

# **Module-2: Metal complexes and Organometallics**

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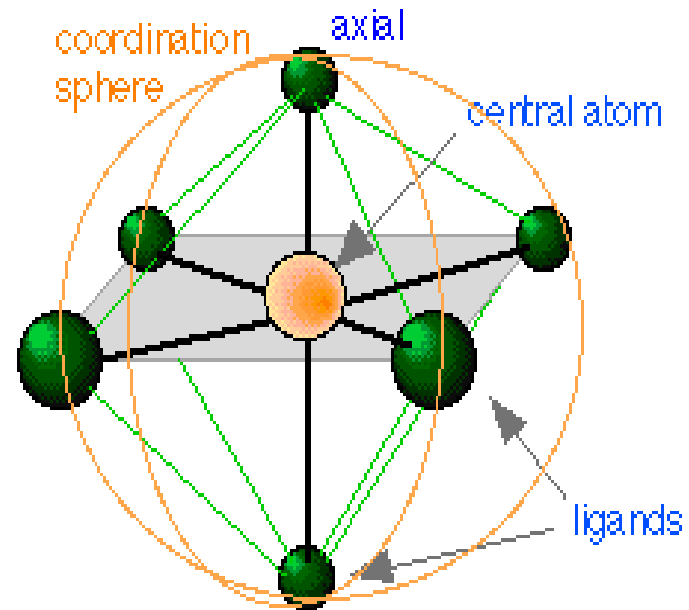
**Prof. G. Buvaneswari**

# Contents

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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, chlorophyll- structure and property).

# Topic : Metal complexes: structure, bonding and applications





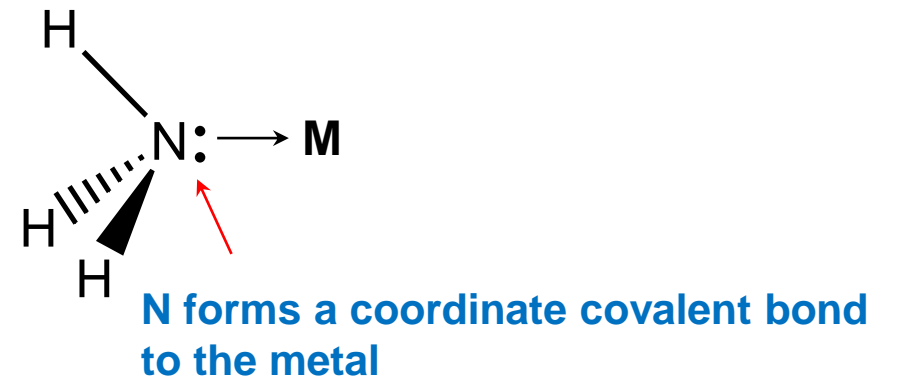
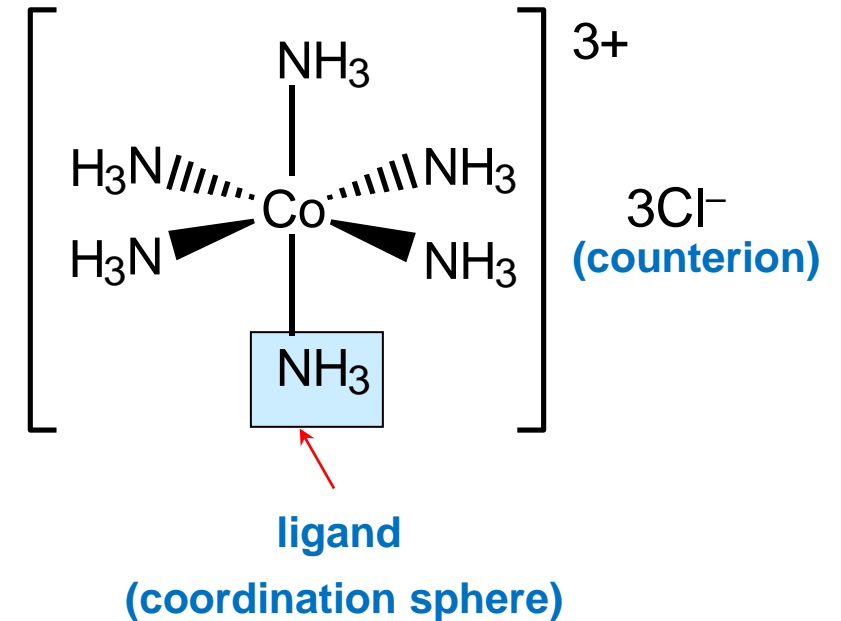
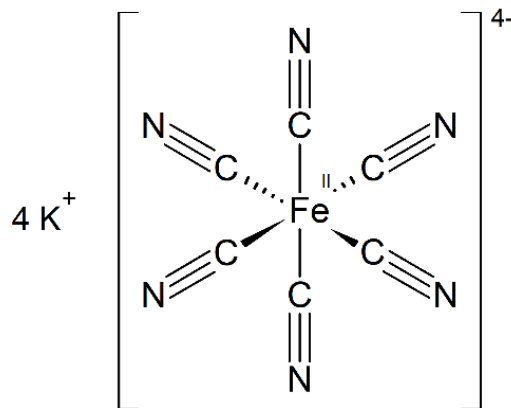
# Double Salts and Co-Ordination Compounds

## ❖ Double Salt:

Ferric alum  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$

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

## ❖ Co-ordination Compounds







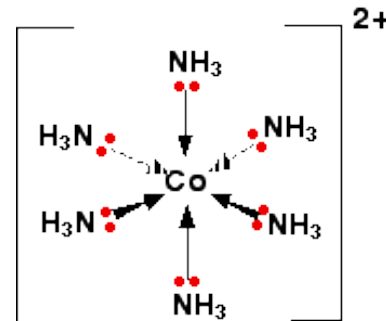
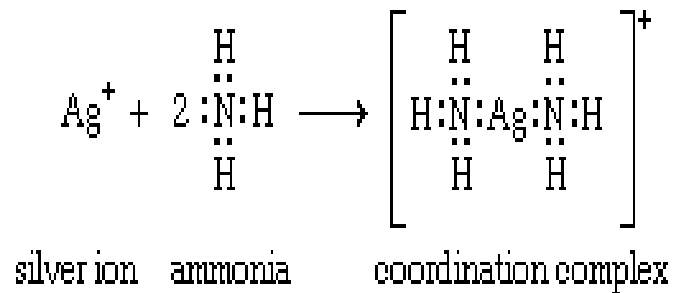




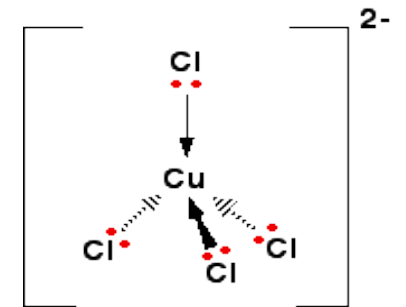


## Lewis Acid Base Theory - Gilbert N. Lewis, 1920s

- 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
- Provided the first electronic interpretation of bonding in coordination compounds.
- Coordination reaction between silver ions and ammonia illustrates that the metal ion can be regarded as Lewis acid and the ligands as Lewis bases.



**[ Co(NH<sub>3</sub>)<sub>6</sub> ]<sup>2+</sup>**



**[ CuCl<sub>4</sub> ]<sup>2-</sup>**

- Denoted by an arrow pointing from the donor to the acceptor.

# Sidgwick's rule

- **Sidgwick's Effective atomic number (EAN) rule** : based on the octet theory of Lewis this is the first attempt to account for the bonding in complexes
- EAN = The sum of the electrons on the central atom (Lewis acid)  $\pm$  No of electrons gained or lost in ion formation + including those donated from the ligands (Lewis base) = AN of next higher inert gas [Ni(CO)<sub>4</sub>], [V(CO)<sub>6</sub>]<sup>-</sup>,
- [Ni(CO)<sub>4</sub>] = 28-0+8 =36 (Next inert gas Krypton(AN-36))
- [Fe(CN)<sub>6</sub>]<sup>4-</sup> = 26-2+12 = 36
- [Zn(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> = 30-2+8 = 36
- [V(CO)<sub>6</sub>]<sup>-</sup> = 23 +1+12=36
- **Exceptions:** [Fe(CN)<sub>6</sub>]<sup>3-</sup>; [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup>
- **Failure: Ionic nature of the complexes**





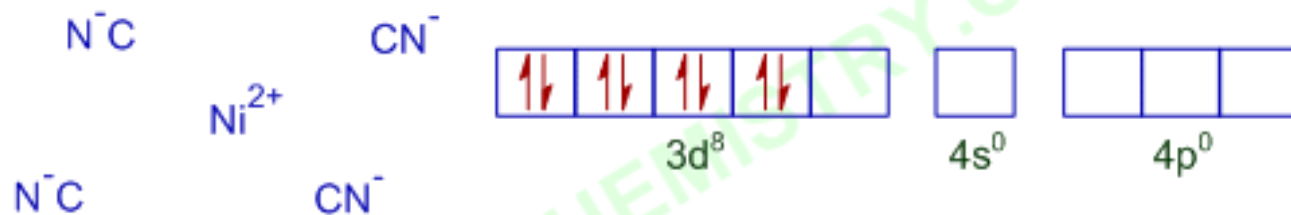


# $[\text{Ni}(\text{CN})_4]^{2-}$

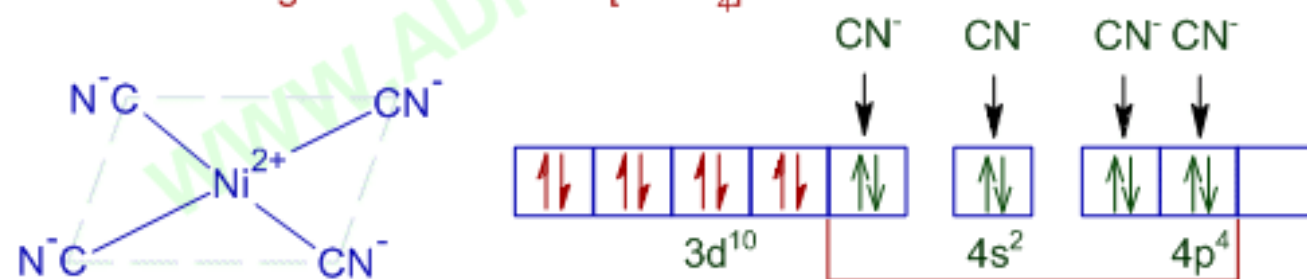
Electronic configuration of  $\text{Ni}^{2+}$  ion



Change in electronic configuration of  $\text{Ni}^{2+}$  ion when  $\text{CN}^-$  ligands approach it



Electronic configuration of  $\text{Ni}^{2+}$  in  $[\text{Ni}(\text{CN})_4]^{2-}$



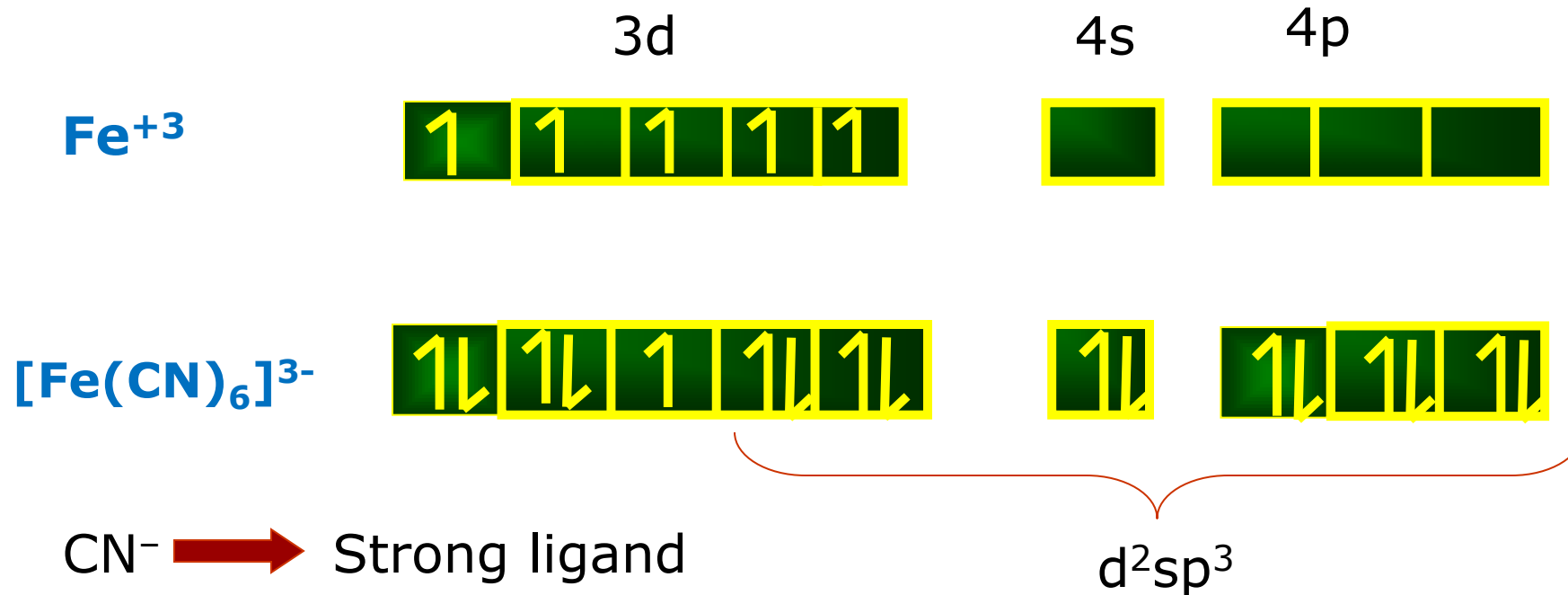
$[\text{Ni}(\text{CN})_4]^{2-}$   
Tetrahedral & Diamagnetic

$dsp^2$  hybridization

Prepared by: V. Aditya vardhan



# Octahedral $d^2sp^3$ Geometry

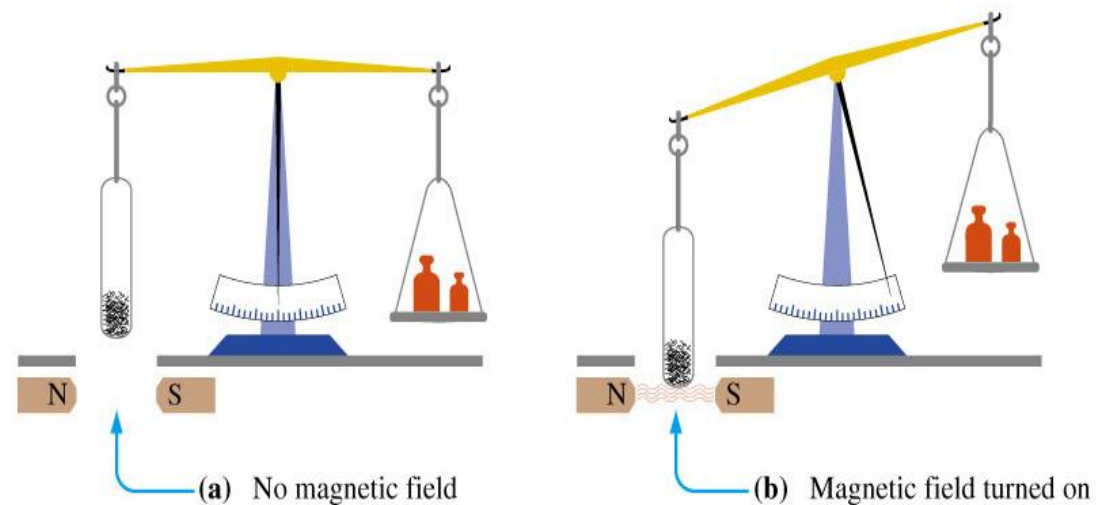


No. of d electrons = AN of central metal – number of electrons lost – AN of previous inert gas (Argon -18) – **Fe: 26-3-18 =  $d^5$**

# Hybridization

- The difference between  $sp^3d^2$  and  $d^2sp^3$  hybrids lies in the principal quantum number of the  $d$  orbital.
- In  $sp^3d^2$  hybrids, the  $s$ ,  $p$ , and  $d$  orbitals have the same principal quantum number—**High Spin**.
- In  $d^2sp^3$  hybrids, the principal quantum number of the  $d$  orbitals is one less than  $s$  and  $p$  orbitals—**Low Spin**.
- **A complex's magnetic properties determine which hybrid is being used.**

# Magnetic behaviour



$$\mu_M = \sqrt{n(n+2)}$$

Where  $n$  is the number of unpaired electrons

## Failures:

- Does not account for
- splitting of  $d$ -orbital
- spectra of complexes
- Reaction rates and mechanisms
- Outer field (or) Inner field
- Tetrahedral (or) square planar
- Magnetic properties

## Bonding in Coordination Compounds

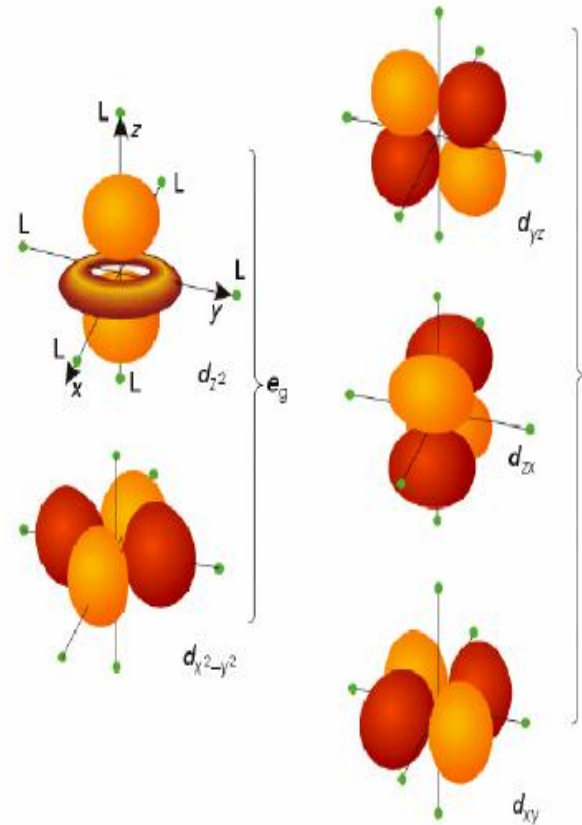
- Many of the properties of metal complexes are dictated by their electronic structures.
- Electronic structure can be explained by an ionic model that attributes formal charges on to the metals and ligands. This forms basis of crystal field theory (CFT), which is considered as the core concept in inorganic chemistry.
- 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.
- CFT provides better understanding of formation of complexes. However, MO and LF theories, though more complicated, provides a more realistic perspective.

# Crystal Field Theory

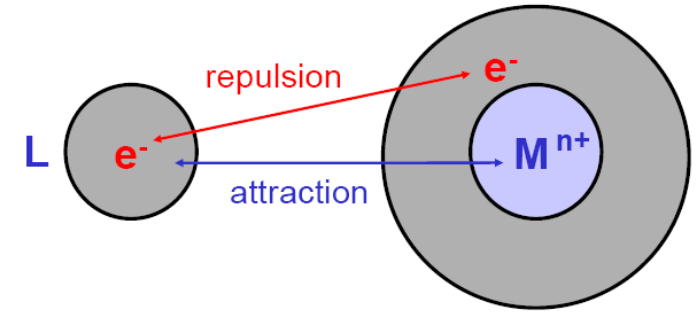
- Crystal field theory largely replaced VB theory for interpreting the chemistry of coordination compounds.
- Proposed by physicist Hans Bethe in 1929
- Further modifications were proposed by J.H. Van Vleck in 1935 to allow for some covalency in the interactions. These are referred to as Ligand Field Theory
- 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.

# CFT Assumptions

- Interaction between the metal ion and the ligands are purely electrostatic (ionic)
- Ligands are considered as point charges
- Ion-ion interaction, if the ligand is negatively charged and ion-dipole interaction, if the ligand is neutral
- Electrons on the metal are under repulsive from those on the ligands
- Electrons on metal occupy those d-orbitals farthest away from the direction of approach of ligands.

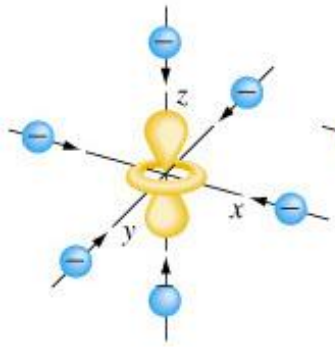


## Crystal Field Theory

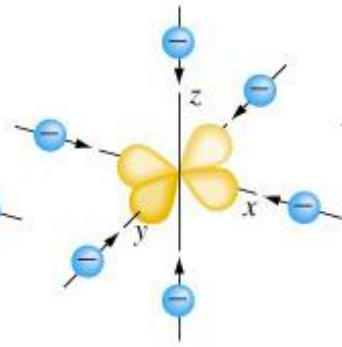


- Interaction between electrons of the cation and those of ligands are entirely repulsive. This is responsible for splitting of d orbitals.
- CFT does not consider the overlapping between metal and ligand orbitals.
- d-orbitals lose their degeneracy due to the approach of ligands during the formation of complex

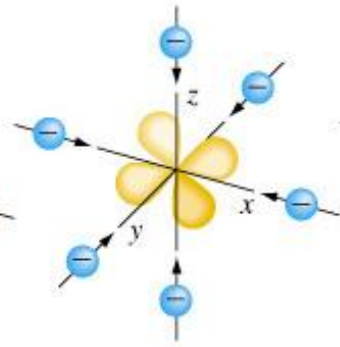
# Octahedral Complex



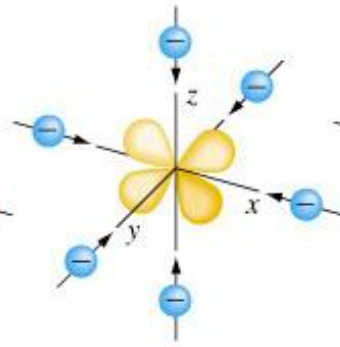
(a)  $d_{z^2}$



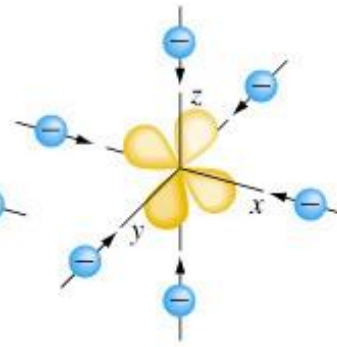
(b)  $d_{x^2-y^2}$



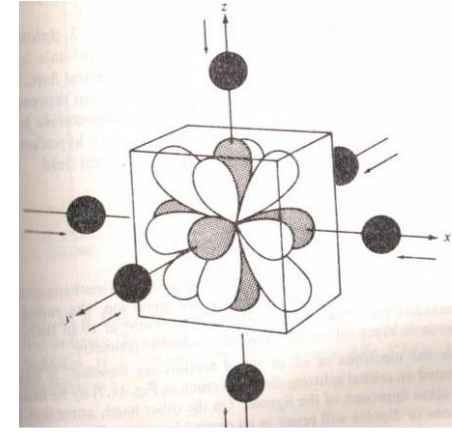
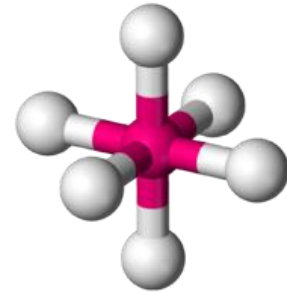
(c)  $d_{xy}$



(d)  $d_{xz}$



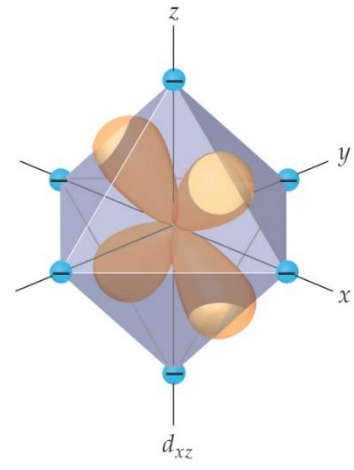
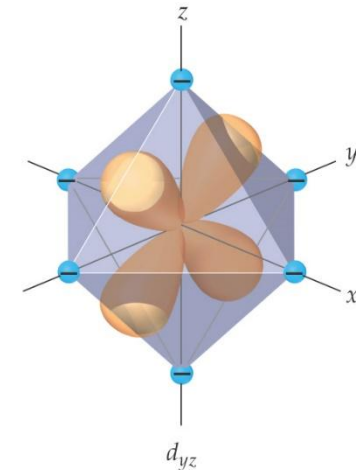
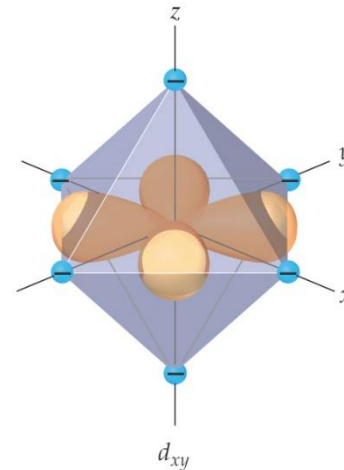
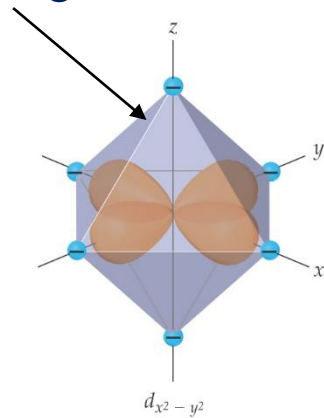
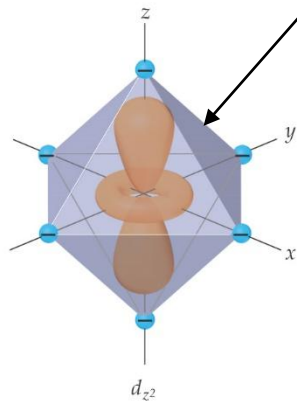
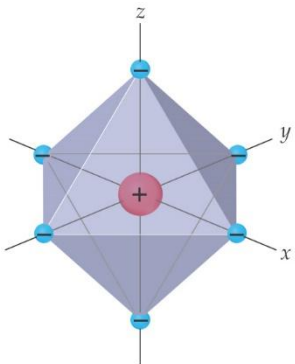
(e)  $d_{yz}$



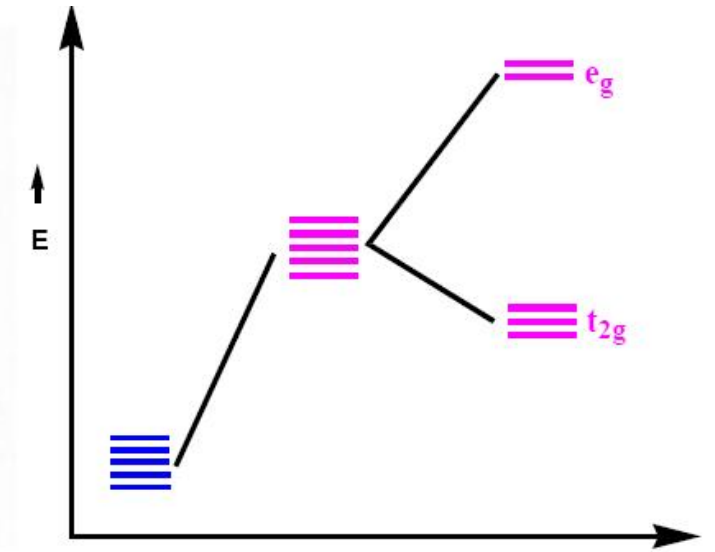
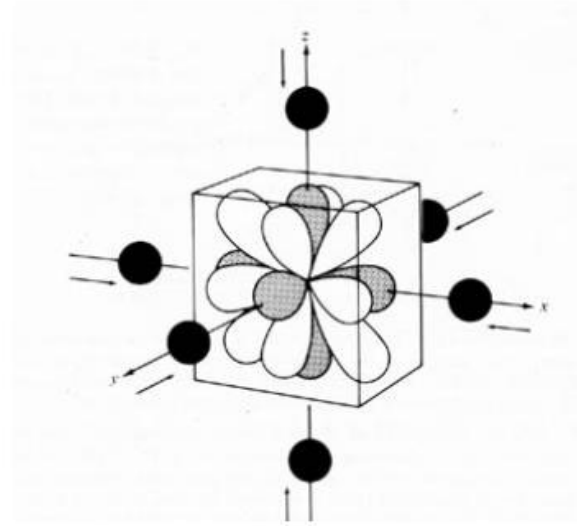
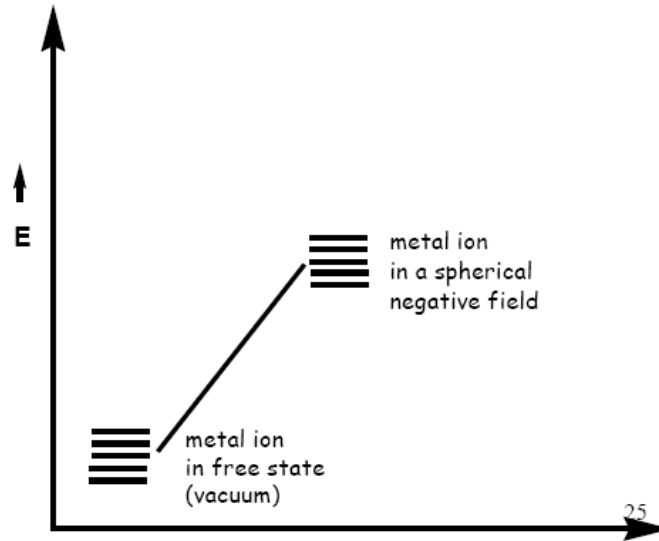
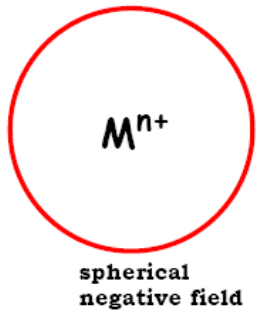
- Ligands will interact with some d orbitals more than others
- Depends on relative orientation of orbital and ligand

- In these orbitals, the ligands are between the lobes, interact less strongly

Ligands point right at lobes



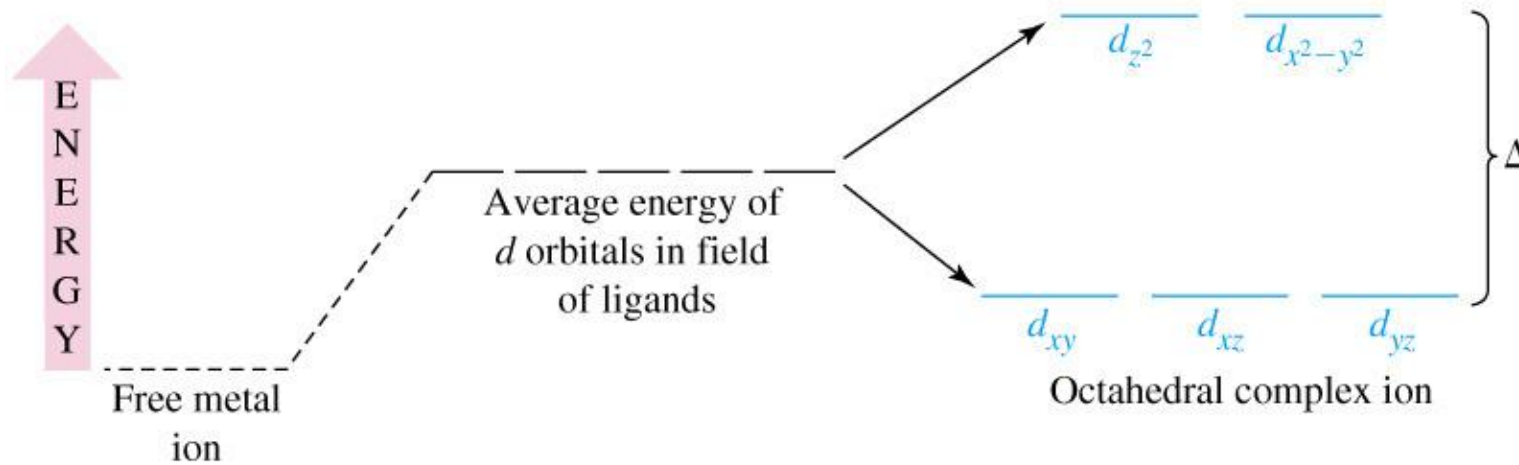
# Octahedral Field



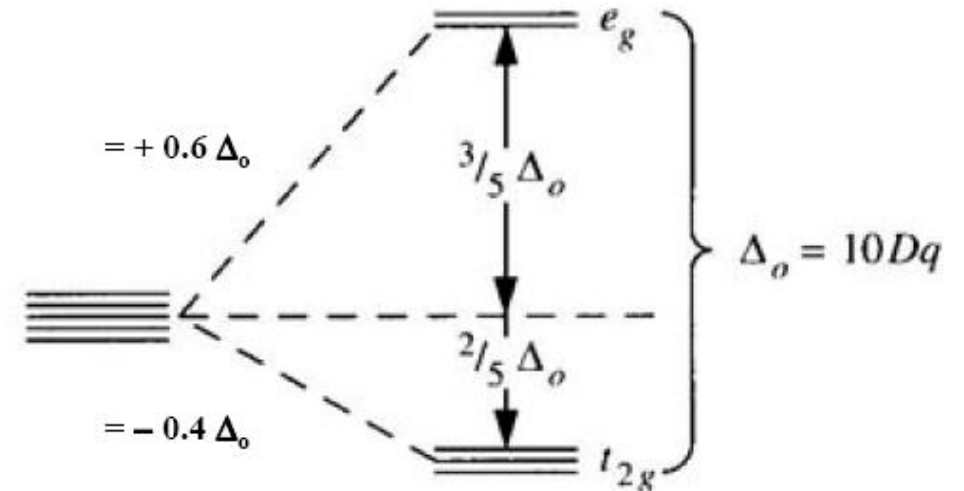
- d-orbitals in the isolated gaseous metal are degenerate.
- If a spherically symmetric field of negative charges is placed around the metal, these orbitals remain degenerate, but all of them are raised in energy as a result of the repulsion between the negative charges on the ligands and in the d orbitals.

- discrete point charges (ligands) are allowed to interact with the metal, the degeneracy of the d orbitals is removed.
- Not all d orbitals interact with the six point charges to the same extent.
- Those orbitals along the axes will be destabilized more than that of the orbitals that lie in between the axes.

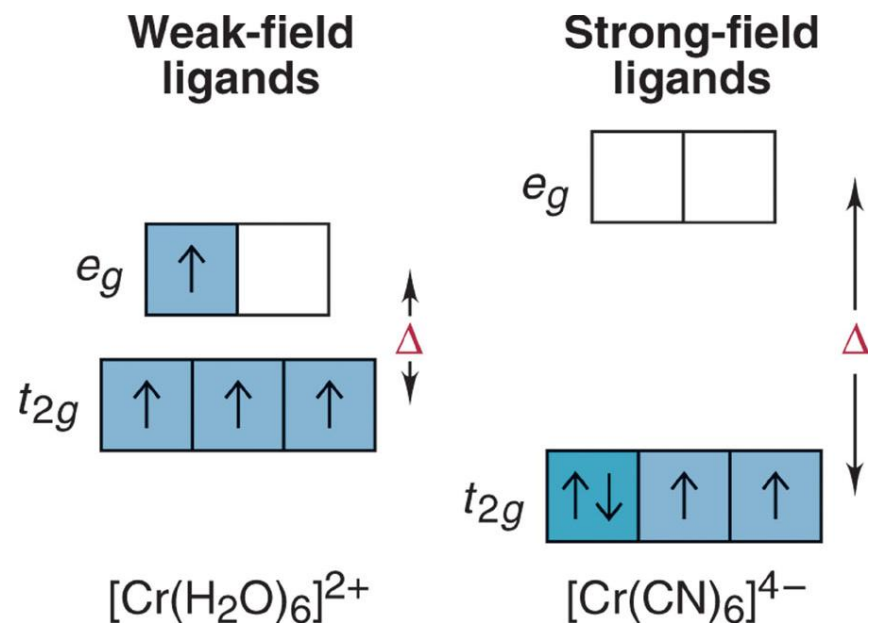
# Octahedral Complex and $d$ -Orbital Energies



- For the  $O_h$  point group, the  $x^2-y^2$ ,  $z^2$  orbitals belong to the  $E_g$  irreducible representation and  $xy$ ,  $xz$ ,  $yz$  belong to the  $T_{2g}$  representation
- The extent to which these two sets of orbitals are split is denoted by  $\Delta_o$  or  $10 Dq$ . As the barycenter must be conserved on going from a spherical field to an octahedral field, the  $t_{2g}$  set must be stabilized as much as the  $e_g$  set is destabilized.



- For  $d^1$ - $d^3$  systems: Hund's rule predicts that the electrons will not pair and occupy the  $t_{2g}$  set.
- For  $d^4$ - $d^7$  systems (2 possibilities) : Either pairing the electrons in  $t_{2g}$  set (low spin or strong field) or electrons in  $e_g$  set, higher in energy, but do not pair (high spin or weak field).
- Pairing energy ( $P$ ) and  $e_g$ - $t_{2g}$  splitting ( $\Delta_0$  or  $10 Dq$ )



## For an octahedral complex, CFSE

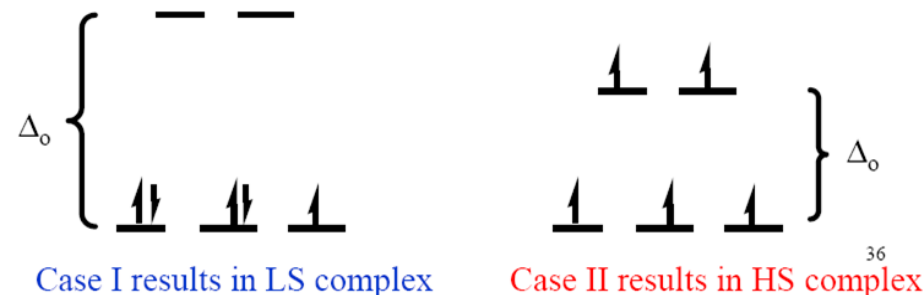
$$\text{CFSE} = -0.4 \times n(t_{2g}) + 0.6 \times n(e_g) \Delta_0$$

Where,  $n(t_{2g})$  and  $n(e_g)$  are the no. of electrons occupying the respective levels

If CFSE is very large, pairing occurs (i.e.  $\text{CFSE} > P$ )

If CFSE is rather small, no pairing occurs (i.e.  $\text{CFSE} < P$ )

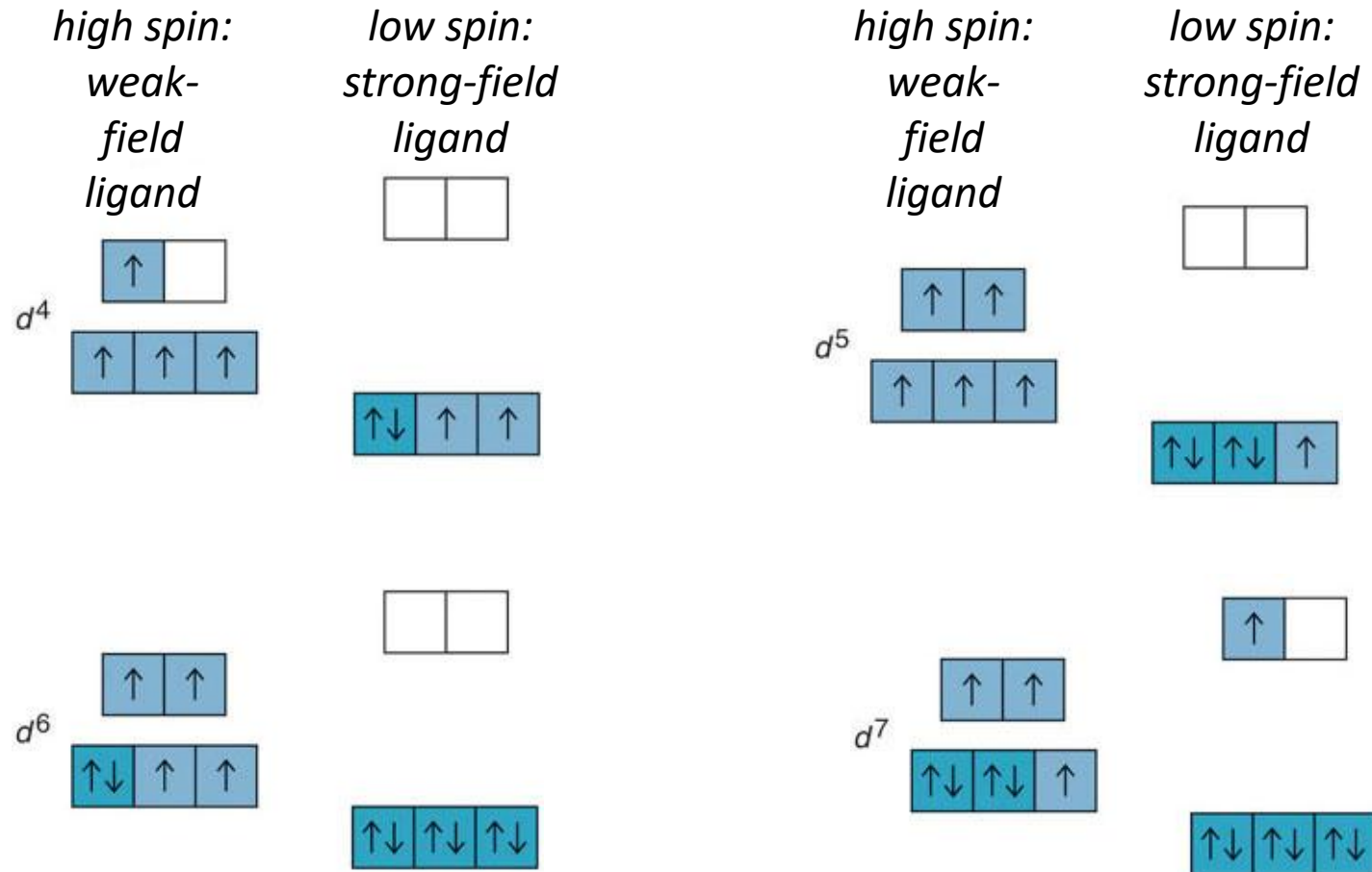
### d<sup>5</sup> system



### $\Delta_0$ vs Pairing Energy

Complex	Config.	$\Delta_0, \text{cm}^{-1}$	$P, \text{cm}^{-1}$	spin-state
$[\text{Fe}(\text{OH}_2)_6]^{2+}$	$d^6$	10,400	17,600	high-spin
$[\text{Fe}(\text{CN})_6]^{4-}$	$d^6$	32,850	17,600	low-spin
$[\text{CoF}_6]^{3-}$	$d^7$	13,000	21,000	high-spin
$[\text{Co}(\text{NH}_3)_6]^{3+}$	$d^7$	23,000	21,000	low-spin

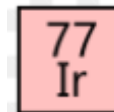
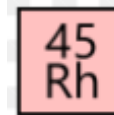
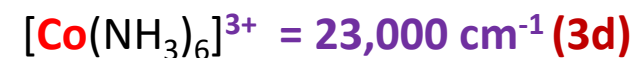
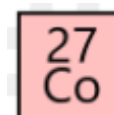
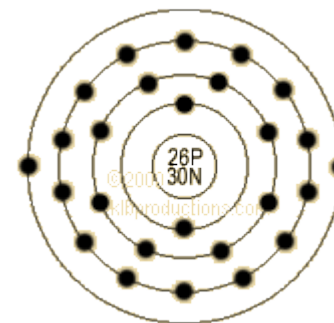
# Orbital occupancy for high- and low-spin complexes of $d^4$ through $d^7$ metal ions



Number of $d$ electrons	Arrangement in weak ligand field				Arrangement in strong ligand field			
	$t_{2g}$	$e_g$	CFSE $\Delta_o$	Spin only magnetic moment $\mu_s(D)$	$t_{2g}$	$e_g$	CFSE $\Delta_o$	Spin only magnetic moment $\mu_s(D)$
$d^1$	$\uparrow \square \square$	$\square \square$	-0.4	1.73	$\uparrow \square \square$	$\square \square$	-0.4	1.73
$d^2$	$\uparrow \uparrow \square$	$\square \square$	-0.8	2.83	$\uparrow \uparrow \square$	$\square \square$	-0.8	2.83
$d^3$	$\uparrow \uparrow \uparrow$	$\square \square$	-1.2	3.87	$\uparrow \uparrow \uparrow$	$\square \square$	-1.2	3.87
$d^4$	$\uparrow \uparrow \uparrow \uparrow$	$\square$	-1.2 +0.6 = -0.6	4.90	$\uparrow \downarrow \uparrow \uparrow$	$\square$	-1.6	2.83
$d^5$	$\uparrow \uparrow \uparrow \uparrow \uparrow$	$\square$	-1.2 +1.2 = -0.0	5.92	$\uparrow \downarrow \uparrow \uparrow \square$	$\square$	-2.0	1.73
$d^6$	$\uparrow \downarrow \uparrow \uparrow \uparrow$	$\uparrow \uparrow$	-1.6 +1.2 = -0.4	4.90	$\uparrow \downarrow \uparrow \downarrow \uparrow \square$	$\square$	-2.4	0.00
$d^7$	$\uparrow \downarrow \uparrow \downarrow \uparrow \uparrow$	$\uparrow \uparrow$	-2.0 +1.2 = -0.8	3.87	$\uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \square$	$\square$	-2.4 +0.6 = -1.8	1.73
$d^8$	$\uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow$	$\uparrow \uparrow$	-2.4 +1.2 = -1.2	2.83	$\uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow$	$\square$	-2.4 +1.2 = -1.2	2.83
$d^9$	$\uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow$	$\uparrow \downarrow \uparrow$	-2.4 +1.8 = -0.6	1.73	$\uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow$	$\square$	-2.4 +1.8 = -0.6	1.73
$d^{10}$	$\uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow$	$\uparrow \downarrow \uparrow \downarrow$	-2.4 +2.4 = 0.0	0.00	$\uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$	$\square$	-2.4 +2.4 = 0.0	0.00

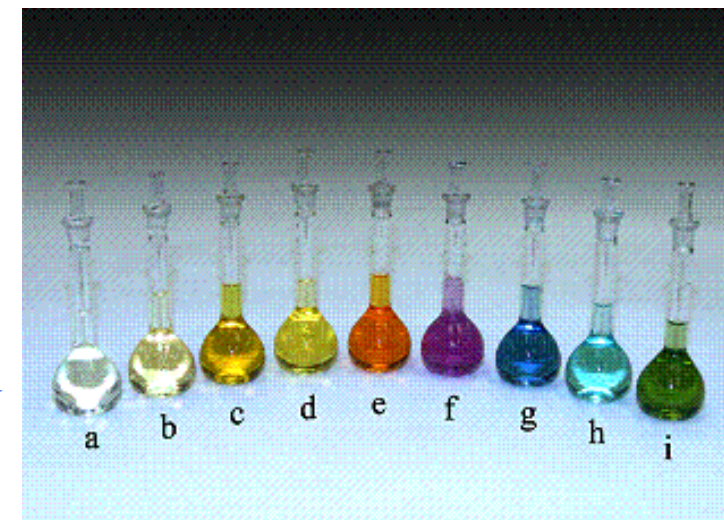
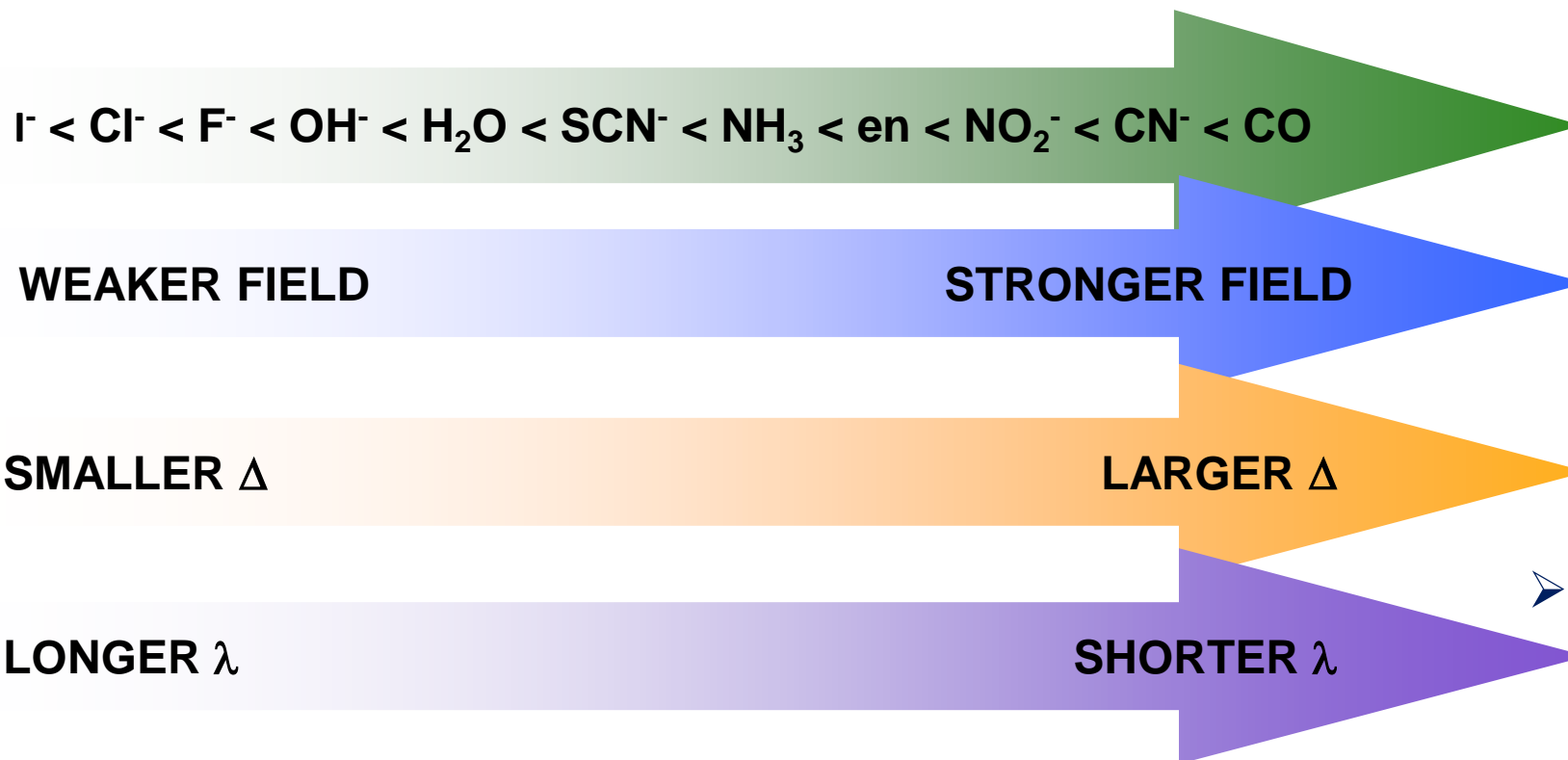
$\Delta_o$  is dependent on:

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



# Spectrochemical series

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



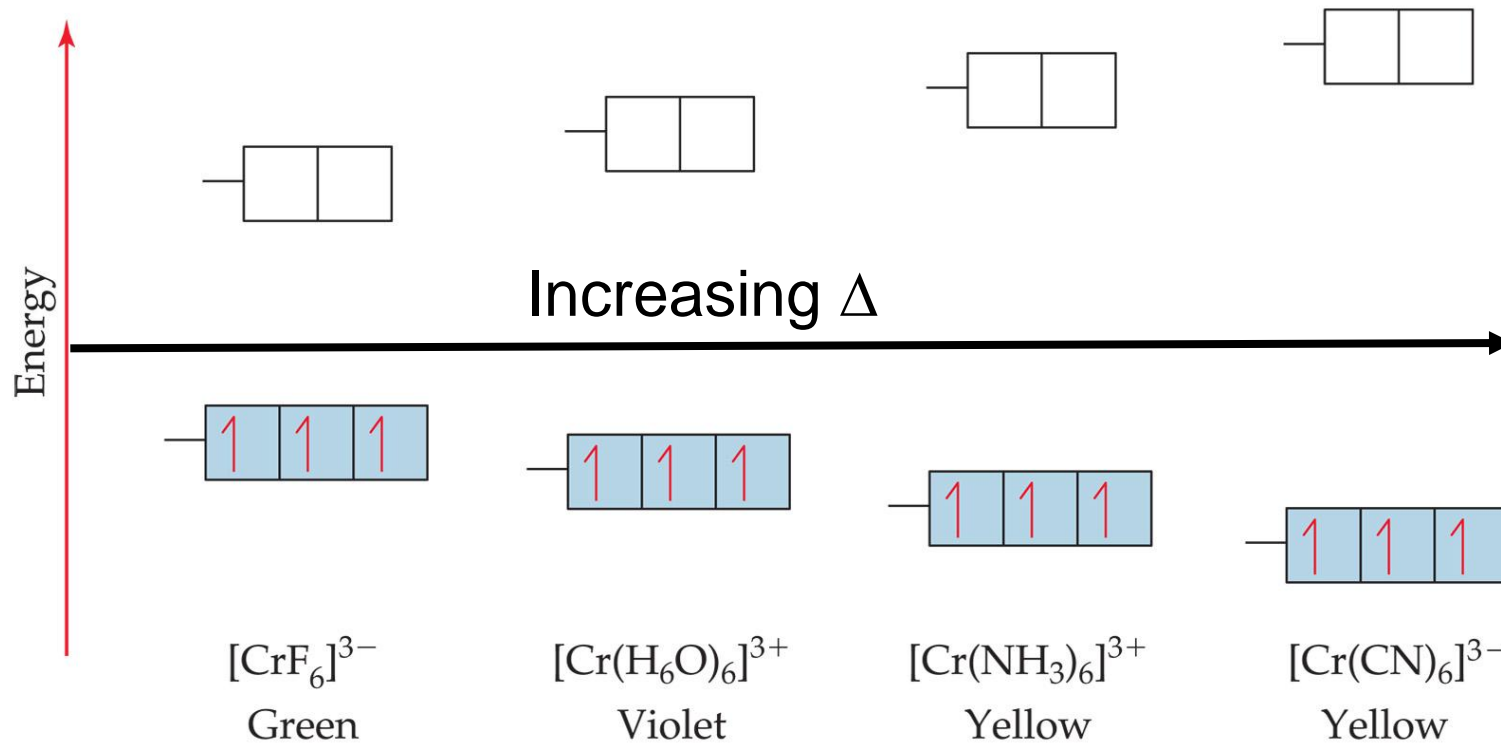
➤ Complexes of cobalt (III) show the shift in color due to the ligand.  
(a)  $CN^-$ , (b)  $NO_2^-$ , (c) phen, (d) en, (e)  $NH_3$ , (f) gly, (g)  $H_2O$ , (h)  $ox^{2-}$ , (i)  $CO_3^{2-}$

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

# Effect of Ligand Field Strength on the Color of the Complexes

- Transition metal complexes are colored generally. Associated with the promotion of an electron from one energy state to another. The energy required is obtained by absorbing light of a particular wavelength.
- In transition elements, there are **partially filled d levels**. The d levels split into different energy levels depending on the geometry of complex.
- To promote the electron from one d level to another d level which corresponds to a **small energy difference**. This results in absorption of light of higher wavelength in the visible region and the complex appear colored.
- The energy difference between split d levels in a transition element **depends on nature of ligand to a larger extent**.
- Depending upon the **CFSE**, the light of **difference wavelengths** will be absorbed to effect d-d transitions and hence the complexes have **different colors** depending upon the wavelength of light absorbed.
- Complexes of s and p block elements are colorless. No d-d transition as all the d levels are doubly occupied. The energy required to remove an electron from s or p level to a higher level is much greater. This may correspond to UV region, in which case it is colorless.

# Chemistry of Colors

- Thus, the Ligand Field Strength is related to the Color of the Complexes
- $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  : light blue ;  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  : deep blue ;  $[\text{CuCl}_4]^{2-}$  : yellow ;  $[\text{Cu}(\text{en})_2]^{2+}$  : violetcolorless
- In all the above complexes, Cu is in +2 oxidation state, but the ligand field strength differ. Hence they have different colors.
- d-d transitions take place by the absorption of visible radiation by transition metal ions and transmitted light is colored with the complementary color of the color of the light absorbed. e.g., when red-light is removed from the white light, the eye sees its complementary color – blue-green.

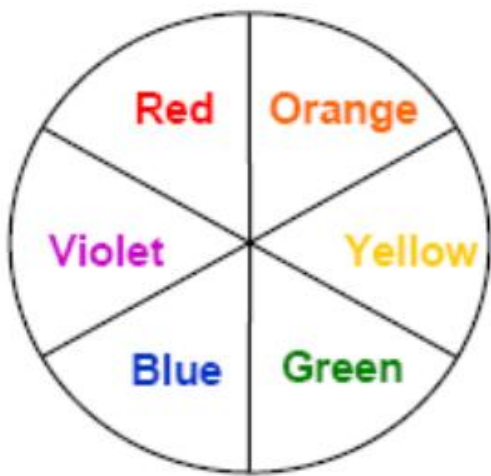
## Color of various Ni(II) complexes in aqueous solutions



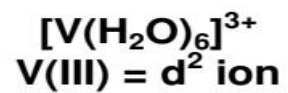
- From left to right, hexaamminenickel(II) -  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ; tris(ethylenediamine)nickel(II) -  $[\text{Ni}(\text{en})_3]^{2+}$  ; tetrachloronickelate(II) -  $[\text{NiCl}_4]^{2-}$  ; hexaaquanickel(II) -  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ .
- Reactions starting from  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  can be used to form a variety of nickel coordination complexes because the  $\text{H}_2\text{O}$  ligands are rapidly displaced.

**$[\text{Co}(\text{NH}_3)_6]^{3+}$   $[\text{Co}(\text{en})_3]^{3+}$   $[\text{Co}(\text{NO}_2)_6]^{3-}$  are orange yellow while  $[\text{CoF}_6]^{3-}$   $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$  are blue**

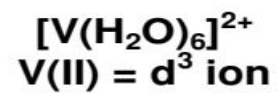
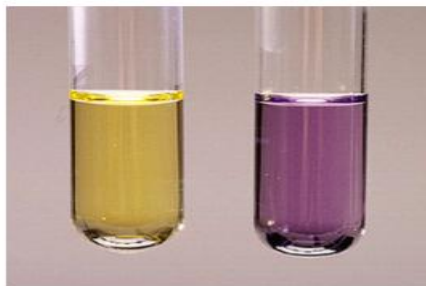
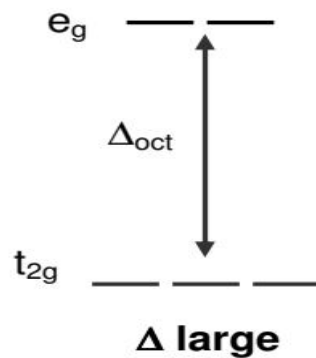
- $\text{Co}^{3+} = 27 - 3 - 18 = d^6$
- **$\text{NH}_3$ , en and  $\text{NO}_2$  are strong field ligands (more splitting –  $(t_{2g})^6 (e_g)^0$  - Large  $\Delta_o$ )**
- To favour d-d transition, the energy required is high. Hence absorbs violet color or blue color and will appear yellow or orange.
- **$\text{F}^-$  and  $\text{H}_2\text{O}$  are weak field ligands (less splitting -  $(t_{2g})^4 (e_g)^2$  - small  $\Delta_o$ )**
- Because of small  $\Delta_o$ , lower energy radiations are required for d-d transition. The complex absorbs yellow or orange (lower energy) and appear as blue.



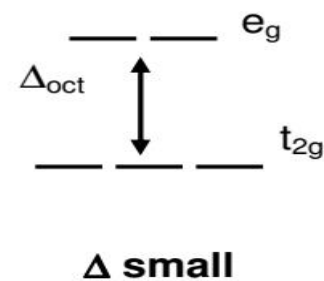
Colour of light absorbed	Approx. $\lambda$ ranges / nm	Colour of light transmitted
Red	700-620	Green
Orange	620-580	Blue
Yellow	580-560	Violet
Green	560-490	Red
Blue	490-430	Orange
Violet	430-380	Yellow



violet light absorbed  
complex appears yellow



yellow light absorbed  
complex appears violet



$[\text{Cr}(\text{NH}_3)_6]^{3+}$   
Strong  $\Delta_{\text{oct}}$   
High energy,  
violet light absorbed  
Complex: yellow

$[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$   
Weak  $\Delta_{\text{oct}}$   
Low energy,  
yellow light absorbed  
Complex: magenta



## Colors of Coordination Complexes

	Fe <sup>II</sup>	Fe <sup>III</sup>	Co <sup>II</sup>	Cu <sup>II</sup>	Al <sup>III</sup>	Cr <sup>III</sup>
<b>Hydrated Ion</b>	[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> Pale green Soln	[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> Yellow/brown Soln	[Co(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> Pink Soln	[Cu(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> Blue Soln	[Al(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> Colourless Soln	[Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> Green Soln
<b>OH<sup>-</sup>, dilute</b>	[Fe(H <sub>2</sub> O) <sub>4</sub> (OH) <sub>2</sub> ] Dark green Ppt	[Fe(H <sub>2</sub> O) <sub>3</sub> (OH) <sub>3</sub> ] Brown Ppt	[Co(H <sub>2</sub> O) <sub>4</sub> (OH) <sub>2</sub> ] Blue/green Ppt	[Cu(H <sub>2</sub> O) <sub>4</sub> (OH) <sub>2</sub> ] Blue Ppt	[Al(H <sub>2</sub> O) <sub>3</sub> (OH) <sub>3</sub> ] White Ppt	[Cr(H <sub>2</sub> O) <sub>3</sub> (OH) <sub>3</sub> ] Green Ppt
<b>OH<sup>-</sup>, concentrated</b>	[Fe(H <sub>2</sub> O) <sub>4</sub> (OH) <sub>2</sub> ] Dark green Ppt	[Fe(H <sub>2</sub> O) <sub>3</sub> (OH) <sub>3</sub> ] Brown Ppt	[Co(H <sub>2</sub> O) <sub>4</sub> (OH) <sub>2</sub> ] Blue/green Ppt	[Cu(H <sub>2</sub> O) <sub>4</sub> (OH) <sub>2</sub> ] Blue Ppt	[Al(OH) <sub>4</sub> ] <sup>-</sup> Colourless Soln	[Cr(OH) <sub>6</sub> ] <sup>3-</sup> Green Soln
<b>NH<sub>3</sub>, dilute</b>	[Fe(H <sub>2</sub> O) <sub>4</sub> (OH) <sub>2</sub> ] Dark green Ppt	[Fe(H <sub>2</sub> O) <sub>3</sub> (OH) <sub>3</sub> ] Brown Ppt	[Co(H <sub>2</sub> O) <sub>4</sub> (OH) <sub>2</sub> ] Blue/green Ppt	[Cu(H <sub>2</sub> O) <sub>4</sub> (OH) <sub>2</sub> ] Blue Ppt	[Al(H <sub>2</sub> O) <sub>3</sub> (OH) <sub>3</sub> ] White Ppt	[Cr(H <sub>2</sub> O) <sub>3</sub> (OH) <sub>3</sub> ] Green Ppt
<b>NH<sub>3</sub>, concentrated</b>	[Fe(H <sub>2</sub> O) <sub>4</sub> (OH) <sub>2</sub> ] Dark green Ppt	[Fe(H <sub>2</sub> O) <sub>3</sub> (OH) <sub>3</sub> ] Brown Ppt	[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup> Straw coloured Soln	[Cu(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup> Deep blue Soln	[Al(H <sub>2</sub> O) <sub>3</sub> (OH) <sub>3</sub> ] White Ppt	[Cr(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> Green Soln
<b>CO<sub>3</sub><sup>2-</sup></b>	FeCO <sub>3</sub> Dark green Ppt	[Fe(H <sub>2</sub> O) <sub>3</sub> (OH) <sub>3</sub> ] Brown Ppt + bubbles	CoCO <sub>3</sub> Pink Ppt	CuCO <sub>3</sub> Blue/green Ppt		

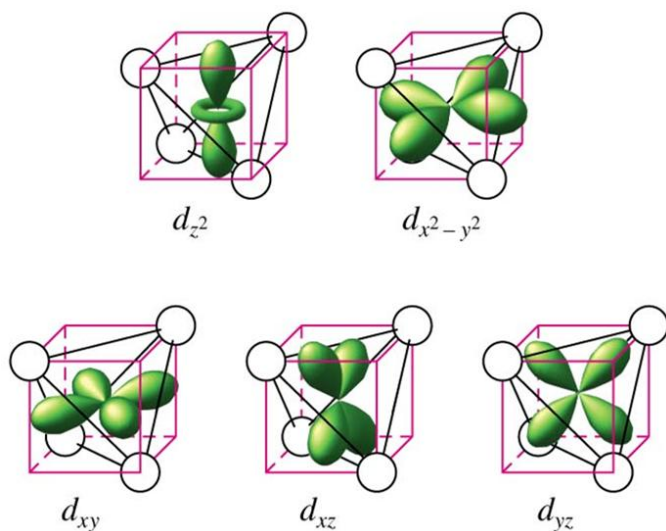
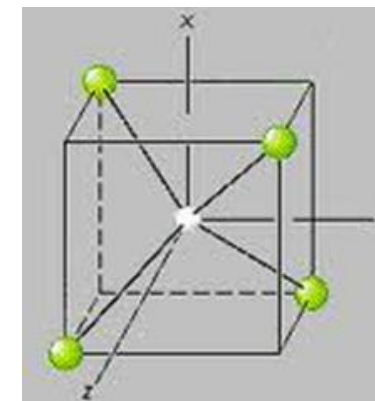
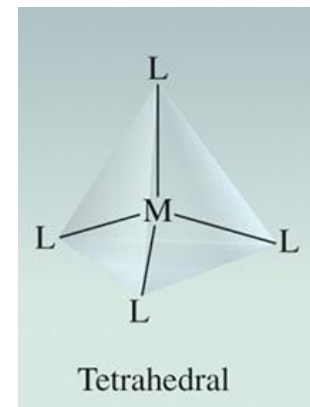
# Charge-Transfer (CT) Bands

- Metal d-orbitals are involved in charge-transfer (CT) transitions too as like d-d transitions
- Observed when filled empty ligand- and metal-centered orbitals have similar energies
- Occurs due to the movement of electrons between metal and ligand. Often stronger than d-d bands
  
- **Direction of the electron transfer is determined by the relative energy levels of these orbitals:**
- **i) Ligand to Metal (LMCT) -  $\text{MnO}_4^-$ ,  $\text{CrO}_4^{2-}$** 

$\text{MnO}_4^-$ , the d-electron count on Mn(VII) is  $d^0$ . The origin of the color in this species is not due to d-d transition, rather, charge transfer from  $\text{O}^{2-}$  to Mn(VII), described as LMCT band. Favored when metal is in high oxidation state attached to  $\pi$ -donor ligands such as oxide, hydroxide, fluoride.
- **ii) Metal-to Ligand (MLCT) -  $[\text{Fe}(\text{bpy})_3]^{2+}$**  - charge transfer occurs from Fe(II) to the empty  $\pi^*$  orbitals of bpy ligand. Favored in electron rich metal centers attached to  $\pi$ -acceptor ligands. Bands occur in UV region (higher in energy) – metal carbonyls

# Tetrahedral Crystal Field

- Imagine a tetrahedral molecule inside a cube with metal ions in the center of the cube. The ligands occupy the four alternate corners of the cube leaving the rest four corners empty.
- Tetrahedral complex -  $\Delta_t$  is relatively small even with strong field ligands as there are fewer ligands to bond with.
- Usually, electrons will move up to the higher energy orbitals rather than pair. Because of this, *most tetrahedral complexes are high spin.*



- The two 'e' orbitals point to the center of the face of the cube while the three 't<sub>2</sub>' orbitals point to the center of the edges of the cube.
- Therefore, the angle between the e orbitals, metal and ligand is **54°44'**. But the angle between the t<sub>2</sub> orbitals, metal and ligand is **35°16'**.
- Thus the t<sub>2</sub> orbitals are nearer to the direction of approach of the ligands than the e orbitals.
- Hence, t<sub>2</sub> orbitals have higher energy compared to e-orbitals.

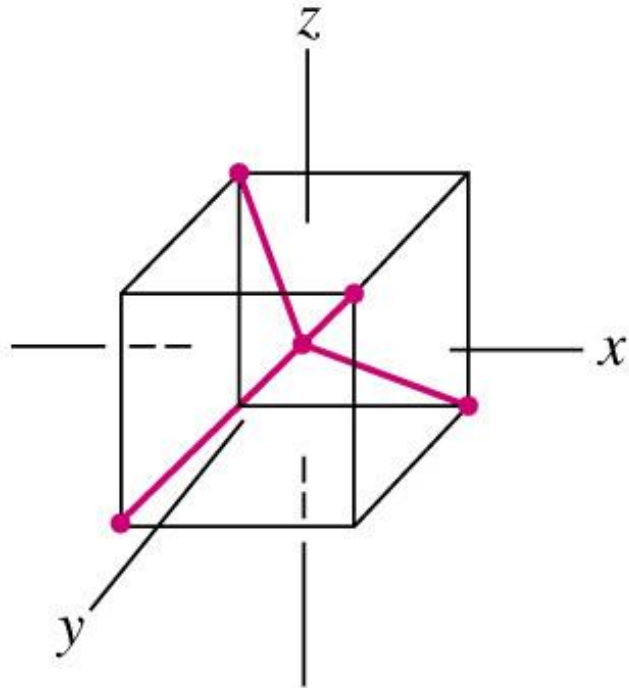
## Tetrahedral Crystal Field

- Position of four ligands with respect to the d orbitals of the central metal ion.
  - The d orbitals having their lobes oriented in between the axes ( $t_2$  orbitals) are nearer to four ligands. Hence interact with the ligand orbitals to a greater extent and hence higher energy.
  - whereas the two d orbitals having their lobes oriented along the axes ( $e$ ) are away from the ligands. Interact only to a lesser extent with the ligand orbitals.
- Splitting of d orbitals just the reverse of splitting observed in oh complexes.
- Difference in energy -tetrahedral crystal field splitting energy [ $\Delta_t = (4/9) \Delta_0$ ]

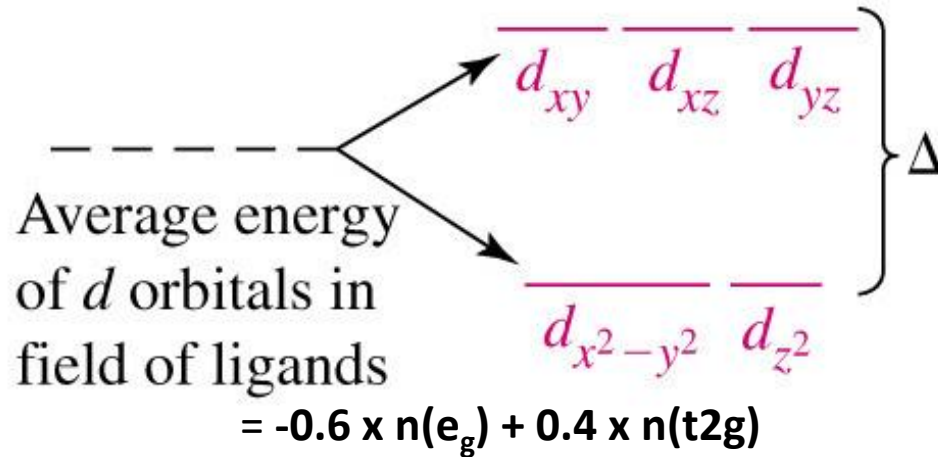
### Reason:

- Only 4 ligands. Hence  $1/3^{\text{rd}}$  decrease in the number of ligands decreases the  $\Delta_t$
- High energy  $t_2$  orbitals although nearer to the ligands, do not point directly to the ligands. Hence the extent of interaction is less. But in oh complex, the  $e_g$  orbitals point directly at the ligands.

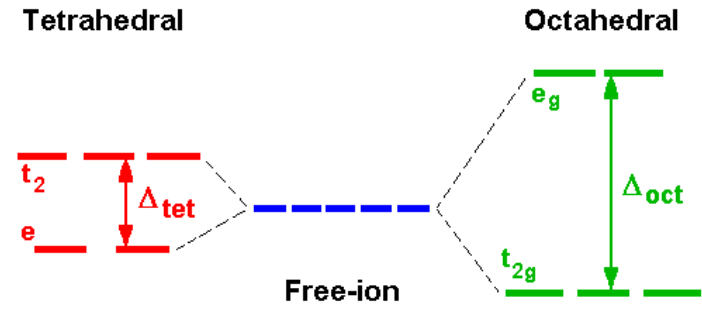
# Tetrahedral Crystal Field



(a)



(b)



$$= -0.4 \times n(t_2) + 0.6 \times n(e) \Delta_o$$

- All tetrahedral complexes are high spin since the CFSE is smaller than the pairing energy.
- Low spin configurations are rarely observed.
- If a very strong ligand is present, the square planar geometry will be favored.

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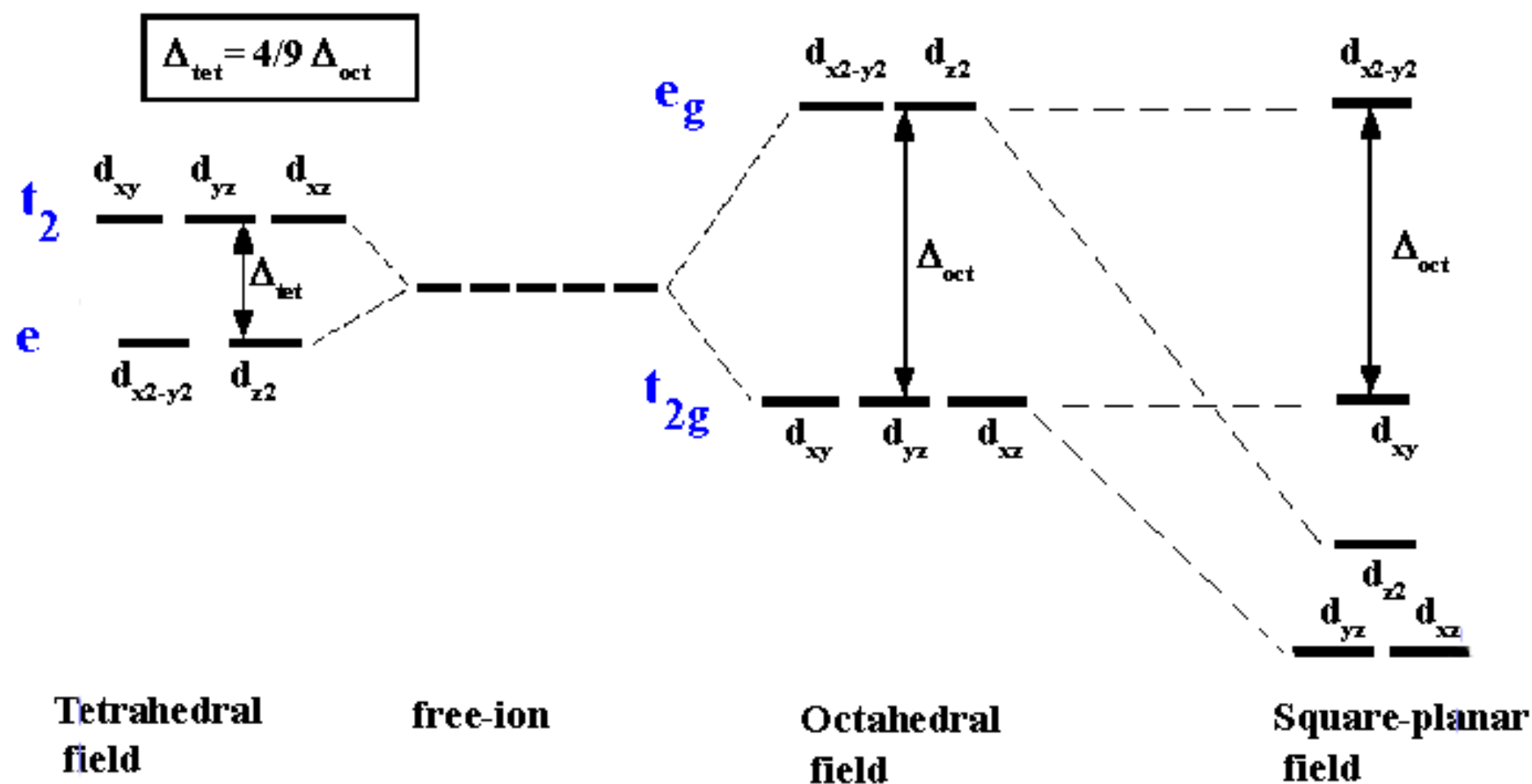
A table showing the crystal field stabilization energies for tetrahedral complexes with different numbers of d-electrons is given below:

### Crystal Field Stabilization Energies for Tetrahedral Complexes of $d^1 - d^{10}$ Ions

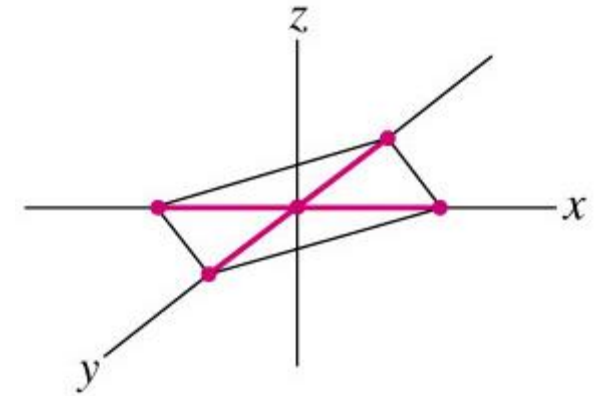
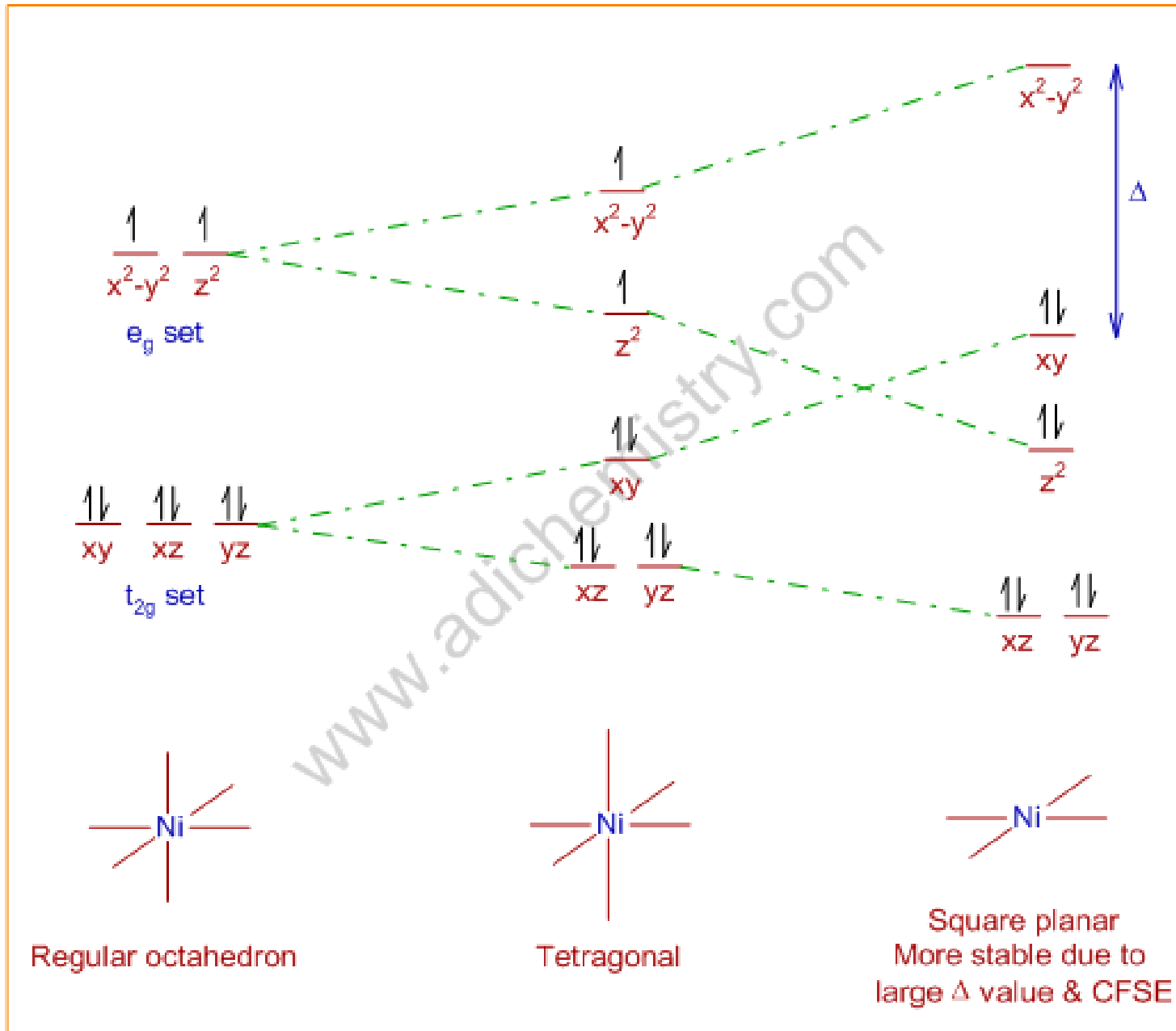
# of d-electrons	Tetrahedral CFSE	# of d-electrons	Tetrahedral CFSE
1	$-0.6 \Delta_t$	6	$-0.6 \Delta_t$
2	$-1.2 \Delta_t$	7	$-1.2 \Delta_t$
3	$-0.8 \Delta_t$	8	$-0.8 \Delta_t$
4	$-0.4 \Delta_t$	9	$-0.4 \Delta_t$
5	zero	10	zero

$$= -0.6 \times n(e_g) + 0.4 \times n(t_{2g})$$

# Crystal field d orbital splitting diagrams for common stereochemistries.



# Square Planar Crystal Field



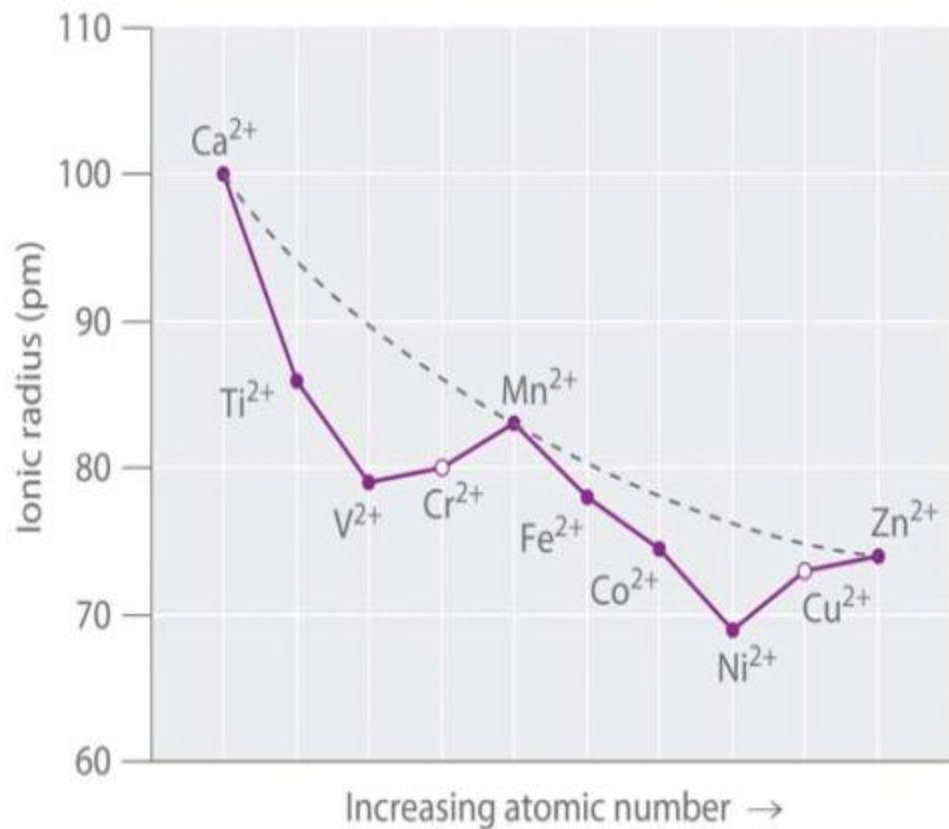
Note: Whichever orbitals come in direct contact with the ligand fields will have higher energies than orbitals that slide past the ligand field and have more of indirect contact with the ligand fields.

# Consequences of Crystal Field Splitting

Crystal Field theory to explain observed properties of complexes:  
Variation of some physical properties across a period:

1. Lattice energy of transition metal ions in a complex
2. Ionic radii of transition metal ions in a complex
3. Enthalpy of hydration of transition metal ions
4. Site preference of Spinel and Inverse spinels

## Ionic radii of transition metals in complexes



Ti<sup>2+</sup> (d<sup>2</sup>) electrons occupy only t<sub>2g</sub>  
V<sup>2+</sup> (d<sup>3</sup>) electrons occupy only t<sub>2g</sub>  
Cr<sup>2+</sup> (d<sup>4</sup>HS) electrons start occupying the e<sub>g</sub> orbitals

As the e<sub>g</sub> orbitals point directly towards the ligands, the repulsion between the metal electrons and ligand electrons will be higher than normal leading to the eventual increase in the ionic radius.

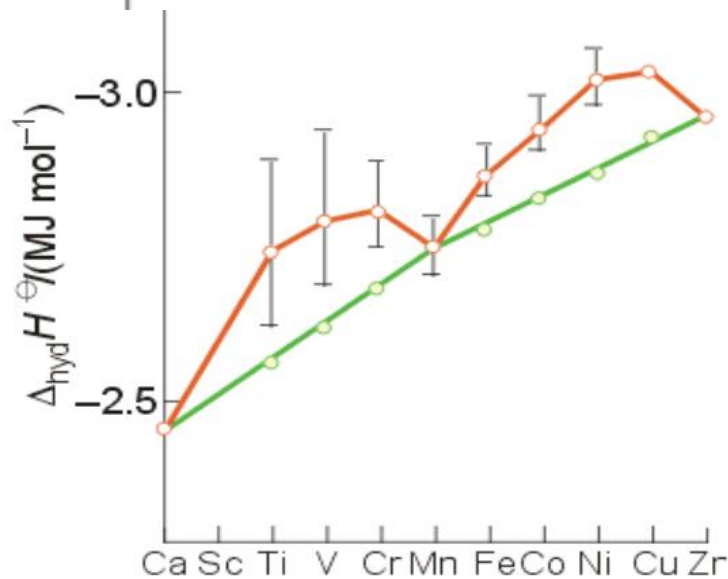
**Enthalpy of hydration** of transition metal ions

It is the heat exchange involved when 1 mole of gaseous ions become hydrated



The amount of energy released when a mole of the ion dissolves in a large amount of water forming an infinite dilute solution in the process.

Higher the charge on the ions and smaller **the size**, more exothermic will be the hydration energy. So it is expected to increase smoothly on going from left to right of the transition metals (**green line in the graph**)



The heats of hydration show two “humps” consistent with the expected CFSE for the metal ions. The values for d<sup>5</sup> and d<sup>10</sup> are the same as expected with a CFSE equal to 0.

## Lattice Energies (1<sup>st</sup> Row Divalent Transition Metal Halides)

Lattice Energy: **Energy released when one mole of an ionic solid is formed from isolated gaseous ions**

Calculated theoretically using the Born- Lande Equation

$$U_o = \frac{A N Z^+ Z^- e^2}{4\pi\epsilon_o r_o} \left(1 - \frac{1}{n}\right)$$

Where

A = Madelung constant ( related to the geometry of the crystal)

N = Avogadro's number

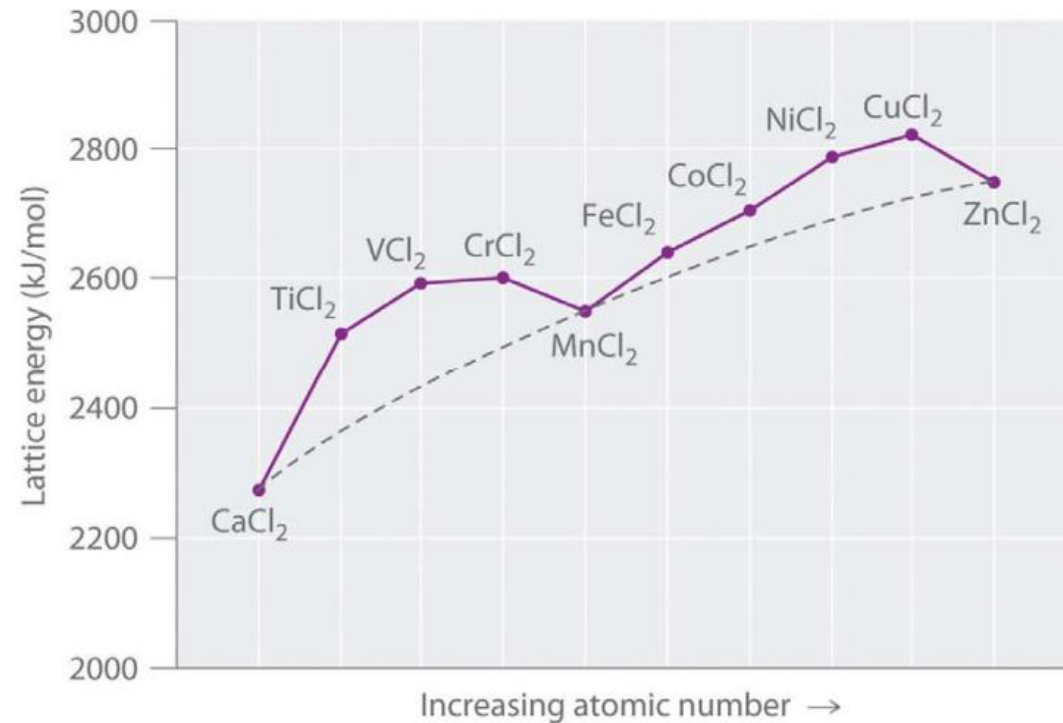
Z= Charge on the M+ and M- ions

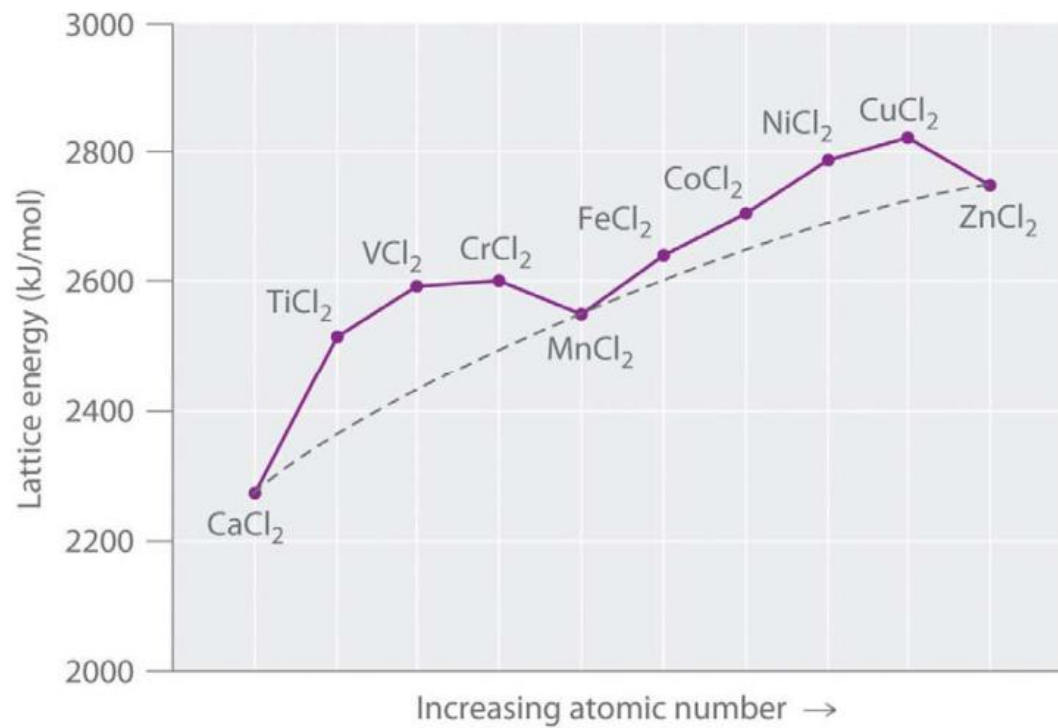
$\epsilon_o$  = permittivity of free space

$r_o$  = distance to the closest ion

n = Born exponent (a number between 5 and 12)

Experimentally determined using the Born- Haber cycle





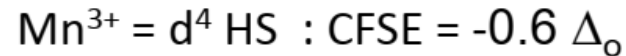
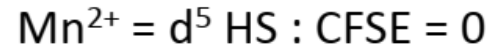
- According to the Born –Lande Equation one can expect a smooth increase in lattice energies as we go from left to right due to decrease in ionic radius of the metal ions
- As anticipated a smooth curve is not seen: instead a double hump shaped curve is obtained
- $\text{Ca}^{2+}$  ( $d^0$ ),  $\text{Mn}^{2+}$  ( $d^5$  HS) and  $\text{Zn}^{2+}$  ( $d^{10}$ ) which in common have CFSE = 0 lie almost on the expected line.
- Ions such as  $\text{V}^{2+}$  which show high CFSE in a weak field situation with high lattice energy values show significant deviation from the calculated lattice energies

# Site Preference for Spinel and Inverse Spinel

Question: **Why does some  $AB_2O_4$  compounds having transition elements as A and /or B prefer the inverse Spinel structure and some others normal Spinel structure?**



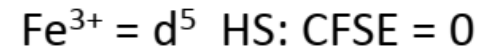
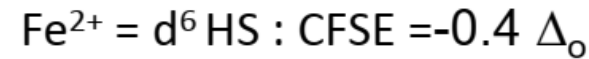
$O^{2-}$  = a weak field ligand



$Mn^{2+}$  by exchanging positions with  $Mn^{3+}$  in an octahedral hole is **not going to gain** any extra crystal field stabilization energy.

While  $Mn^{3+}$  by being in the octahedral hole will have CFSE.

Therefore  $Mn_3O_4$  will be **Normal Spinel**



$Fe^{2+}$  by exchanging positions with  $Fe^{3+}$  to an octahedral hole is going to gain extra crystal field stabilization energy. While  $Fe^{3+}$  by being in the octahedral hole will not have any CFSE. Therefore  $Fe_3O_4$  will be **Inverse Spinel**

- **Based on CFSE values, it is possible to predict the type of compounds having the formula  $AB_2O_4$  whether it belongs to normal spinels or Inverse Spinel**

## Merits of crystal Field Theory

- Predict most favorable geometry of a complex
- Accounts for four coordinated complexes (tetrahedral and square planar)
- Explains the ligands forming outer / inner orbital complexes (high spin / low spin)
- Interprets magnetic properties taking in to consideration the orbital contributions also
- Interprets color of transition metal complexes
- Explains spectral properties of many transition metal complexes
- Predict site selection in spinel and antispinel structures

## Limitations of CFT

- CFT considers only the metal ion d-orbitals and gives no consideration at all to other metal orbitals such as s-, p-orbitals and the ligand  $\pi$ -orbitals. Therefore, to explain all the properties of the complexes dependent on the  $\pi$ -ligand orbitals will be outside the scope of CFT. This does not consider the formation of  **$\pi$ -bonding in complexes**.
- Less accurate when **covalent bonding increases or partly covalent nature of the metal-ligand bonds** (As ligand orbital and electrons become more important). Bonding strength and chemical properties cannot be explained in some complexes based on only electrostatic interactions (purely ionic) as assumed by the theory
- CFT is unable to account satisfactorily for the **relative strengths of ligands**, e.g. it gives no explanation as to why  $\text{H}_2\text{O}$  appears in the spectrochemical series as a stronger ligand than  $\text{OH}^-$

## Preparation of Complex Compounds

➤ Complexes are prepared by the following types of reactions:

➤ **Connection Reactions:**



➤ **Substitution Reactions:**



➤ **Exchange Reactions:**



➤ **Redox Reactions:**



# Properties of Complex Compounds

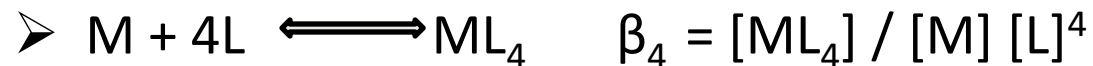
- **Dissociation of complexes:** Complexes are strong electrolytes.
- Readily dissociate to a complex ion and the counter ion – Primary dissociation



- Formed complex ion may also dissociate – weak dissociation – Secondary dissociation  $[\text{Ag}(\text{NH}_3)_2]^+ \rightleftharpoons \text{Ag}^+ + 2 \text{NH}_3$

- **Stability of complexes:** Formation constant ( $K_f$ ) describes the formation of complex ion from central metal and the ligands attached to it

- Known as stability constant or association constant.



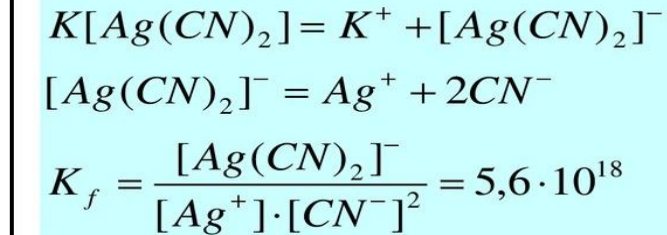
- Stepwise stability constant ( $K_n$ ) and overall stability constant ( $\beta_n$ ) are therefore related as follows.  $\beta_n = K_1 K_2 K_3 K_4 \dots K_n$

- Dissociation constant is the reciprocal of formation constant

# Stability of Complex Compounds

- **Formation constant ( $K_f$ )** describes the formation of complex ion from central metal and the ligands attached to it. Known as stability constant or association constant
- $K_f$  can be explained simply as given below, where M is a metal ion, L is a ligand and x and y are coefficients.
- **Larger the  $K_f$  value of a complex ion, greater the stability**

$$K_f = \frac{[M_x L_y]}{x[M^{+n}] \cdot y[L]}$$



- Experimental methods - potentiometry, voltammetric methods (polarography and anodic stripping voltammetry), pH-metry, spectrophotometric methods, and nuclear magnetic resonance spectroscopy.
- pH-metry is the most sensitive and accurate of all the methods
- **Extraction metallurgy, nuclear energy industry, analytical methods, and medical, environmental, and industrial research.**
- The above applications require stability constant values of high reliability

# Application of coordination compounds

- Coordination compounds are of great importance.
- Play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine.
  - Extraction of metal
  - Analytical chemistry
  - Biological importance
  - Medicinal application
  - Industrial application
  - Hardness estimation

## 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.



- **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.

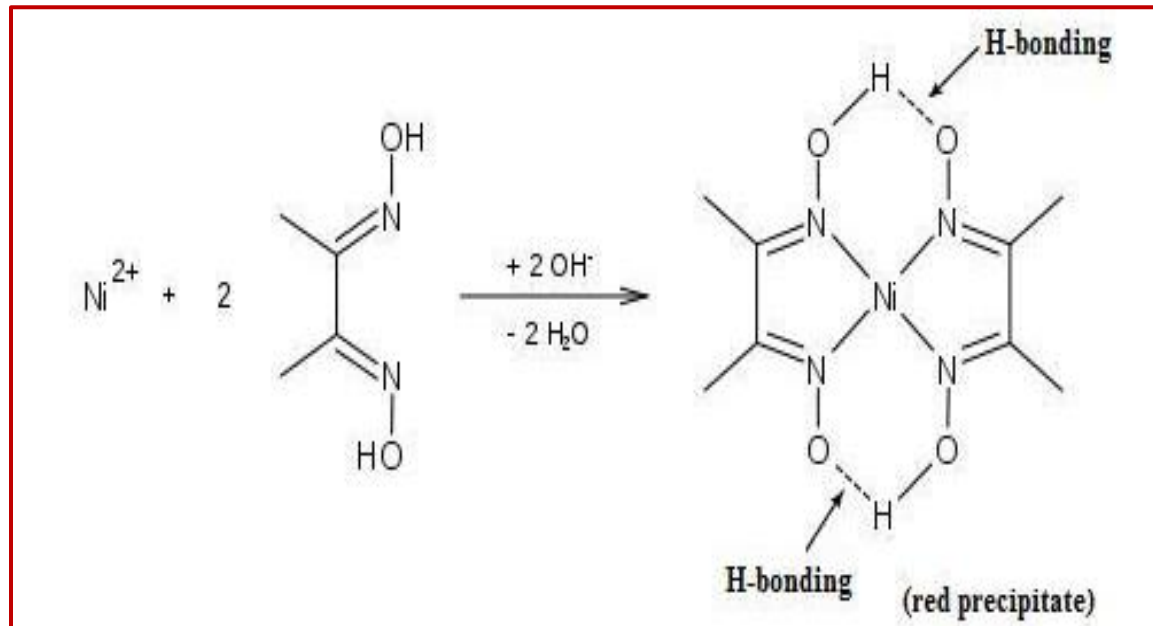
# Analytical chemistry

- 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.
  - $Cu^{2+} + 4CN^- \rightarrow [Cu(CN)_4]^{2-}$
  - $Cd^{2+} + 4CN^- \rightarrow [Cd(CN)_4]^{2-}$
- Presence of **Co and Fe can be detected by the formation of blue and blood red color thiocyanate complexes respectively**



# Detection of Complex formation

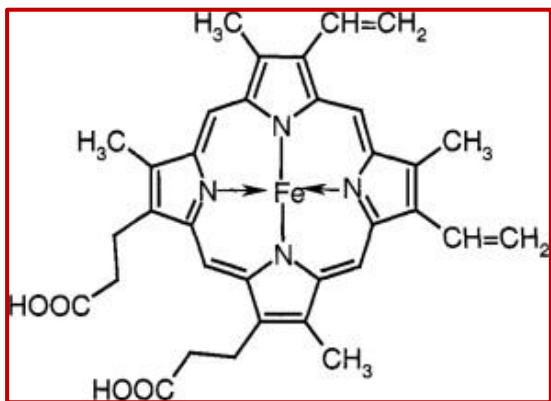
- Formation of Precipitate



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

## 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.

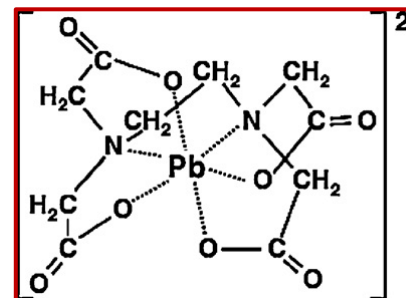


**Heme B:** Heme B is a porphyrin (four linked pyrrole rings) that readily binds iron, as shown. This is an example of a biomolecule that contains non-protein ligands for a transition metal.

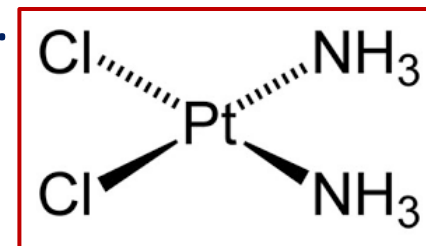
## Medicinal Application

- 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.

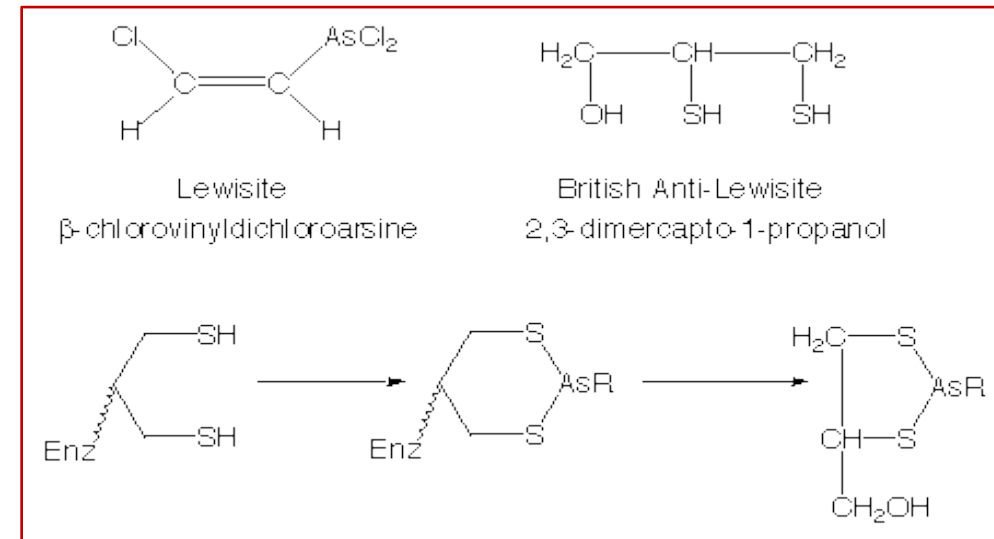
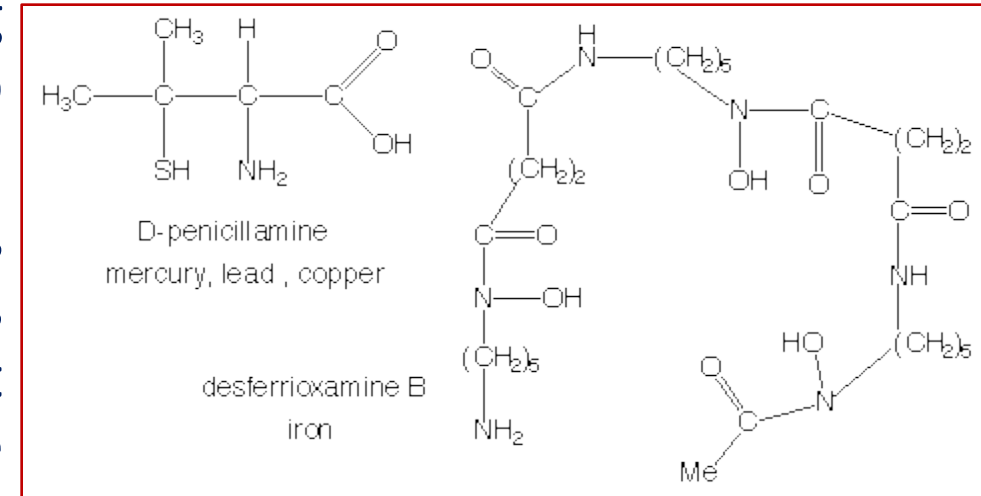


- Coordination compound of platinum effectively inhibit the growth of tumours.  
**cisplatin** - **cis**  $[PtCl_2(NH_3)_2]$ , and related compounds.



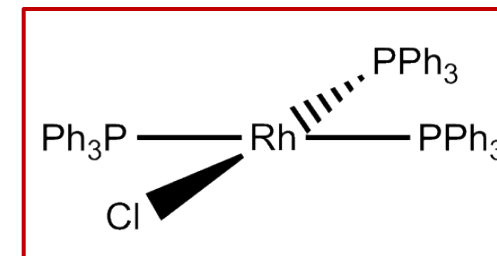
## Chelation therapy

- 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.
- First World War - poisonous gases used in the war was  $\beta$ -chlorovinyl dichloroarsine (Lewisite).
- Reacts with the SH groups of various important enzymes
- **British Anti-Lewisite (BAL)**, 2,3-dimercaptopropanol, forms stronger complex with arsenic – acts as an antidote.



## 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)



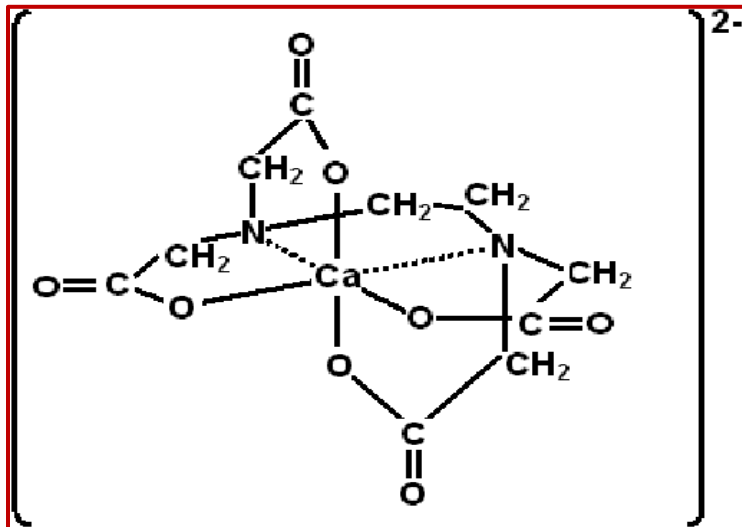
### History of Prussian blue:

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.



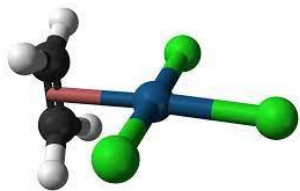
## Hardness of water

- 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.



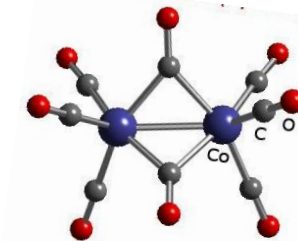
**Organometallics** – Introduction, stability, structure and applications of metal carbonyls, ferrocene and Grignard reagent

# Organometallic Chemistry



Zeise's Salt

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



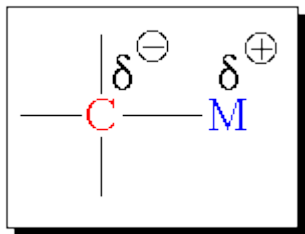
dicobalt (0) octacarbonyl

## ❖ What is organometallic compounds?

*Edward Frankland coined the term "Organometallic"*

- The designation "**Organometallic**" generally denotes compounds in which organic groups are linked directly to the metal through at least one carbon atom.
- Metal hydrides are often included, H being considered as the "**smallest organic group**"
- Therefore:
  - $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ,  $\text{Ca}\{\text{N}(\text{CH}_3)_2\}_2$  and  $\text{Fe}(\text{SC}_5\text{H}_{11})_3$  are not considered as organometallic
  - However,  $\text{C}_6\text{H}_5\text{Ti}(\text{OC}_4\text{H}_9)_3$ , and  $(\text{C}_5\text{H}_5)_2\text{Zr}(\text{OOCCH}_3)_2$  would be organometallic
- As in many other areas of chemistry, there are some obvious exceptions to this simple definition of organometallic compounds; for example, in spite of species like  $\text{CaC}_2$ ,  $\text{Hg}(\text{CNO})_2$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$  having metal-carbon bonds, these are not considered organometallic compounds for traditional or/and some other obvious reasons!

# What all compounds are considered as Organometallic?



C always 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.
- ❖ It is also understood that the element to which carbon is bound is **more electropositive than carbon** in organometallic chemistry.
- ❖ Traditional chemists do not agree for classifying **metal cyanide complexes** as organometallic

# History of Organometallic Compounds

1760

Cacodyl



Cacodyl (tetramethyldiarsine) was probably the first organometallic derivative isolated by Prussian military apothecary

The first transition metal organometallic compound

Zeise's Salt  $\text{K}^+[(\text{C}_2\text{H}_4)\text{PtCl}_3]^-$

1827

1900

Grignard Reagents  
 $\text{RMgX}$



Awarded Nobel Prize in 1912

1951

Ferrocene



Awarded Nobel Prize in 1973

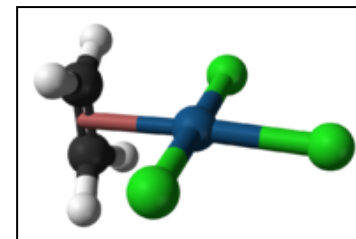
1930

Gilman Reagents  $\text{R}_2\text{Cu-Li}^+$

# Zeise's Salt- The first transition metal organometallic compound



- ❖ Discovery 1827
- ❖ Structure ~ 150 years later



W. C. Zeise, Danish  
pharmacist, **1789- 1847**

Also father of the  
chemistry of  
mercaptans R-SH



*'The breakthrough, the isolation of a pure, crystalline compound came when Zeise added potassium chloride to a concentrated PtCl<sub>4</sub> /ethyl alcohol reaction solution and evaporated the resulting solution. Beautiful lemon yellow crystals, often one half inch or more in length were isolated. On longer exposure to air and light, they gradually became covered with a black crust. They contained water of hydration, which was lost when they were kept over concentrated sulfuric acid in vacuo or when heated to around 100°C. Chemists in those days often reported how the compounds that they had prepared tasted. Zeise described the taste of this potassium salt as metallic, astringent and long lasting.'*

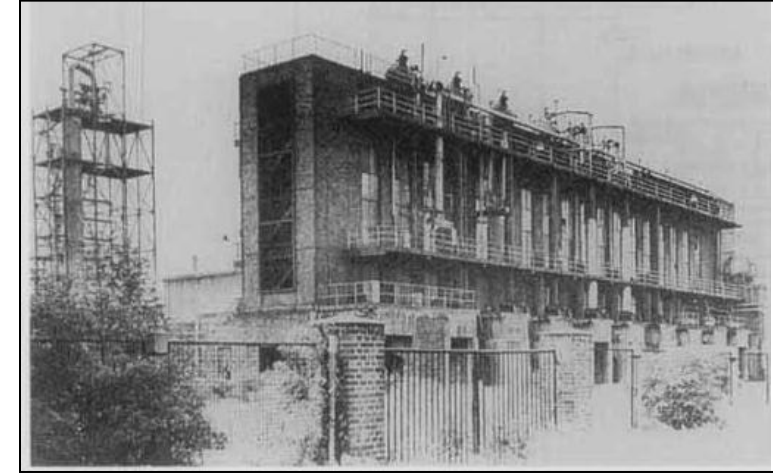
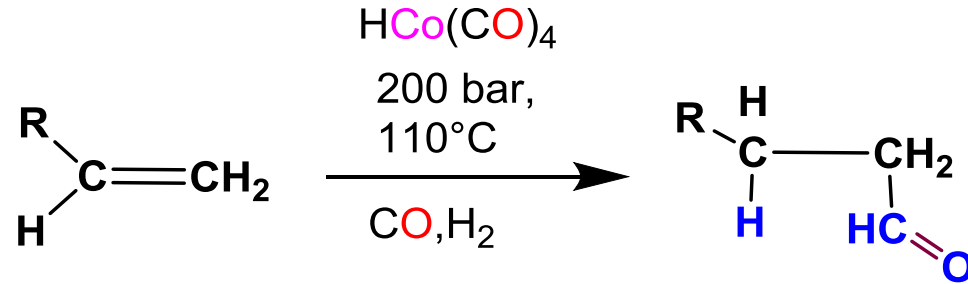
Dietmar Seyferth, *Organometallics*, 2001, 20, 2

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

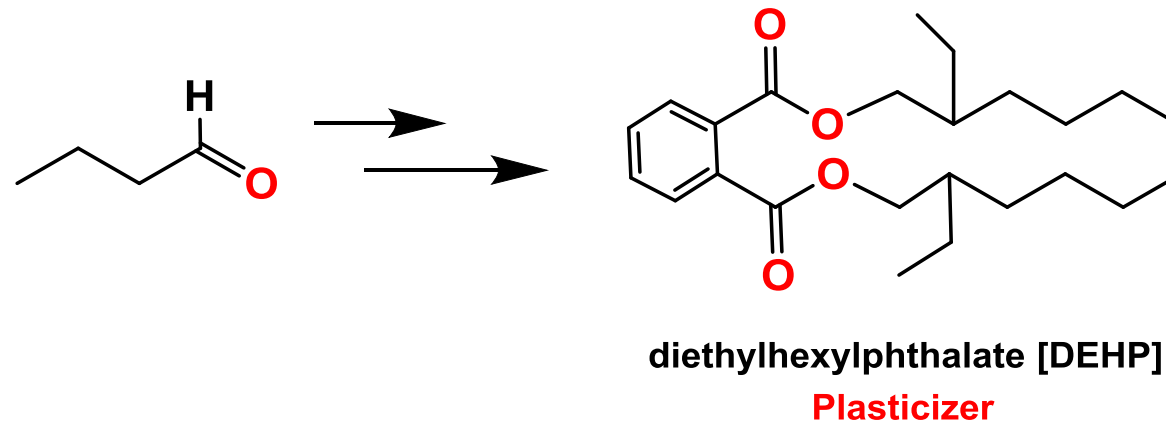


**Otto Roelen**

Pioneer in Industrial  
homogeneous catalysis  
(1897-1993)



First Industrial plant-  
**hydroformylation**



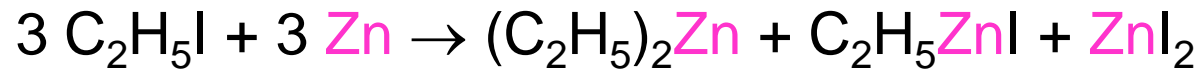
detergents

# First $\sigma$ -bonded Organometallic Compound- Diethyl zinc

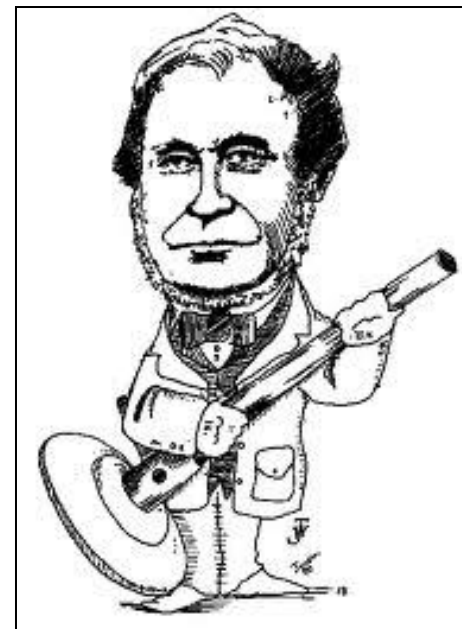
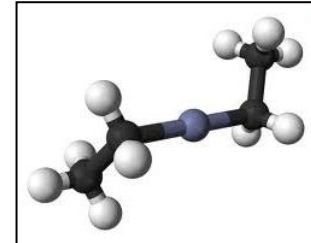


Edward Frankland  
1825-1899

*Frankland coined the term "Organometallic"*



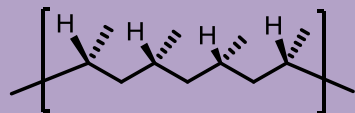
- ❖ Student of Robert Bunsen (Bunsen burner fame!). Prepared diethyl zinc while trying to make ethyl radicals.



As the early 1850s English chemist Edward Frankland described flasks exploding, throwing bright green flames across his lab, as he heroically distilled dialkylzinc compounds under an atmosphere of **hydrogen**.

# Nobel Prizes in Organometallic Chemistry

## Ziegler-Natta polymerization



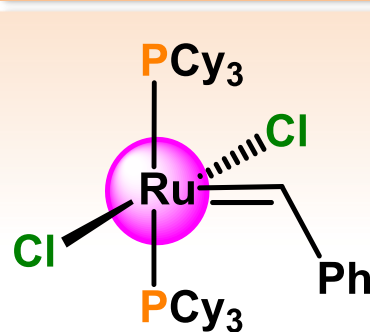
- ❖ **1963**: Zeigler and Natta
- ❖ **1973**: Wilkinson and E. O. Fischer
- ❖ **1976**: W. Lipscomb
- ❖ **1979**: Herbert Brown, G. Wittig
- ❖ **1981**: Fukui and R. Hoffman
- ❖ **2001**: Sharpless, Knowles and Noyori
- ❖ **2005**: Schrock, R. H. Grubbs, and Chauvin
- ❖ **2010**: Heck, Negishi and Suzuki



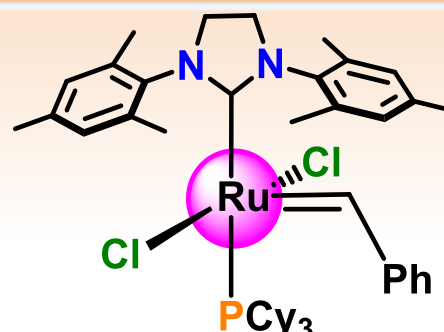
1963

## Olefin Metathesis

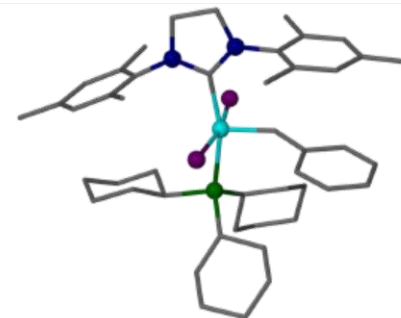
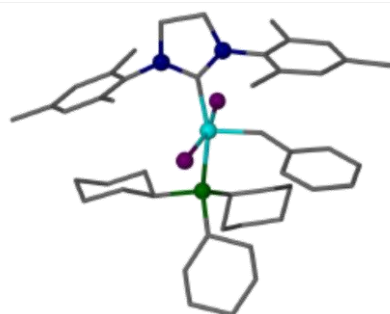
### Grubbs-Schrock-Chauvin



1st generation



2nd generation



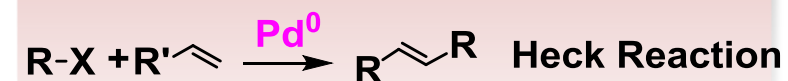
2005

## Cross Coupling

### Heck-Negishi-Suzuki

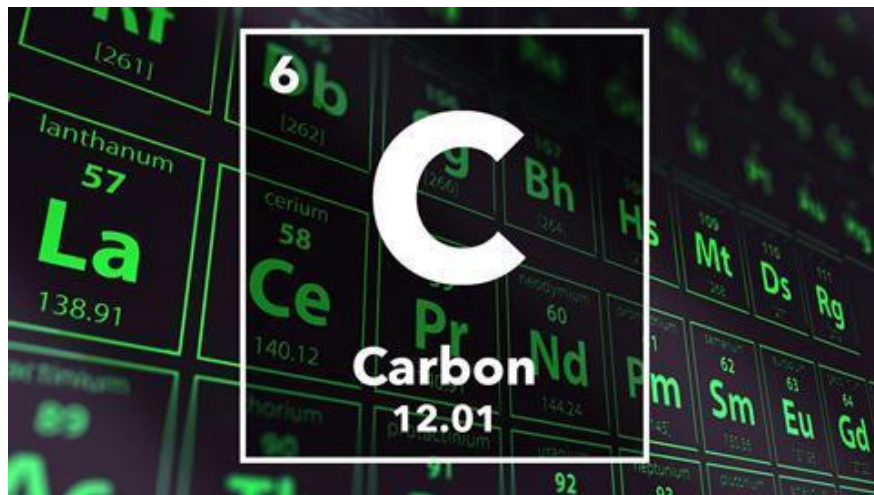


2010



# Why the subject is 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!

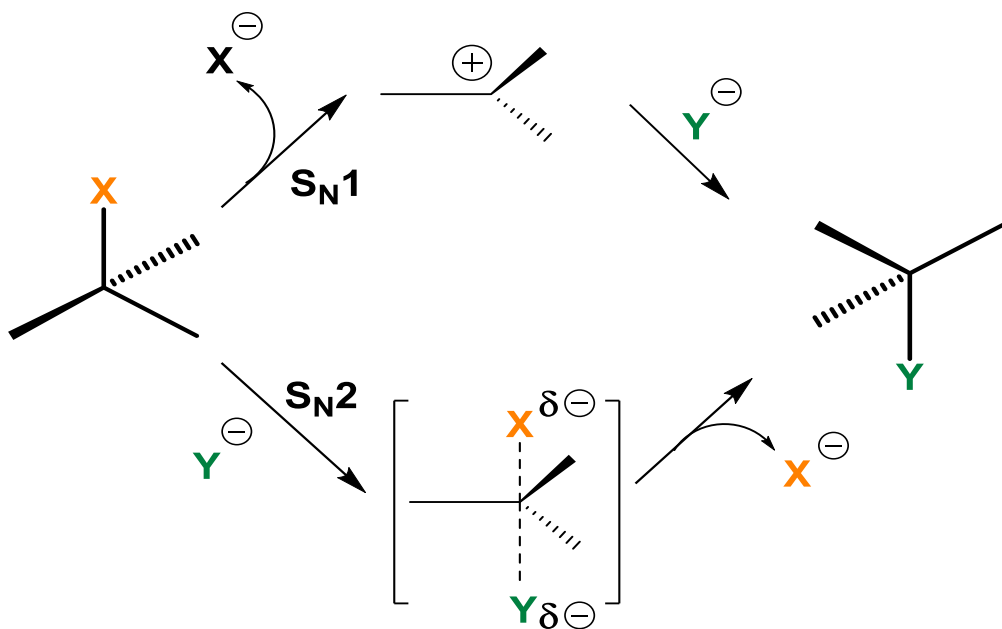


❑ Why is this special ?

- 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**

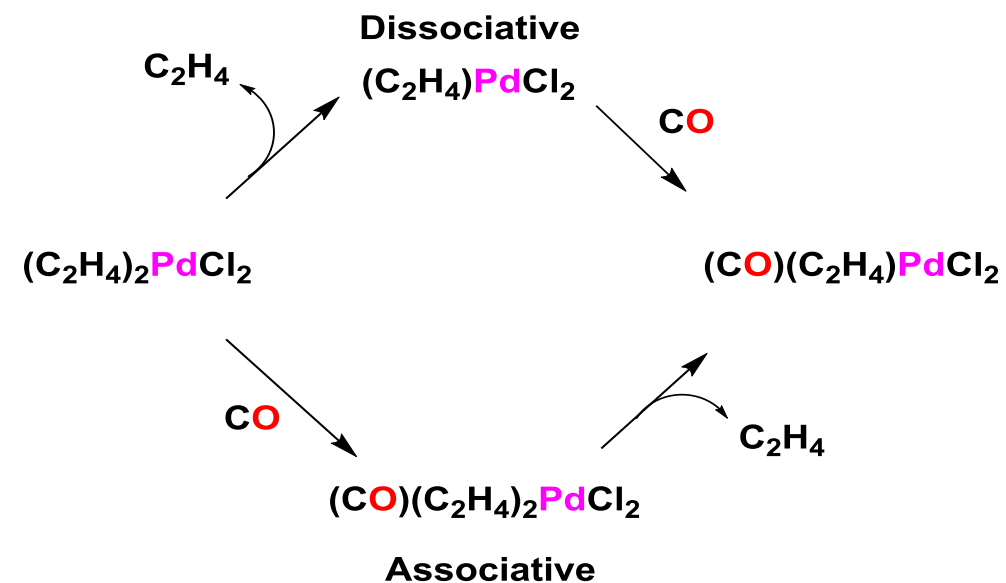
# Organic vs Organometallic reactivity

## 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 substitution at M

# General Periodic Trends of Organometallic Compounds

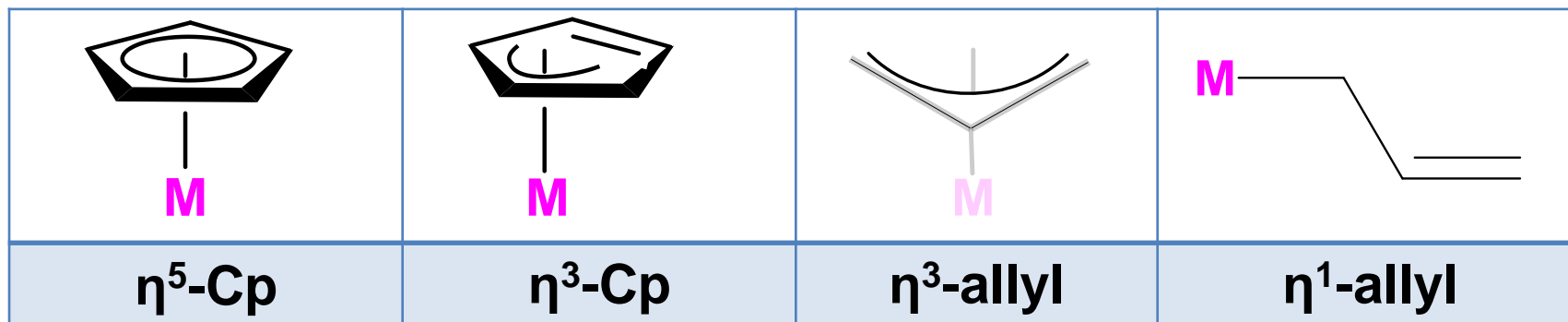
<b>Group 1</b>	Except lithium, ionic compounds
<b>Li, Be, Mg, B, Al</b>	Covalent and multi centre (e.g., $2e-3C$ ) bonds
<b>Group 2-11</b>	M-C bond : $\sigma$ -bond (e.g., B-CH <sub>3</sub> ) $\pi$ -bond ((e.g. (CO) <sub>5</sub> Cr=CH <sub>2</sub> ) $\delta$ -bond ([R <sub>4</sub> Re $\equiv$ ReR <sub>4</sub> ] <sup>2-</sup> ) $\eta$ -bond (e.g., Cp <sub>2</sub> Fe)
<b>Lanthanides</b>	M-C bond predominantly ionic
<b>Actinides</b>	M-C bond predominantly covalent
<b>Group 12-16</b>	mainly M-C $\sigma$ bonds

## 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  $x$ .





“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.

**Ordering** There is no set method of naming or ordering the listing of metal and ligands in a metal/ligand complex that most authors follow. There are IUPAC formalisms, but hardly anyone follows them. There are some qualitative rules that most authors seem to use in American Chemical Society (ACS) publications:

1) in formulas with Cp (cyclopentadienyl) ligands, the Cp usually comes first, followed by the metal center:  $\text{Cp}_2\text{TiCl}_2$

2) other anionic multi-electron donating ligands are also often listed in front of the metal

3) in formulas with hydride ligands, the hydride is sometimes listed first. Rules # 1 & 2, however, take precedence over this rule:  $\text{HRh}(\text{CO})(\text{PPh}_3)_2$  and  $\text{Cp}_2\text{TiH}_2$

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

# Stability of Organometallic Compounds

# Stability of Organometallic Compounds

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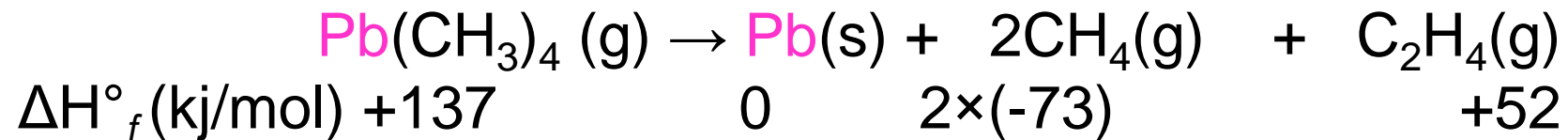
- ❖ In general terms, the stability of an organometallic compound may refer to either its thermal stability, or resistance to chemical attack (by air and moisture). Obviously, these different types of stabilities would depend both on **thermodynamic** as well as **kinetic** factors.
- ❖ Most metal alkyls and aryls,  $MR_n$ , are thermodynamically unstable to oxidation and hydrolysis and, therefore, need protection from the atmosphere during their synthesis, isolation and storage.
- ❖ There are few other examples of organometallic compounds like tetramethyllead which are thermodynamically unstable with respect to oxidation and hydrolysis, yet they survive exposure to air or/and moisture possibly because of kinetic factors.

# 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.,

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

## Stability to Oxidation

- ❖ The thermodynamic instability of organometallic compounds may be ascribed to the large value of free energies of formation of the metal oxides, carbon dioxide and water. Actually the combustion of organometallic compounds is a highly exothermic process, e.g.,



- ❖ It is worth noting that dimethylzinc is a spontaneously inflammable compound whereas tetramethyltin is air stable. The greater reactivity of dimethylzinc can be easily understood on the basis of its strong Lewis acid character. In addition to ZnMe<sub>2</sub>, the lighter alkyls of Li, Na, Be, Mg, Zn, B, Al, Ga, In, Tl, As, Sb and Bi are also spontaneously inflammable. Thus the presence of empty low-lying orbitals (e.g., 4*p* orbital of GaMe<sub>3</sub>) or a lone pair of electrons (as in SbMe<sub>3</sub>) appears to be a source for kinetic reactivity to oxidation by air. The Group IVB tetraalkyls such as SnMe<sub>4</sub> possess neither of these characteristics and, therefore, they resist oxidation at ambient temperatures.

## Stability to Hydrolysis

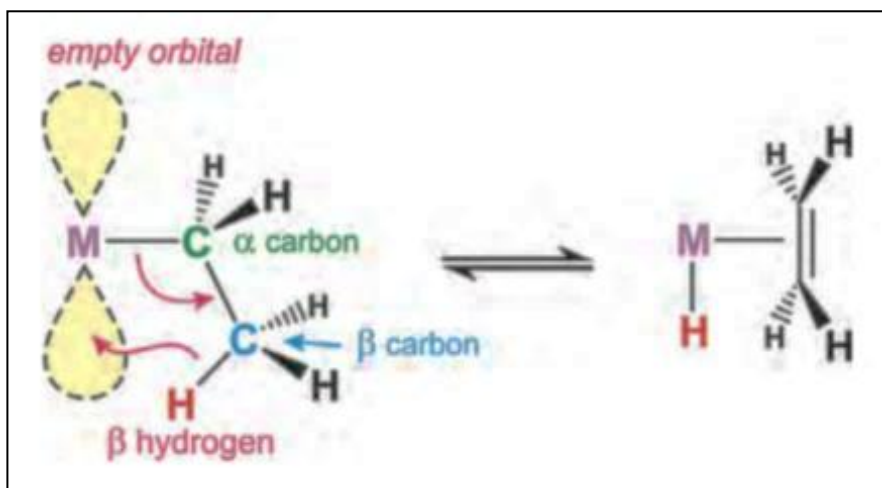
The organometallic compounds are generally hydrolysed via nucleophilic attack by water, which is facilitated by:

- (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

As a consequence of these factors, the organoderivatives of alkali and alkaline earth metals as well as of Zn, Cd, Al, Ga and In are readily hydrolyzed. By contrast, the trialkylboranes although coordinatively unsaturated (the empty 2p orbitals on the boron atom provides a site for nucleophilic attack) are unaffected by water at ambient temperatures, possibly due to comparatively very low polarity of boron-carbon bonds. The alkyls and aryls of the Group IV and V elements are also kinetically inert to hydrolysis by water.

# 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

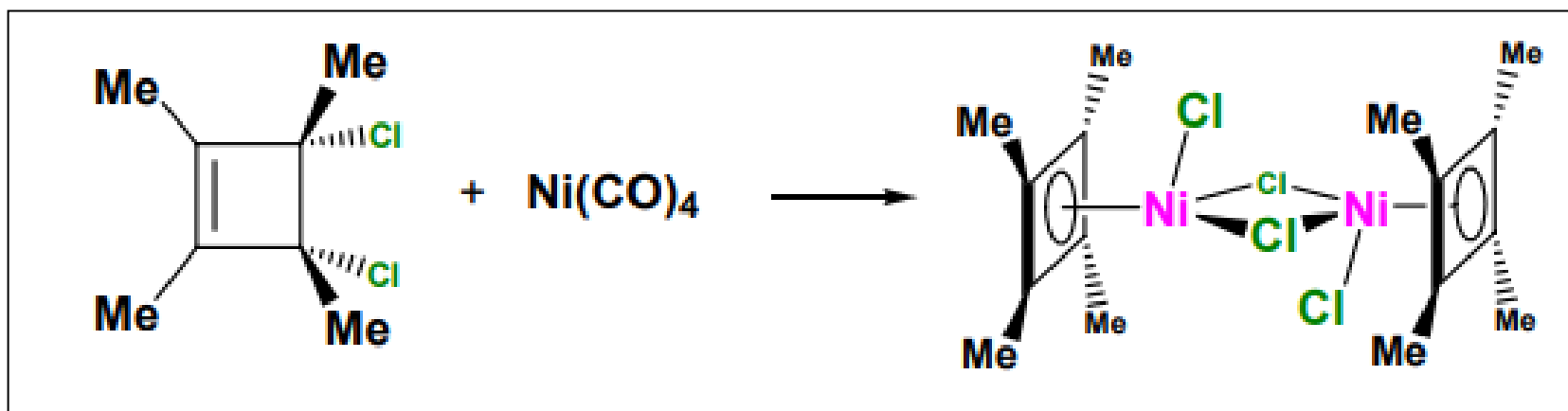


- The main driving force for  $\beta$ -hydride elimination is the formation of a stronger M-H bond (almost always stronger than M-alkyl) and the generation of an alkene ligand that reduces the unsaturation of the metal complex. The reverse reaction, however, also can occur and is called a migratory insertion.
- 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).

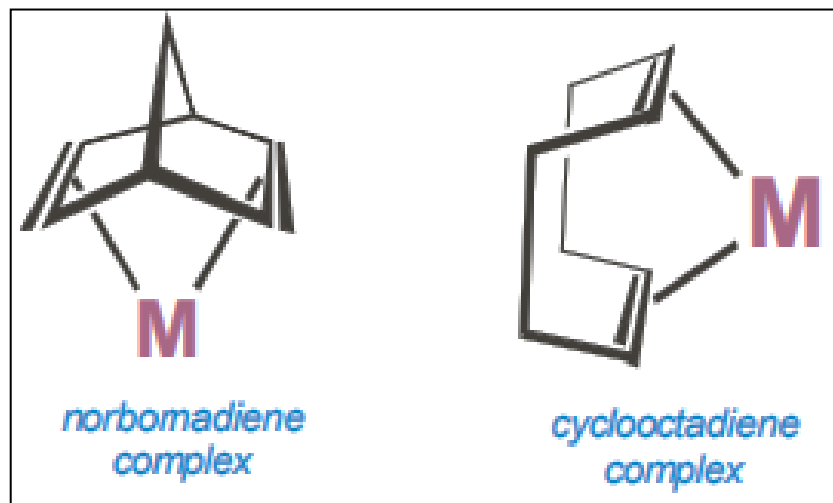
4. Metal complexes of ring-strained cycloalkenes (e.g., cyclopropene) display higher than expected stability. The ring strain raised the energy of the cycloalkene ring system making it a better donor to the metal center (better orbital energy matching). See the next section on cyclobutadiene for a particularly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



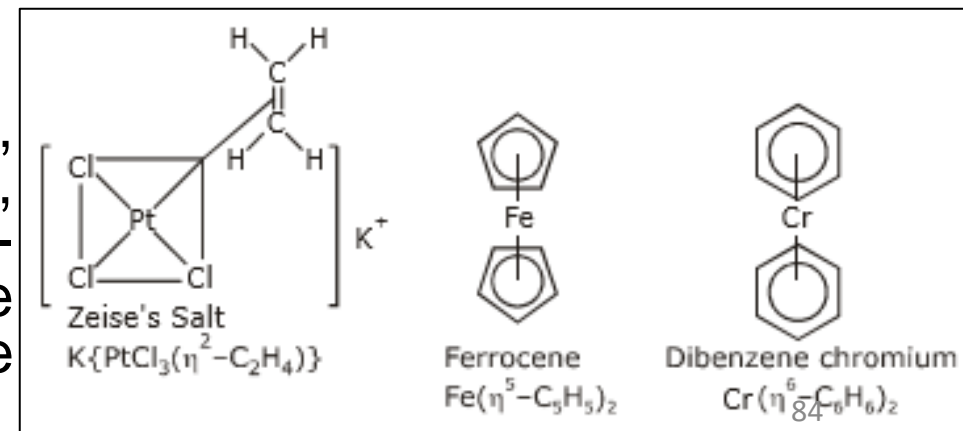
# Classification of Organometallic Compounds

❖ Organometallic compounds are classified in 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 compound are  $(CH_3)_4Sn$ ,  $(C_2H_5)_4Pb$ ,  $Al_2(CH_3)_6$ ,  $Al_2(C_2H_5)_6$ ,  $Pb(CH_3)_4$  etc.  $(CH_3)_4Sn$ ,  $(C_2H_5)_4Pb$ ,  $Al_2(CH_3)_6$ ,  $Al_2(C_2H_5)_6$ ,  $Pb(CH_3)_4$  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.

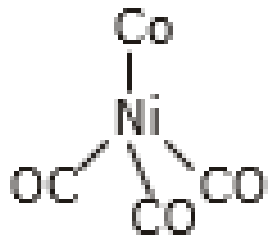
**(ii) Pi ( $\pi$ ) bonded organometallic compounds:**

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.

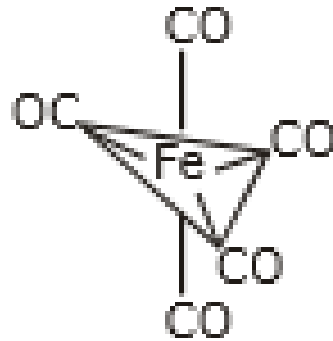


### (iii) Sigma and $\pi$ -bonded organometallic compounds

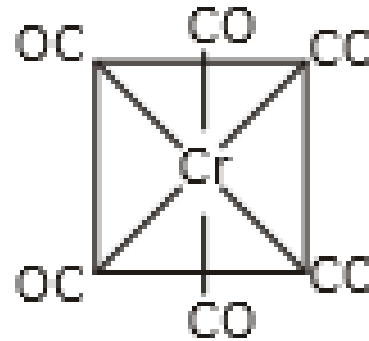
- Metal carbonyl compounds formed between metal and carbon monoxide, belong to this class. These compounds possess both  $\sigma$ -and  $\pi$ -bonding. Generally oxidation state of metal atoms in these compounds is zero. Carbonyls may be mononuclear, bridged or polynuclear.



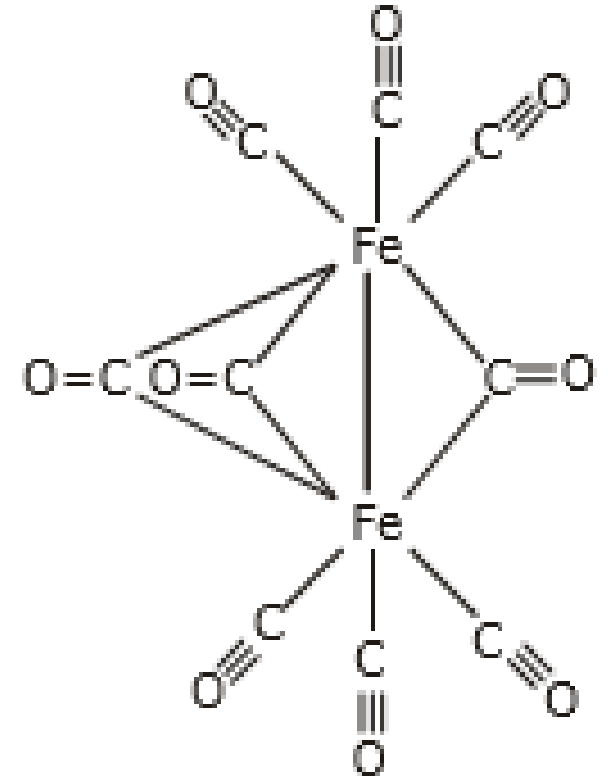
$\text{Ni}(\text{CO})_4$



$\text{Fe}(\text{CO})_5$



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



$\text{Fe}(\text{CO})_9$

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

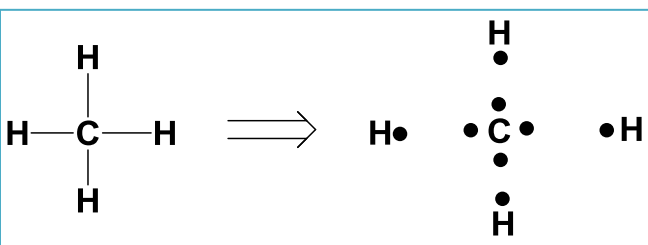
- ❖ The 18e rule is a way to help us decide whether a given d-block transition metal organometallic complex is likely to be stable. Not all the organic formulas we can write down correspond to stable species. **Recall:** Second row elements (B, C, N, O, F) have 4 valence orbitals ( $1s + 3p$ ) so they 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 formulas of coordination compounds are 'complex' – for example,  $\text{CoCl}_3 \cdot 6\text{NH}_3$ , which in Warner's term, has the primary valence satisfied by  $\text{Cl}^-$  and secondary valence satisfied by  $\text{NH}_3$ . The nature of secondary valence follows from G. N. Lewis's treatment of the coordinate covalent bond in which the ligand atom furnishes an electron pair that is shared with the central metal ion. Sidgwick argued that coordination process provided the opportunity for the transition metal ion to reach a noble gas configuration. **The effective atomic number** (EAN) of a metal ion is calculated by adding the electrons of the metal ions to those shared with it through coordination. This electron-counting scheme is also called "**eighteen-electron 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

There are two models for counting electrons. Both give the same answer, but offer different advantages and disadvantages.

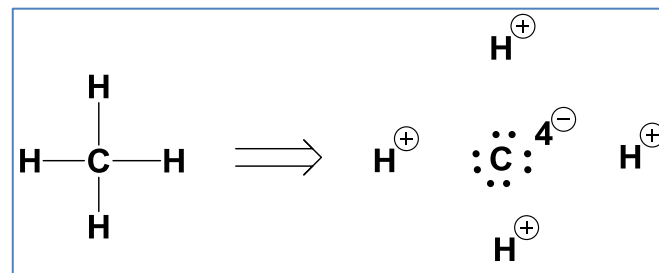
Example: CH<sub>4</sub>

❖ **Covalent model:** Since C-H bonds are covalent, assume that the electrons are shared equally between carbon and hydrogen. To count the electrons, we dissect the molecule giving each atom 1 electron of the bonding pair.



H:  $4 \times 1e = 4e$   
C:  $4e$   
Total = 8 electrons

❖ **Ionic model:** Alternatively, we can treat the bonds as being ionic. This allows us to assign a formal oxidation state to the carbon atom. This can be useful to determine whether a particular transformation is an oxidation or a reduction. In this model, both electrons are given to the atom with the higher electronegativity. For a C-H bond, this is the carbon.



H<sup>+</sup>:  $4 \times 0e = 0e$   
C (-4):  $8e$   
Total = 8 electrons

## Counting electrons for metal complex

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, and L and X are both 2 e donors. See the table below.

In my opinion, the ionic model is easier and gives a clearer picture of the actual chemistry, since the formal oxidation state is part of the calculation. All discussions in this class will use the ionic model, so I would encourage you to learn that one. You should also be aware of the covalent method, since you will encounter it from time to time!

## To determine the electron count for a metal complex

1) Determine the oxidation state of the transition metal center(s) and the metal centers resulting *d*-electron count. To do this 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)

2) Add up the electron counts for the metal center and ligands

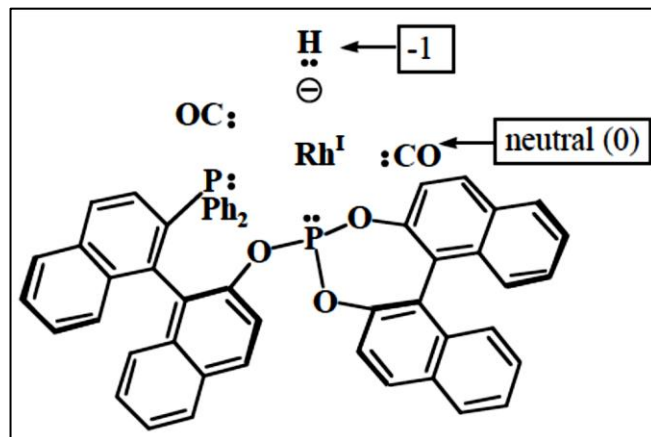
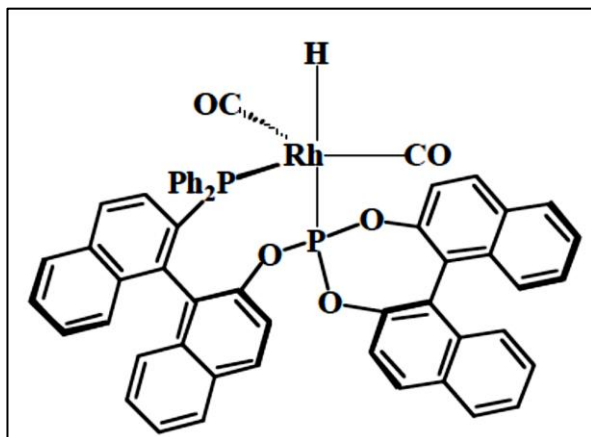
❖ **Complexes with 18 e<sup>-</sup> counts are referred to as *saturated*, because there are no empty low-lying orbitals to which another incoming ligand can coordinate. Complexes with counts lower than 18e<sup>-</sup> are called *unsaturated* and can electronically bind additional ligands.**

○ **Let's take an example and try to understand stepwise (Next page)!!**

# 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.

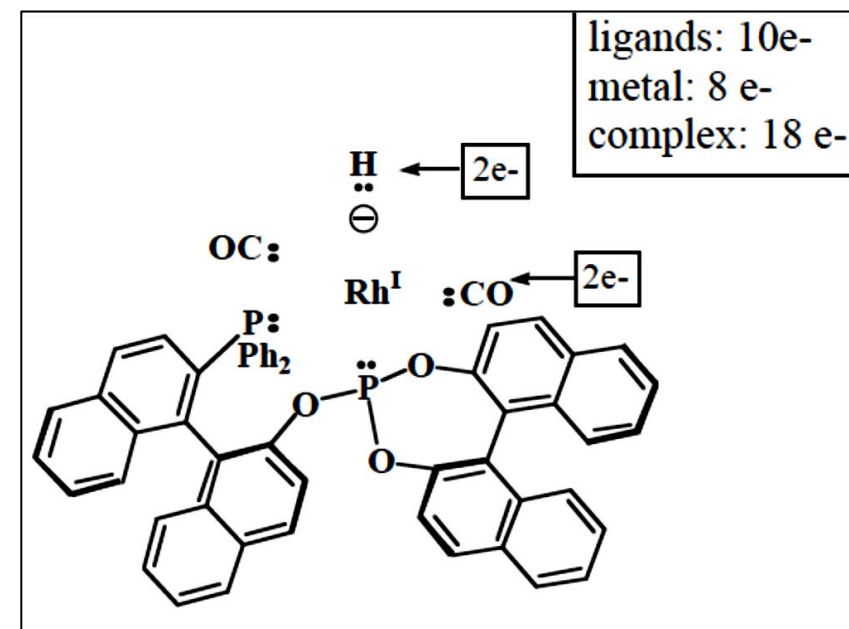
- To determine ligand charges, create an ionic model by assigning each M-L electron pair to the more electronegative atom (L). This should result in stable ligand species or ones known as reaction intermediates in solution.



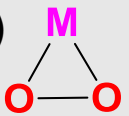
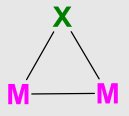

❖ **Step 2: Determine the d electron count.** Recall: subtract the metal's oxidation state from its group #.

9	
Co 3d <sup>9</sup>	
Rh 4d <sup>9</sup>	Rh <sup>I</sup> = d <sup>8</sup>
Ir 5d <sup>9</sup>	

❖ **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.



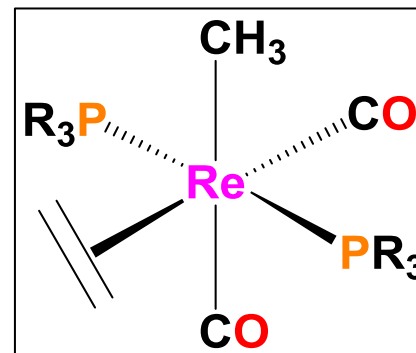
Ligand	Covalent Model	Ionic Model	
	Electron count	Charge	Electron Count
$\eta^2(\sigma)$ -Dihydrogen	2	0	2
Hydride	1	-1	2
Halide (F-, Cl-, Br-, I-) or pseudohalide (-CN, -OTs, etc)	1	-1	2
CO, CNR (bridging or terminal)	2	0	2
PR <sub>3</sub> , AsR <sub>3</sub> , SbR <sub>3</sub> , NR <sub>3</sub> , imines, nitriles, ethers, sulfides, etc.	2	0	2
Terminal dinitrogen (N <sub>2</sub> )	2	0	2
$\eta^2(\pi)$ -Alkene	2	0	2
$\eta^2(\pi)$ -Alkyne	2 or 4	0	2 or 4
$\eta^2(\pi)$ -Carbonyl	2	0	2
$\eta^6(\pi)$ -Arene	6	0	6
$\eta^1$ -Acyl	1	-1	2
$\eta^2$ -Acyl	3	-1	4
$\eta^3$ -Allyl	3	-1	4
$\eta^5$ -Cyclopentadienyl (Cp <sup>-</sup> )	5	-1	6

Ligand	Covalent Model	Ionic Model	
	Electron count	Charge	Electron Count
Imide (M=NR)	2	-2	4
Oxide (M=O)	2	-2	4
Peroxide (terminal or bridging) 	2	-2	4
Alkylidene or carbyne, terminal M≡C-R	3	-3	6
Nitride (M≡N)	3	-3	6
Nitrosyl (linear, NO+), terminal or bridging)	3	+1	2
Halide (X <sup>-</sup> ) μ-bridging 	3	-1	4 (2 to each metal)
Alkoxide, thiolate, amide, phosphide: OR <sup>-</sup> , SR <sup>-</sup> , NR <sub>2</sub> <sup>-</sup> , PR <sub>2</sub> <sup>-</sup>	1	-1	2
η <sup>4</sup> -acyclic diene 	4	0	4

## 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  $\text{Re}^I$ . I prefer the  $\text{Re}(+1)$  nomenclature because it is clearer. Most chemistry journals, however, prefer the Roman numeral notation in parenthesis after the element.



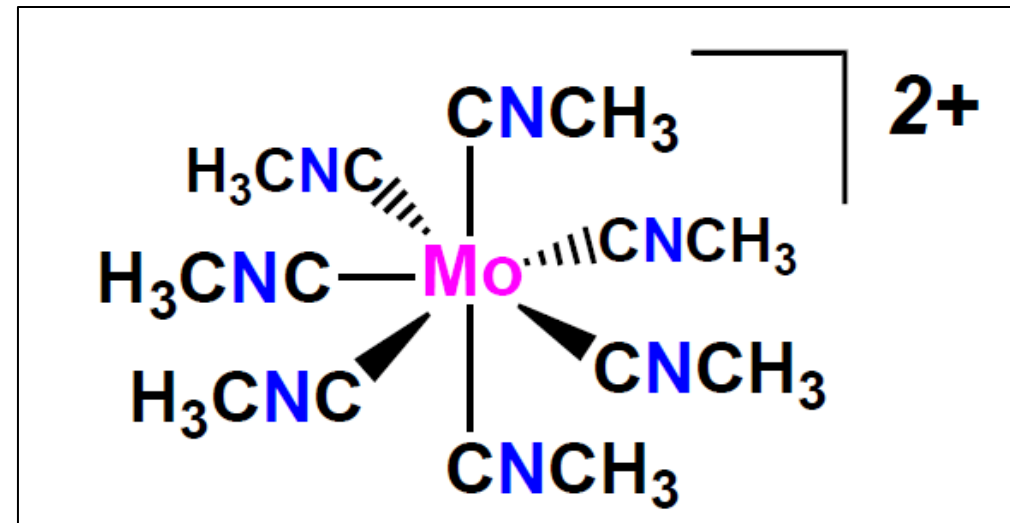
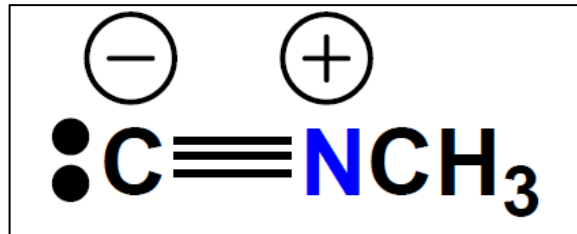
Now we can do our electron counting:

$\text{Re}(+1)$	$d^6$
2 $\text{PR}_3$	4e-
2 $\text{CO}$	4e-
$\text{CH}_3^-$	2e-
$\text{CH}_2=\text{CH}_2$	2e-
<hr/>	
<b>Total: 18e-</b>	

## Example 2

1) There is a +2 charge on the complex

2) The  $\text{CNCH}_3$  (methyl isocyanide) ligand is neutral, but let's check the Lewis Dot structure to make sure that is correct:



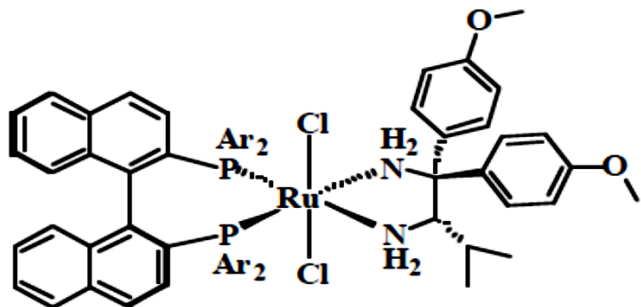
Nitrogen is normally trivalent, that is, it wants to have 3 chemical bonds to it. When it has 4 bonds, one more than usual, the nitrogen atom is assigned a formal **positive** charge. Carbon, on the other hand, is tetravalent and almost always wants 4 bonds. In isocyanides, however, we only have 3 bonds to the C. To keep an even number of electrons around the C we add an extra electron and the carbon gains a formal **negative** charge.

3) Because there is a +2 charge on the complex and there are all neutral ligands present, the Mo has a +2 charge & oxidation state.

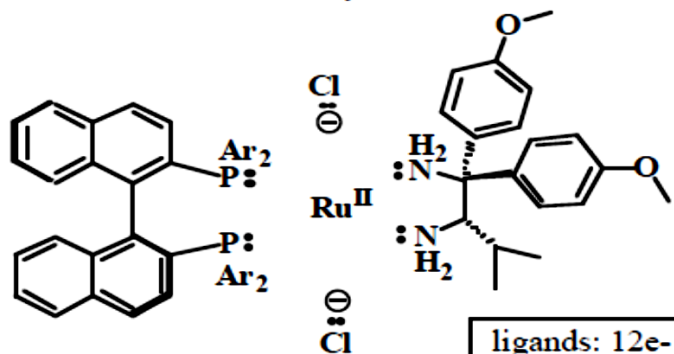
Now we can do our electron counting:

$\text{Mo}(+2)$	$d^4$
$7 \text{CNCH}_3$	$14e^-$
<hr/>	
Total: $18e^-$	

# More Examples

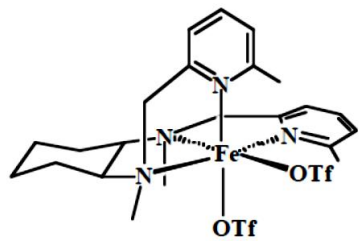


Noyori hydrogenation catalyst



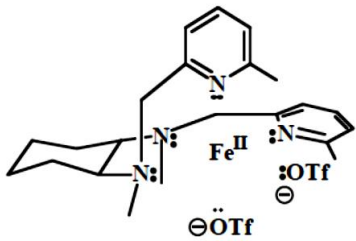
ligands: 12e-  
metal:  $d^6$ , 6e-  
complex: 18 e-

Noyori *JACS* 1998 (120) 13529.

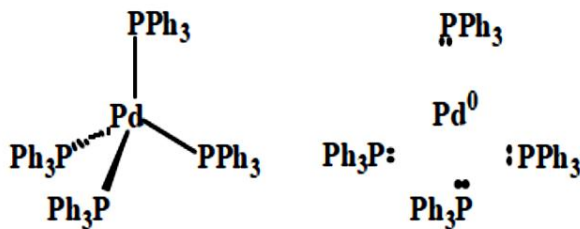


Olefin dihydroxylation catalyst

Que *JACS* 2001 (123) 6722.

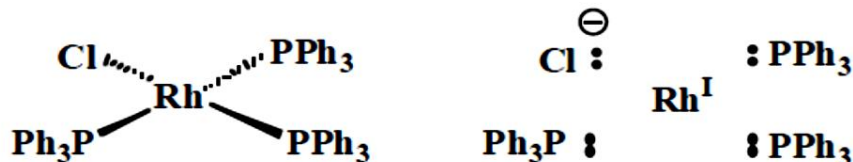


ligands: 12e-  
metal:  $d^6$ , 6e-  
complex: 18 e-



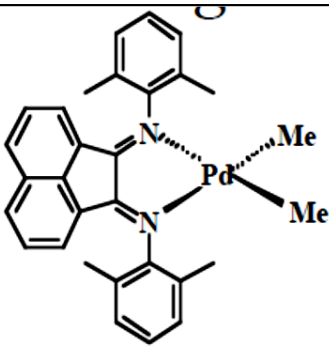
Palladium "tetrakis" triphenylphosphine cross coupling catalyst

ligands: 8e-  
metal:  $d^{10}$ , 10e-  
complex: 18 e-



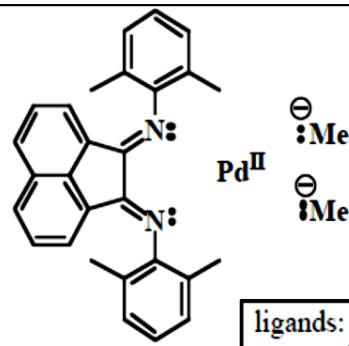
Wilkinson's catalyst  
( $\text{Ph}_3\text{P}$ ) $_3\text{RhCl}$

ligands: 8e-  
metal:  $d^8$ , 8e-  
complex: 16 e-

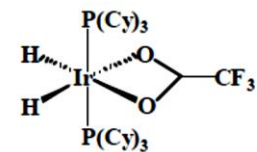


Brookhart polymerization catalyst precursor

Brookhart *JACS* 1995 (117) 6414.

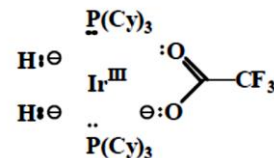


ligands: 8e-  
metal:  $d^8$ , 8e-  
complex: 16 e-

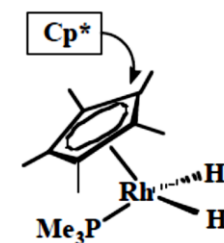


Crabtree's dehydrogenation catalyst

Crabtree *JACS* 1987 (109) 8025.

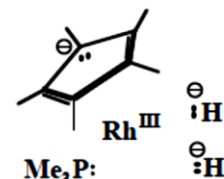


ligands: 12e-  
metal:  $d^6$ , 6e-  
complex: 18 e-

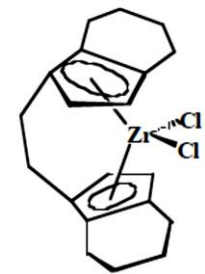


Bergman:  
direct observation  
of C-H  $\rightarrow$  C-M

Bergman *OM* 1984 (3) 508.

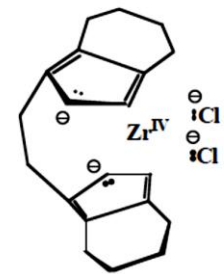


ligands: 12e-  
metal:  $d^6$ , 6e-  
complex: 18 e-

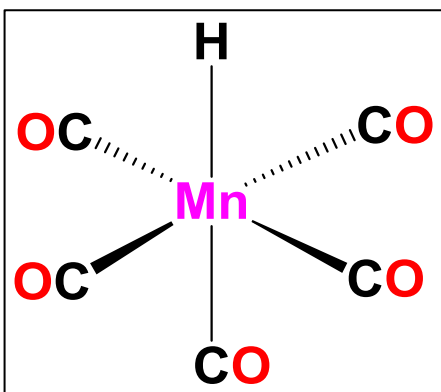


Brintzinger catalyst

Brintzinger *JOMC* 1985 (228) 63.



ligands: 16e-  
metal:  $d^0$ , 0e-  
complex: 16 e-



**Mn(+1) d<sup>6</sup>**

**5 CO**

**H<sup>-</sup>**

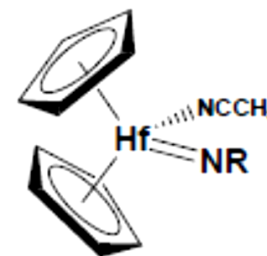
**6e<sup>-</sup>**

**10e<sup>-</sup>**

**2e<sup>-</sup>**

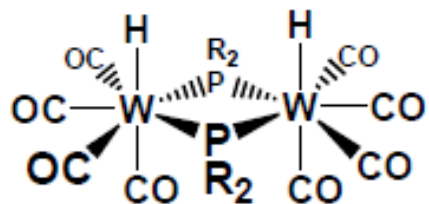
**Total: 18e<sup>-</sup>**

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



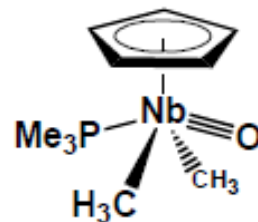
Hf(+4)	0e <sup>-</sup>
NR <sup>2-</sup>	4e <sup>-</sup>
2Cp <sup>-</sup>	12e <sup>-</sup>
NCMe	2e <sup>-</sup>
<b>Total</b>	<b>18 e<sup>-</sup></b>

a) W, μ-PR<sub>2</sub>, CO, H



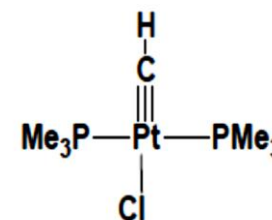
W(+2)	4e <sup>-</sup>
2μ-PR <sub>2</sub> <sup>-</sup>	4e <sup>-</sup>
H <sup>-</sup>	2e <sup>-</sup>
4CO	8e <sup>-</sup>
<b>Total</b>	<b>18 e<sup>-</sup></b>

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



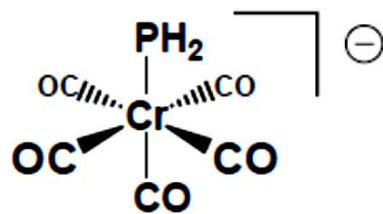
Nb(+5)	0e <sup>-</sup>
Cp <sup>-</sup>	6e <sup>-</sup>
O <sup>2-</sup>	6e <sup>-</sup>
2CH <sub>3</sub> <sup>-</sup>	4e <sup>-</sup>
PMe <sub>3</sub>	2e <sup>-</sup>
<b>Total</b>	<b>18 e<sup>-</sup></b>

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



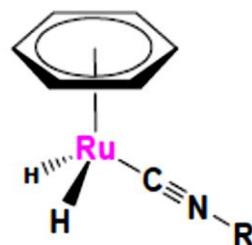
Pt(+4)	6e <sup>-</sup>
CH <sup>3-</sup>	6e <sup>-</sup>
Cl <sup>-</sup>	2e <sup>-</sup>
2PMe <sub>3</sub>	4e <sup>-</sup>
<b>Total</b>	<b>18 e<sup>-</sup></b>

a) [Cr(PH<sub>2</sub>)(CO)<sub>5</sub>]<sup>-</sup>

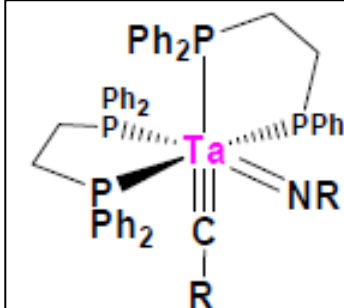


Cr(0)	6e <sup>-</sup>
PH <sub>2</sub> <sup>-</sup>	2e <sup>-</sup>
5 CO	10e <sup>-</sup>
<b>Total</b>	<b>18 e<sup>-</sup></b>

d) Ru, benzene, H, C≡NMe



Ru(+2)	6e <sup>-</sup>
benzene	6e <sup>-</sup>
2H <sup>-</sup>	4e <sup>-</sup>
C≡NMe	2e <sup>-</sup>
<b>Total</b>	<b>18 e<sup>-</sup></b>



Ta(+5)	0e <sup>-</sup>
C-R <sup>3-</sup>	6e <sup>-</sup>
N-R <sup>2-</sup>	4e <sup>-</sup>
2dppe	8e <sup>-</sup>
<b>Total</b>	<b>18 e<sup>-</sup></b>

# Exceptions to the 18 electron rule

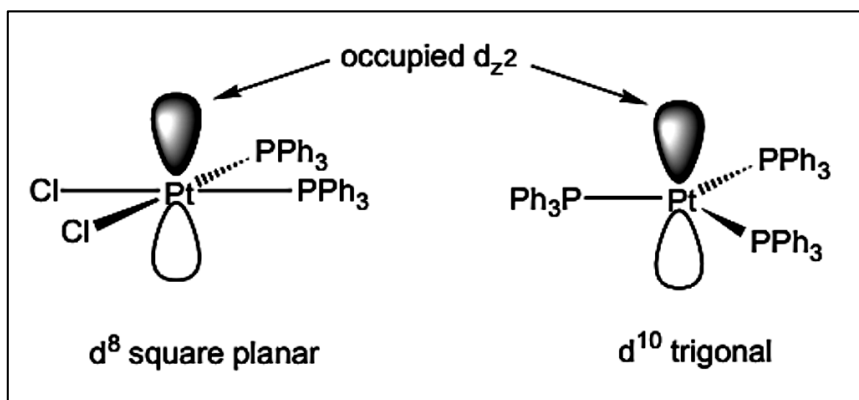
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- ❖ Square planar organometallic complexes of the late transition metals (16e).
- Some organometallic complexes of the early transition metals (e.g.  $\text{Cp}_2\text{TiCl}_2$ ,  $\text{WMe}_6$ ,  $\text{Me}_2\text{NbCl}_3$ ,  $\text{CpWCl}_3$ ) [ A possible reason for the same is that some of the orbitals of these complexes are too high in energy for effective utilization in bonding or the ligands are mostly  $\sigma$  donors
- ❖ Some high valent  $d^0$  complexes have a lower electron count than 18
- ❖ Sterically demanding bulky ligands force complexes to have less than 18 electrons
- ❖ The 18 electron rule fails when bonding of organometallic clusters of moderate to big sizes (6 Metal atoms and above) are considered
- ❖ The rule is not applicable to organometallic compounds of main group metals as well as to those of lanthanide and actinide metals

❖ There are quite a few examples of organometallics which have 16 VE. As with all chemistry, the excuse is either **electronic** or **steric** (or both).

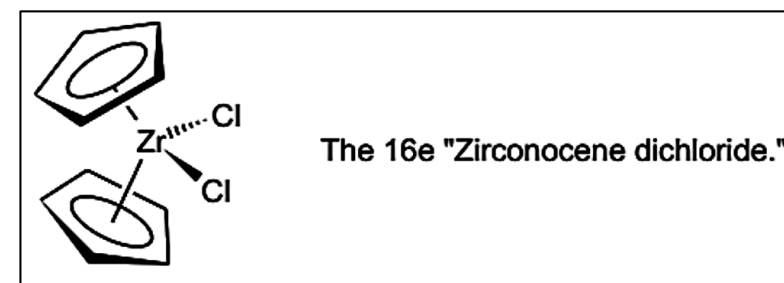
### (i) **Electronic effects**

Late transition metals with  $d^8$  electron configurations e.g. Rh(I), Ir(I), Pd(II), Pt(II) have a strong tendency to form square planar 16 VE complexes. Similarly,  $d^{10}$  complexes tend to form trigonal 16 VE complexes. As the atomic number  $Z$  increases, the  $d$ -shell is stabilized (lowers in energy). The occupied  $d_{z^2}$  orbital (perpendicular to the plane) is no longer involved in ligand bonding.

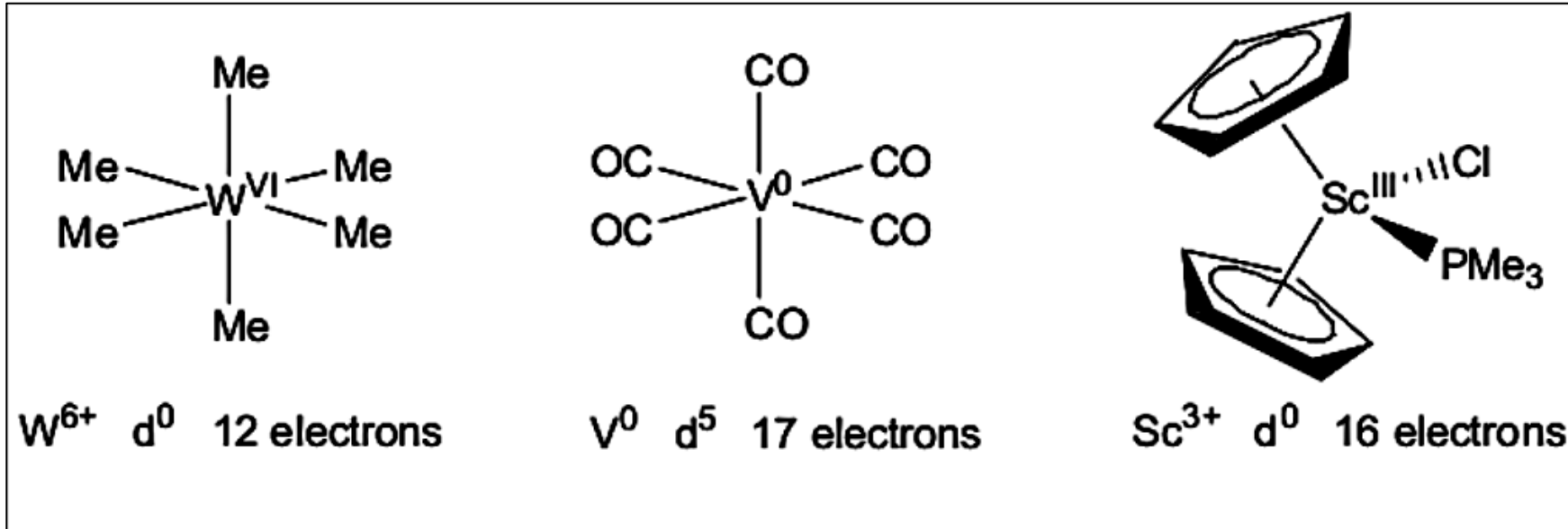


### (ii) **Steric Effects**

Early transition metals have fewer  $d$ -electrons to start with than the middle and late transition metals, so they must achieve their 18e count by coordination of a larger number of ligands. If the ligands involved are too bulky, then low-electron count complexes are formed.



- ❖ For early transition metals (e.g. with  $d^0$  metals) it is often not possible to fit the number of ligands necessary to reach 18 electrons around the metal.



# Unique reactions in organometallic chemistry

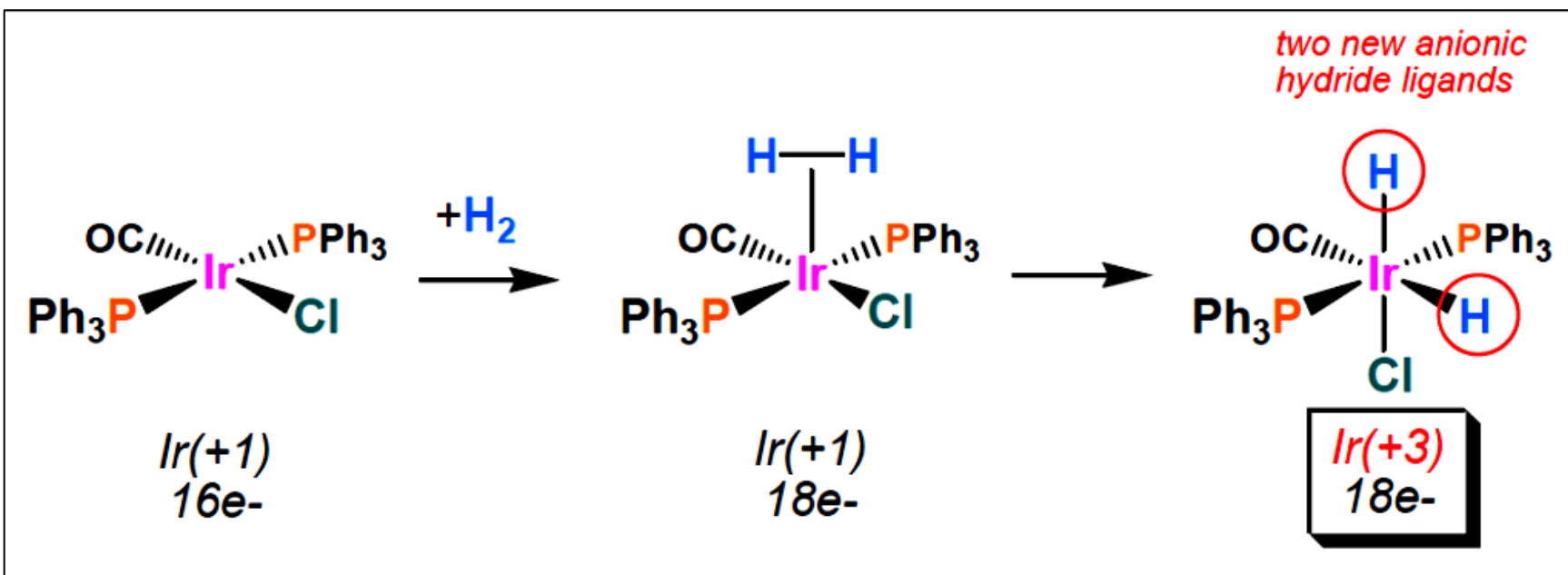
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- **Oxidative Addition**
- **Reductive Elimination**
- **Migratory Insertion**
- **Transmetallation**
- **$\beta$  - Hydride Elimination**

# Common Reactions

## ❖ Oxidative Addition

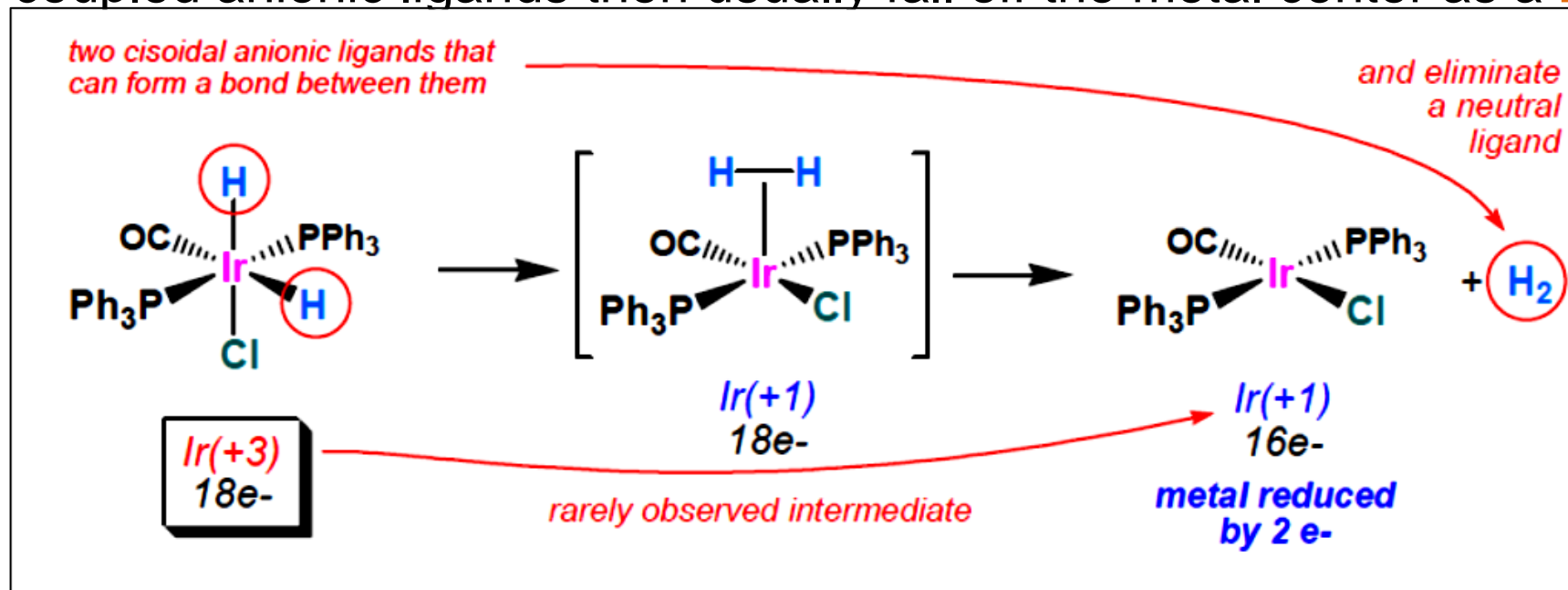
A reaction in which (usually) a neutral ligand adds to a metal center and in doing so oxidizes the metal, typically by  $2e^-$ . The transferring of the two electrons from the metal to the incoming ligand breaks a bond in that ligand forming two new anionic ligands. At least one of these new anionic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

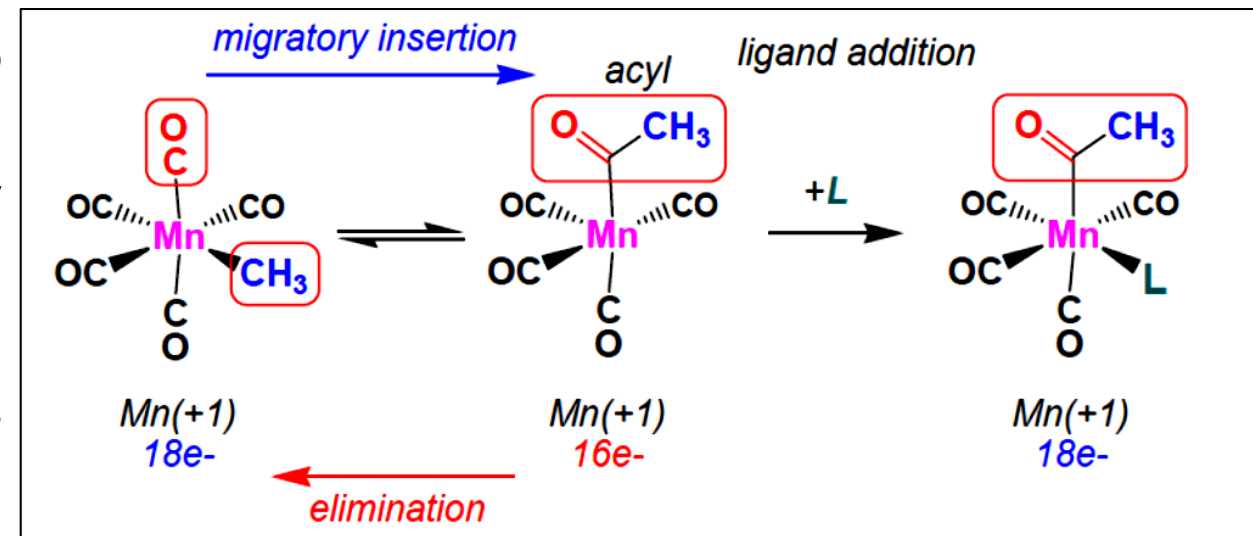
### ▪ General Features:

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

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

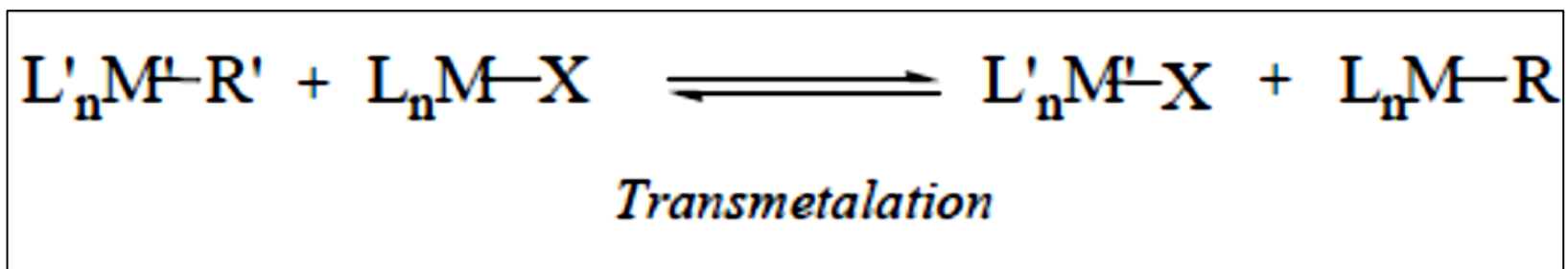
3) A vacant coordination site is generated by the migratory insertion. Therefore, a vacant site is required for the back elimination reaction (e.g.,  $\beta$ -hydride elimination). A trapping ligand is often needed to coordinate to the empty site formed from a migratory insertion in order to stop the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

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

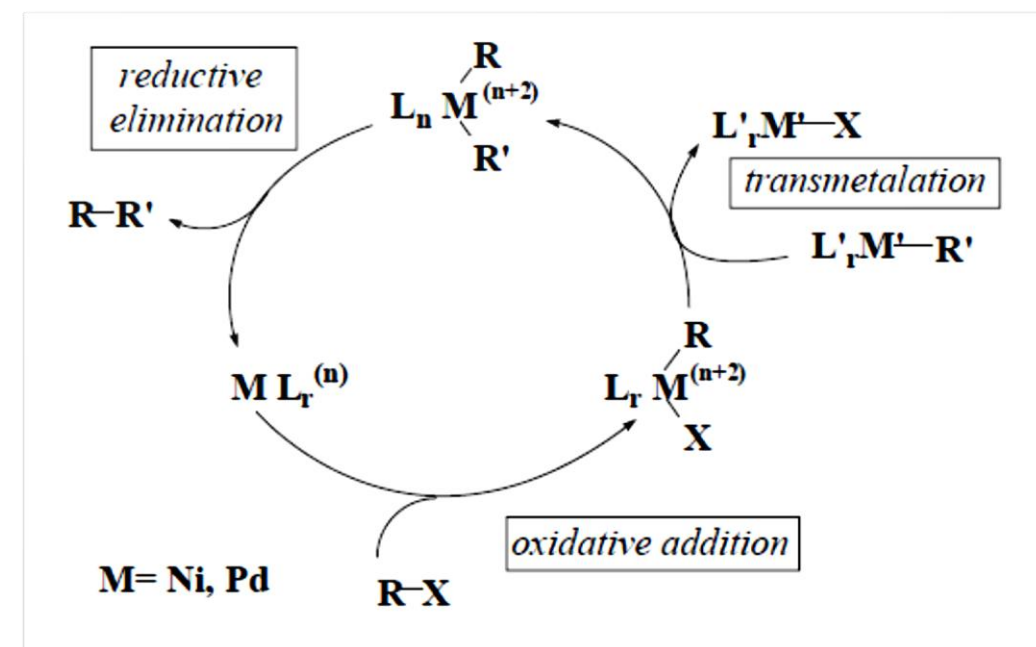


## ❖ Transmetalation

- **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.

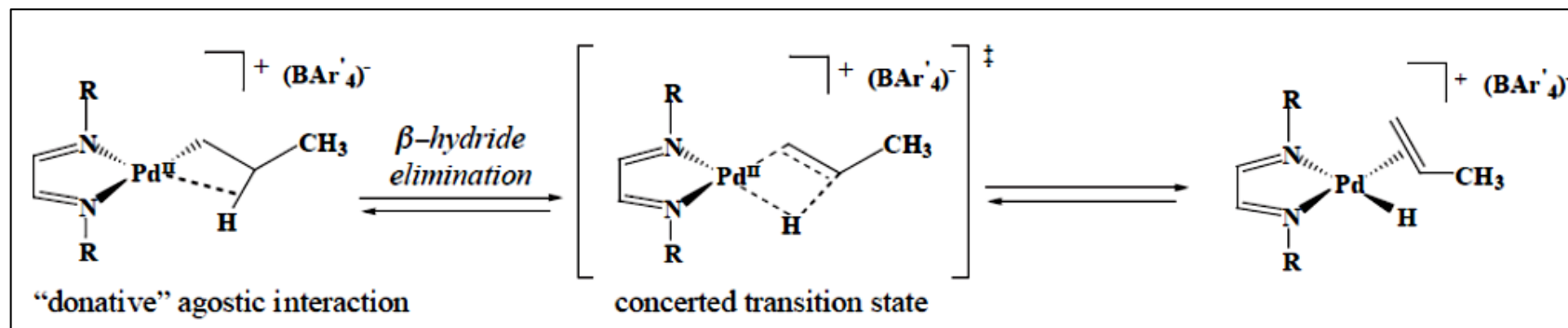


- Transmetalation is often a *reversible process*, with the equilibrium favoring the more ionic M-X bond. Subsequent reactivity of one  $L_n M-R$  species can drive the equilibrium in one direction. This is often exploited in cross-coupling reactions, where a transmetalated intermediate undergoes a reductive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

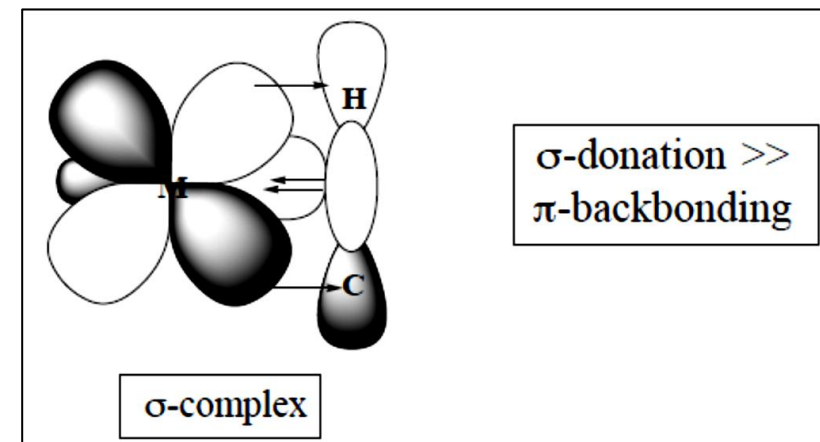


## ❖ $\beta$ -Hydride Elimination

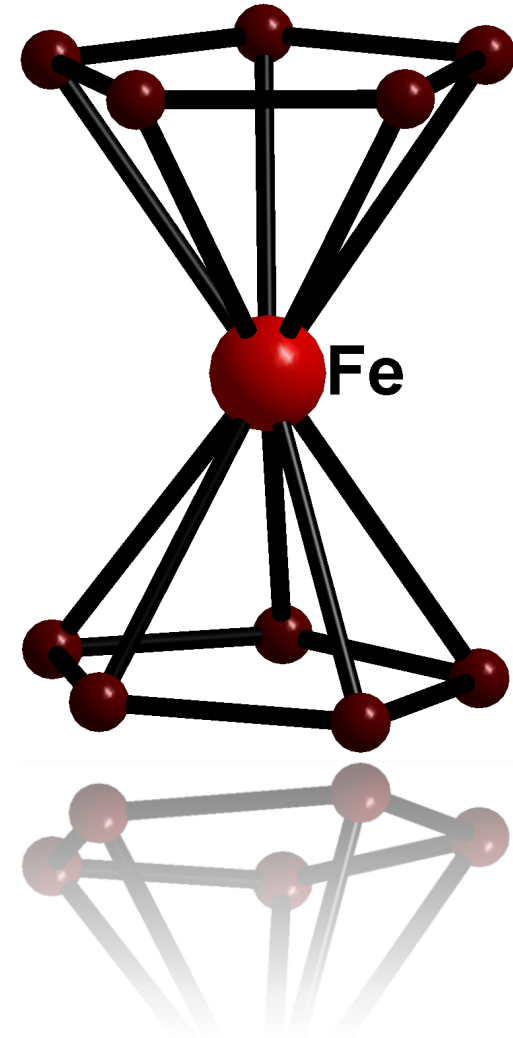
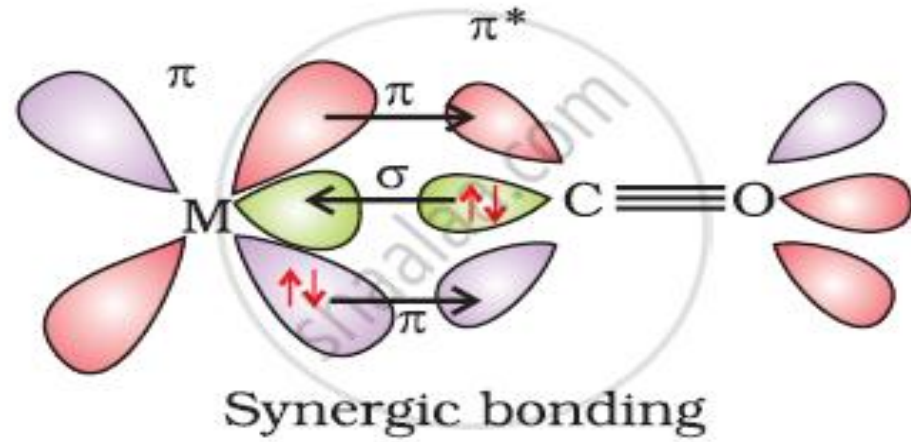
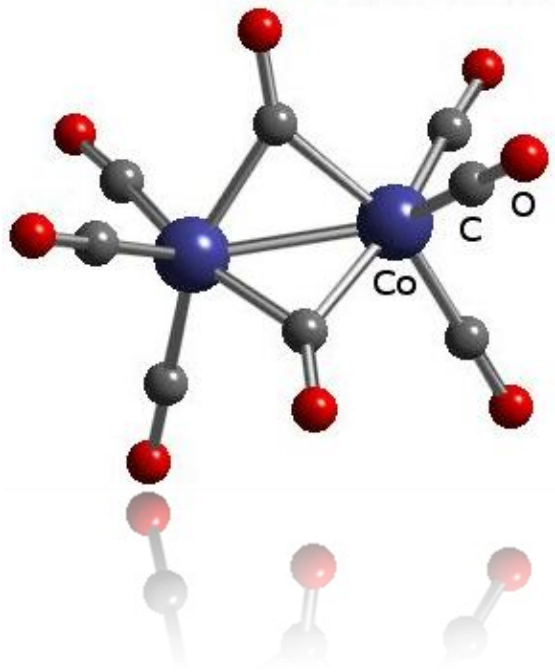
- A significant decomposition pathway for metal alkyls is  $\beta$ -hydride elimination which converts a metal alkyl into a hydrido metal alkene complex.



- **$\beta$ -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  $\gg$   $\pi$ -backbonding).

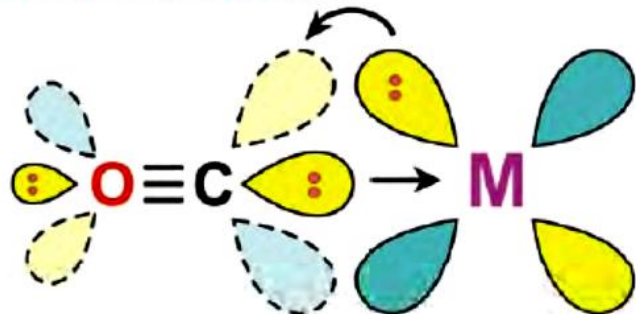


# Metal Carbonyls and Ferrocene



# Carbonyl Ligands

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



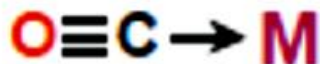
**powerful  $\pi$ -acceptor ligand!**  
**excellent ligand, therefore, for stabilizing electron-rich low-valent metal centers**

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.

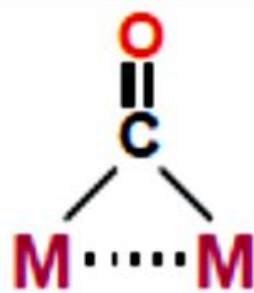
## ❖ Standard Bonding Modes



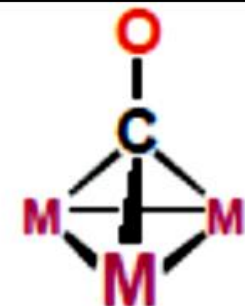
free CO



terminal mode



$\mu_2$ -bridging



$\mu_3$ -bridging

$\nu_{\text{CO}}$  IR ( $\text{cm}^{-1}$ )

2143

2120 - 1850

1850 - 1720

1730 - 1500

(for neutral metal complexes)

2e<sup>-</sup> neutral donor

2e<sup>-</sup> neutral donor

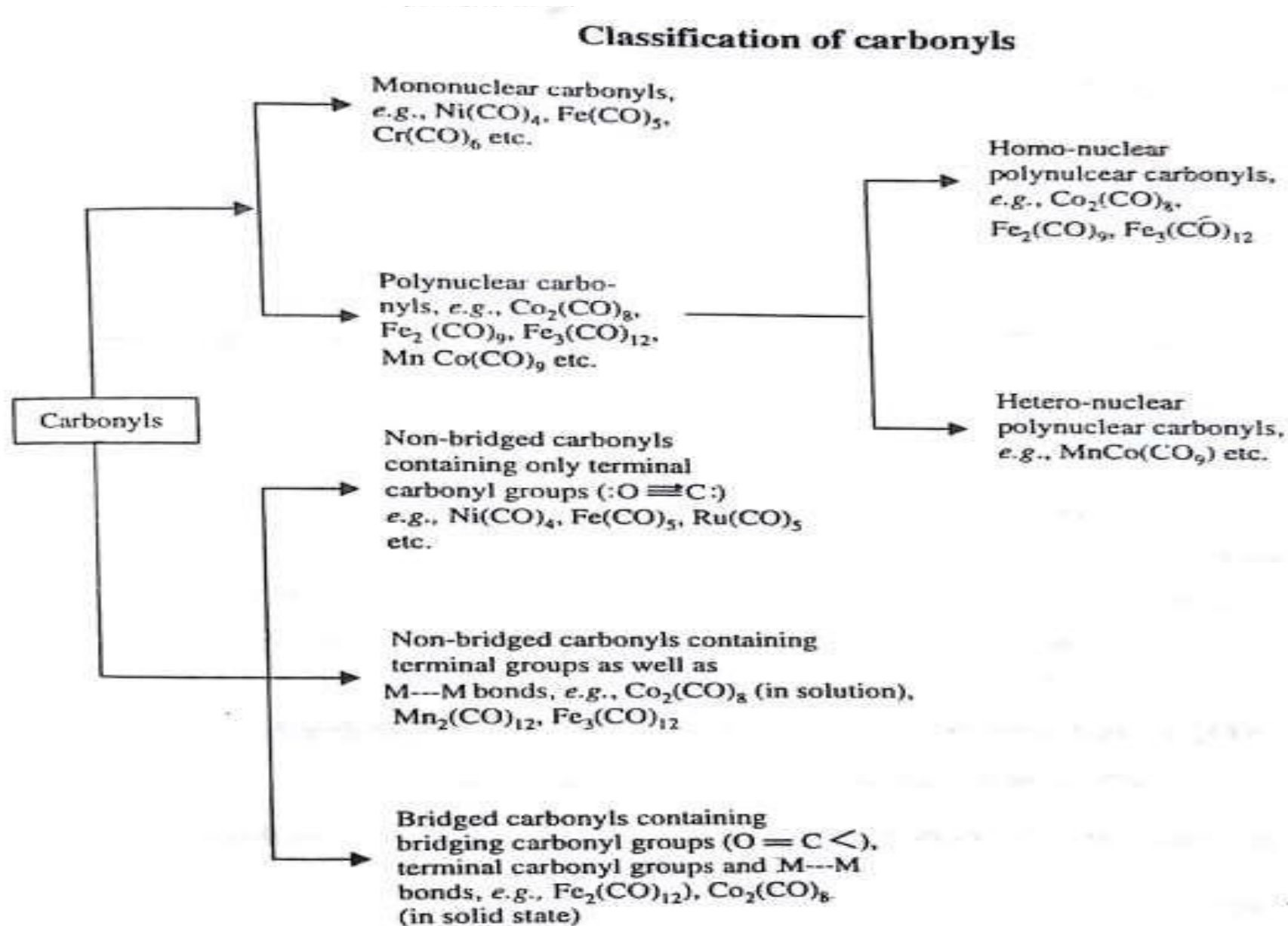
3e<sup>-</sup> neutral donor

# Introduction

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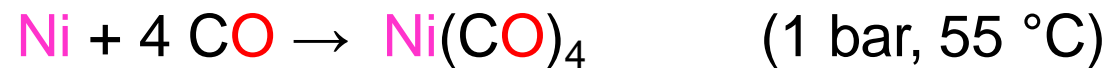
- ❖ Metal carbonyls are coordination complexes of transition metals with carbon monoxide ligands in **low oxidation state** where CO ligand acts as neutral ligands
- ❖ Metal carbonyl compounds were first synthesized in by **Paul** Schützenberger in 1868 by passing chlorine and carbon monoxide over platinum black, where **dicarbonyldichloroplatinum [Pt(CO)<sub>2</sub>Cl<sub>2</sub>]** was formed
- ❖ Although many compounds were produced, they couldn't be fully characterized until
- ❖ the development of X-ray diffraction, IR and NMR spectroscopy.
- ❖ In general, these compounds obey the “**18 electron rule.**”
- ❖ Normally **diamagnetics, Most metal carbonyls are toxic.**
- ❖ Monomerics are **colourless**, whereas polymeric are coloured.
- ❖ Poor conductors of electricity and Sublimated at low temperature.
- ❖ Soluble in organic solvents

# Classification

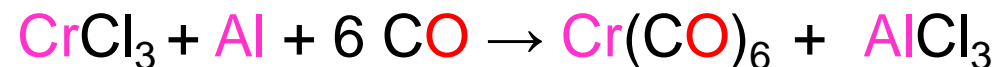


# Preparation

## ❖ Direct reaction of metal with carbon monoxide



## ❖ Reduction of metal salts and oxides



## ❖ Preparation of dinuclear carbonyls from mononuclear carbonyls (Photolysis and thermolysis)



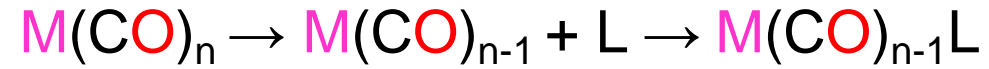
## Physical Properties of Selected Metal Carbonyls

	Color	mp °C	Sym	IR $\nu_{\text{CO}}$ $\text{cm}^{-1}$	Misc
$\text{V}(\text{CO})_6$	blue-black	70(d)	$O_h$	1976	paramagnetic, $S = 1/2$
$\text{Cr}(\text{CO})_6$	white	subl	$O_h$	2000	Cr-CO = 1.91 Å, air-stable
$\text{Mo}(\text{CO})_6$	white	subl	$O_h$	2004	Mo-CO = 2.06 Å, air-stable
$\text{W}(\text{CO})_6$	white	subl	$O_h$	1998	W-CO = 2.06 Å, air-stable in solid state.
$\text{Mn}_2(\text{CO})_{10}$	yellow	154	$D_{4d}$	2044, 2013, 1983	Mn-Mn = 2.89 Å, bond is easily broken.
$\text{Tc}_2(\text{CO})_{10}$	white	160	$D_{4d}$	2065, 2017, 1984	Tc-Tc = 3.03 Å
$\text{Re}_2(\text{CO})_{10}$	white	177	$D_{4d}$	2070, 2014, 1976	Re-Re = 3.04 Å
$\text{Fe}(\text{CO})_5$	yellow	-20	$D_{3h}$	2034, 2013	bp = 103°C, <i>toxic</i> , Fe-CO (ax) = 1.81 Å, Fe-CO (eq) = 1.83 Å, $h\nu$ produces $\text{Fe}_2(\text{CO})_9$
$\text{Fe}_2(\text{CO})_9$	gold plates	d	$D_{3h}$	2082, 2019, 1829	Fe-Fe = 2.46 Å, insoluble in most solvents except for THF where it dissociates to produce $\text{Fe}(\text{CO})_4 + \text{Fe}(\text{CO})_5$
$\text{Fe}_3(\text{CO})_{12}$	green	d	low	complex	
$\text{Ru}(\text{CO})_5$	colorless	-16	$D_{3h}$	2035, 1999	unstable, forms $\text{Ru}_3(\text{CO})_{12}$
$\text{Ru}_3(\text{CO})_{12}$	orange	150(d)	$D_{3h}$		
$\text{Os}(\text{CO})_5$	colorless	2	$D_{3h}$	2034, 1991	v. unstable, forms $\text{Os}_3(\text{CO})_{12}$
$\text{Os}_3(\text{CO})_{12}$	yellow		$D_{3h}$		
$\text{Co}_2(\text{CO})_8$	orange-red	51(d)	$D_{3d}$	2107, 2069, 2042, 2031, 2023, 1991	solid state structure has 2 $\mu$ -CO's (1886, 1857 $\text{cm}^{-1}$ ). Solution structure is unbridged. Co-Co = 2.54 Å in solid-state.
$\text{Rh}_4(\text{CO})_{12}$	red		$C_{3v}$		3 $\mu$ -CO's around one triangular $\text{Rh}_3$ face.
$\text{Ni}(\text{CO})_4$	colorless	-25	$T_d$	2057	bp 34°C, <i>highly toxic</i> , CO's quite labile, Ni-CO = 1.84 Å

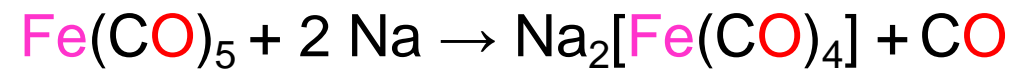
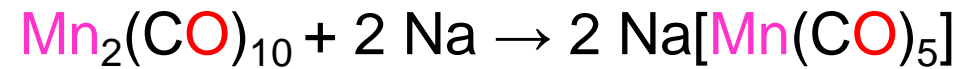
# Chemical properties

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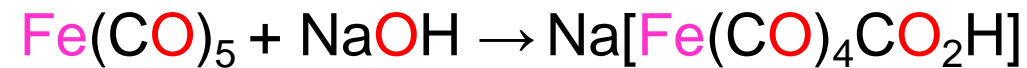
## 1. CO substitution



## 2. Reduction



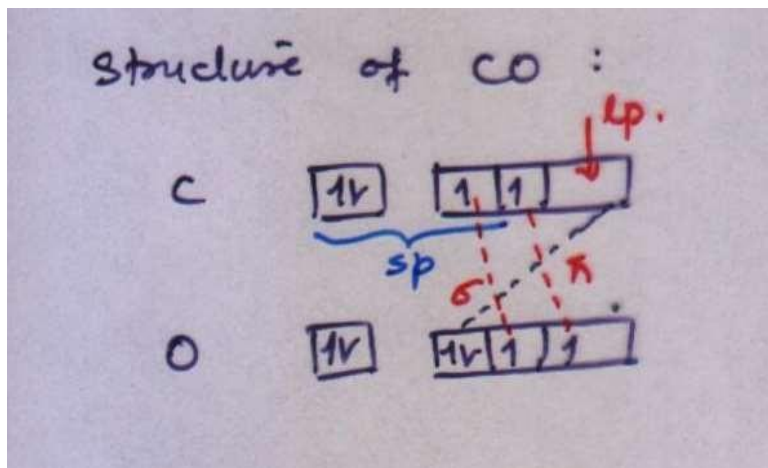
## 3. Nucleophilic attack at CO



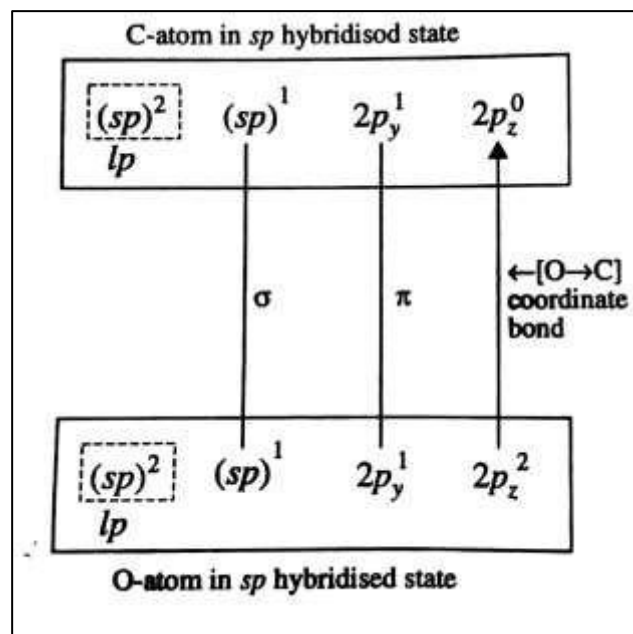
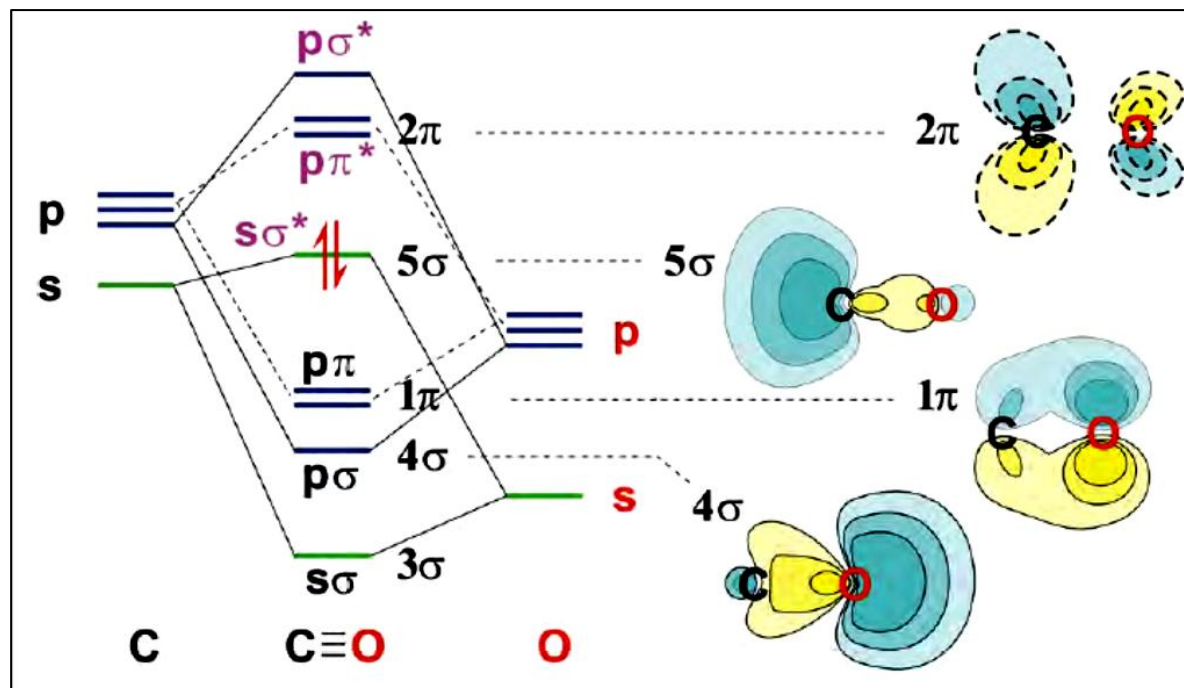
## 4. With electrophiles



# Structure of CO According to VBT & MOT

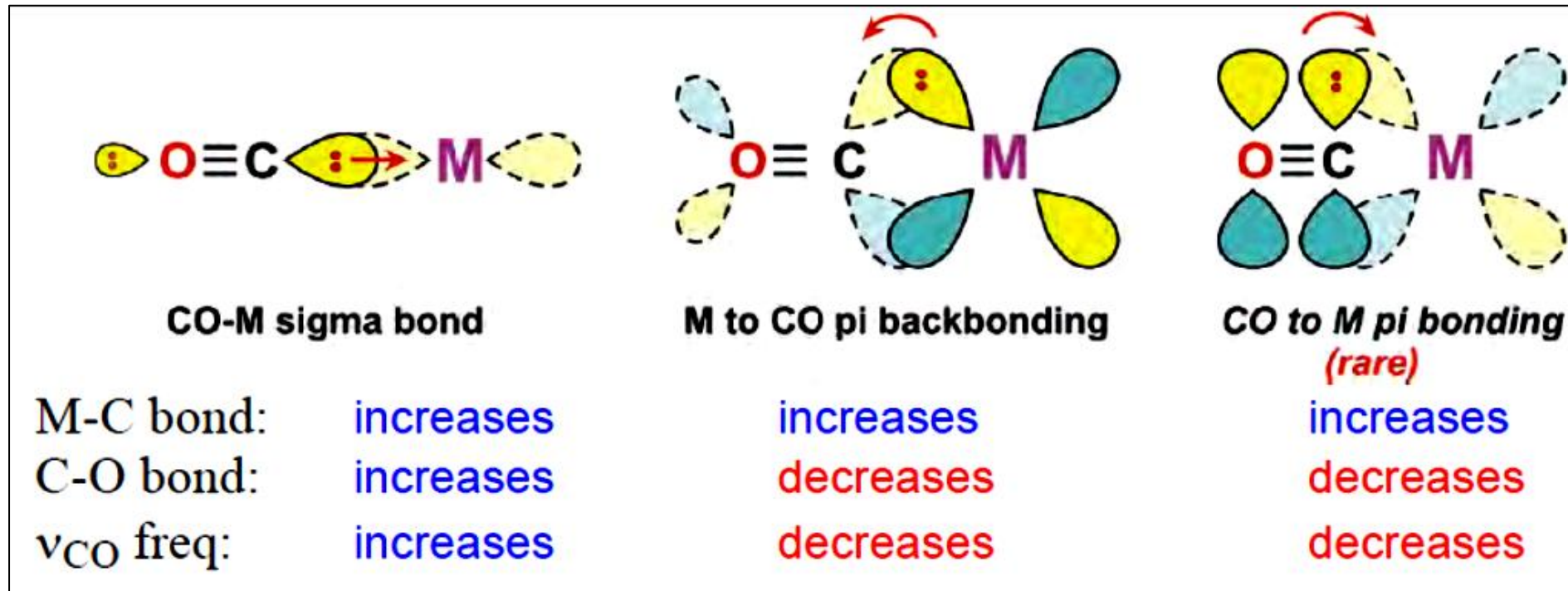


## ❖ Molecular Orbital Diagram for CO



A simple MO diagram for CO is shown above. The highest occupied molecular orbital (**HOMO**) is indicated by the pair of electrons. This is the  $5\sigma$  lone pair orbital mainly centered on the carbon and weakly antibonding with respect to the C-O bond (although that isn't too clear from the orbital contour plot). The **LUMO** is strongly  $\pi^*$  antibonding and is low enough in energy to act as a good acceptor orbital for interacting with filled  $d$ -orbitals on metals.

# 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←CO  $\sigma$ -bond.

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

- This bond is formed because of overlapping of filled dπ orbitals or hybrid dπ orbitals of metal atom with antibonding π orbitals on CO molecule.

# Structure of Ni(CO)<sub>4</sub>

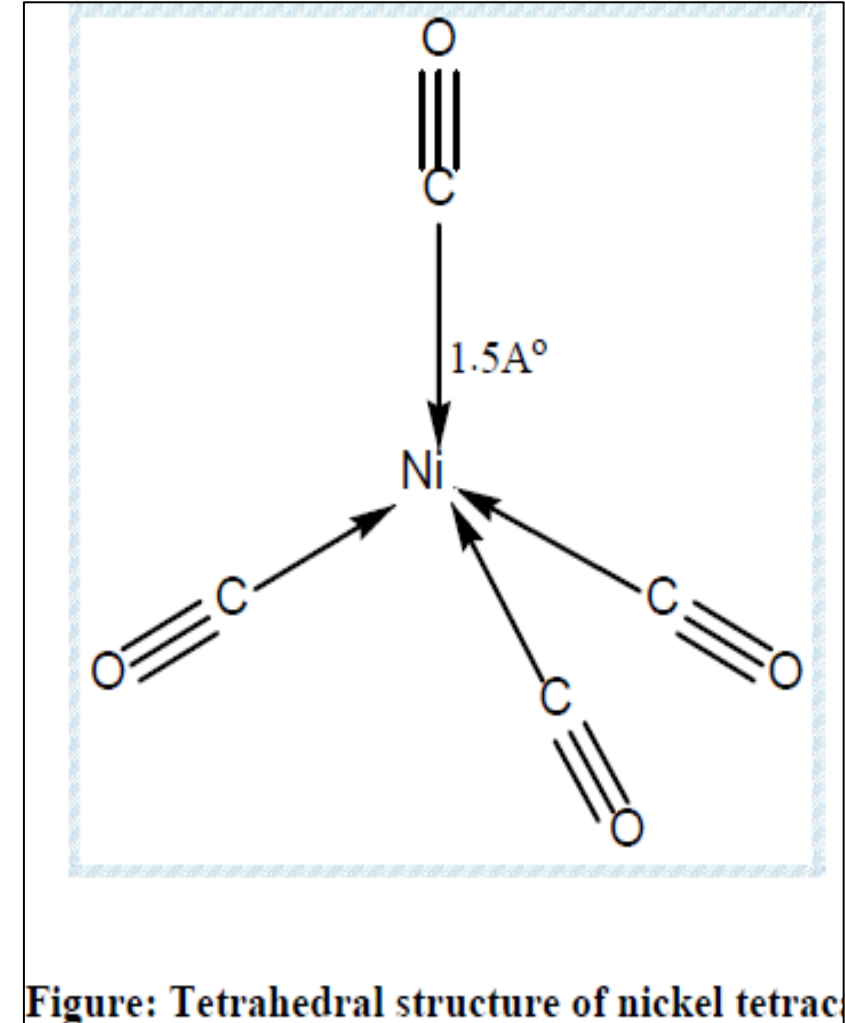
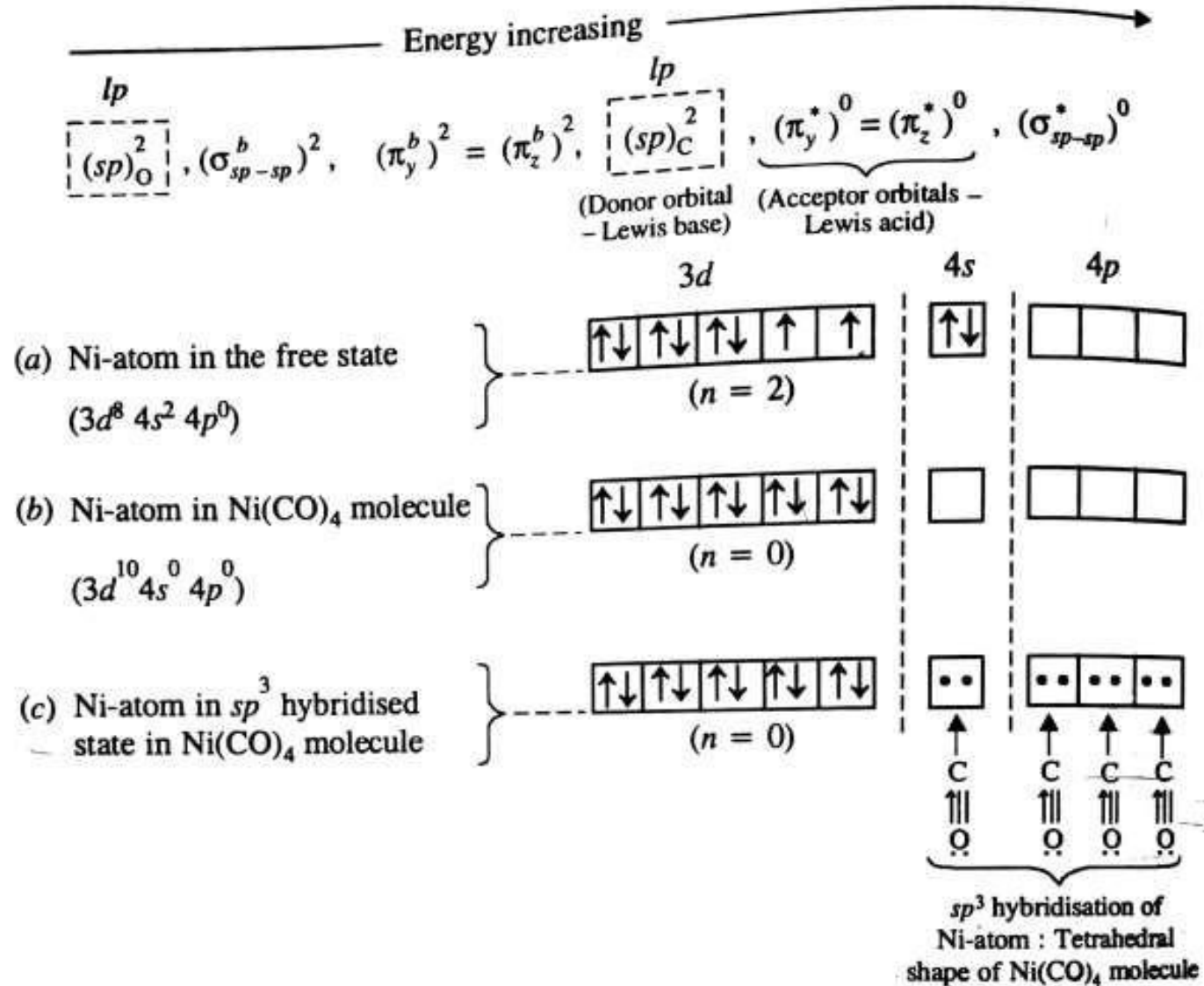
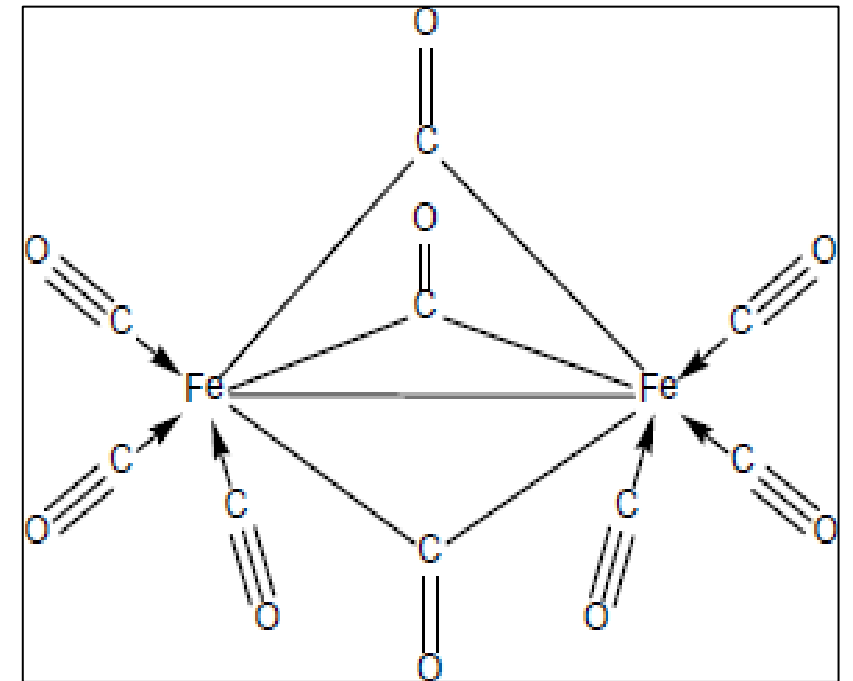
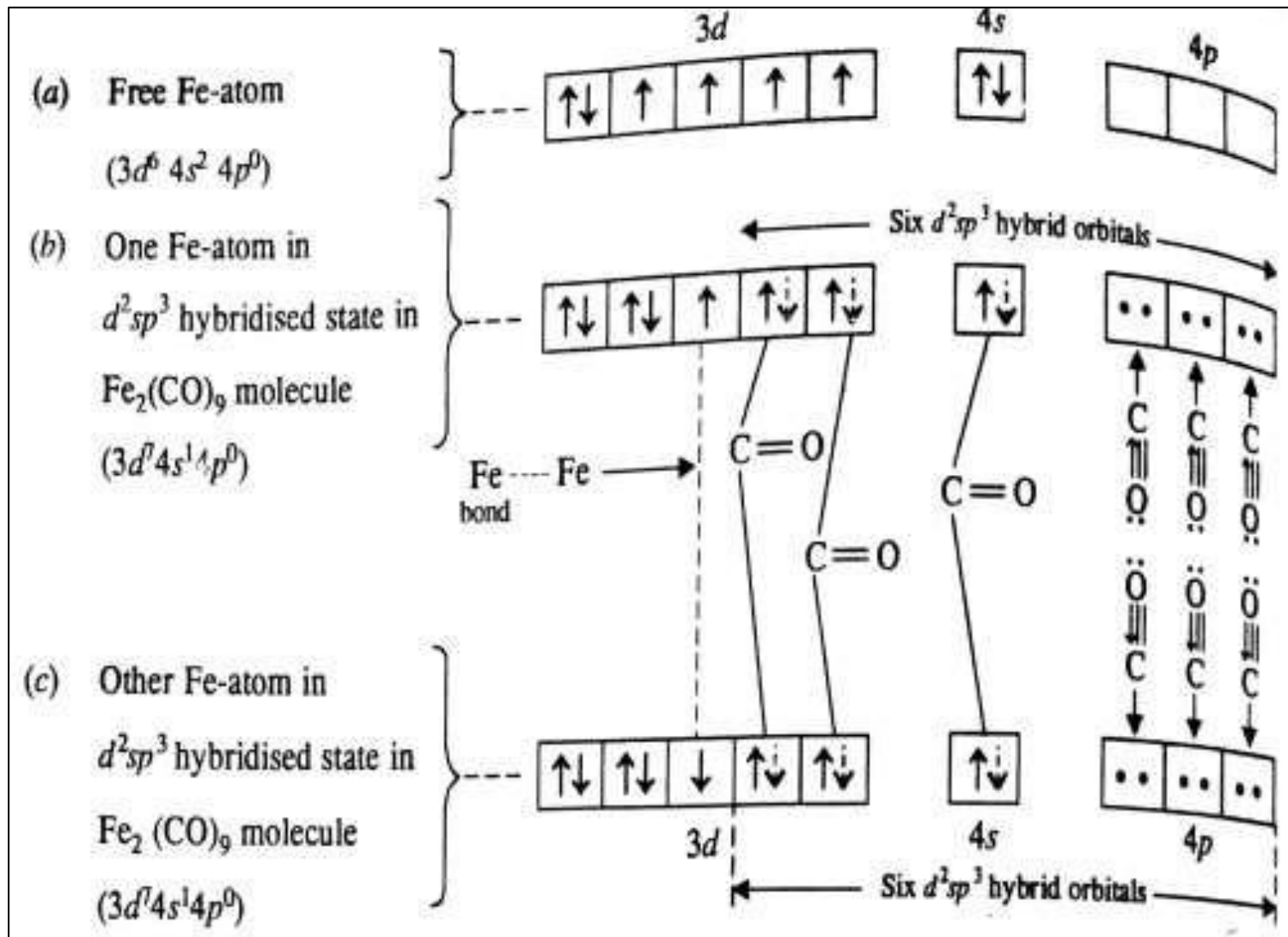


Figure: Tetrahedral structure of nickel tetracarbonyl

# Structure of $\text{Fe}_2(\text{CO})_9$


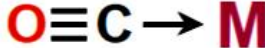
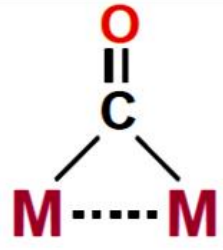
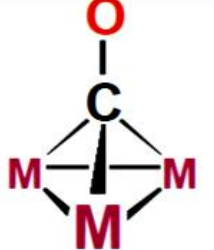


# Carbonyl IR Stretching Frequencies

- ❖ The **position** of the carbonyl bands in the IR depends mainly on the **bonding mode** of the CO (terminal, bridging) and the **amount of electron density on the metal being  $\pi$ -backbonded to the CO**.
- ❖ The **number** (and intensity) of the carbonyl bands one observes depends on **the number of CO ligands present** and the **symmetry** of the metal complex. There are also secondary effects such as Fermi resonance and overtone interactions that can complicate carbonyl IR spectra.

## ❖ **Bonding Modes:**

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.

				
	free CO	terminal mode	$\mu_2$ -bridging	$\mu_3$ -bridging
$\nu_{\text{CO}}$ IR ( $\text{cm}^{-1}$ )	2143	2120 - 1850	1850 - 1720	1730 - 1500
<i>(for neutral metal complexes)</i>				

Note that these ranges are typical for “**neutral**” transition metal complexes with an average amount of electron density on the metal center (see *discussion in next page*). Bridging carbonyls tend to have weaker and broader IR bands.

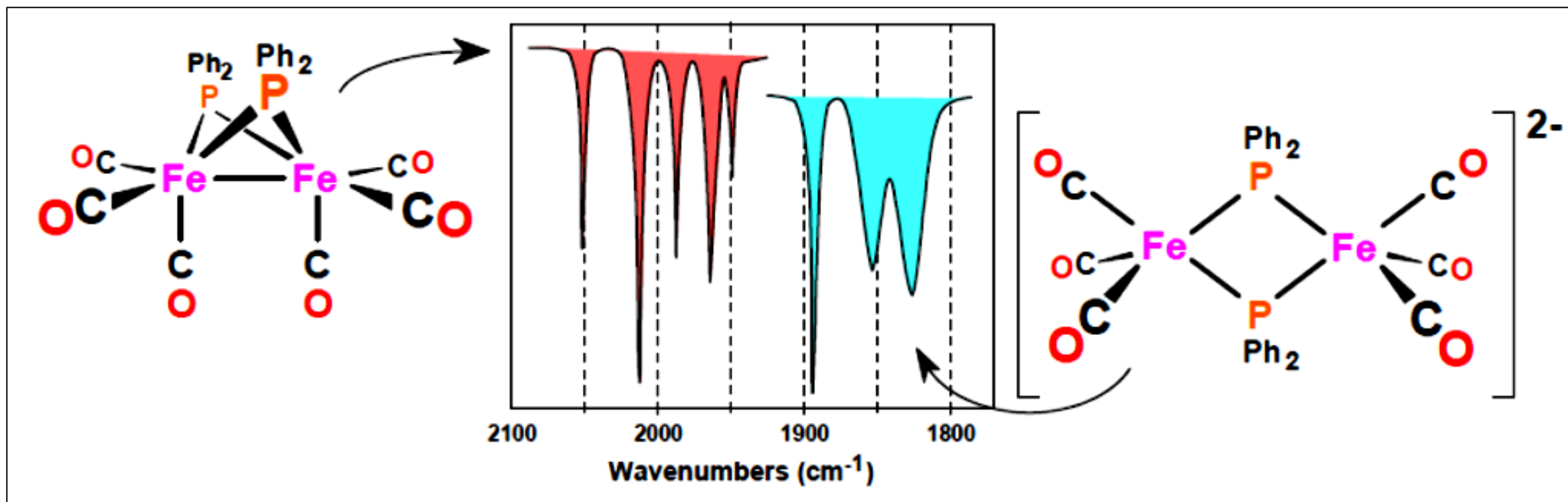
# Effect of Electron Density on Metal

❖ As the electron density on a metal center increases, more  $\pi$ -backbonding to the CO ligand(s) takes place. This further weakens the C-O bond by pumping more electron density into the formally empty carbonyl  $\pi^*$  orbital. This increases the M-CO bond strength making it more double-bond-like, i.e., the resonance structure **M=C=O** assumes more importance. This can clearly be seen on the table to the right that illustrates the effect of charge and electronegativity on the amount of metal to CO  $\pi$ -backbonding and the CO IR stretching frequency.

$d^x$	Complex	$\nu_{\text{CO}}$ $\text{cm}^{-1}$
	free CO	2143
$d^{10}$	$[\text{Ag}(\text{CO})]^+$	2204
	$\text{Ni}(\text{CO})_4$	2060
	$[\text{Co}(\text{CO})_4]^-$	1890
	$[\text{Fe}(\text{CO})_4]^{2-}$	1790
$d^6$	$[\text{Mn}(\text{CO})_6]^+$	2090
	$\text{Cr}(\text{CO})_6$	2000
	$[\text{V}(\text{CO})_6]^-$	1860

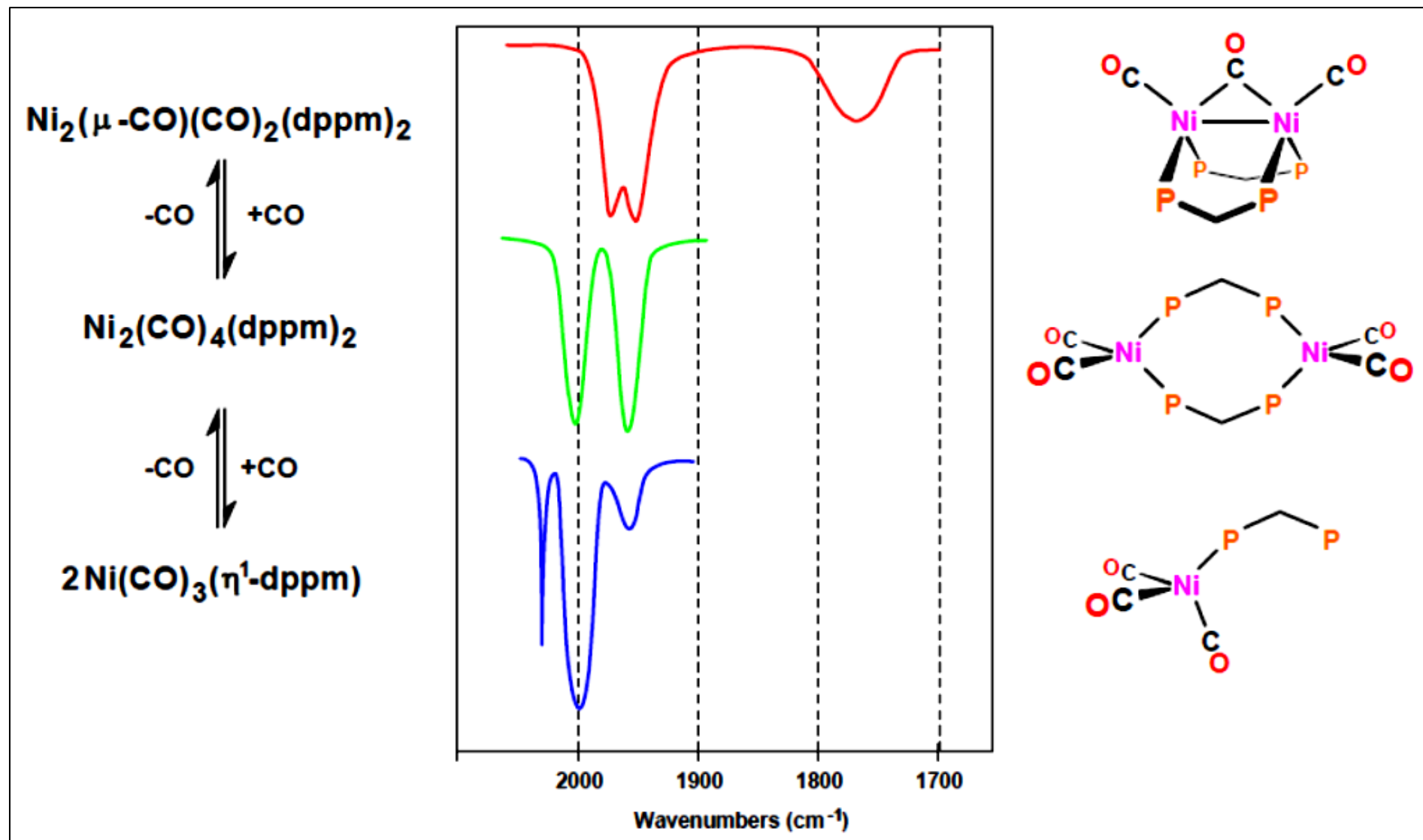
# More examples

Shown below is another example of the dramatic effect on the  $\nu_{\text{CO}}$  IR stretching frequencies on reducing  $\text{Fe}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$  by 2 electrons to form the dianionic complex  $[\text{Fe}_2(\mu\text{-PPh}_2)_2(\text{CO})_6]^{2-}$ . The average  $\nu_{\text{CO}}$  frequency shifts almost  $150\text{ cm}^{-1}$  to lower energy on reduction.



# More examples

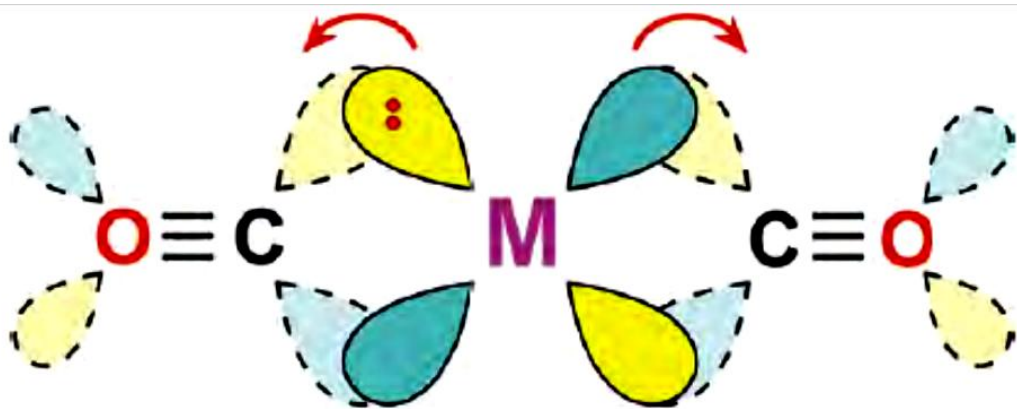
The carbonyl region in the IR spectrum can be very distinctive and useful for help in assigning structures and for indicating the relative amount of electron density present on the metal:



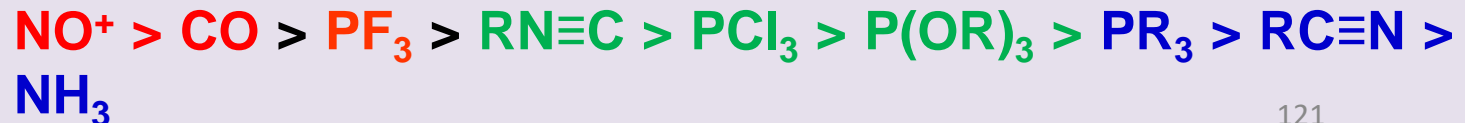
# Ligand Donation Effects

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  $\nu_{\text{CO}}$  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.

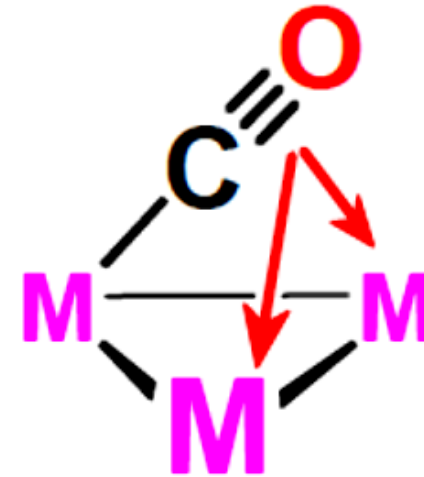
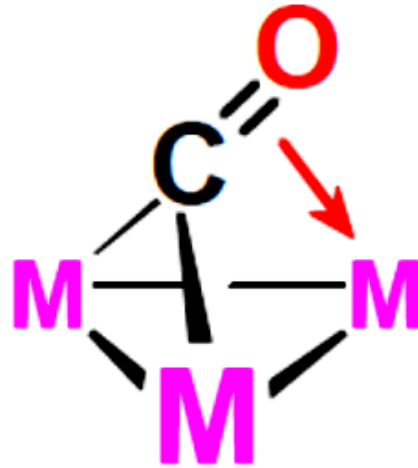
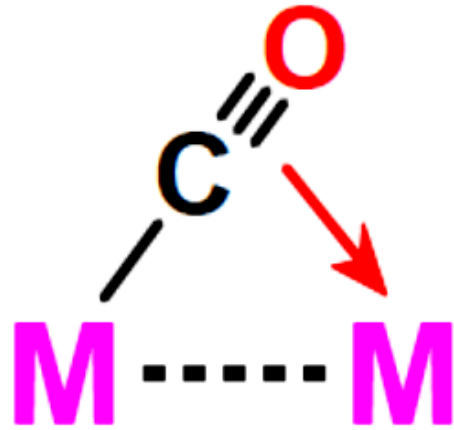
Complex	$\nu_{\text{CO}} \text{ cm}^{-1}$
$\text{Mo}(\text{CO})_3(\text{PF}_3)_3$	2090, 2055
$\text{Mo}(\text{CO})_3(\text{PCl}_3)_3$	2040, 1991
$\text{Mo}(\text{CO})_3[\text{P}(\text{OMe})_3]_3$	1977, 1888
$\text{Mo}(\text{CO})_3(\text{PPh}_3)_3$	1934, 1835
$\text{Mo}(\text{CO})_3(\text{NCCH}_3)_3$	1915, 1783
$\text{Mo}(\text{CO})_3(\text{triamine})_3$	1898, 1758
$\text{Mo}(\text{CO})_3(\text{pyridine})_3$	1888, 1746



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

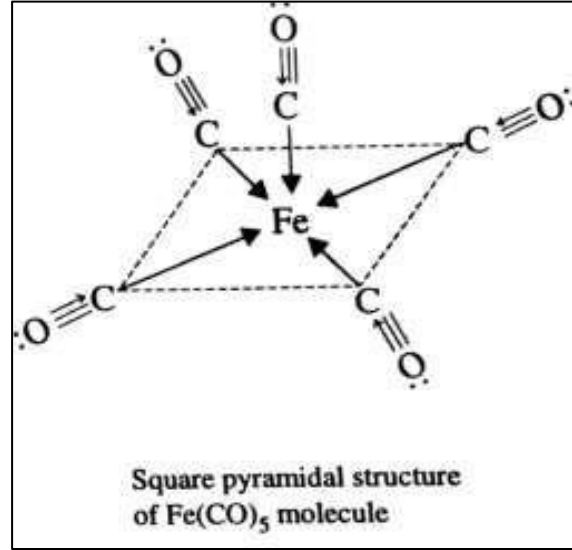
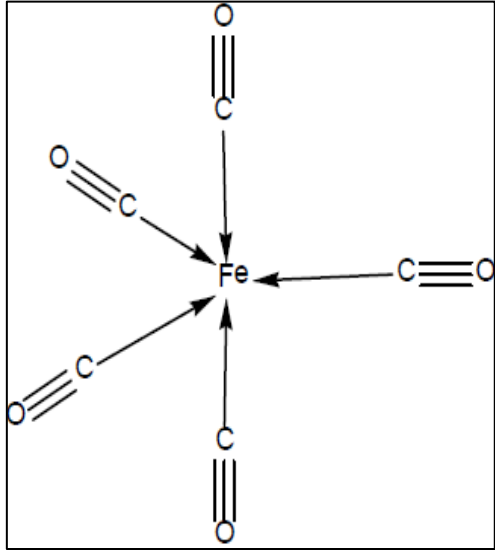


This is where the CO not only acts as a traditional  $\sigma$ -donor/ $\pi$ -acceptor to one or more metal centers, but also as a  $\pi$ -donor to additional metals. This will occur for more electron deficient metal complexes where the metal centers have less need to  $\pi$ -backbond to the carbonyl, 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

- Calculating number of IR active bands with Raman active bands and then tally with number of bands predicted theoretically



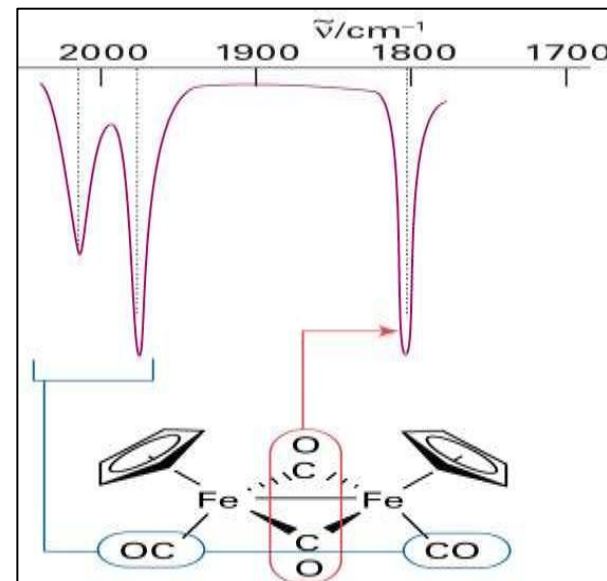
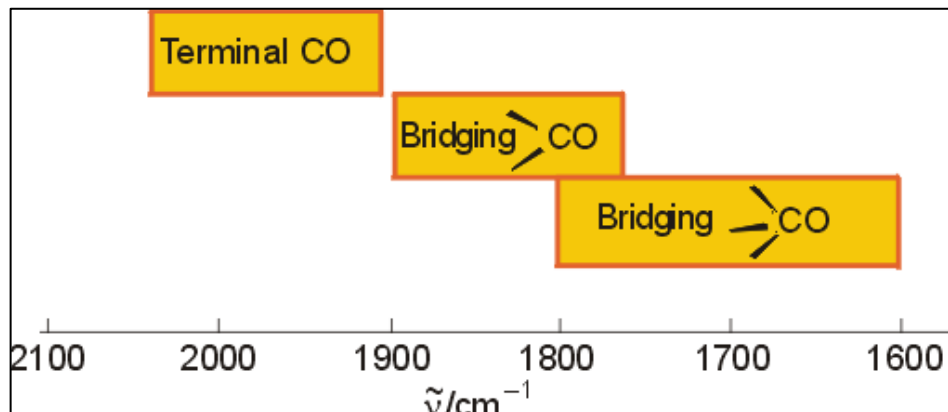
## 2. Determination of Bond orders

- 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  $2220\text{-}1700\text{ cm}^{-1}$ , 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

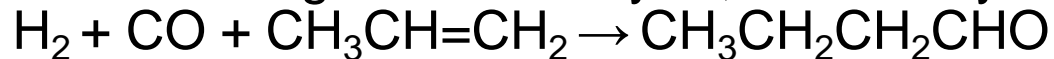


### 4. To study reaction rates

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.



Dicobalt octacarbonyl acts as catalyst.

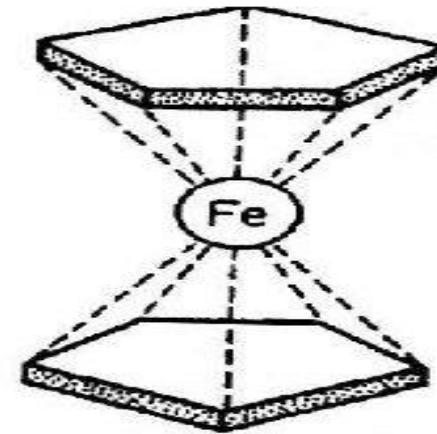
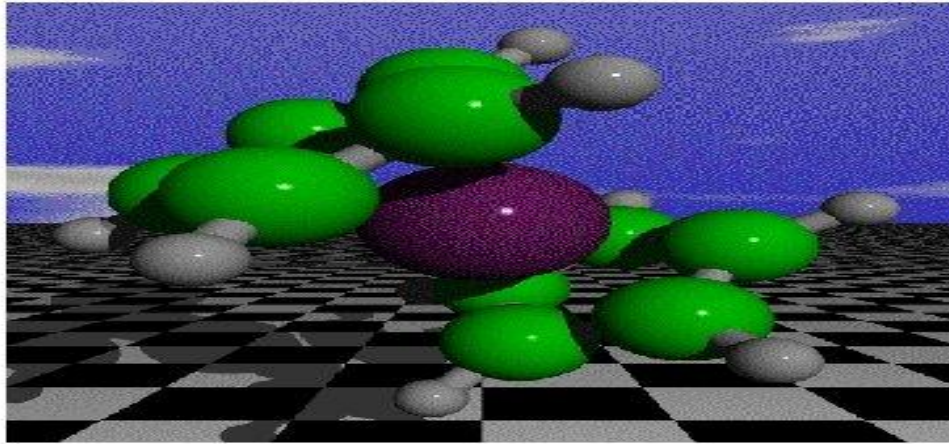
$\text{Co}_2(\text{CO})_8$  could be used for hydrosilation of olefins also.

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

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

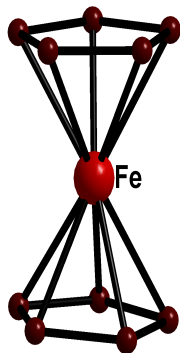
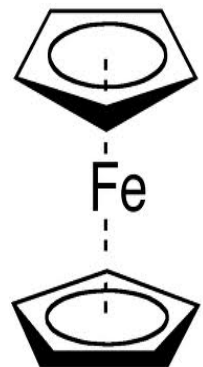
# Ferrocene

The compound  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ , bis (cyclopentadienyl) iron, popularly known as ferrocene was discovered in 1951. It has famous sandwich structure.

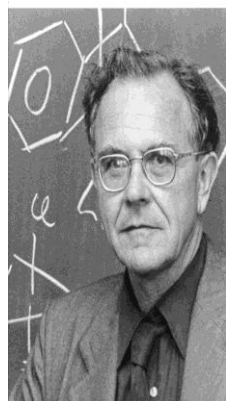
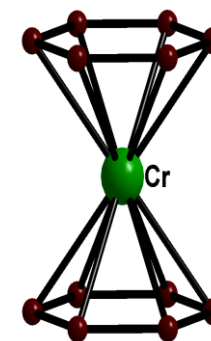
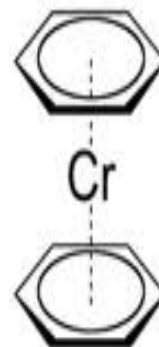
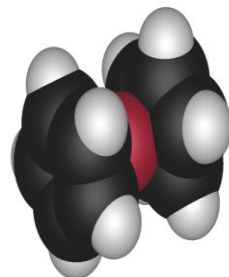


# Sandwich Compounds

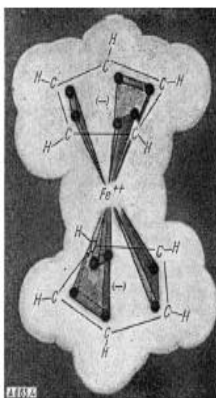
The **hapto** symbol,  $\eta$ , with a numerical superscript, provides a topological description by indicating the number of carbon atoms at a bonding distance to the metal



Sandwich



G. Wilkinson



1973 Nobel Prize  
'sandwich compounds'



E. O. Fischer



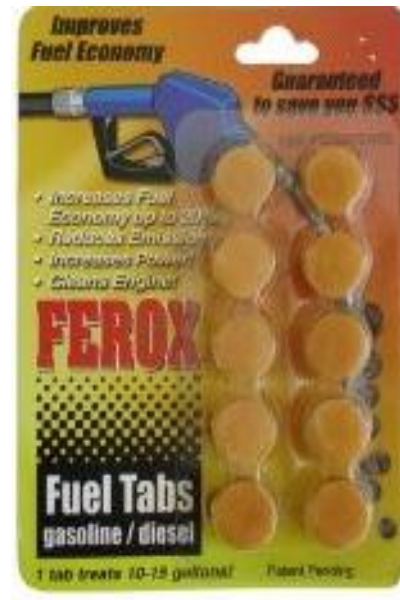
# Ferrocene's Applications: Fuel additive, smoke suppressant and chiral catalyst precursor



Ferrocene powder



Ferrocene crystals



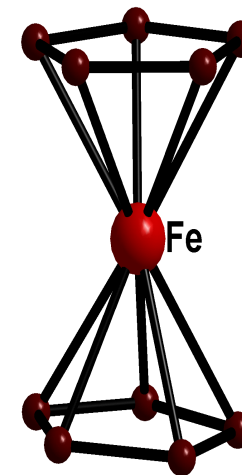
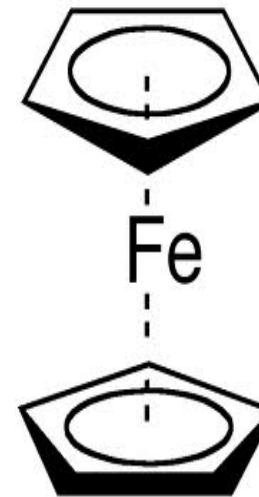
**Ferox Gas & Diesel Fuel Additive is a catalyst that is an eco-friendly fuel additive and horsepower booster. It allegedly increases mileage from between 10 and 20% while also significantly reducing harmful emissions.**

# Ferrocene

- It is popular Organometallic compound with the formula  $\text{Fe}(\text{C}_5\text{H}_5)_2$ .
- The molecule consists of two cyclopentadienyl rings bound on opposite sides of a central iron atom.
- It is an orange diamagnetic solid and is soluble in most organic solvents e.g.  $\text{C}_6\text{H}_6$ .
- It is remarkable for its stability: unaffected by air, water, strong bases, can be heated to  $400\text{ }^\circ\text{C}$  without decomposition, m. p.  $174\text{ }^\circ\text{C}$
- **Preparation:**
- $2\text{C}_5\text{H}_5\text{MgBr} + \text{FeCl}_2 \rightarrow \text{Fe}(\text{C}_5\text{H}_5)_2 + \text{MgBr}_2 + \text{MgCl}_2$

# Structure and Bonding

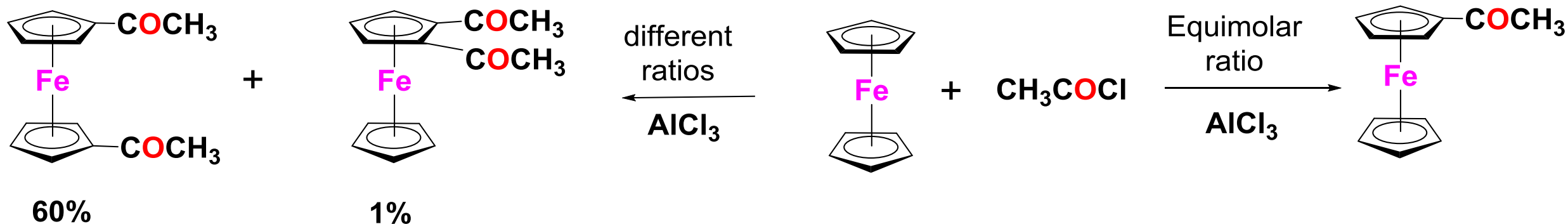
- Mössbauer spectroscopy indicates that the iron center in ferrocene should be assigned the +2 oxidation state. Each cyclopentadienyl (Cp) ring should then be allocated a single negative charge. Thus ferrocene could be described as iron(II) bis(cyclopentadienide)  $\text{Fe}^{2+}[\text{C}_5\text{H}_5^-]_2$ .
- 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  $\text{Fe}^{2+}$  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  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$ .
- Crystallography reveals that the cyclopentadienide rings are in staggered conformation.
- Hybridization:  $d^2sp^3$
- Magnetic Nature: Diamagnetic



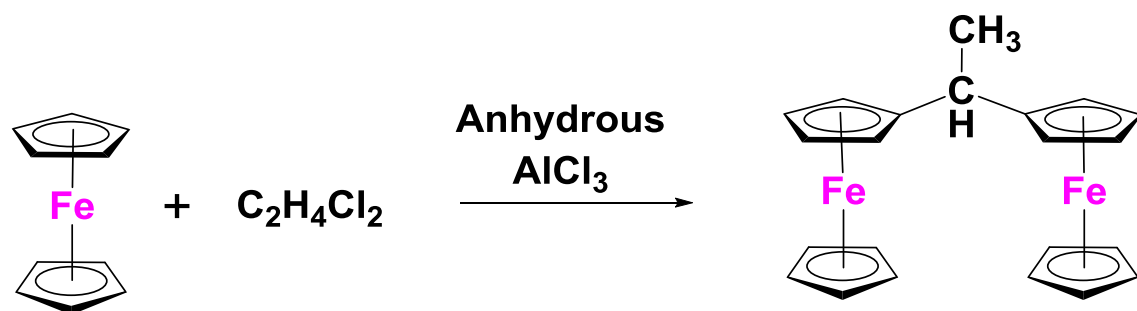
# Chemical reactions of Ferrocene

## ❖ Friedel crafts Acylation

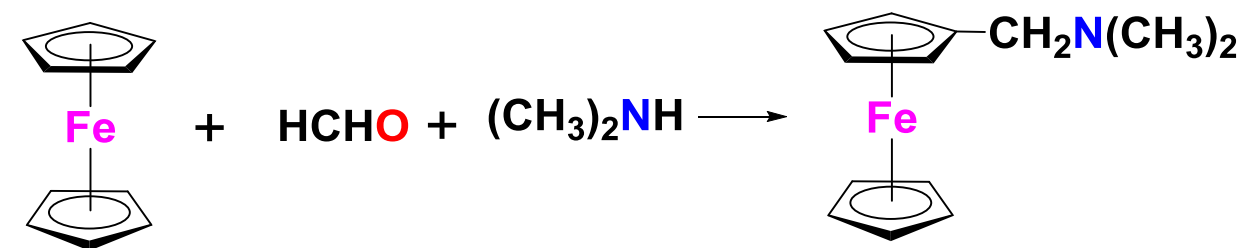
- Ferrocene and acetyl chloride in the equimolar quantities give the mono substituted derivative while in the double quantities resulted in distributed derivatives



## ❖ Friedel crafts Alkylation



## ❖ Mannich condensation



# Importance

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- Ferrocene was not the first organometallic compound known. Zeise's salt  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$  was reported in 1831.
- Mond's discovery of  $\text{Ni}(\text{CO})_4$  occurred in 1888 and organolithium compounds were developed in the 1930s.
- **However, it can be argued that it was ferrocene's discovery that began organometallic chemistry as a separate area of chemistry. It also led to an explosion of interest in compounds of d-block metals with hydrocarbons.**
- The discovery was considered so significant that Wilkinson and Fischer shared the 1973 Nobel Prize for Chemistry "for their pioneering work, performed independently, on the chemistry of the organometallic, so called **SANDWICH** compounds."
- The rapid growth of organometallic chemistry is often attributed to the excitement arising from the discovery of ferrocene and its many analogues (metallocenes).

# Applications of Ferrocene

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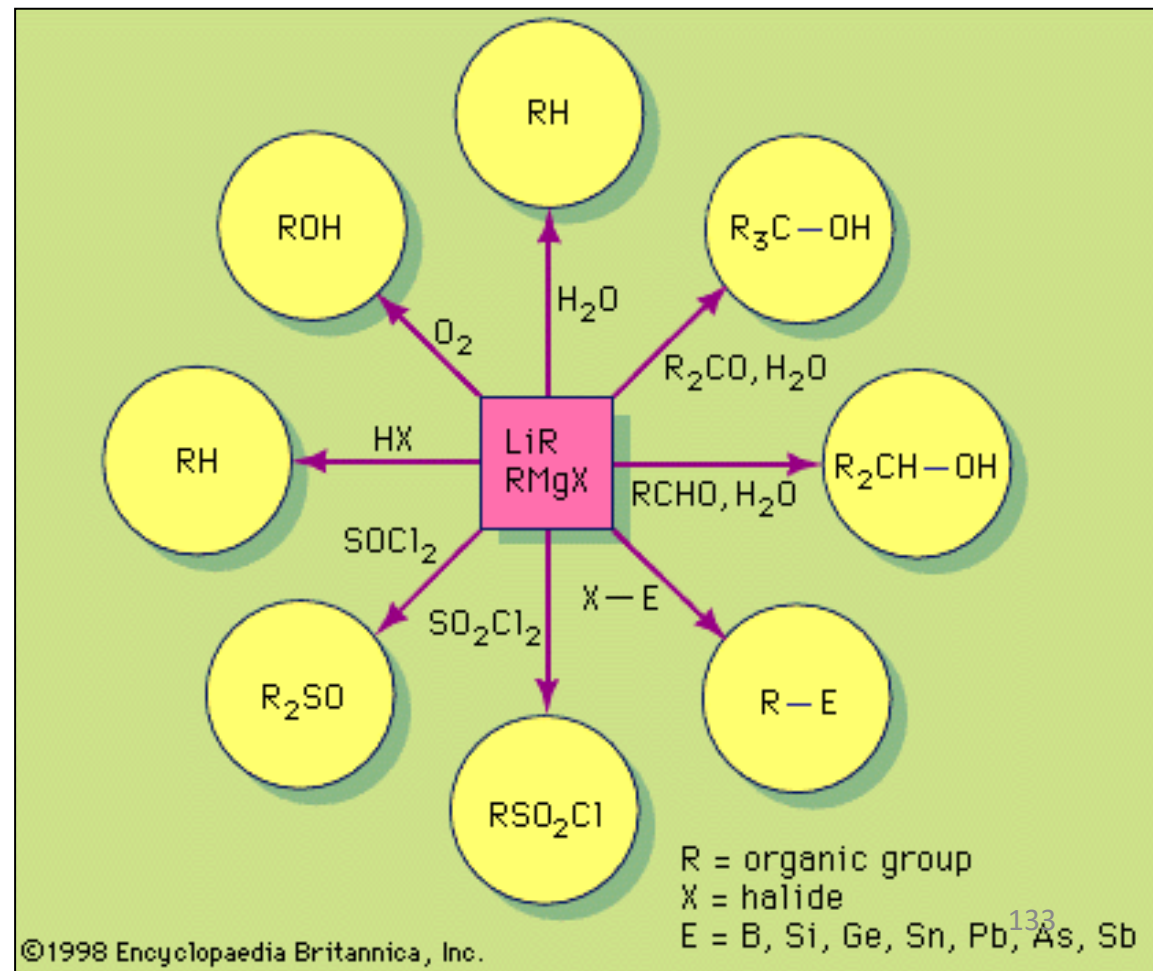
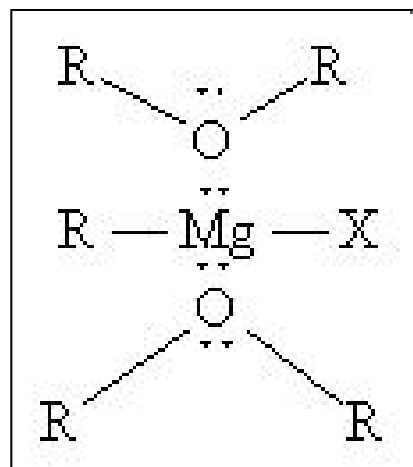
- 1. Fuel additives:** Ferrocene and its derivatives could be used as antiknock agents in the fuel for petrol engines. They are safer than previously TEL.
- 2. Pharmaceutical:** Ferrocene derivatives have been investigated as drugs e.g. one drug has entered clinic trials, Ferroquine (7-chloro-N-(2-((dimethylamino)methyl)ferrocenyl)quinolin-4-amine), 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.

# The Grignard Reagent



François Auguste  
Victor Grignard 1871-  
1935

- He was the student of Philippe Barbier (Barbier reaction [Zn]) He discovered the Grignard reaction [Mg] in 1900. He became a professor at the University of Nancy in 1910 and was awarded the Nobel Prize in Chemistry in 1912.



- **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).

### ❖ Preparation of Grignard reagents

- Grignard reagents are made through the addition of magnesium metal to alkyl or alkenyl halides. The halide can be Cl, Br, or I (not F). It's slightly easier to make Grignards from the iodides and bromides, however. Note what's happening here – the magnesium is “inserting” itself between the carbon and the halide. This halide the “X” referred to when we refer to Grignard reagents as “RMgX”.

#### Example 1: Formation of Grignard reagents



*Grignards can be formed from alkyl or alkenyl chlorides, bromides or iodides (never fluorides)*

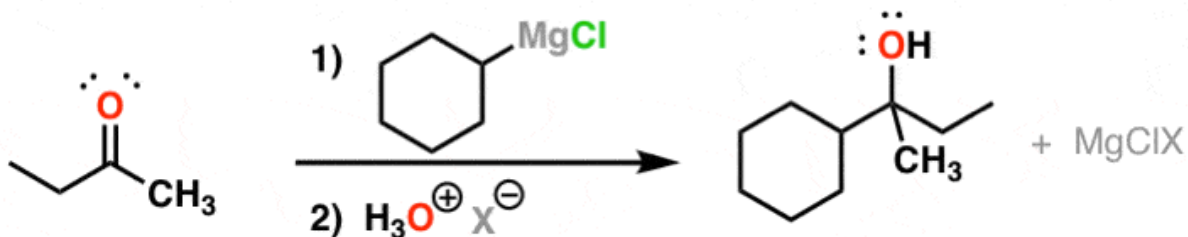
# Applications of Grignard reagents

## ❖ Reaction with aldehydes to form secondary alcohols

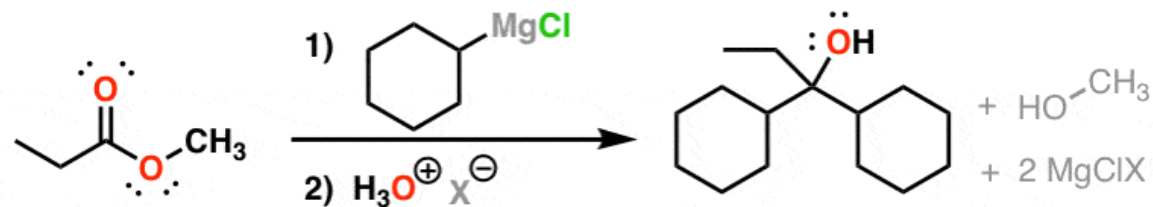


Acid is added in the second step to protonate the negatively charged oxygen

## ❖ Reaction with ketones to form tertiary alcohols

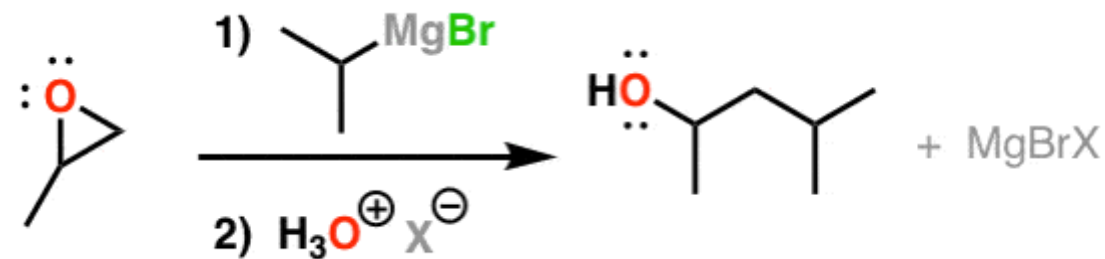


## ❖ Reaction with esters to give tertiary alcohols



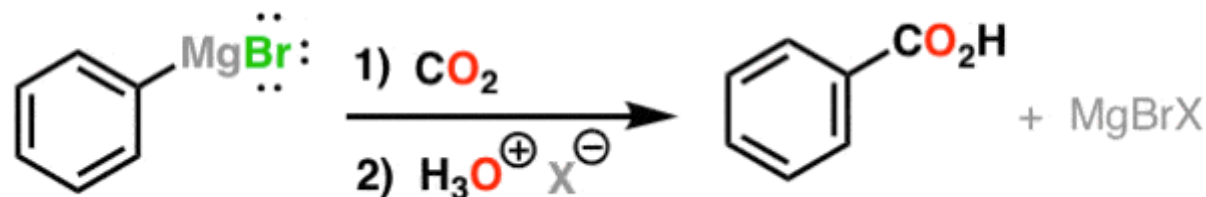
Grignard reagents add twice to esters, acid halides, and anhydrides

## ❖ Reaction with epoxides



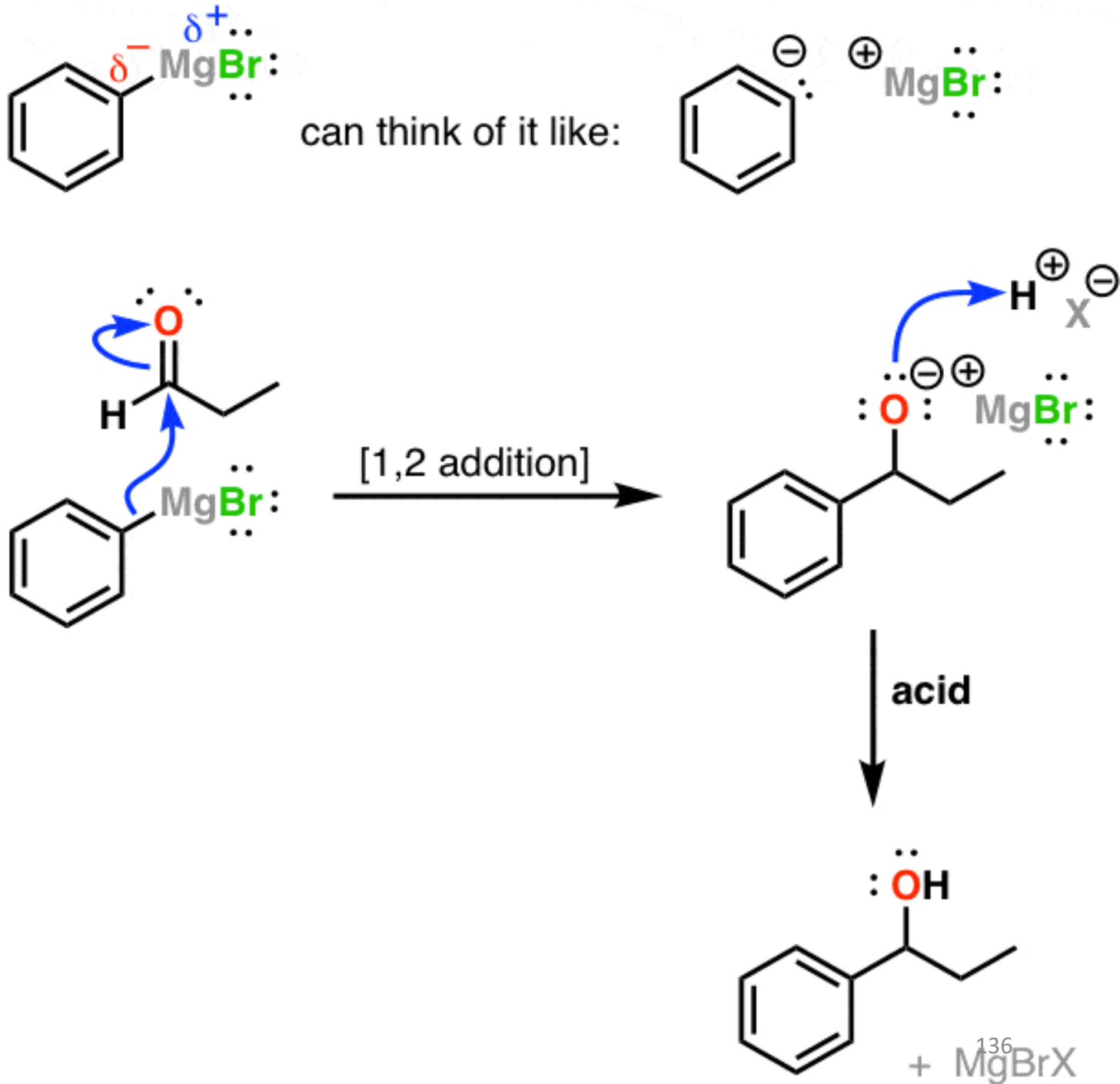
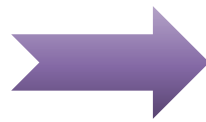
Grignard reagents add to the less substituted end of epoxides

## ❖ Reaction with CO<sub>2</sub> to make carboxylic acids



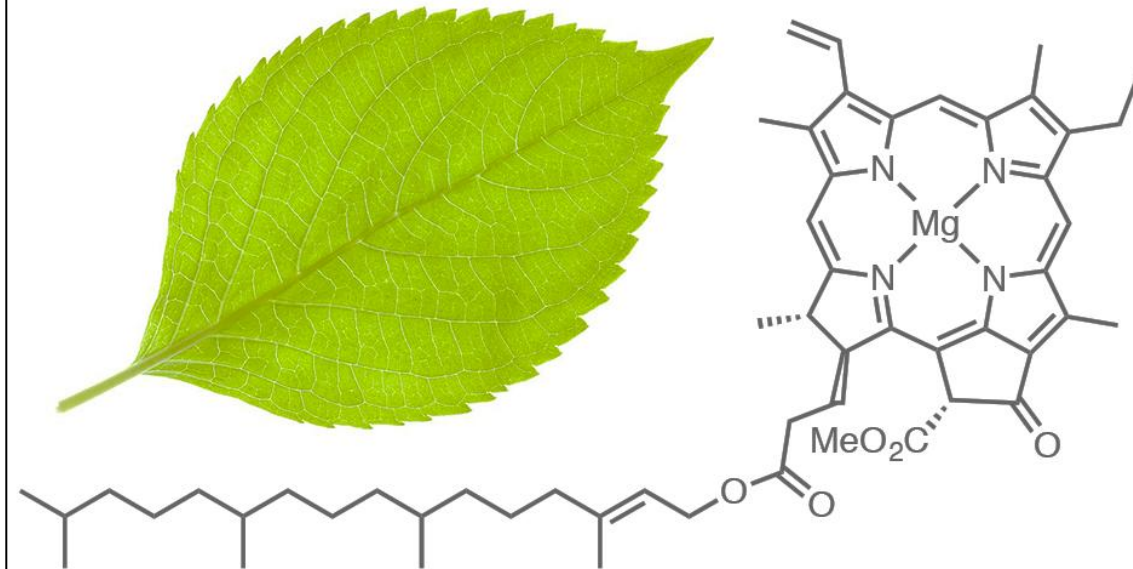
# Reaction Mechanism

- **How it works:** Addition to aldehydes/ketones Grignard reagents are extremely strong nucleophiles – the electrons in the C–Mg bond are heavily polarized toward carbon

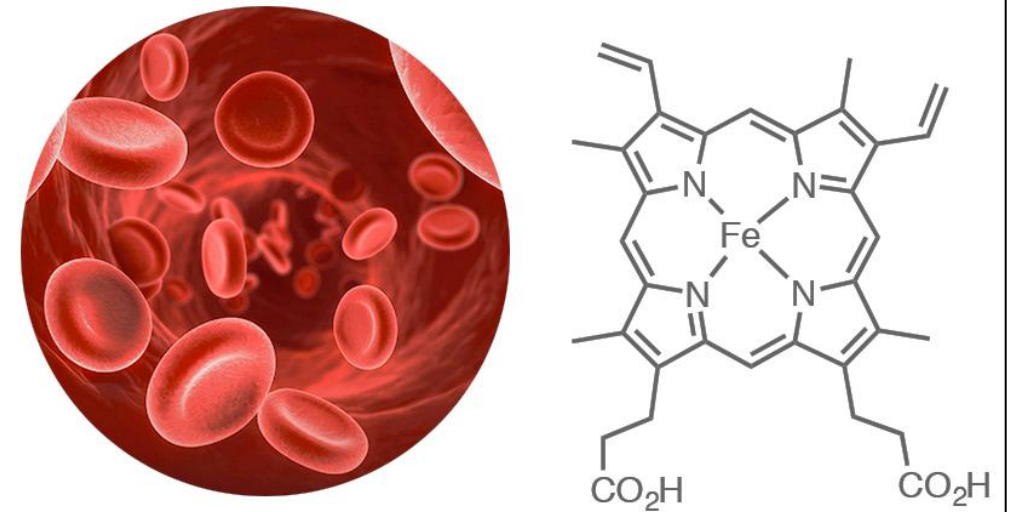


# Metals in biology

*Chlorophyll a*



*Heme b*



# Essential metal ions and their functions

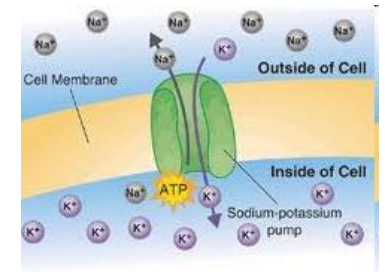
1												18					
<b>H</b>	2											13	14	15	16	17	He
Li	Be											B	<b>C</b>	<b>N</b>	<b>O</b>	F	Ne
<b>Na</b>	<b>Mg</b>	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
<b>K</b>	<b>Ca</b>	Sc	Ti	V	<b>Cr</b>	<b>Mn</b>	<b>Fe</b>	<b>Co</b>	Ni	<b>Cu</b>	<b>Zn</b>	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	<b>Mo</b>	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	<b>I</b>	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac*															

*A biological periodic table of the elements indicating the essential elements. The essential elements for most forms of life are shown in black with the exception of chromium (Cr), which is shown with an upward diagonal pattern, and essential elements that are more restricted for some forms of life shown in gray.*

- Most living organisms require some 25 elements.
- In the case of Homo sapiens, there are 10 essential metal ions (sodium, potassium, calcium, magnesium, manganese, iron, cobalt, copper, zinc, and molybdenum).
- Of these, the first four are considered as “bulk elements” ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ), representing 112 g, 160 g, 1.1 kg, and 25 g, respectively, in an “average” person of body weight 80 kg Together, they constitute some 99% of the metal ion content of the human body.
- The others, manganese, iron, cobalt, copper, zinc, and molybdenum, designated “trace elements,” are present in much lower amounts than the bulk elements (respectively, 16 mg, 4.8 g, 1.6 mg, 80 mg, 2.6 g, and 8 mg in an 80-kg person).
- The essential alkali metal ions  $\text{Na}^+$  and  $\text{K}^+$  only weakly bind organic ligands, rendering them extremely mobile, as with  $\text{H}^+$  and  $\text{Cl}^-$ . This enables them to generate ionic gradients across biological membranes.
- The alkaline earth metal ions,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , have greater binding strengths to organic ligands than  $\text{Na}^+$  and  $\text{K}^+$ , and therefore are less mobile. Both play important structural and catalytic roles, with 99% of the body’s  $\text{Ca}^{2+}$  found in bone and teeth.

11  
**Na**  
22.98

19  
**K**  
39.09



20  
**Ca**  
40.08

12  
**Mg**  
24.31



26  
**Fe**  
55.85

Hemoglobin  
Myoglobin  
Cytochromes  
Ferredoxin

27  
**Co**  
58.94

Vit B12

29  
**Cu**  
63.55

Hemocyanin

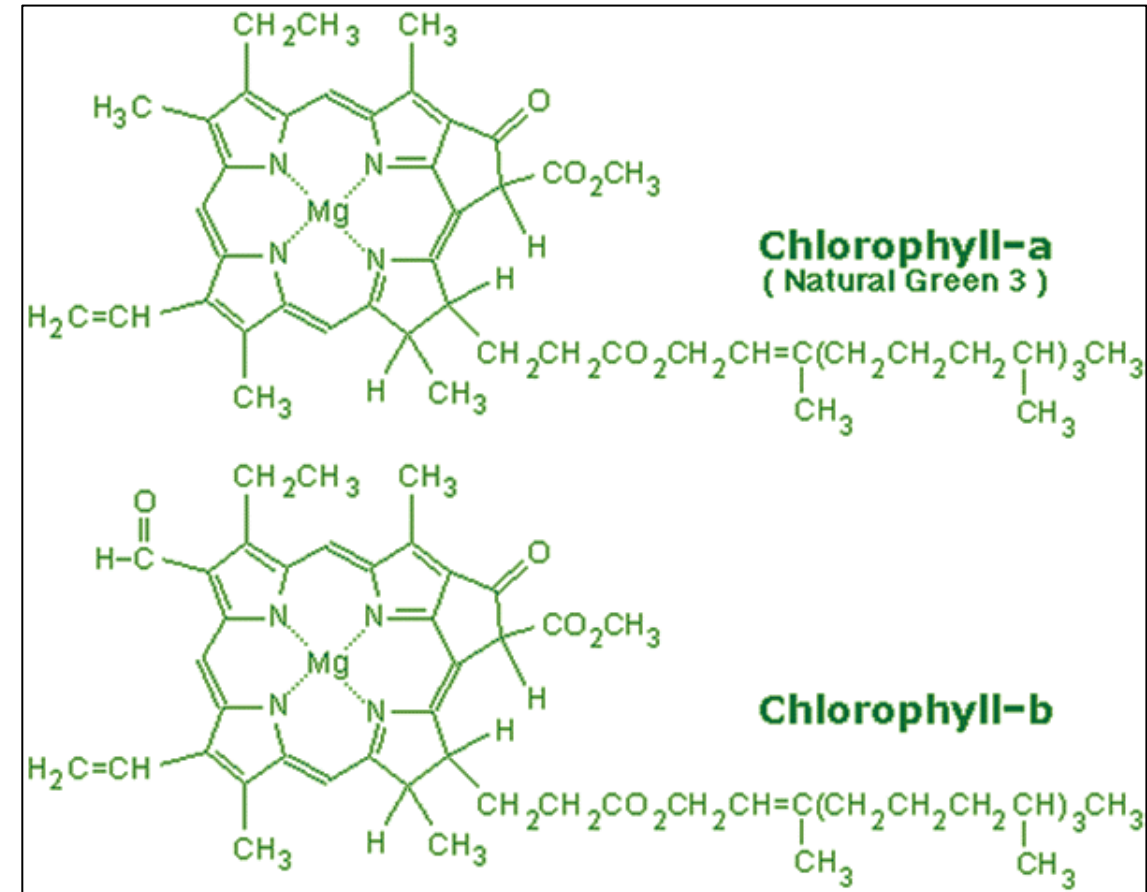
30  
**Zn**  
65.38

Carbonic anhydrase  
Carboxypeptidase

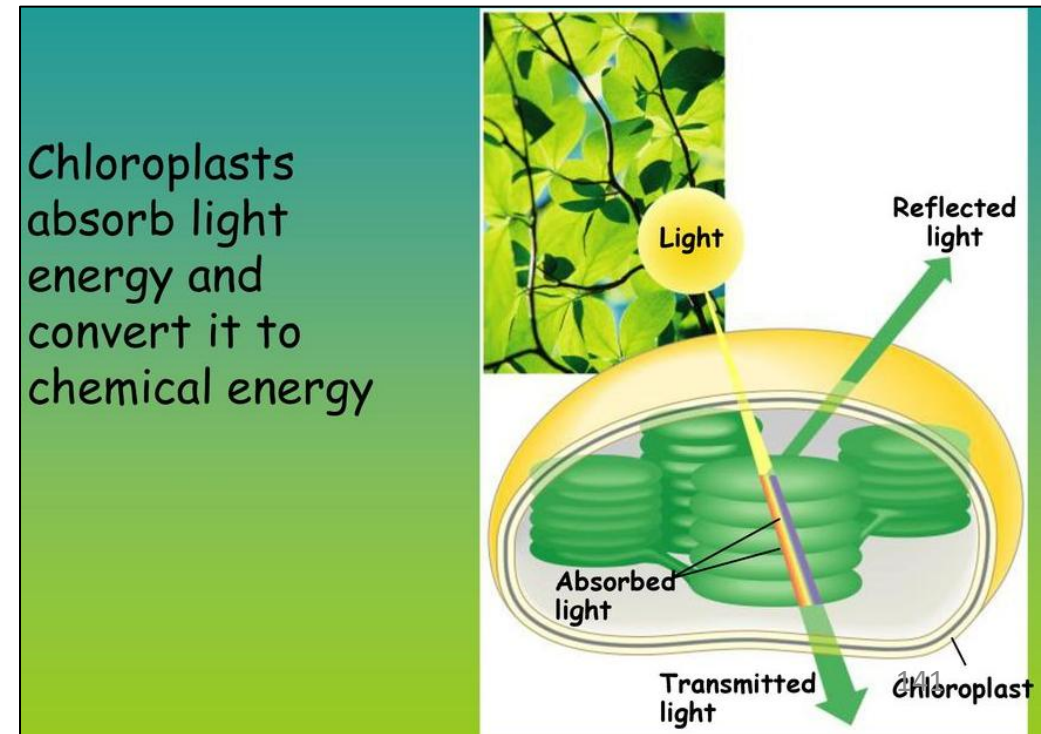
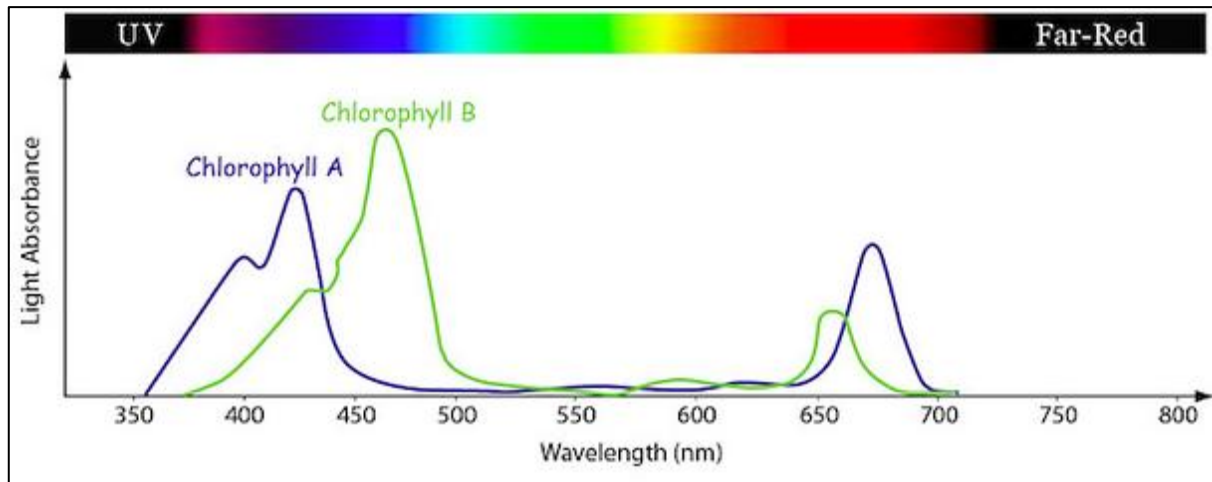
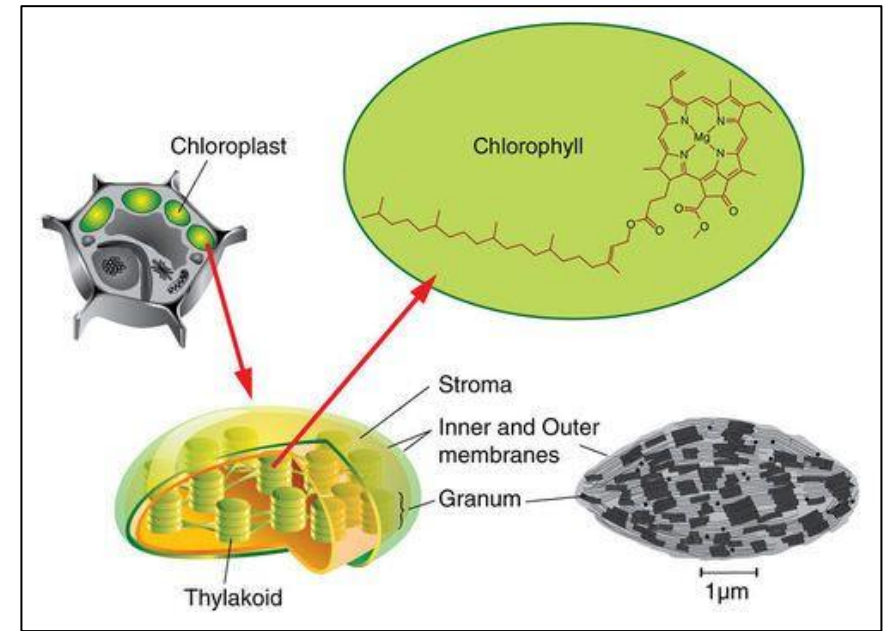
# Chlorophyll- Structure and Property

## ❖ 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

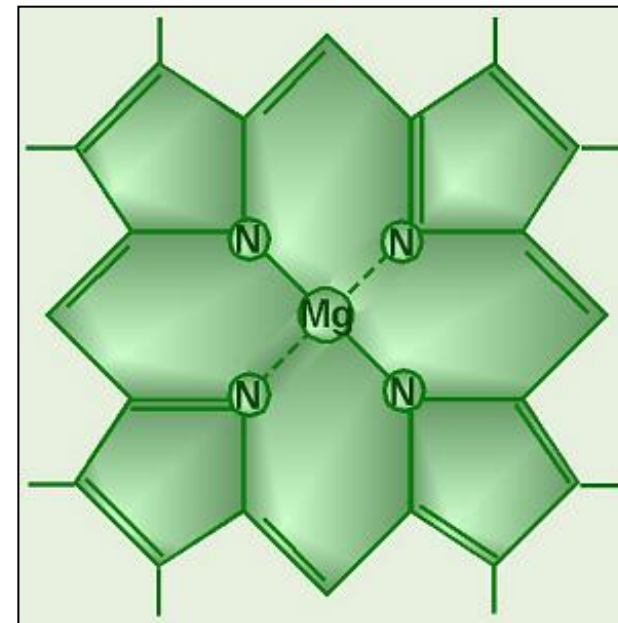
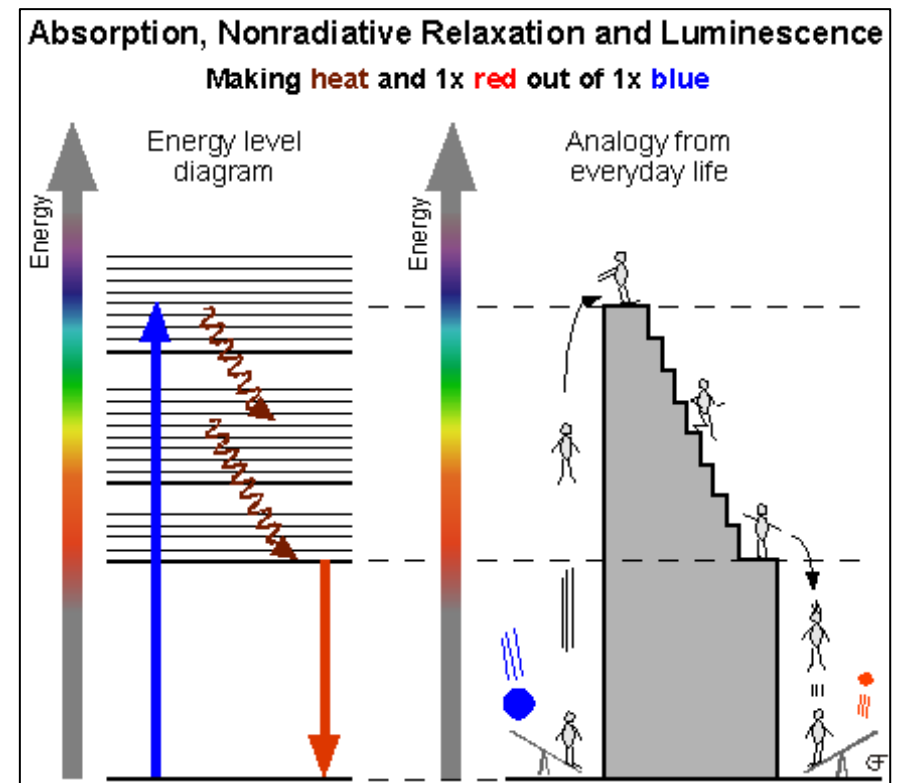


- ❖ Chloroplasts always contain both chlorophyll a and chlorophyll b
- ❖ Both are green, their absorption spectra are sufficiently different that they complement each other's range of light absorption in the visible region
- ❖ Both chlorophyll a & b absorb in the blue and red region so that the remaining 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.

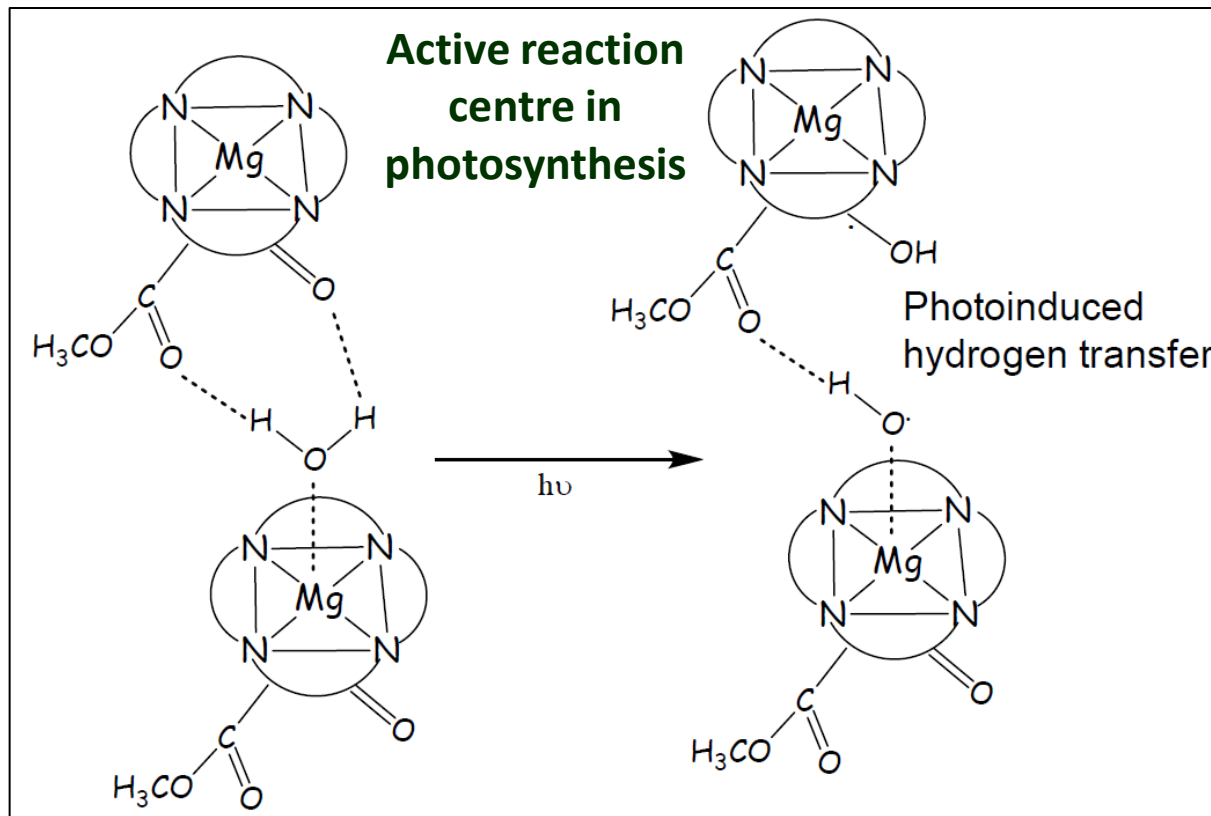


# Role of Mg in chlorophyll

- ❖ 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

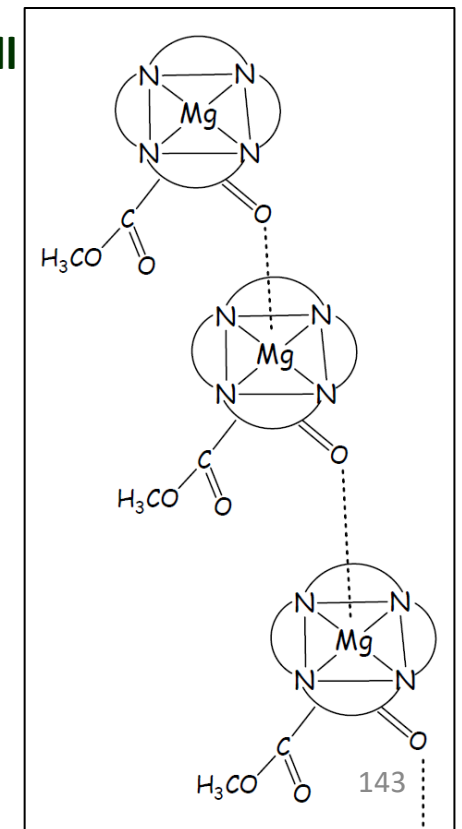


- **Mg(II) prefers tetrahedral geometry rather than square planar geometry. But in Chlorophyll it is in square planar geometry**
- So Mg(II)-N bonds in chlorophyll is strained – the electrons involved in bonding can be excited upon light absorption as **strain is relived in excited state**
- Antenna chlorophylls—polymers of chlorophyll are formed due to the **coordination of the carbonyl** part one chlorophyll with Mg(II) of other chlorophyll. The polymer is terminated when there is water coordinated with Chlorophyll at axial position
- The coordination of water in the axial position with **Mg(II) favours splitting of water** to form H atom that provides electron for photosynthetic process – active reaction centre in photosynthesis



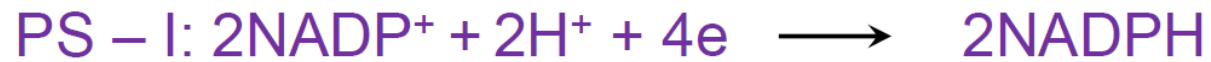
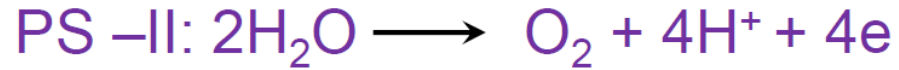
**Antenna chlorophyll**

This transformation provides **electron required** for photosynthesis reaction

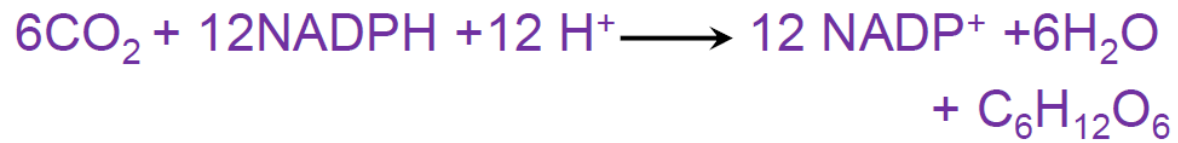


# Photosynthesis Reaction

## Light reaction

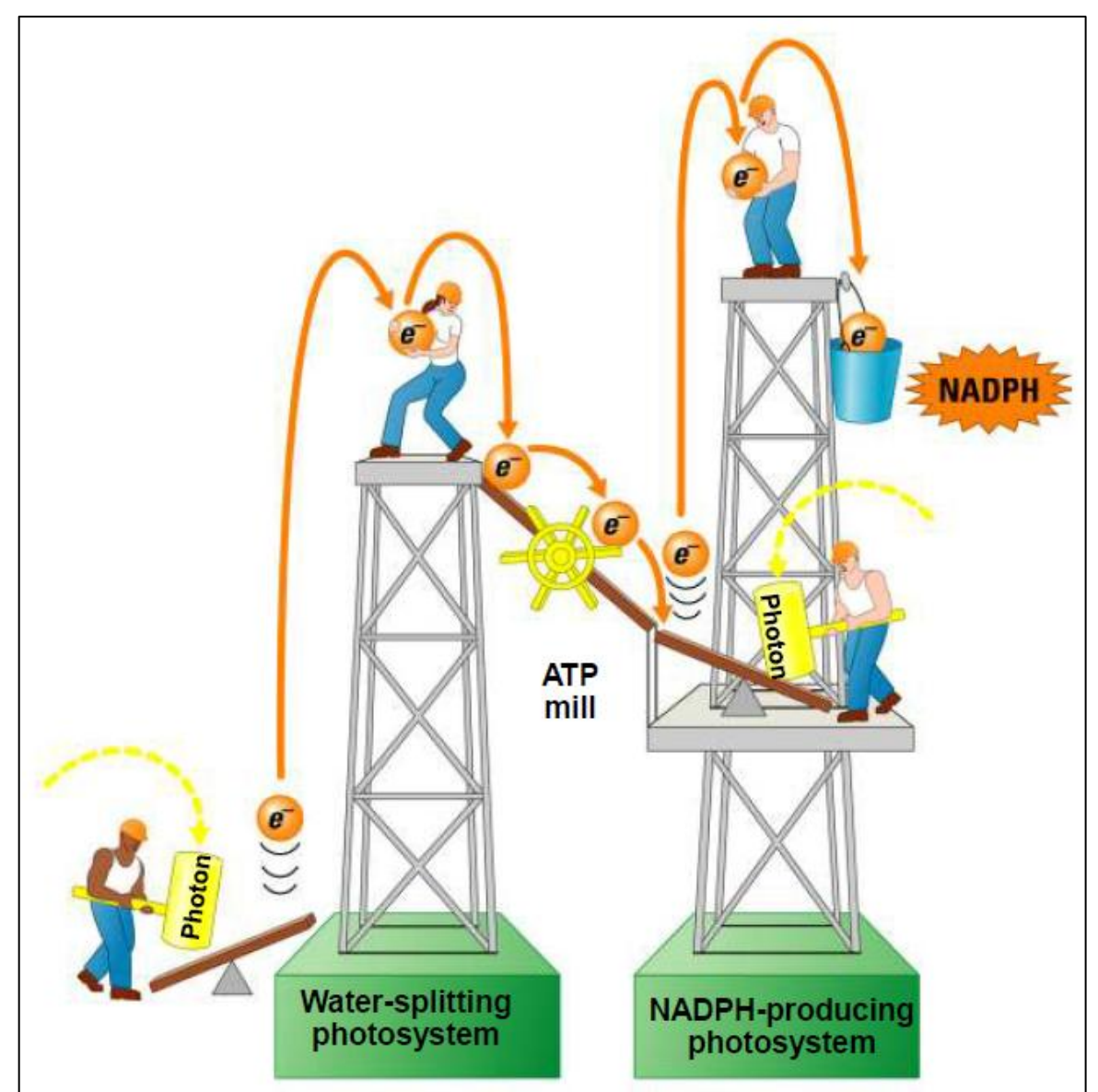
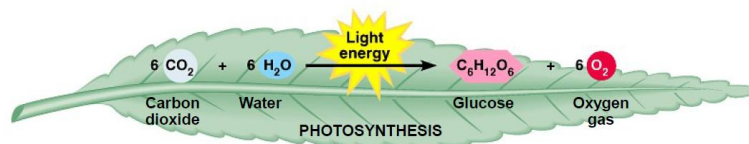


## Dark reaction



### 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

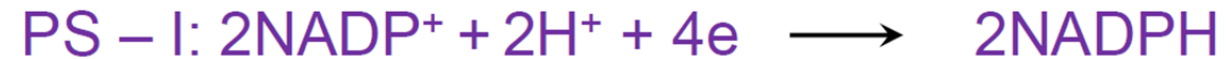
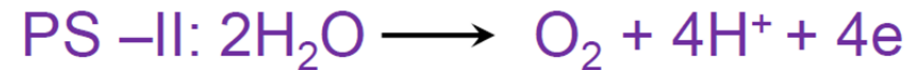


Two types of photosystems cooperate in the light reactions

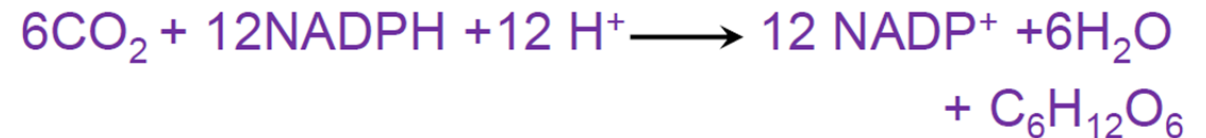
# Photosynthesis Reaction: Mechanism of PS-I and PS-II Reactions

- ❖ It absorbs light at 680 nm so the name P680. When one photon hit P680, it goes to the excited state and one electron is transferred to electron transfer chain, where the electron is transported via different electron transfer molecules. During this transport ATP is synthesized
- ❖ Finally the electrons are transferred to P700 complex. P700 absorbs light at 700 nm
- ❖ In PS-I also the electron are transported via a different electron transfer chain and finally NADPH is produced from NADP<sup>+</sup>
- ❖ This NADPH is used to reduce CO<sub>2</sub> in to carbohydrates in the dark reaction. During this reaction ATP is converted in to ADP & energy. This energy is utilized to convert CO<sub>2</sub> to carbohydrate
- ❖ The electrons lost by P680 is compensated by the electrons produced by splitting of water in to O<sub>2</sub> and H<sup>+</sup> as shown in the reaction

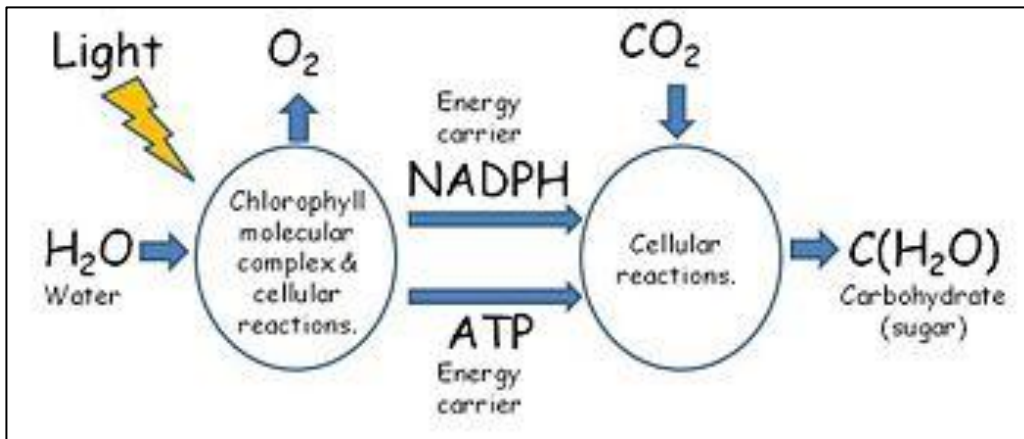
## Light reaction



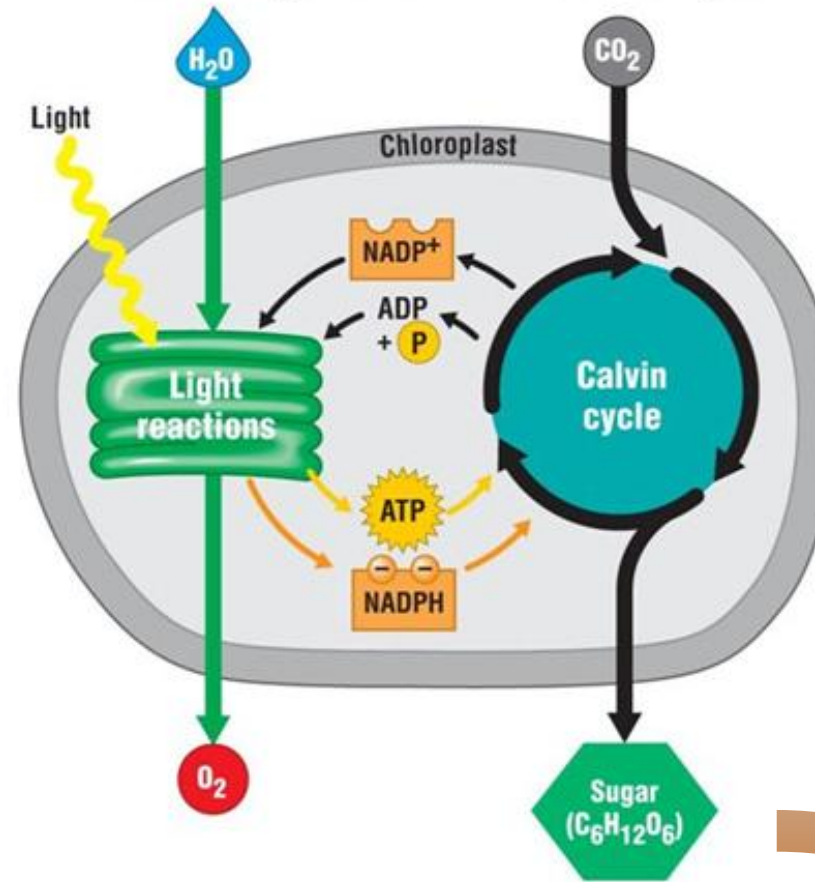
## Dark reaction



# A Photosynthesis Road Map



Photosynthesis is composed of two



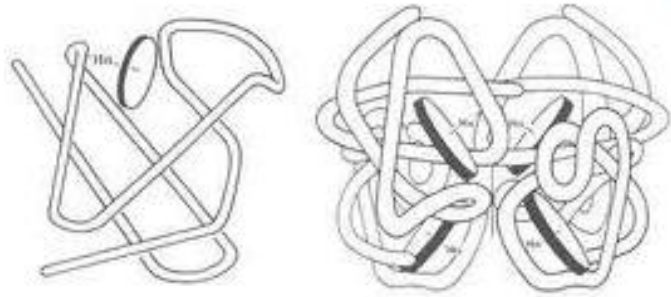
- The light reactions convert solar energy to chemical energy.

- 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

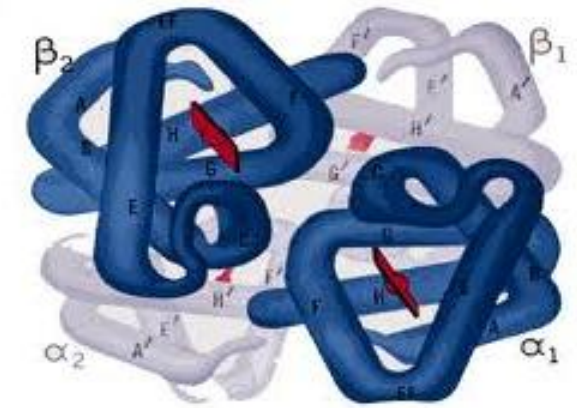


Myoglobin

Haemoglobin

Figure 3 Myoglobin versus haemoglobin

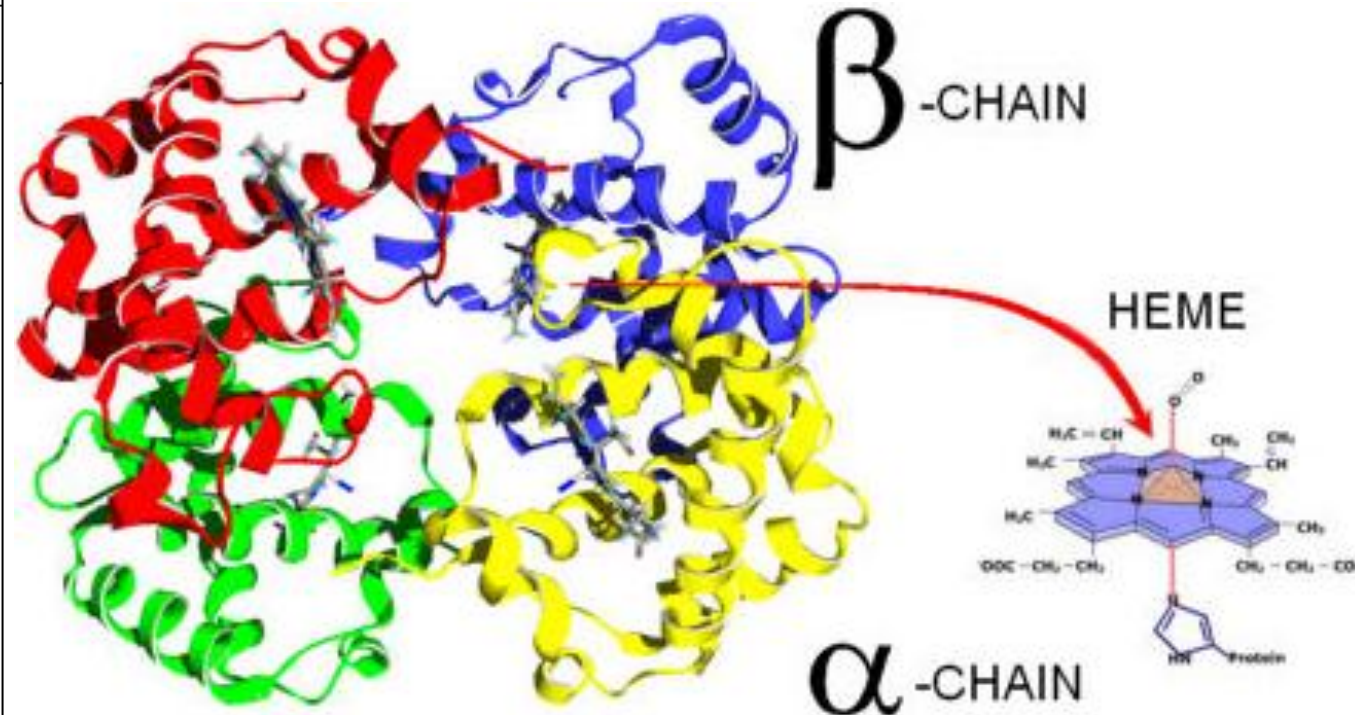
$\alpha$  141 Amino acid  
 $\beta$  146 Amino acid  
 Mb 153 Amino acid



Four units of Hb

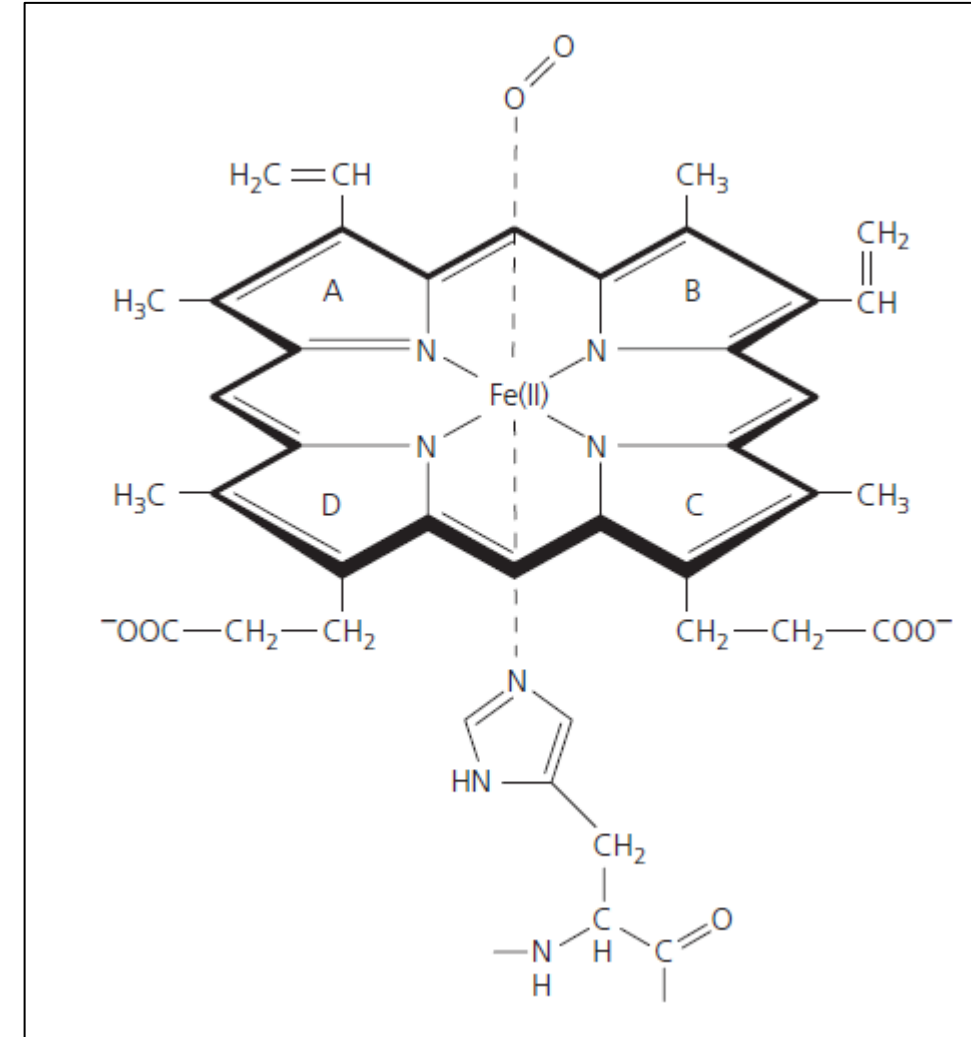
Hb is not an exact tetramer of Mb

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

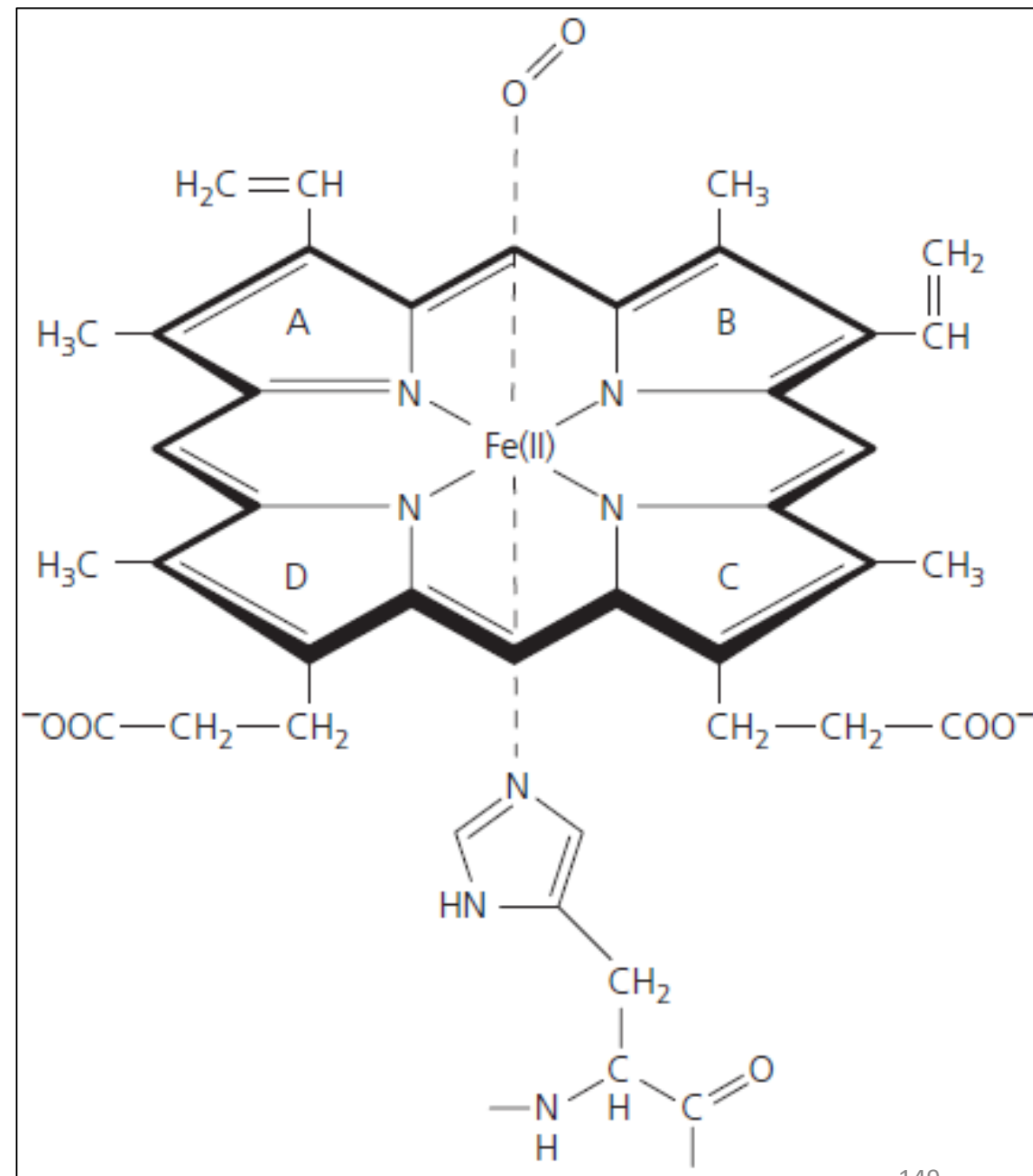


3 major types of Hb  
 Hb A (Adult)  
 Hb F (Fetal)  
 Hb S (Sickle cell)

- ❖ 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.



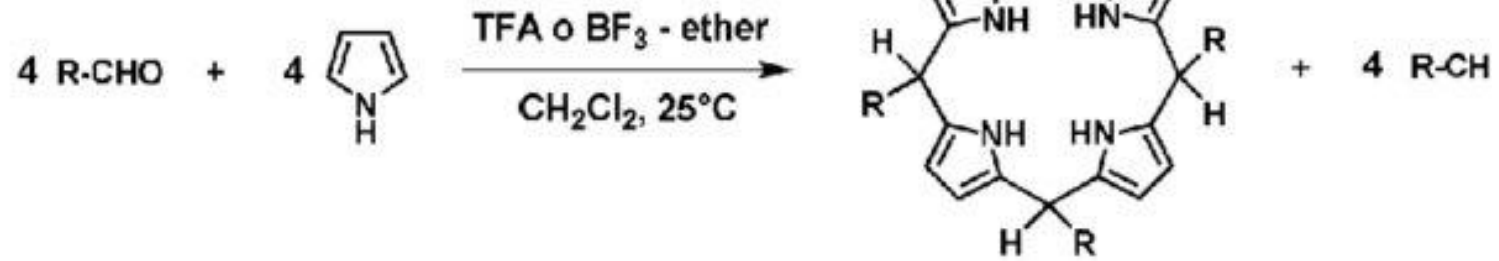
- ❖ The organic component of the heme group—the protoporphyrin—is made up of four pyrrole rings (A, B, C & D) linked by methine bridges to form a tetrapyrrole ring. Four methyl groups, two vinyl groups, and two propionate side chains are attached.
- ❖ The iron atom at the center of the protoporphyrin 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 (CO, NO,
- ❖  $\text{CN}^-$ , and  $\text{H}_2\text{S}$



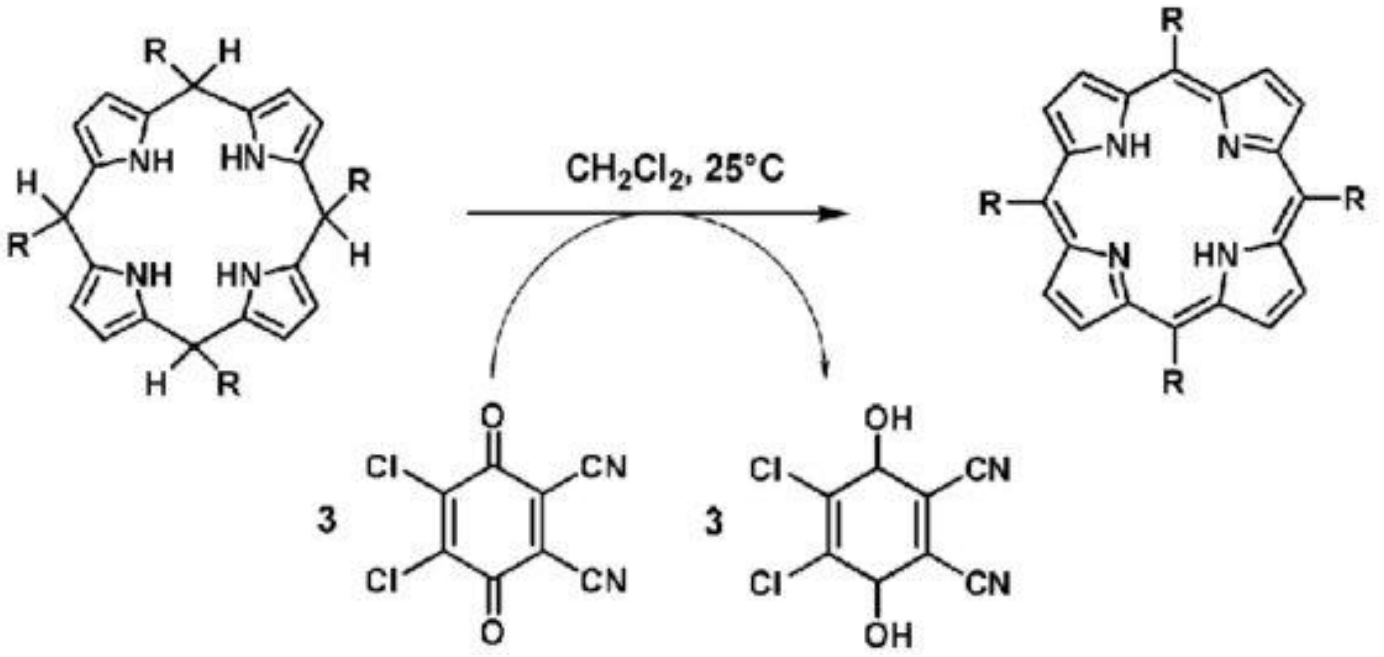
# Synthesis of Porphyrins

Porphyrins are molecules with four pyrrole units linked by four methine bridges having a square planar conformation. An unsubstituted porphyrin, known as porphin, represents the simplest porphyrin. Numerous functional groups can be substituted onto porphin macrocycles at the meso-position or the  $\beta$ -position producing a wide variety of porphyrin derivatives. In addition, free-base porphyrins can be coordinated with numerous metal ions at the porphyrin center to form metal complexes, known as **metalloporphyrins**

## 1. Condensation

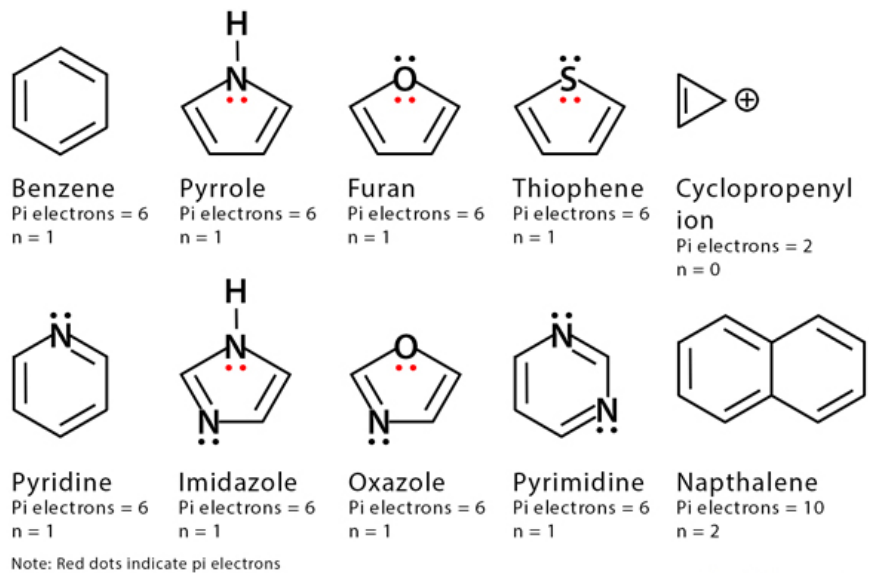


## 2. Oxidation

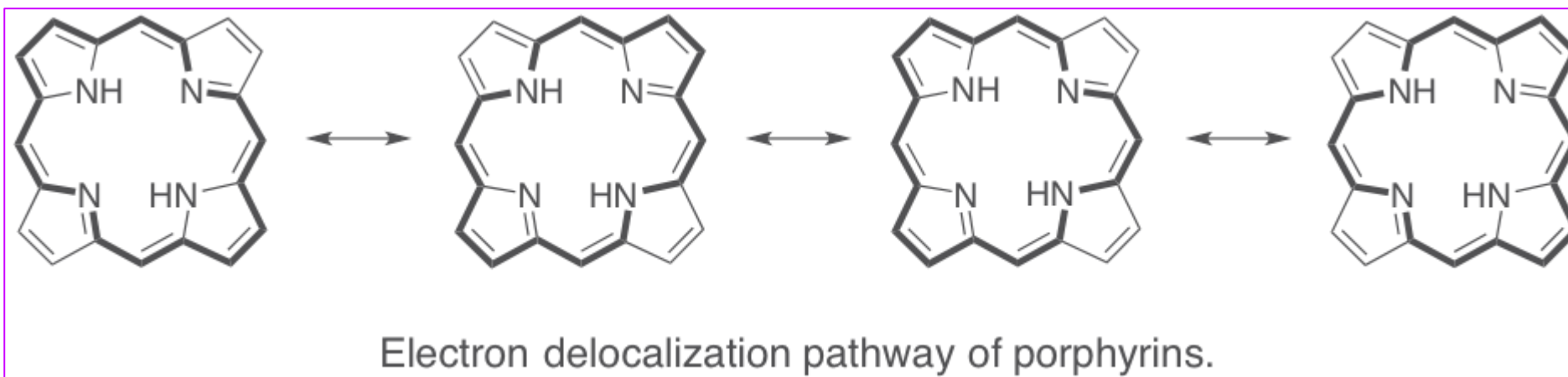
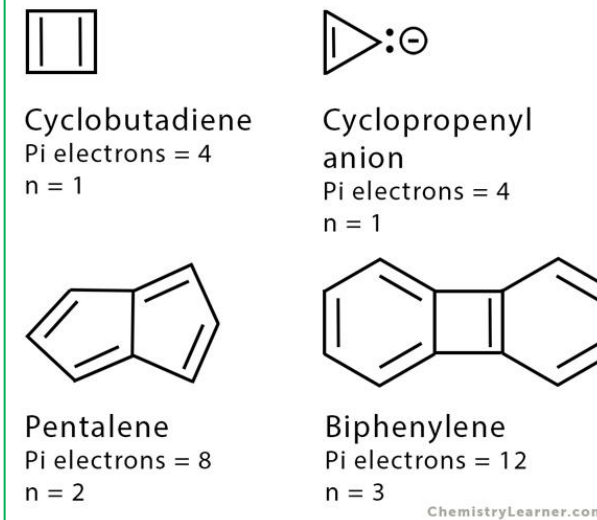


- The porphyrin macrocycle contains 18 delocalized  $\pi$ -electrons, that are in accord with Hückel's rule of aromaticity with the  $(4n + 2)$   $\pi$ -electrons of the porphyrin corresponding to an aromatic system.

### Huckel's Rule for Aromatic Compounds (Number of Pi Electrons = $4n + 2$ )

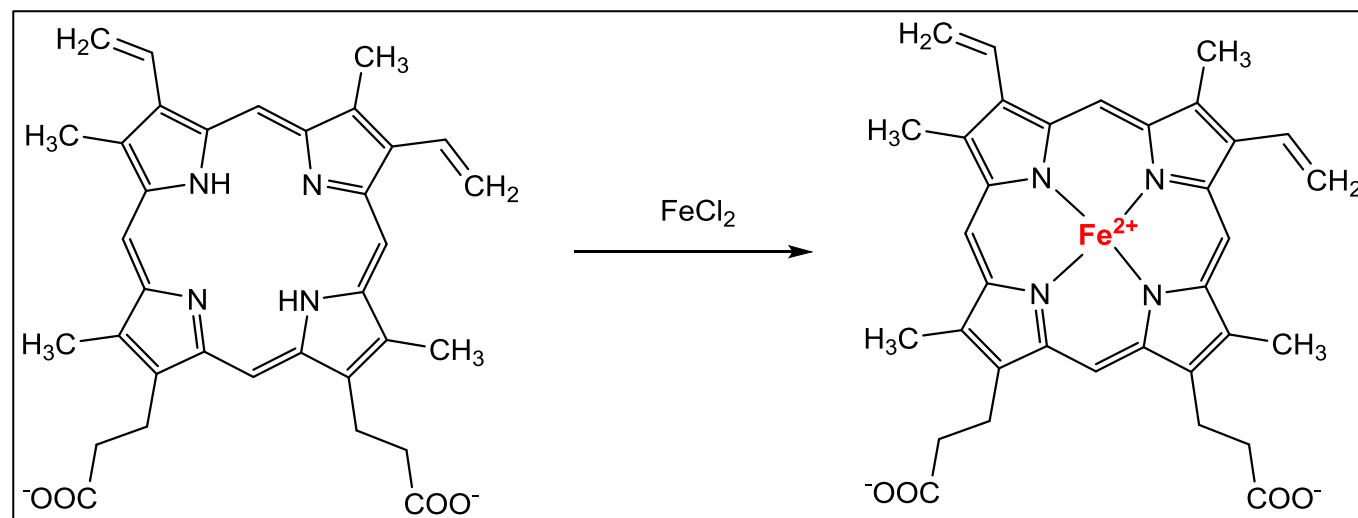


### Huckel's Rule for Antiaromatic Compounds (Number of Pi Electrons = $4n$ )



# Preparation of metalloporphyrins

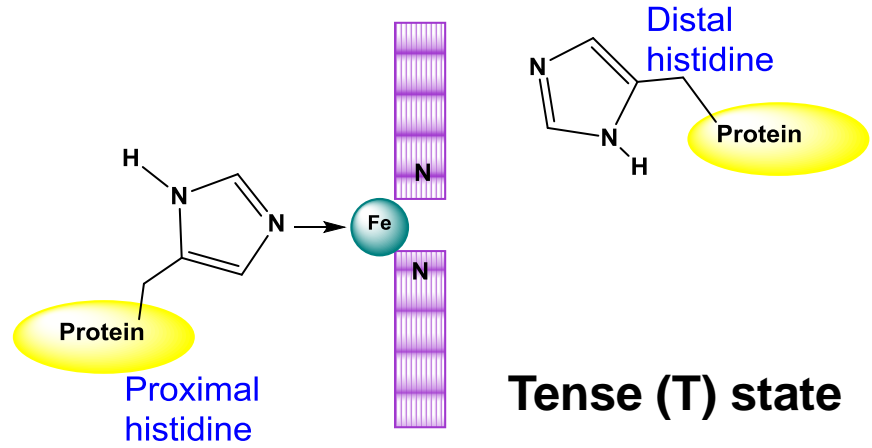
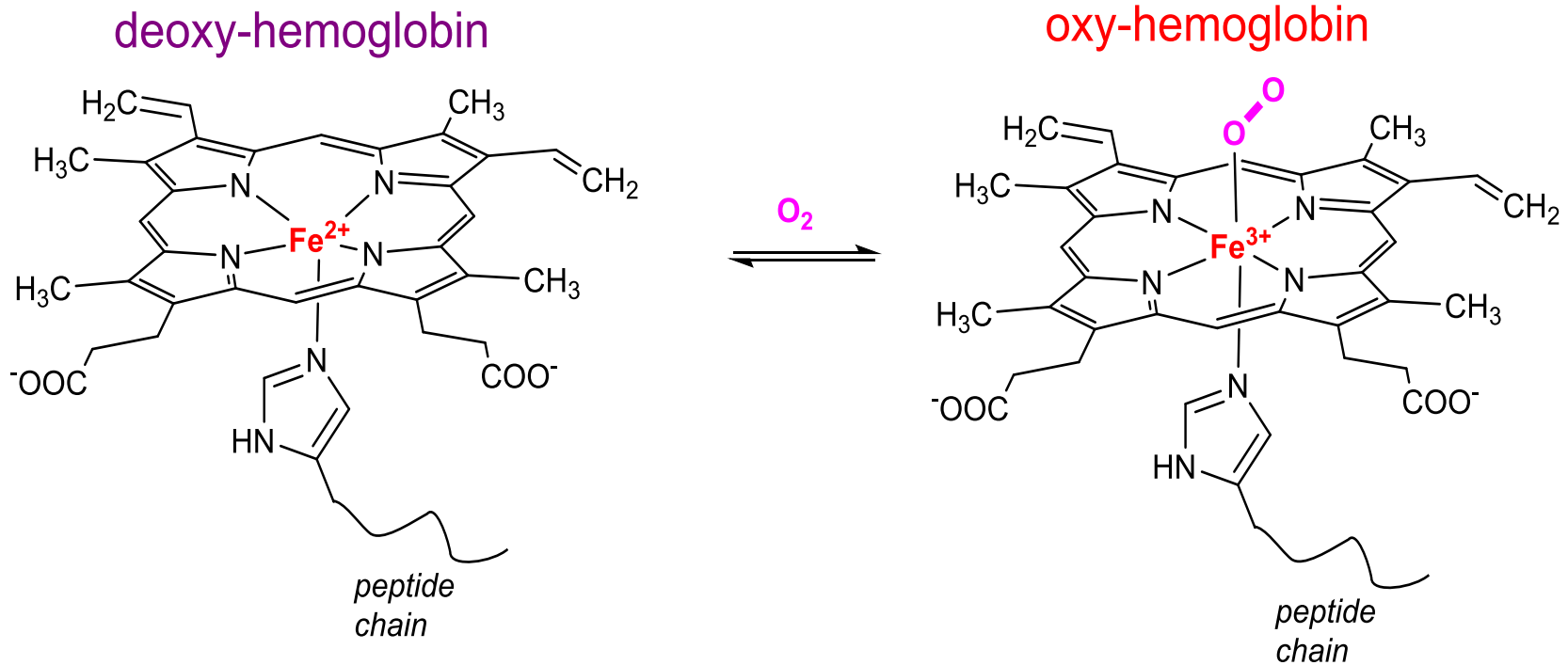
❖ Deprotonated, porphyrins are some excellent tetradentate ligands. They can be metalated by almost all the metals from the periodic table by reaction with the corresponding metal salts. In biological systems, the properties of metalloporphyrins often depend on the nature of the coordinated metal. Under its dianionic form, the four electron pairs of the nitrogen atoms are oriented toward the center of the macrocycle. Thus, the metal is often located at the center of the porphyrin cavity.



❖ The minimum coordination number of the metal is equal to four but it can increase to six thanks to the coordination in axial positions. Axial positions play a central role in the reversible axial ligation of adducts.

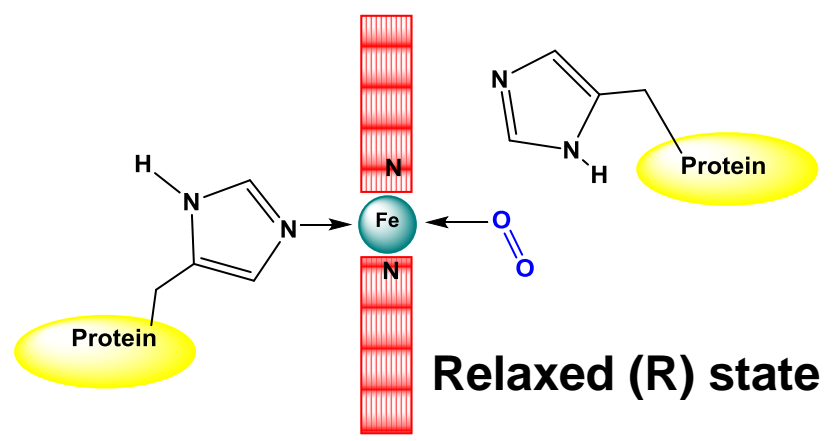
- Role of distal histidine: **Makes O<sub>2</sub> to bind in a bent fashion and makes it difficult for CO to bind in a linear fashion.**

- An isolated heme binds CO 25000 times as strongly as O<sub>2</sub> 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



$Fe^{2+} t_{2g}^4 e_g^2$ , High spin, radius 92 pm  
Paramagnetic

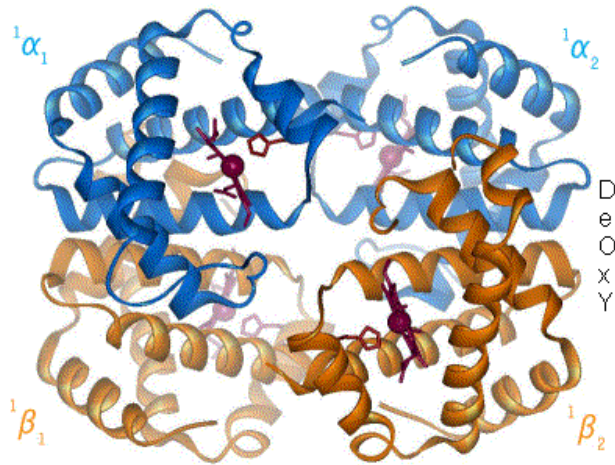
Fe 42 pm outside porphyrin plane



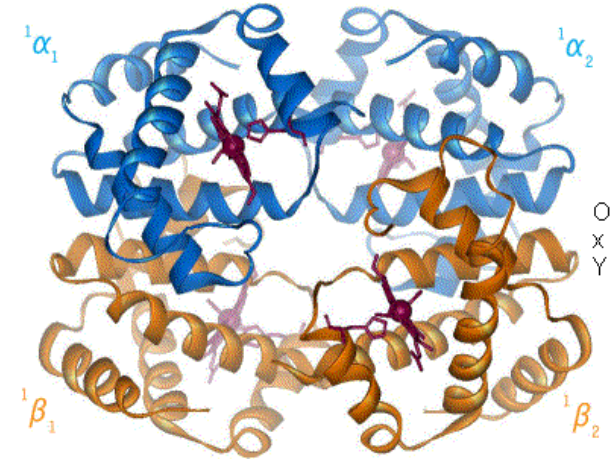
$Fe^{3+} t_{2g}^5 e_g^0$ , Low spin, radius 75 pm  
Diamagnetic

Fe fits inside the porphyrin plane

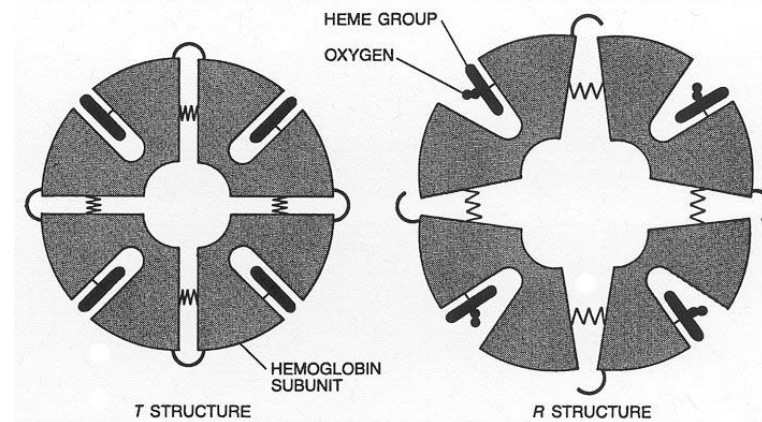
# Hemoglobin: Tense (T) and Relaxed (R) States; Deoxy versus Oxy: The cooperative effect



- Binding of  $O_2$  to Hb is cooperative. The presence of bound oxygen favor addition of more  $O_2$ . The Hb molecule goes from a tense to a relaxed state. Pockets of heme gets more easy for the following  $O_2$  units to access due to breaking of some weak interactions.
- This happens like chain and pulley. The pulling of the proximal histidine along with the activity of Fe getting into the plane of the porphyrin triggers this activity



Removing the first stamp requires more effort



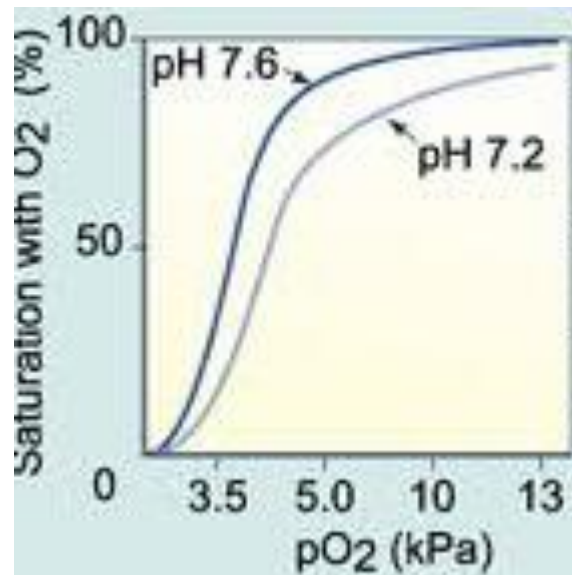
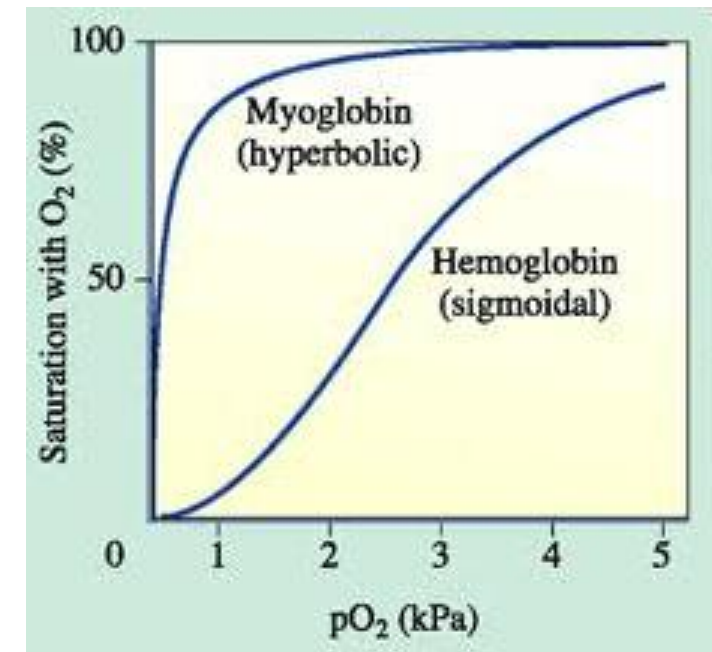
Deoxy Hb

Oxy Hb

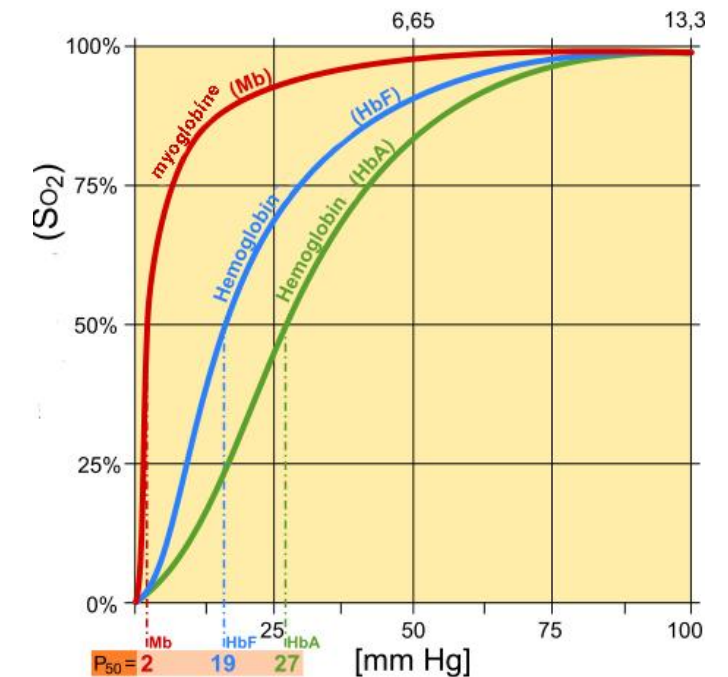
Courtesy: Prof. Anil J. Elias,  
IIT Delhi

# Hemoglobin: An allosteric protein

- An allosteric protein does not have fixed properties. Its functional characteristics are regulated by specific molecules present in its environment. **Hemoglobin is an allosteric protein while Myoglobin is not.**
- Function of Hemoglobin in the living system is regulated by oxygen partial pressure,  $H^+$  concentration and 2, 3 biphosphoglycerate presence (BPG)



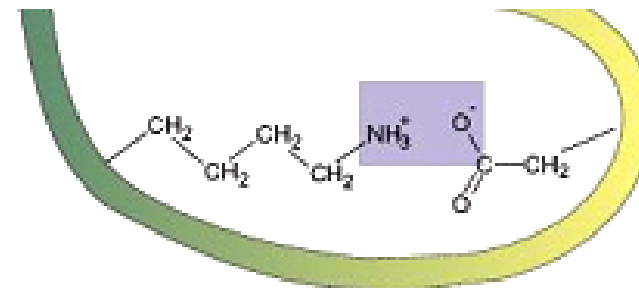
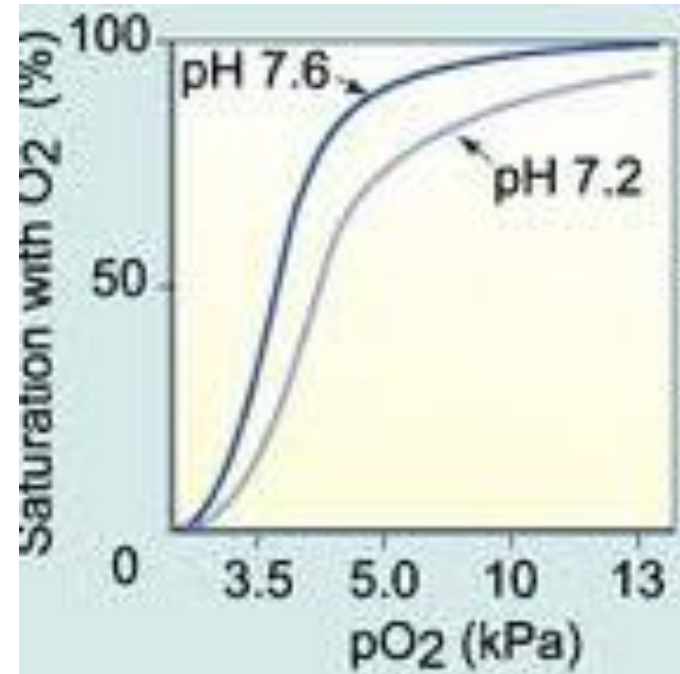
**Bohr Effect (effect of H<sup>+</sup> on Hb)**



**2,3-BPG (saturation of O<sub>2</sub> on Hb-F)**

# The Bohr Effect

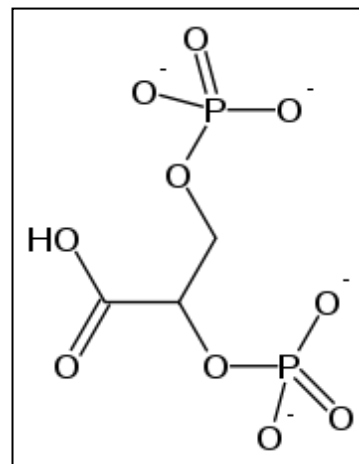
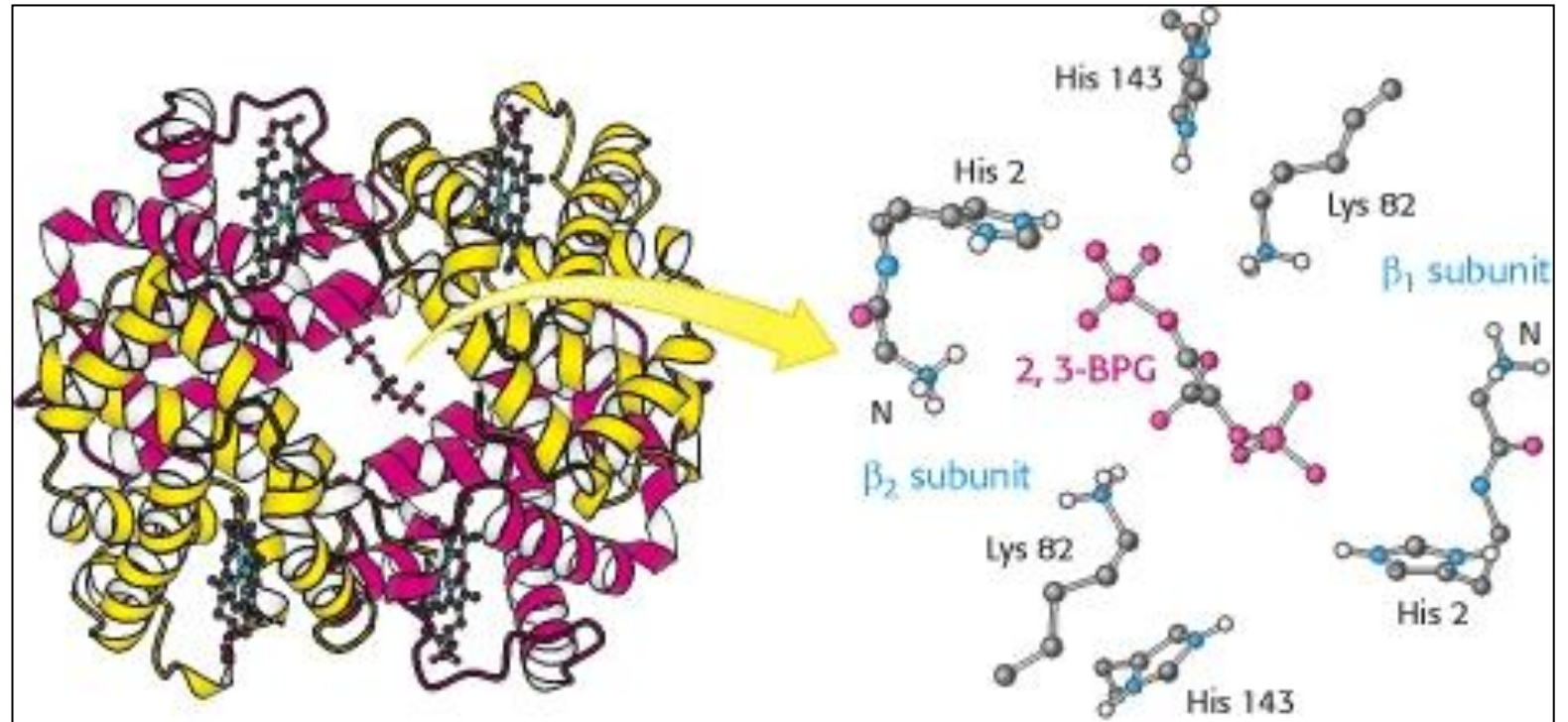
- Christian Bohr, father of Niels Bohr discovered this effect. An increase in concentration of protons and/or carbon dioxide will reduce the oxygen affinity of hemoglobin
- The chemical basis for the Bohr effect is due to the **formation of two salt bridges of the quaternary structure**. One of the salt bridges is formed by the interaction between Histidine 146 and Lysine 40. This connection will help to orient the histidine residue to also interact in another salt bridge formation with the negatively charged aspartate 94. The second bridge is formed with the aid of an additional proton on the histidine residue.
- Below a pH of 6, the imidazole ring of histidine is mostly protonated thus favoring salt bridge formation**



A salt bridge ( weak electrostatic interaction)

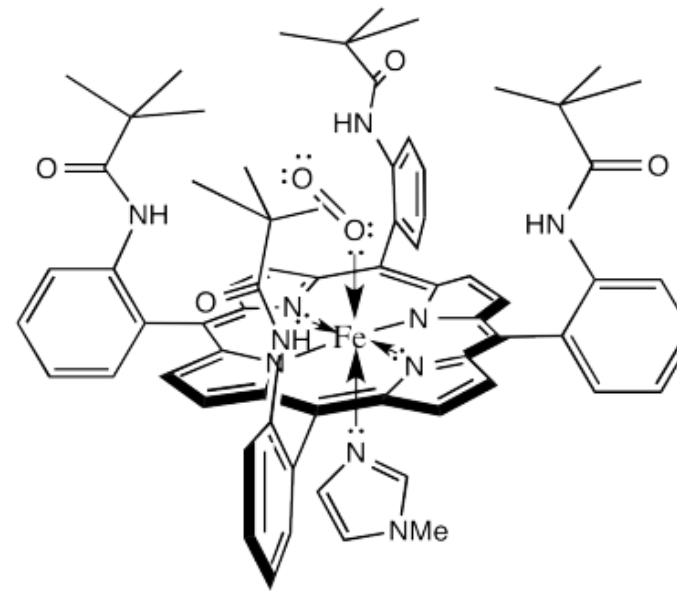
## 2, 3 biphospho glycerate (BPG)

- The organic compound **2, 3 biphospho glycerate (BPG)** binds to hemoglobin A and reduces its  $O_2$  affinity by a factor of 26. This at the first instance will make one wonder why? Interestingly, this increases the oxygen-binding affinity of fetal hemoglobin (Hb-F) relative to that of maternal (Hb-A) hemoglobin. This difference in oxygen affinity allows oxygen to be effectively transferred from maternal to fetal red cells, the transport of oxygen from mother to fetus.

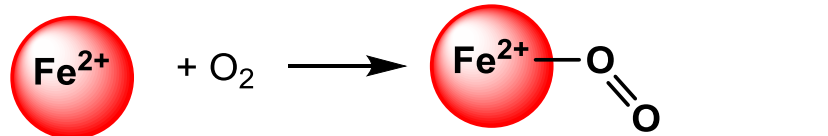


**2,3-  
Biphospho  
glycerate**

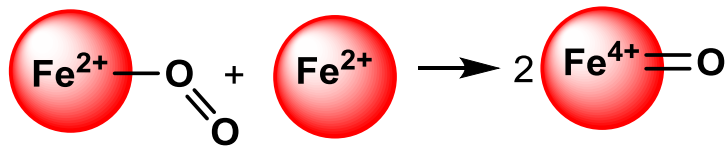
# Can the prosthetic unit part of a metalloprotein perform its normal function without the protein unit around it ?



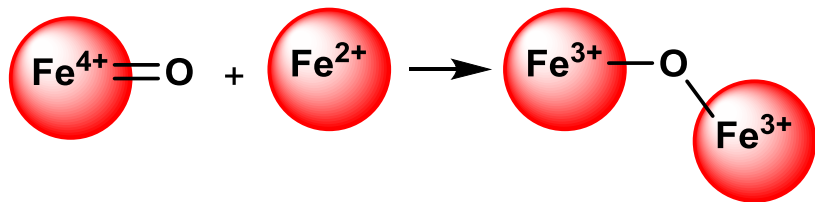
James Collman at Stanford University succeeded in demonstrating reversible oxygen binding to the "picket fence" porphyrin complex shown below. The bulky tert-butyl groups serve to keep the bound oxygen from bridging to another complex.



Free Heme



*Highly reactive!*



$\mu$ -oxodimer (hematin)

- Steric hindrance:** The globin part of the molecule prevent one oxoheme from attacking another heme. The embedded heme will reversibly bind dioxygen. And more recently, this same result has been achieved by "picket-fence" – that reversibly binds oxygen

- Lighter elements are more abundant in general and therefore utilized more.
- 3d metals, rather than 4d, are used as catalytic centers in metalloenzymes.
- ❖ Why has Mo (4d) rather than Cr (3d) been utilized more biologically?
  - Although Mo is rare in the earth's crust, Mo is the most abundant transition metal in sea water as  $\text{MoO}_4^-$  has fairly high solubility in water. Better correlation exists between the abundance of elements in human body and in sea water than between the human body and the earth's crust. Taken as evidence for the oceans as the site of evolution of life.
- ❖ Despite the high abundance of Si, Al and Ti (the 2<sup>nd</sup>, 3<sup>rd</sup> and 10<sup>th</sup> most abundant elements on earth). Why are they not utilized biologically?
  - Because of the insolubility of their naturally occurring oxides ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ) under physiological conditions. A lower oxidation state is unavailable for Si and Al and unstable for Ti in an aerobic environment and is readily oxidized to Ti(IV) at pH 7.
- ❖  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  have very similar coordination chemistry and ionic size and can be interchanged in many Zn enzymes without loss of activity. Why is Co not utilized more biologically?
  - Zn is much more abundant and therefore has been utilized more.
- ❖ Why has cobalt been given an essential role in cobalamins despite its very low availability?
  - The unique properties of cobalt (e.g. its oxidation states, redox potentials and coordination chemistry) is needed to achieve essential functions of  $\text{B}_{12}$  coenzymes

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