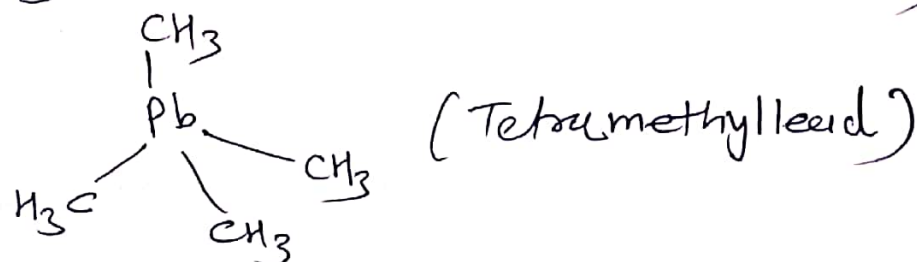


* Organometallic compounds of transition elements.

- The compounds containing at least one direct metal-carbon bond are called organometallic compounds.
- The term 'metal' in this definition includes all those ~~metals~~ elements which are less electronegative than carbon.
- The electronegativity of carbon is 2.5.
The electronegativities of Si (1.8), B (2.0), As (2.0), Ge (1.8) etc.

→ examples



Ferrocene

→ Hapticity (η)

— "The no. of carbon atoms of an organic ligands which are directly attached to (or closely associated with) the metal in organometallic comp. is called the hapticity of the organic group."

* The 18-Electron Rule:

- Sidwick made an attempt to explain the nature of bonding in transition metal complexes on the basis of electronic concept.
- According to him, the ligand acts as a Lewis base and the metal ion acts as Lewis acid.
- The complex compound in which the central metal atom or ion acquires noble gas electronic configuration are stable.
- Effective Atomic Number (EAN)
"The sum of the electrons on the central metal atom or ion and the electrons donated from the ligands is called effective atomic number of the metal. It is equal to the atomic number of noble gases i.e. 36 (Kr), 54 (Xe), or 86 (Rn)."

$$\text{EAN} = \text{No. of electrons in central metal atom or ion} + \text{No. of electrons donated by ligands.}$$

→ For example: The EAN of Cr in $[\text{Cr}(\text{CO})_6]$.

No. of electron in Cr atom = 24 (Atomic No.)

No. of electron donated by 6 CO = $2 \times 6 = 12$

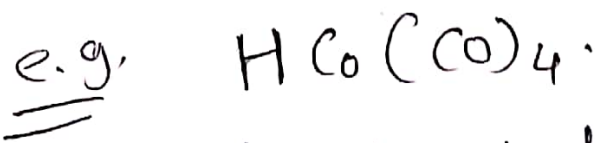
$$\text{EAN of Cr in } [\text{Cr}(\text{CO})_6] \quad 36$$

- "When the central metal atom or ion of a complex compound acquires an outer shell electronic configuration $(n-1)d^{10} ns^2 np^6$, there will be 18-electrons in the valence orbitals. & the electronic configuration will be closed and stable. It is known as the 18-electron rule.
- The complexes obeying the 18-electron rule are quite stable.

(*) Counting electrons in Complexes:

- The 18-electron rule is very useful in predicting stabilities and structure of organometallic compounds.
- These are two methods for counting electrons in complexes

- ① Neutral atom or covalent model
- ② Oxidation state or ionic model.



According to Neutral atom;

- There is a covalent bond betⁿ Co & H, atom in $HCo(CO)_4$ & H atom acts as 1e donor ligand.

- Accordingly, no. of electrons in the valence orbitals of Co in.

$$\begin{aligned} \text{HCo}(\text{CO})_4 &= 9 + (4 \times 2) + 1 \times 1 \\ &\quad \text{Co} \quad (\text{CO}) \quad (\text{H}) \\ &= 9 + 8 + 1 \\ &= 18 \text{ elec.} \end{aligned}$$

[Note: Co (Atomic no. 27), so valence electron = 9]
As $(18) + 9 = 27$

→ According to Oxidation state or ionic model, there is a ionic bond betⁿ $(\text{OC})_4\text{Co}^{\oplus}$ & H^{\ominus} ions in $\text{HCo}(\text{CO})_4$ & H^{\ominus} ion acts as $2e^-$ donor ligand. Therefore no. of electrons in the valence orbitals of Co in

$$\begin{aligned} \text{HCo}(\text{CO})_4 &= 8 + 4 \times 2 + 1 \times 2 \\ &\quad (\text{Co}^{\oplus}) \quad (\text{CO}) \quad (\text{H}^{\ominus}) \\ &= 8 + 8 + 2 = 18 \text{ electrons.} \end{aligned}$$


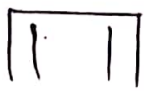
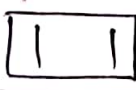
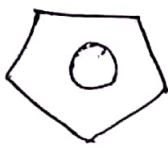
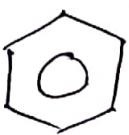
→ Complex which follow 18 electron rule is stable

→ Complex which follow 17 electron rule is strong oxidizing agent.

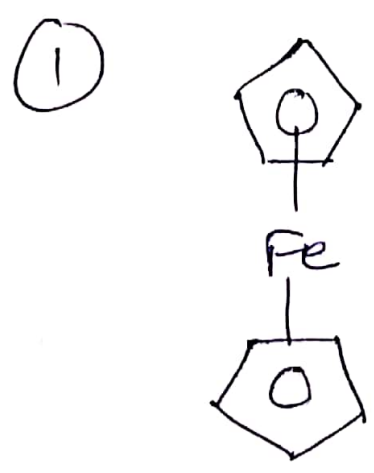
→ Complex which follow 19 electron rule is strong reducing agent.

Some common organic ligands & their electron counts.

Ligand	Available electrons. Covalent model or Neutral atom method
Carbonyl [M-CO]	2
Phosphine [M-PR ₃]	2
Amine [M-NR ₃]	2
Amide [M-NH ₂]	1
Hydrogen [M-H]	1
Methyl [M-CH ₃]	1
Alkene	2
Alkyne	2
η^2 -C ₆₀	2
Carbene [M=CH ₂]	2
Halogen [M-X]	1
Alkyl [M-R]	1
Aryl [M-Ar]	1

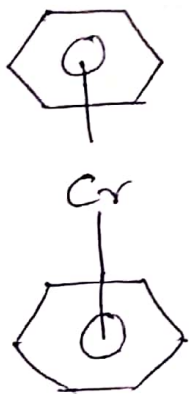
$\text{CH}_2 = \text{CH} - \text{CH}_2 -$ (σ -Allyl)	1
Ethene $\text{CH}_2 = \text{CH}_2$	2
 (π -Allyl)	3
 (1,3-Butadiene)	4
 (Cyclobutadiene)	4
 (Cyclopentadienyl)	5
 (Benzene)	6
Carbyne ($\text{M} \equiv \text{CH}$)	3

* Some examples of electron Counts :-
(Neutral atom method)



$$\begin{aligned} \text{Fe} &= 8 \\ 2(\text{C}_2\text{H}_5) &= \frac{2 \times 5 = 10}{18 \text{ ele}} \end{aligned}$$

②



$$C_2 = 6 e^-$$

$$2 C_6H_6 = \frac{2 \times 6 = 12 \text{ ele}}{18 \text{ ele}}$$

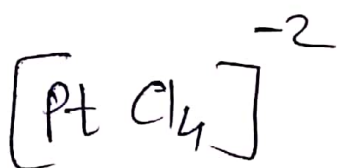
③



$$Ni = 10 \text{ ele}$$

$$2 C_5H_5 = \frac{2 \times 5 = 10 e^-}{16 e^-}$$

④



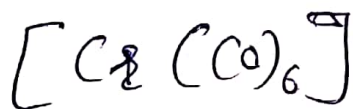
$$Pt = 10 e$$

$$4 Cl = 4 e^-$$

$$\text{charge} = 2 e^-$$

$$\frac{16 e^-}{16 e^-}$$

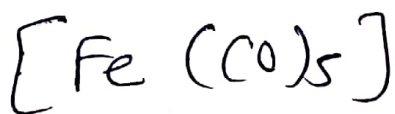
⑤



$$C_2 = 6 e$$

$$6 CO = \frac{12 e}{18 e^-}$$

⑥



$$Fe = 8 e^-$$

$$5 CO = \frac{5 \times 2 = 10}{18 e^-}$$

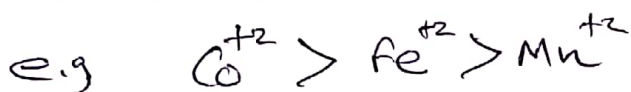
* Stability of Complexes :-

→ Factors affecting stability of complexes are as follows.

[A] Effect of central metal ion

① Ionic Size

→ Smaller an ion → greater its electrical field → More stable complex. $\left[\text{stability} \propto \frac{1}{\text{size}} \right]$



② Ionic charge

→ Higher the charge → high stability

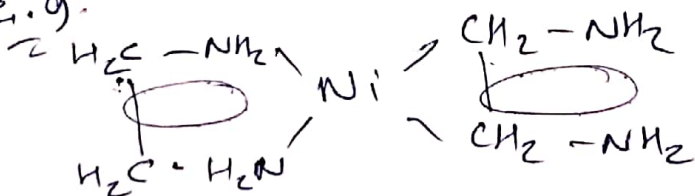


③ Chelate effect :-

⇒ The attainment of ~~a metal~~ extra stability by formation of ring structure by bi or poly dentate ligands which include the metal is termed as chelate effect

⇒ The poly dentate ligands form ring type of structure.

e.g.



- Five & six membered ring are more stable

⇒ ④ Electronegativity - (Acidity)

- Higher the electronegativity of metal →
Higher the stability of complexes.

→ [B] Ligands

① Basic character

- Greater the basic character of ligand,
more stable will be complex.

② charge on ligand

- In case of anionic ligand, greater the
charge, more stable will be complex.

③ Size

- stability $\propto \frac{1}{\text{size}}$

④ Nature of ligand

- Strong field ligand will ~~form~~ form
more stable complex.

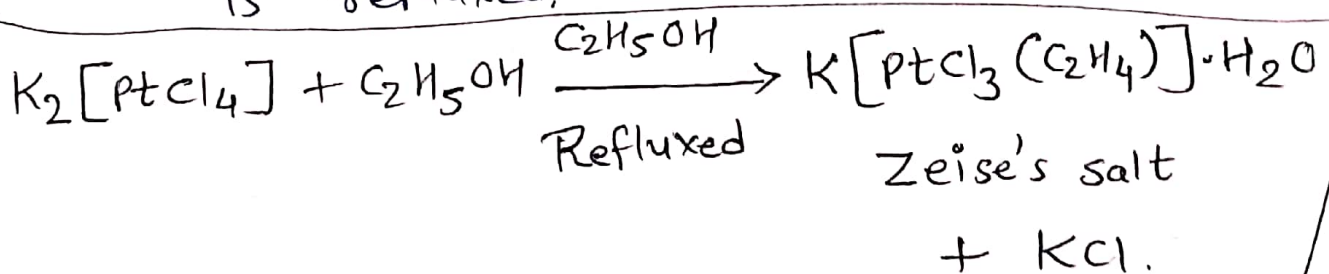
* Synthesis, uses and structure of organometallic compound of π bonding organic ligands.

→ The molecules that have multiple bonds such as $C=C$, $C\equiv C$, $N=O$, $N\equiv N$ etc. can form complexes with transition metals which are called π -complexes.

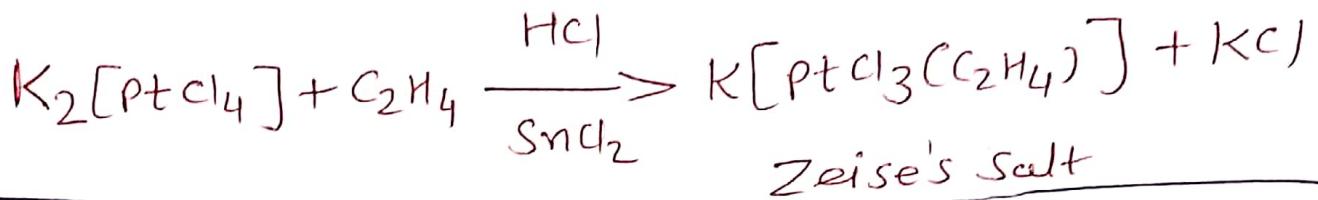
[1] Transition Metal - Alkene complexes:- [2-electron ligands]

- The complexes of transition metals with alkenes (i.e. olefins) have been known since 1827.
- The Danish chemist W.C. Zeise isolated stable yellow crystals of platinum (II)-ethylene complex. It was called Zeise's salt.
- ⇒ Method of preparation of Zeise's salt

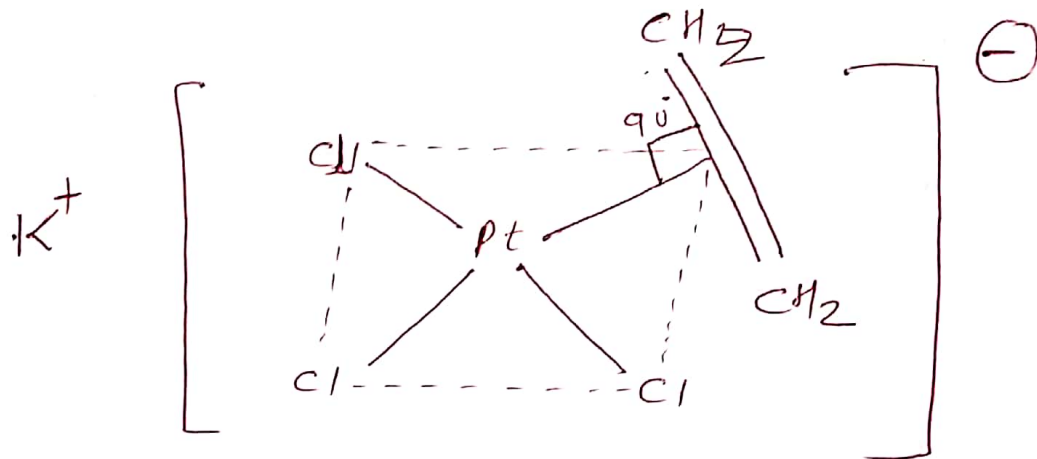
- (a) Zeise's salt is isolated as stable yellow crystals when an ethanolic solⁿ of potassium tetrachloroplatinate (II) is refluxed.



\Rightarrow (b) Zeise's salt may be obtained by shaking of a solⁿ of $K_2[PtCl_4]$ in dilute HCl with ethylene. This reacⁿ is generally slow. It can be speeded up by the addition of small amount of stannous chloride ($SnCl_2$)



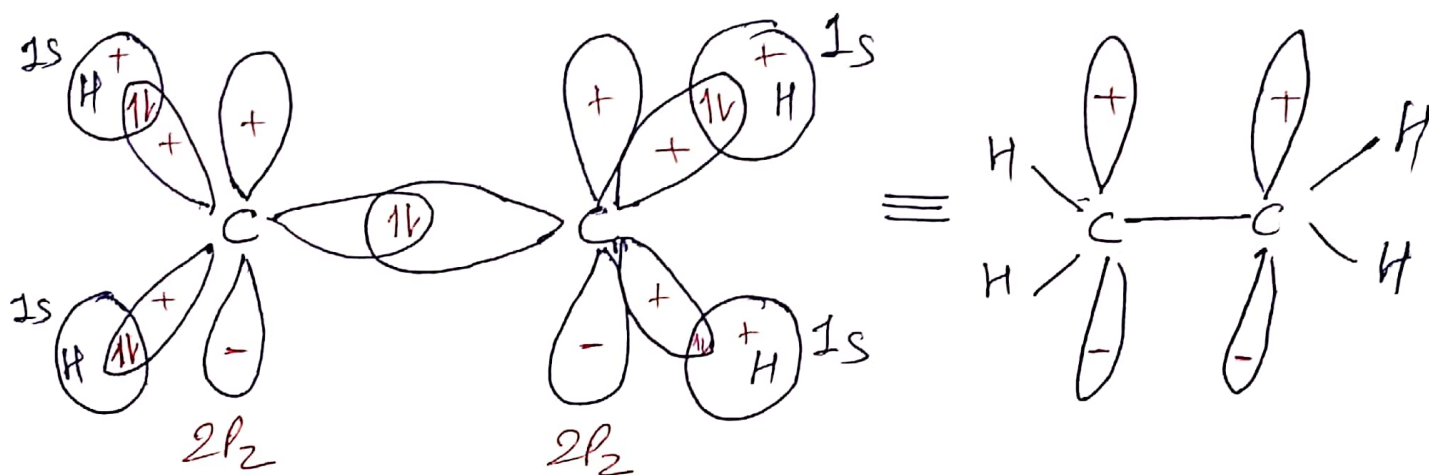
\Rightarrow Structure:



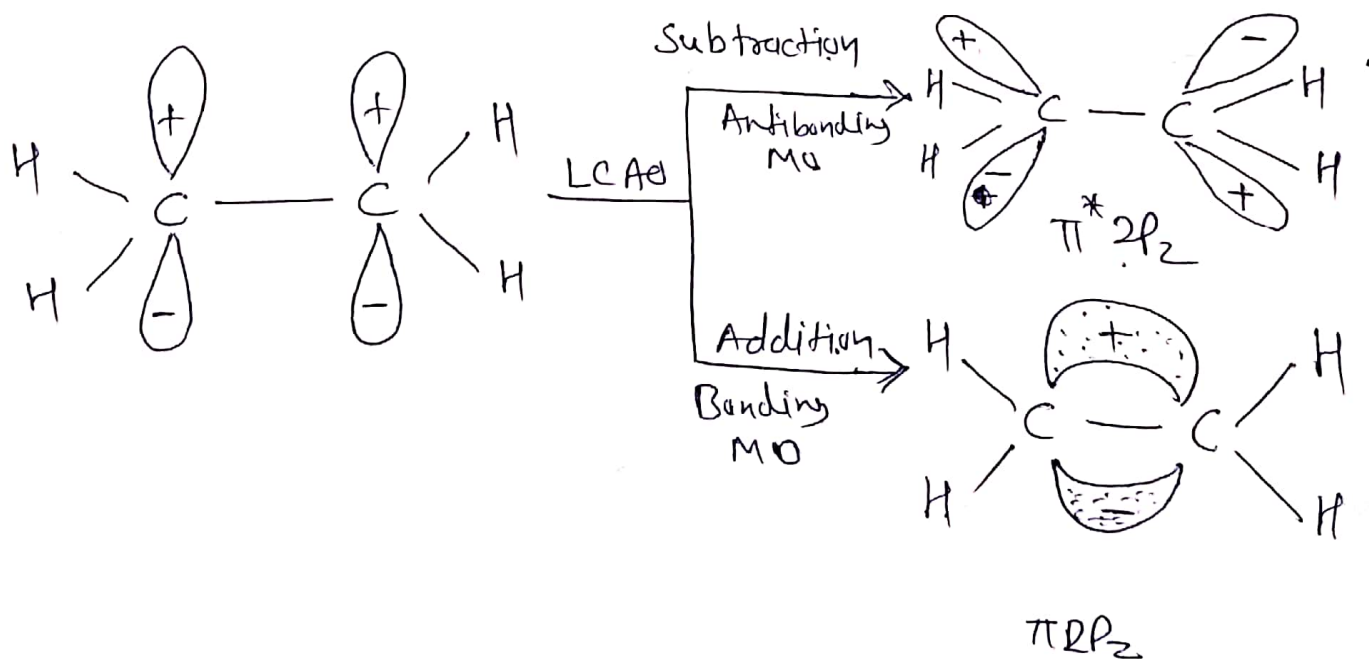
- Pt^{+2} ion is present at the centre of a square plane
- Three corners of square-plane are occupied by Cl^- ions
- C_2H_4 occupies the fourth coordination site of the square-planar complex with $C=C$ bond perpendicular to the $PtCl_3$.
- The two carbon atoms of the coordinated C_2H_4 molecule are almost equidistant from the Pt^{+2} ion.

→ Bonding

- The nature of bonding between Pt^{+2} ion & C_2H_4 molecules in the anion of Zeise's salt.
- First of all, let us consider the nature of bonding in C_2H_4 .
- Each carbon atom forms three σ -bonds, one with other carbon atom and two with Hydrogen atom using its three singly occupied sp^2 hybrid orbitals as follows.

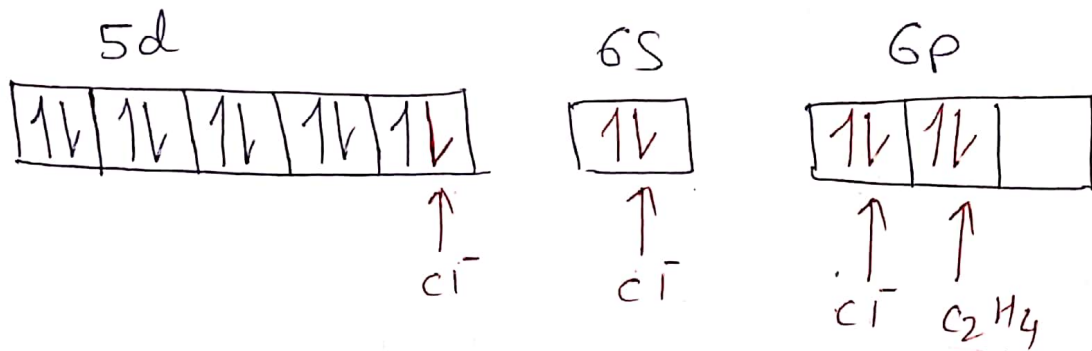


- These two parallel singly occupied $2p_z$ atomic orbitals take part in the linear combination producing two π -molecular orbitals as follows



→ The Pt^{+2} ion of the anion of Zeise's salt is dsp^2 hybridised. Thus Pt^{+2} ion has 4 vacant dsp^2 hybrid orbitals.

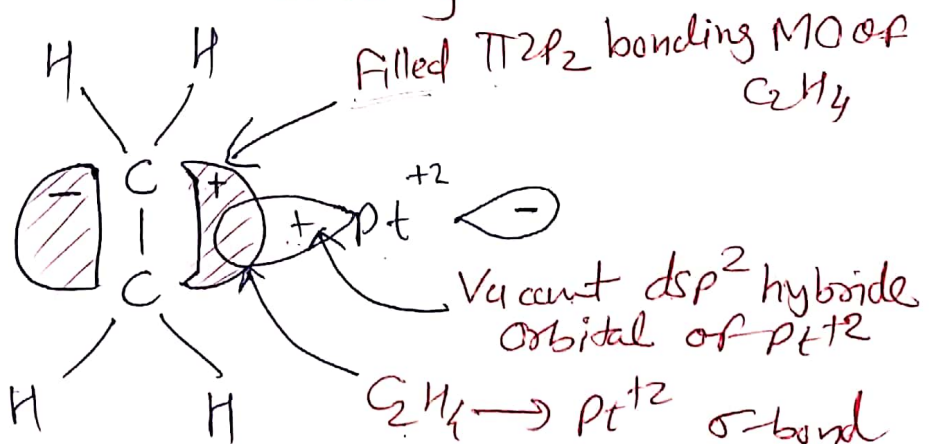
→ Valance Shell Electron Configuration (VSEC) of Pt^{+2} ion $[PtCl_3(C_2H_4)]^{-}$

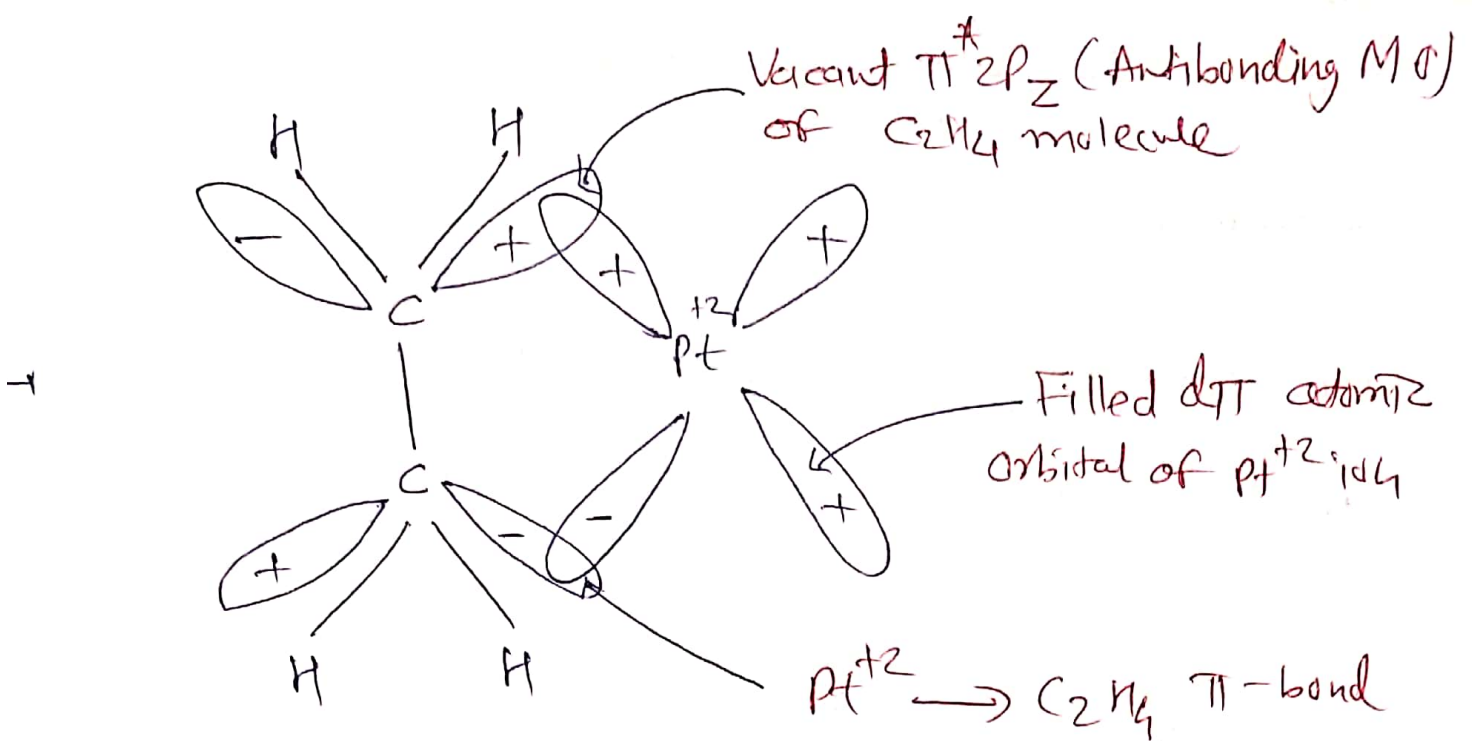


→ The vacant dsp^2 hybrid orbitals of Pt^{+2} ion overlaps with the filled σ - orbitals of Cl^- ion forming $Pt^{+2} \leftarrow Cl^-$ σ bond.

→ Three such σ bonds are formed with 3 Cl^- ions using 3 vacant dsp^2 hybrid orbitals of Pt^{+2} ion.

→ The ~~fourth~~ 4th dsp^2 vacant hybrid orbitals of Pt^{+2} ion overlaps with the filled $\pi 2p_z$ M.O. of C_2H_4 molecule forming $Pt^{+2} \leftarrow C_2H_4$ σ bonds as follows $[\sigma$ -donation from the filled $\pi 2p_z$ in to the vacant dsp^2 hybrid orbitals of $Pt^{+2}]$

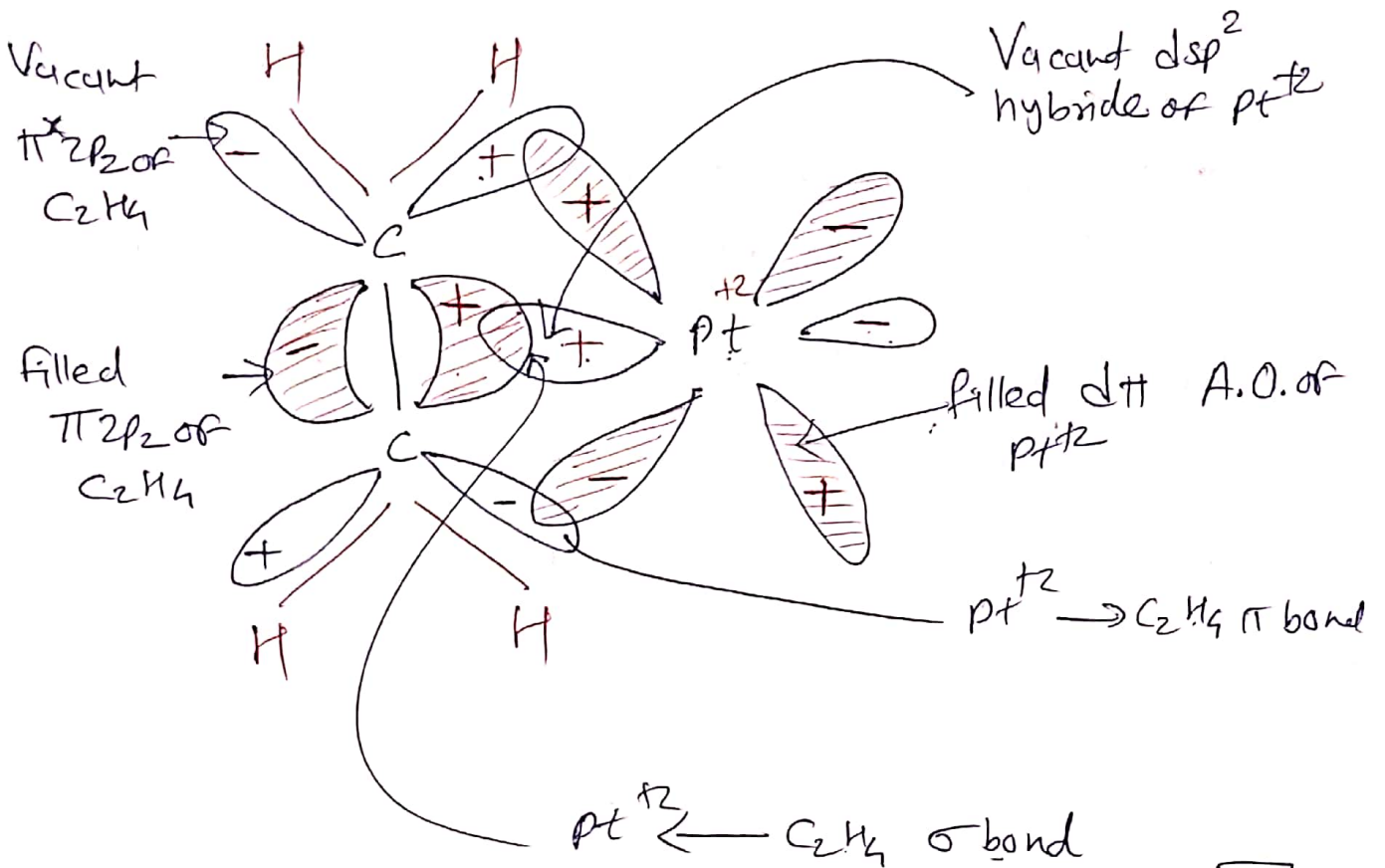




- Now, the filled $d\pi$ atomic orbital ion overlaps with the vacant $\pi^* 2p_z$ M.O. of ethylene molecule forming $Pt^{+2} \rightarrow C_2H_4 \pi$ bond or back bond.

(π -Back-donation from a filled d atomic orbital of Pt^{+2} ion into the vacant $\pi^* 2p_z$ molecular orbital of C_2H_4)

→ The ~~$Pt^{+2} \leftarrow C_2H_4 \sigma$ bond~~ $Pt^{+2} \leftarrow C_2H_4 \sigma$ bond and $Pt^{+2} \rightarrow \pi$ bond reinforce each other. It is called synergic bonding.

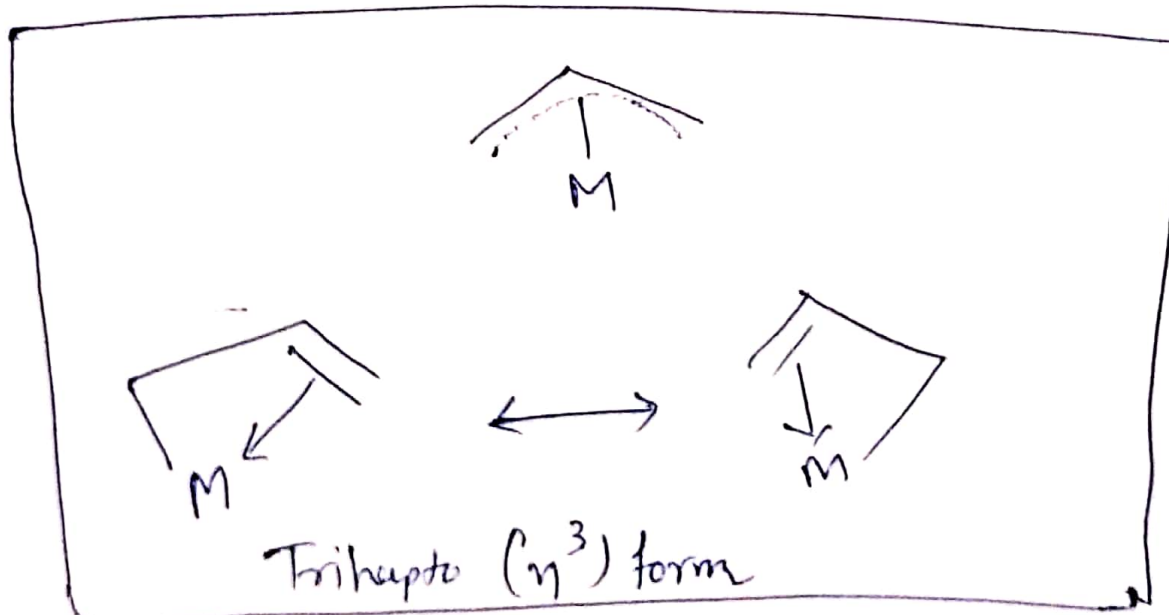
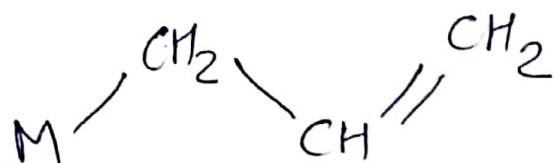
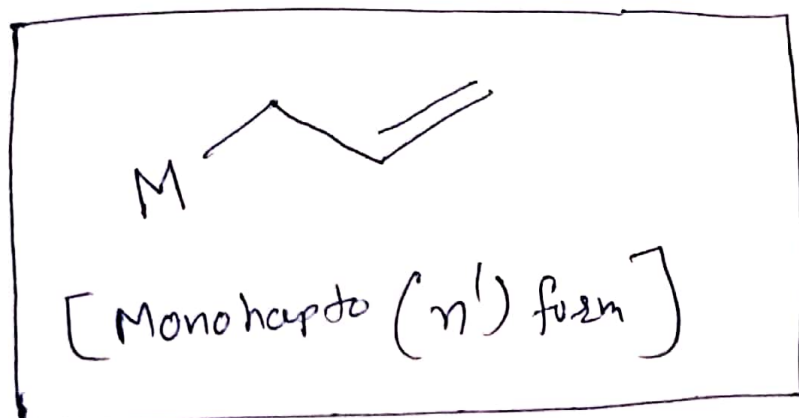


[Synergic bonding betⁿ C_2H_4 & Pt^{+2} in the anion of Zeise's salt]

- For a weakly π -basic metal, this reduction is slight, but for a good π base it can reduce it almost to a single bond.
- Strong donor ligands, a net negative charge on the complex ion, and a particularly low oxidation state for the metal.

(*) Compound with 3 e⁻ ligands (Allyl complexes)

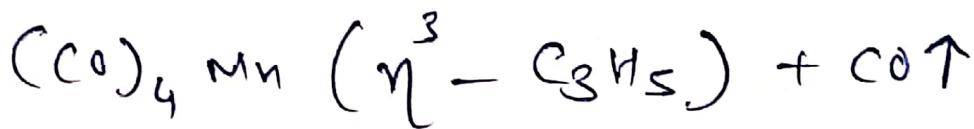
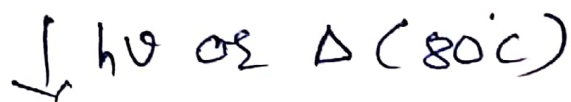
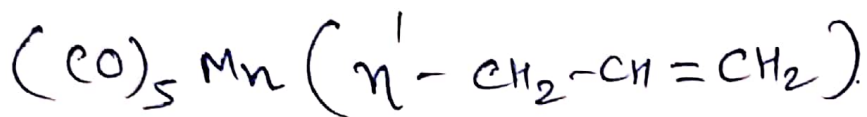
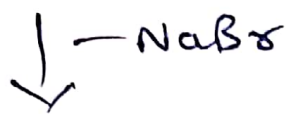
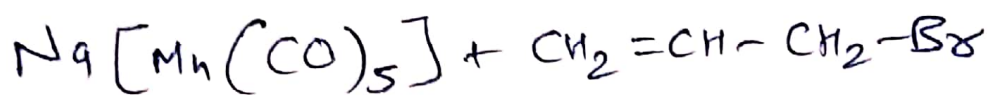
- The allyl ligand is often referred to as an "actor" ligand rather than a "spectator ligand."
- It binds to metals in two ways. i.e. in a η^1 [monohapto] form and a η^3 (trihapto) form.
- In its η^1 form, it behaves as an anionic 1 e-donor X type of a ligand.
- In η^3 form, it acts as an anionic 3 e-donor LX type of ligands.



⇒ (*) General methods of Preparation

- The η^3 -allyl complexes can be prepared by the following routes.

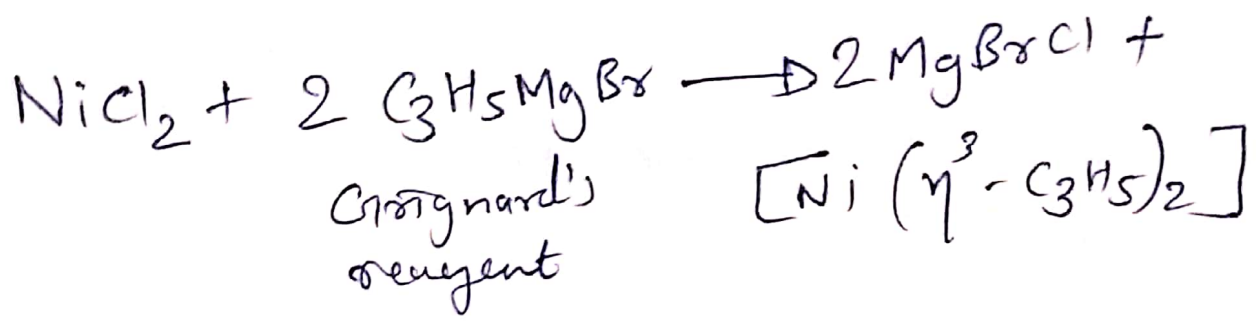
(a) Conversion of η^1 -allyl to η^3 -allyl:-



- Likewise, many other η^1 -allyl carbonyl complexes convert to η^3 -allyl complexes with loss of one CO.

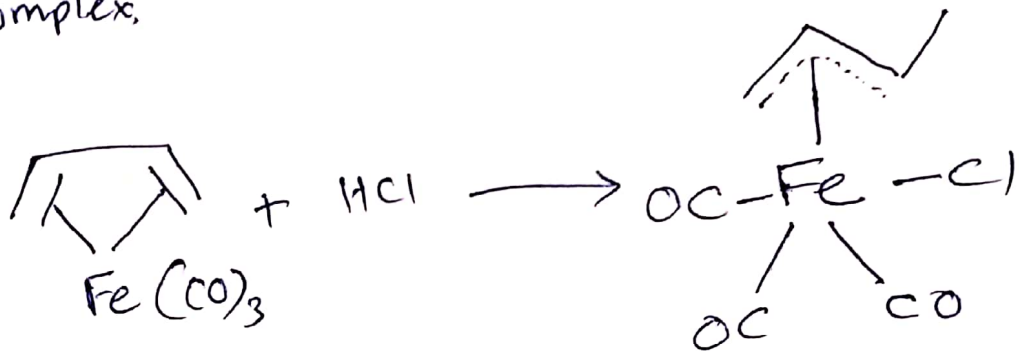
→ (b) Using allyl Grignard's reagents

- When a transition metal halide is treated with an allyl Grignard's reagent in appropriate molar proportion in dry ether solvent at low temperature, η^3 -allyl complex is formed.



→ (c) By protonation of 1,3-butadiene complex:

- If the metal centre is not basic, the protonation of a butadiene complex leads to the formation of a η^3 -allyl complex.

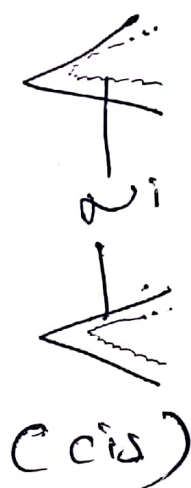
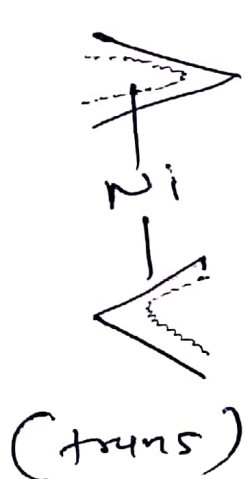


➤ Structure and Bonding

- An allyl group is a substituent with the structural formula $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{R}$, where R is the rest of the molecule.
- It consists of methylene bridge ($-\text{CH}_2-$) attached to a vinyl group ($-\text{CH}=\text{CH}_2$).

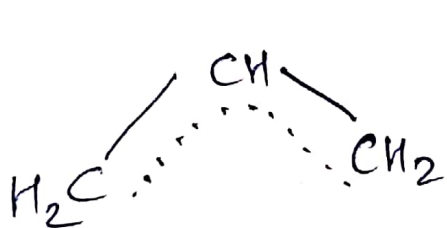
→ The structures of η^3 -allyl complexes of transition metals have been determined by X-ray Diffraction studies. (XRD).

→ In $[\text{Ni}(\eta^3\text{-C}_3\text{H}_5)_2]$, the Ni atom is sandwiched betⁿ two almost ~~parallel~~ parallel allyl groups which may have either cis- or trans- configuration.



→ All the three carbon atoms of the allyl group are almost equidistant from the metal carbon.

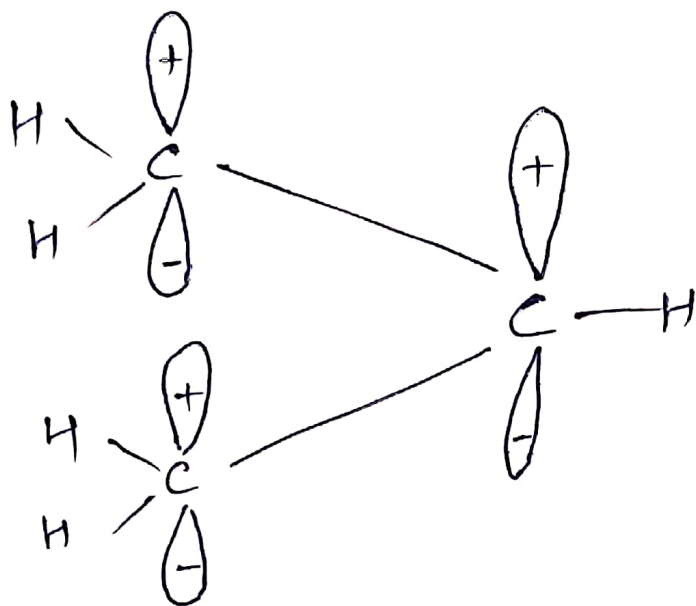
→ All three carbon atoms of the allyl group are sp^2 hybridised.



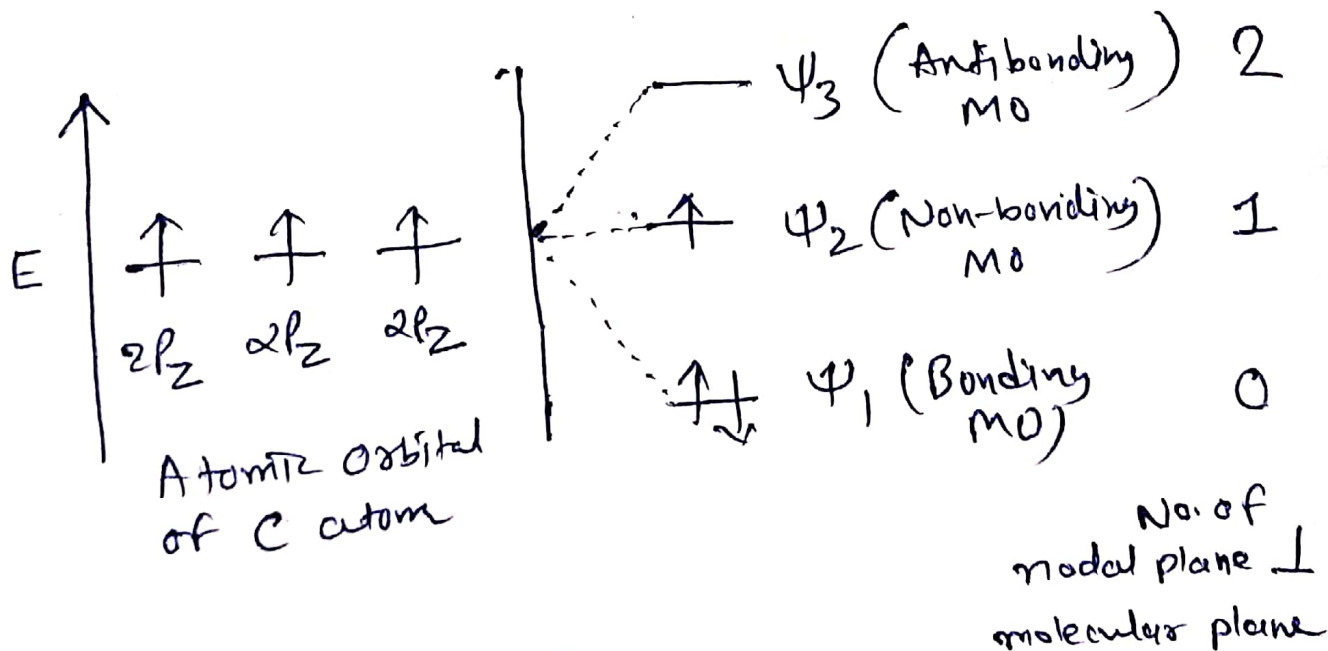
→



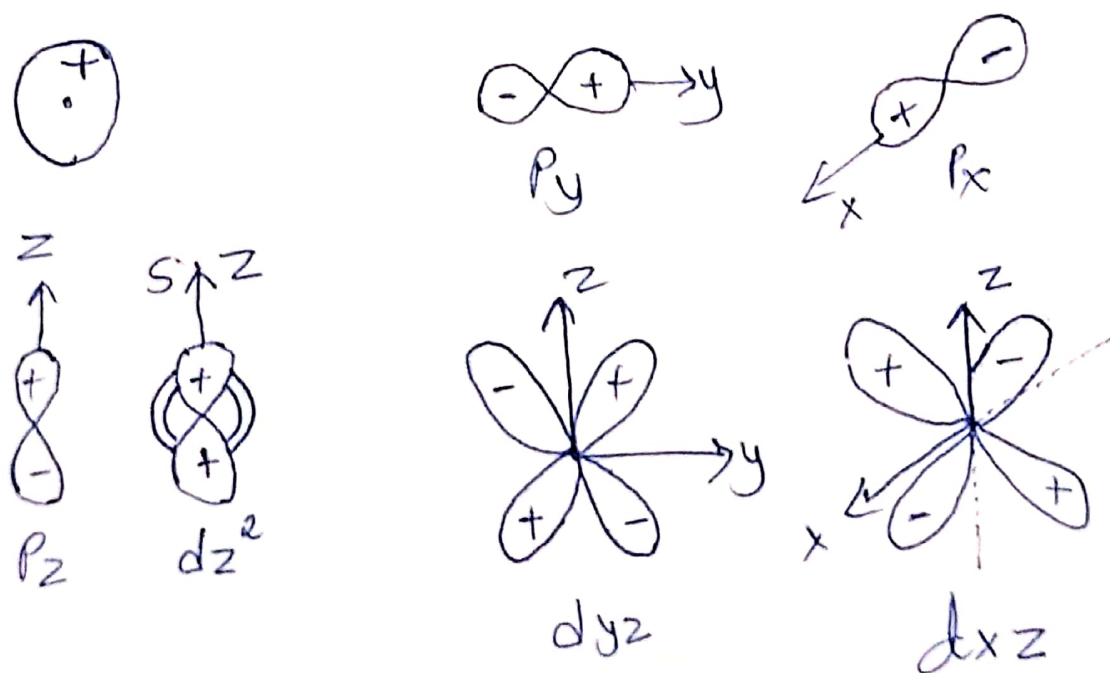
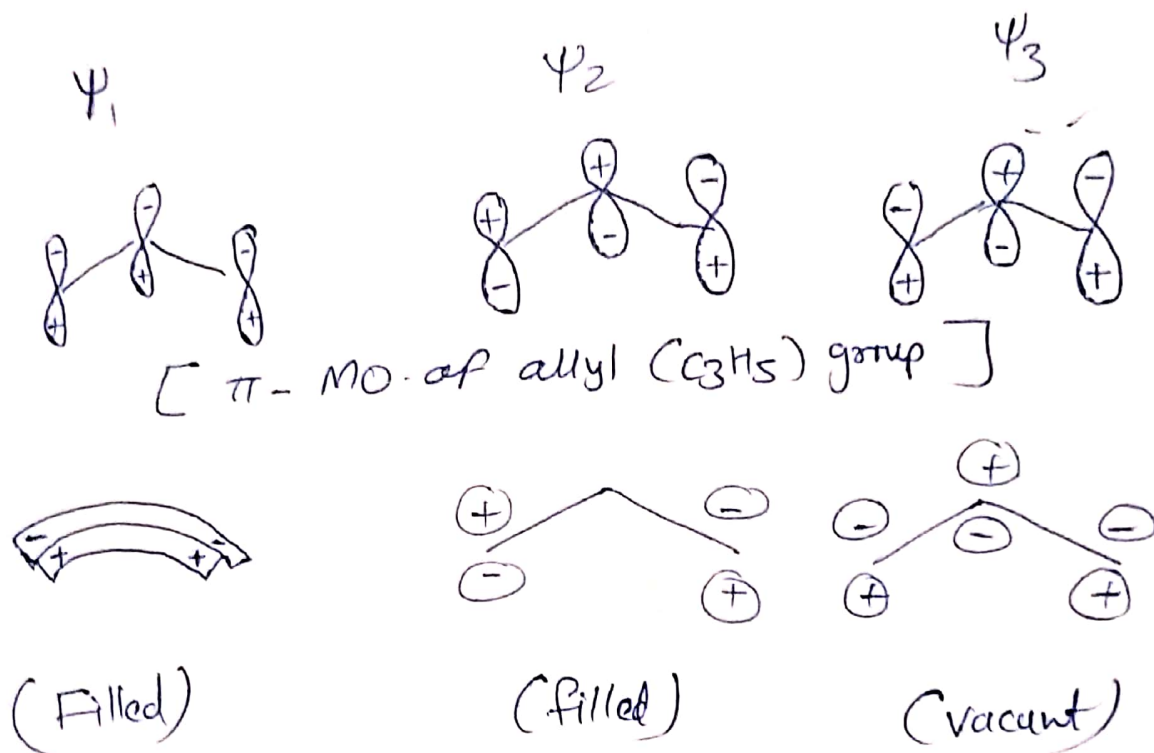
- Each carbon atom forms 3 σ bonds using its 3 singly occupied sp^2 hybrid orbitals.
- The allyl group lies on XY-plane. One singly occupied $2p_z$ atomic orbital perpendicular to the molecular plane remains unused on each carbon atom.



→ These three parallel singly occupied $2p_z$ atomic orbitals take part in the linear combination forming three π molecular orbitals as follows.



- These 3 π molecular orbitals of the allyl group and the atomic orbitals of the metal atom having matching symmetry for overlapping are shown in the following fig.



[Atomic orbitals of matching symmetry]

→ The filled ψ_1 MO of allyl group overlaps with vacant s, p_z & d_z^2 orbitals of the metal atom forming allyl \rightarrow M σ bond.

→ Similarly, the vacant ψ_3 MO of the allyl group overlaps with the filled p_{xz} & d_{xz} AOs of the metal atom forming M \rightarrow allyl π bond.

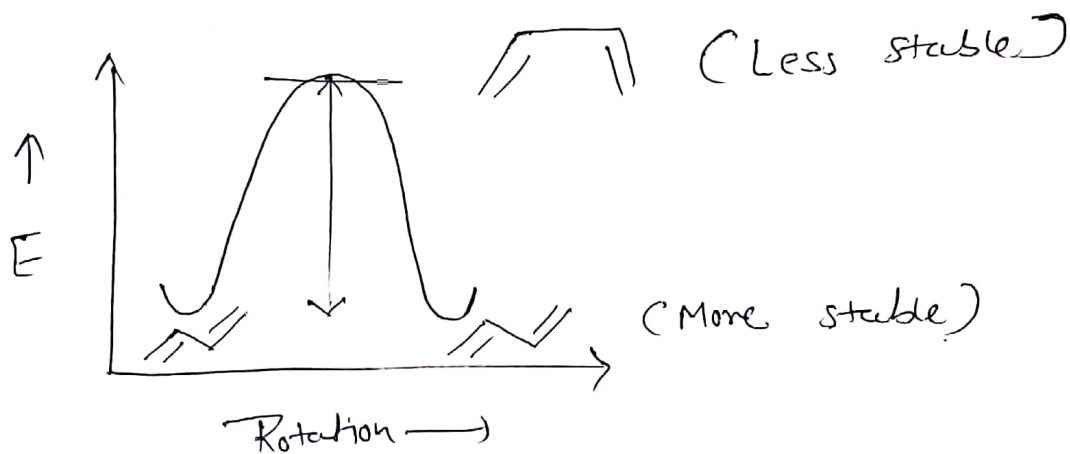
* 4 electron ligand
[Butadiene Complexes]

→ The conjugated dienes such as 1,3 butadiene act as 4 electron donor ligand.

→ 1,3-Butadiene exists as two conformational isomers which are in rapid and dynamic equilibrium with each other. $[CH_2=CH-CH=CH_2]$



→ The energy of s-trans form is 12 ~~kJ~~ KJ mole⁻¹ lower than that of s-cis form.



→ Therefore, the equilibrium mixture contains 95% more stable s-~~trans~~ trans form and only 5% less stable s-cis form.

→ Despite of this difference in the stability, the *S-cis* form is more suitable conformer of 1,3-butadiene to act as 4e donor ligand for a metal atom

→ *S-cis* form of 1,3-butadiene can be bonded to metal atom in two ways.



L_2 -type ligand

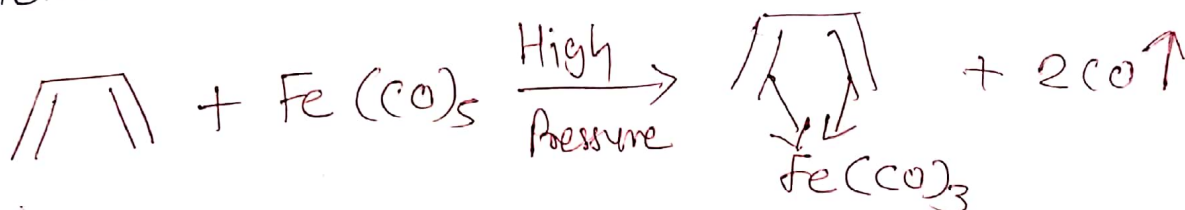


LX_2 -type Ligand,

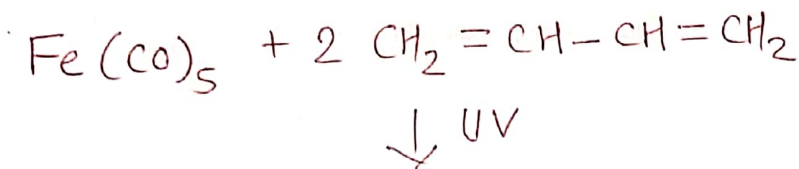
⇒ ⊛ Methods of Preparation

[A] Reaction of metal carbonyl with 1,3-butadiene :-

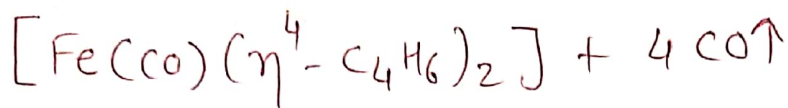
- When a metal carbonyl is treated with 1,3-butadiene, two CO ligands are replaced by the diene molecule forming transition metal-butadiene complex.



- When a mixture of 1,3-butadiene and $\text{Fe}(\text{CO})_5$ is irradiated by UV-light, 4 CO ligands are replaced by two molecules of 1,3-butadiene forming a bis(η^4 -butadiene) complex.

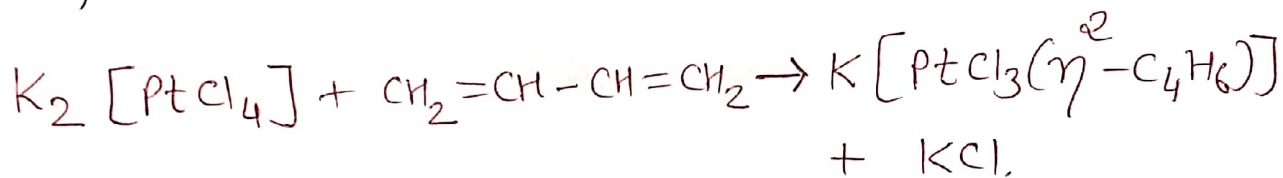


↓ UV

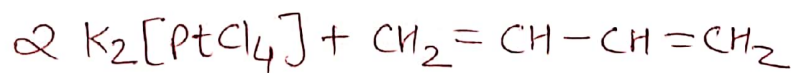


⇒ [B] Reaction of metal halide with
1,3-butadiene :-

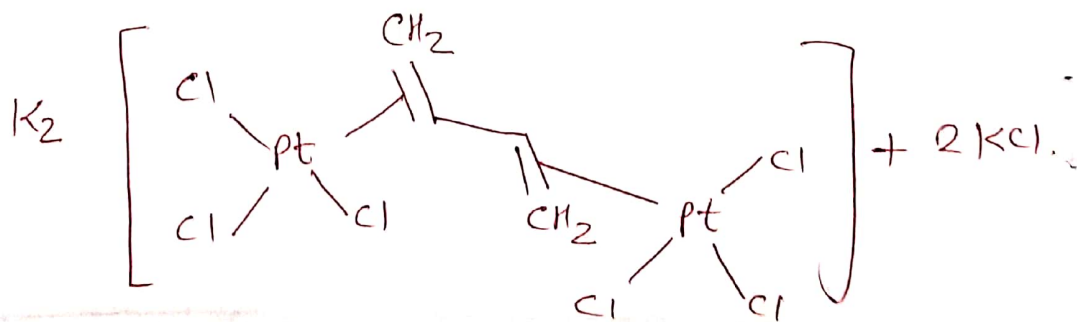
Some 1,3-butadiene complexes can be prepared by the reaction of metal halide with 1,3-butadiene under suitable conditions.



In $\text{K}[\text{PtCl}_3(\eta^2 - \text{C}_4\text{H}_6)]$, 1,3-butadiene acts as a 2e donor dihapto ligand. 1,3-Butadiene may also act as a bridging ligand.

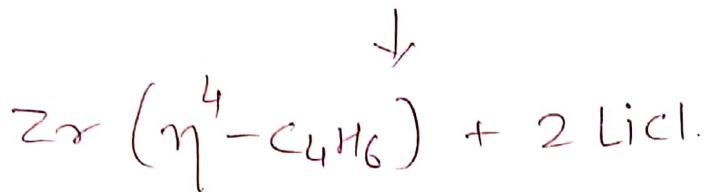
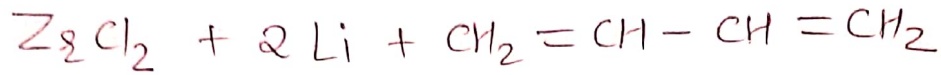


↓



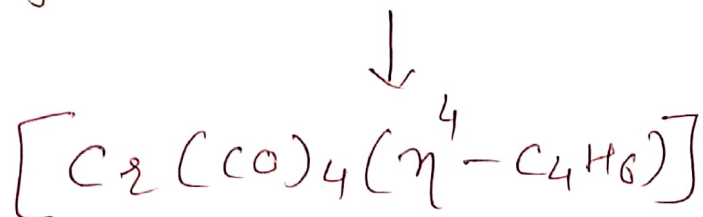
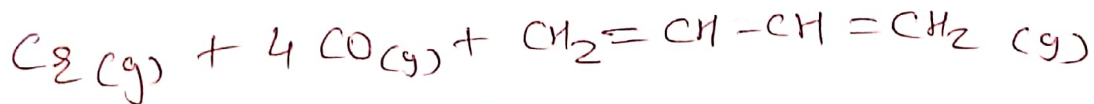
Here, s-trans form of 1,3-butadiene acts as a bridging ligand.

- Early transition metal complexes can be prepared by the reduction of halides in the presence of the ligand.



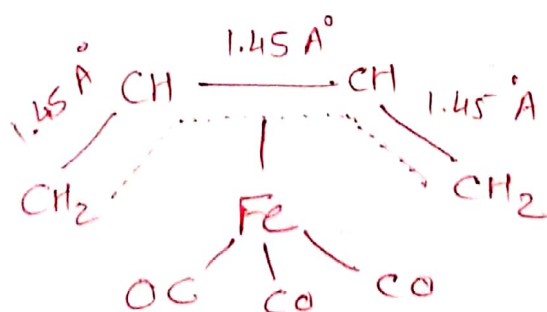
[C] Metal, atom, vapour, phase synthesis:-

- The condensation of vapour of a metal in the presence of 1,3-butadiene and suitable co-ligands (such as CO, PR₃ etc.) produces butadiene complexes.

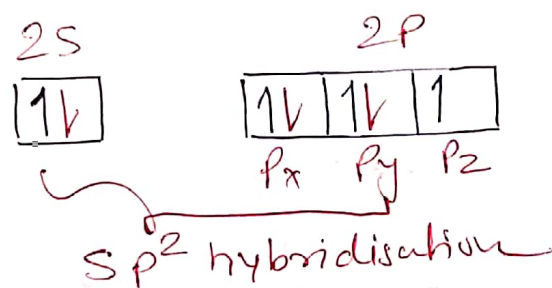


* Structure and Bonding:-

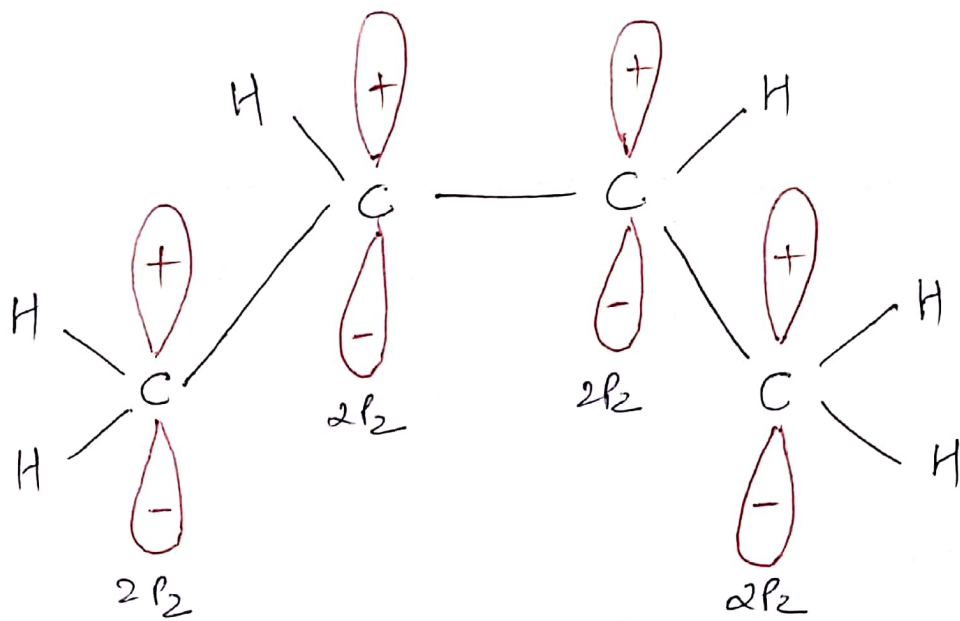
→ The structure of $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_6)]$ is given.



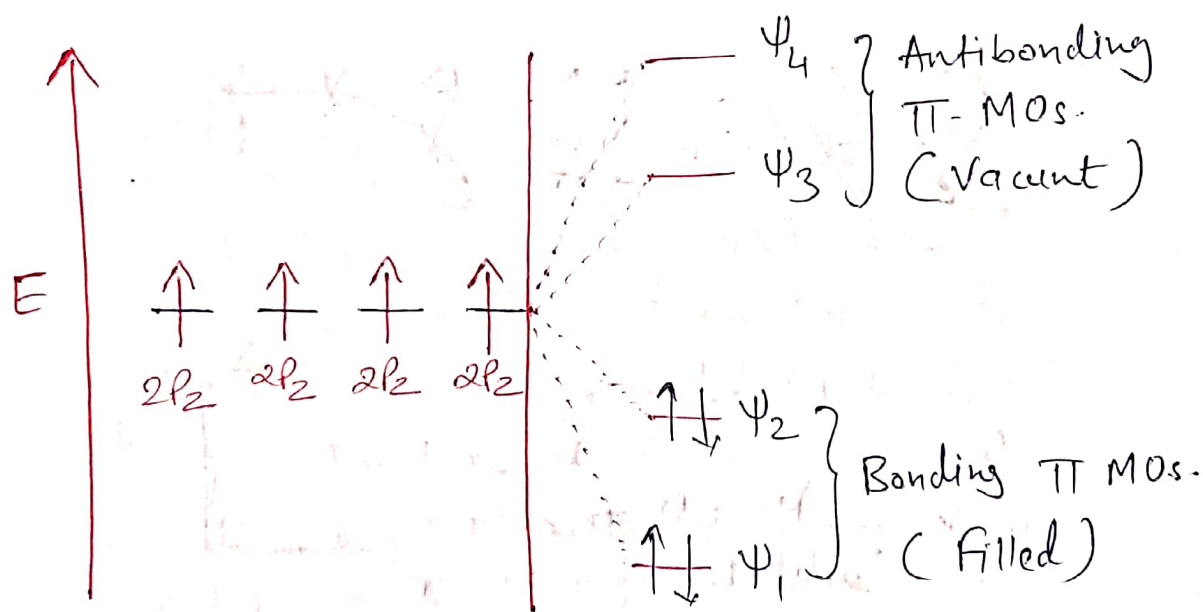
- The ligand 1,3-butadiene, is present in cis-configuration.
- The plane of four carbon atoms of 1,3-butadiene is nearly parallel to that of three carbonyl groups.
- Fe atom is equidistant from each of the four carbon atoms of the diene and all the C-C bonds of the diene are of equal length (1.45 \AA).
- 1,3-Butadiene is a planar molecule with sp^2 hybridisation on each carbon atom.
- VSEC (Valence shell electron Configuration) of C atom in 1,3-butadiene



- Each Carbon atom forms 3 σ -bonds using its three singly occupied sp^2 hybrid orbital.
- One singly occupied $2p_z$ atomic orbital is left unused on each carbon atom which is perpendicular to the molecular plane (i.e. xy -plane).



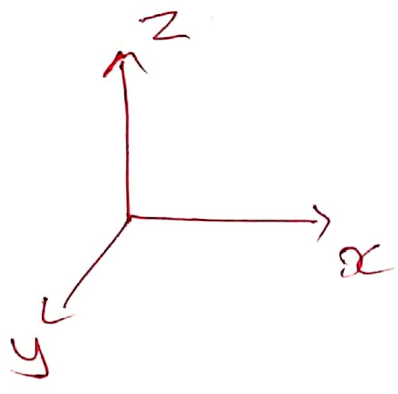
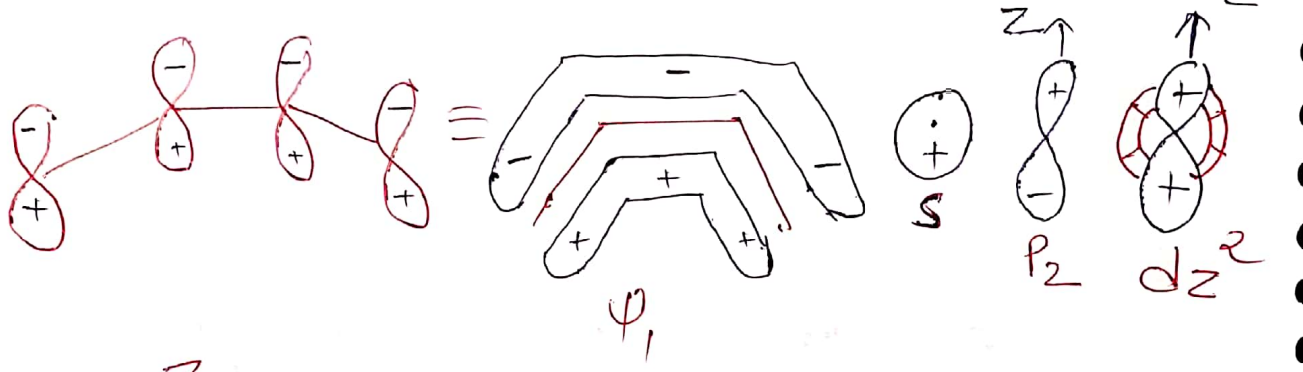
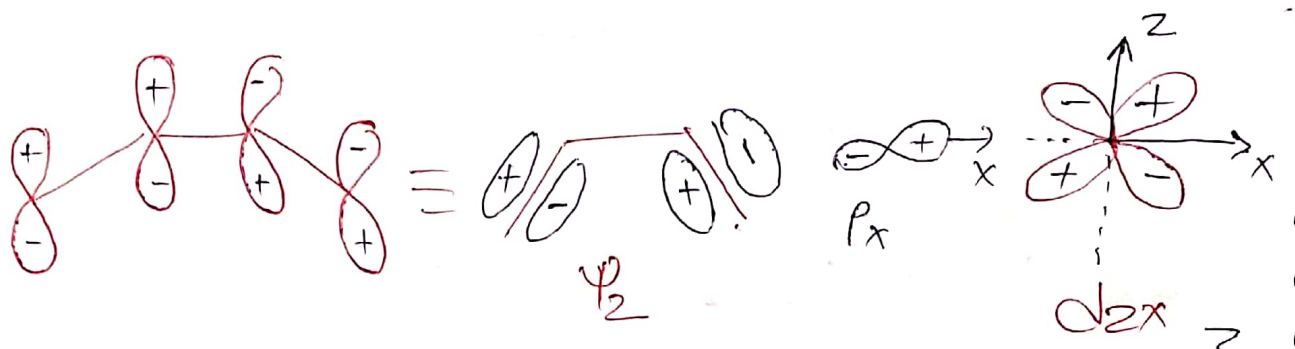
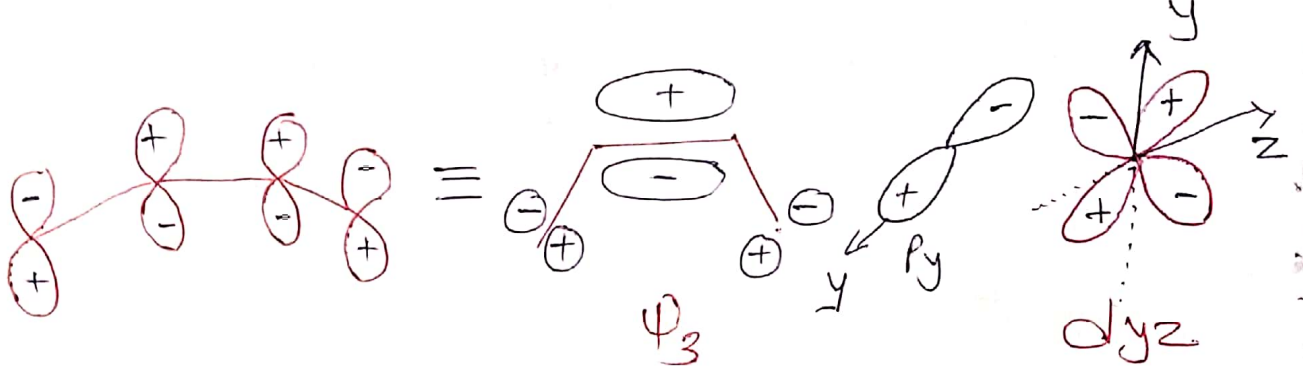
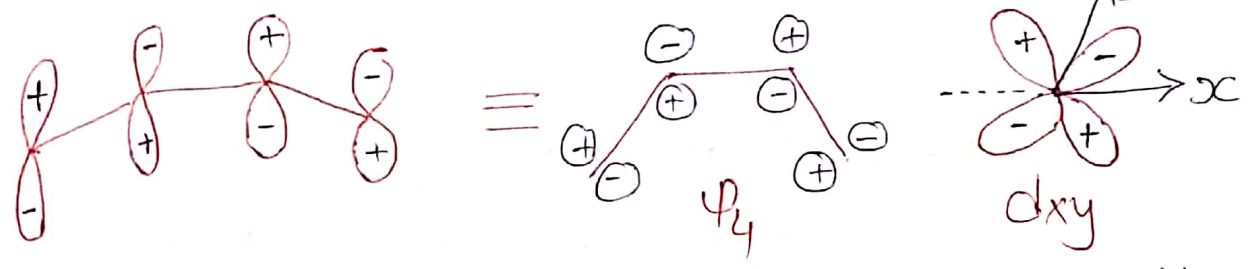
→ These 4 parallel singly occupied $2p_z$ atomic orbitals take part in the linear combination forming four π -molecular orbitals as follows



π -MOs of 1,3-butadiene

→ Appropriate combination of the four π MOs of 1,3-butadiene and metal-based orbitals can be used to construct MOs of transition metal-butadiene complexes, as shown in following fig.

E ↑



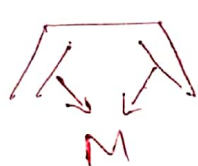
π MOs of 1,3-butadiene

Atomic orbitals of metal atoms with matching symmetry

→ ψ_1 and ψ_2 π MOs of 1,3-butadiene are involved in the formation of $M \leftarrow$ butadiene σ and π bonds respectively.

→ Similarly, ψ_3 and ψ_4 π MOs of 1,3-butadiene are involved in the formation of $M \rightarrow$ butadiene π & σ bond respectively. (back donation)

→ The bonding between metal and 1,3-butadiene may be represented as follows.



[a]



[b]



[c]

→ When the donation from ψ_2 into metal orbitals is important, the bonding may be represented by [a].


→ If donation from ψ_1 into metal orbitals is important, the bonding may be represented by [c].

→ If the interaction of ψ_3 with metal orbitals is important, the structure and bonding may be represented by (b).



5-electron ligand complexes:

[Cyclopentadienyl Complexes] ~~(Cp)~~

→ The cyclopentadienyl group (C_5H_5) is the most important of the polyenyls and it has played a major role in the development of organo-metallic chemistry.  $\leftrightarrow C_5H_5$.

→ The cyclopentadienyl ~~(Cp)~~ ligand is the firmly bound to the metal atom and it is the most inert to nucleophilic or electrophilic reagents.

→ The bis (η^5 -cyclopentadienyl) metal complexes, i.e. $(\eta^5-C_5H_5)_2 M$, formed by the reaction between the cyclopentadienyl anion and suitable derivatives of the transition metals are called metallocene.

→ e.g. $(\eta^5-C_5H_5)_2 Fe$, $(\eta^5-C_5H_5)_2 Ni$, etc.
Ferrocene Nickelocene

→ The C_5H_5 group is generally denoted as "Cp.", Me_5C_5 as $*Cp$. and other substituted species as Cp' or Cp'' .

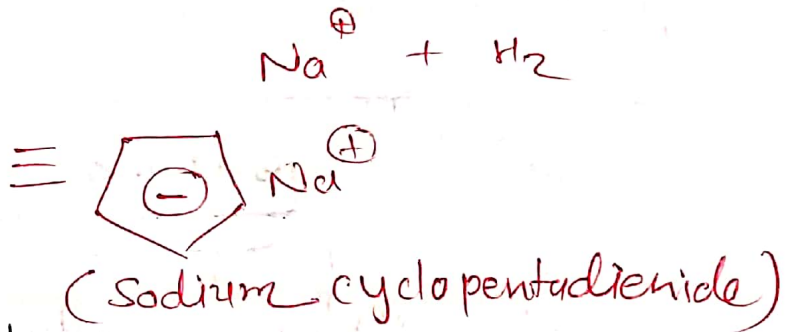
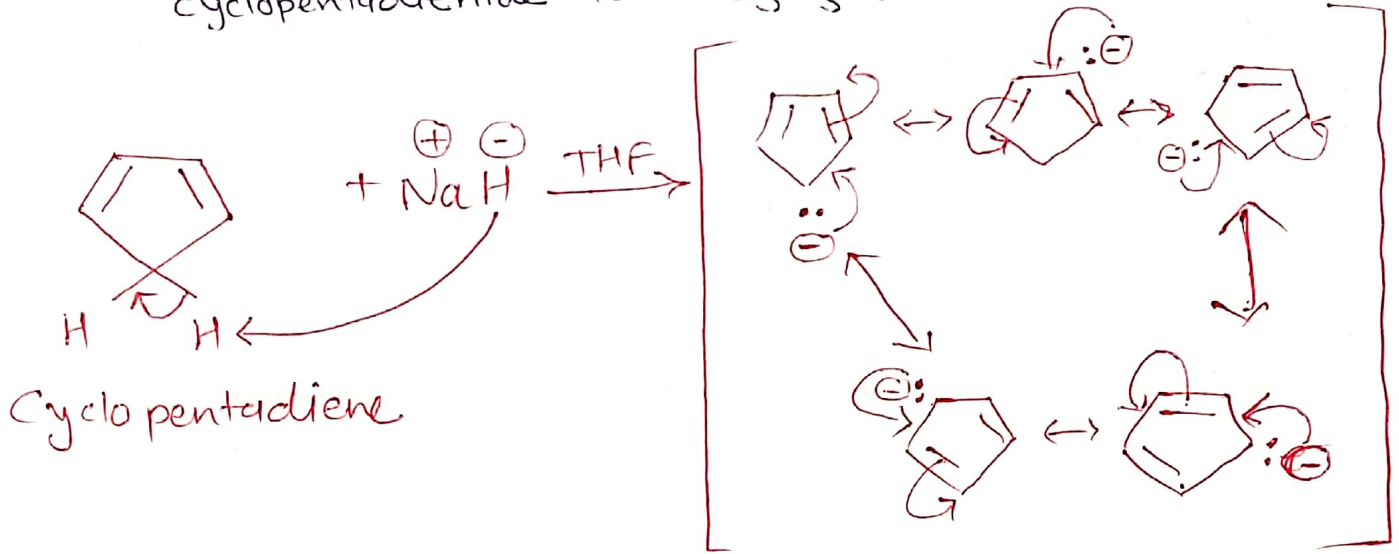
→ Ferrocene is the most important metallocene. It is highly stable.

→ The cyclopentadienyl group can act as mono-hapto (η^1), trihapto (η^3) & pentahapto (η^5) ligand.

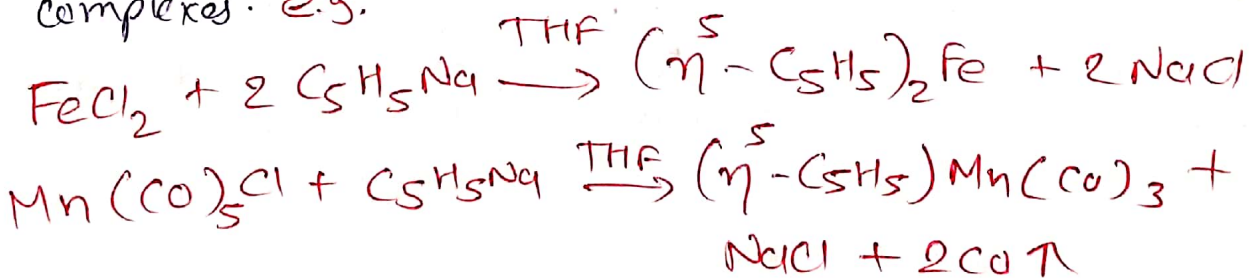
⇒ General Methods of Preparation :-

[A] Starting from sodium cyclopentadienide :-

→ C_5H_5 is a weak acid. Its reaction with the strong base such as NaH (Sodium hydride) or reactive metals such as sodium in aprotic solvent such as THF produces salt of symmetrical cyclopentadienide ion. $C_5H_5^-$.

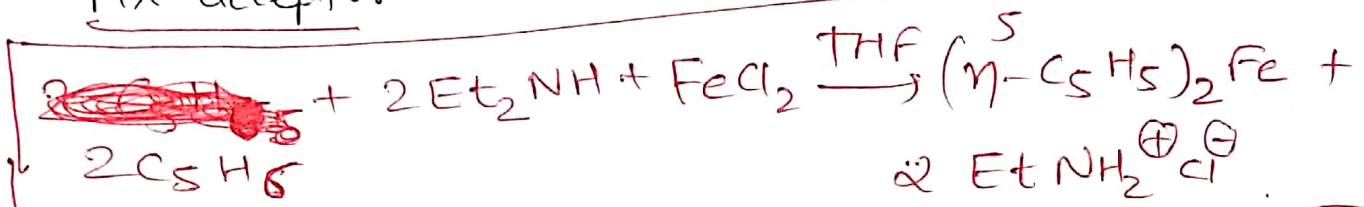


- Sodium cyclopentadienide is a common starting material for the preparation of cyclopentadienyl complexes. e.g.



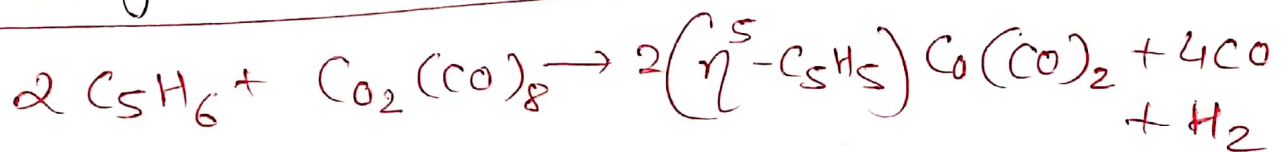
[B] ~~Treatment~~ Treatment with Metal halide

→ Metallocene can be prepared by the treatment of cyclopentadiene with metal halide in the presence of the excess of strong organic base such as diethylamine, Et_2NH , which acts as HX acceptor.



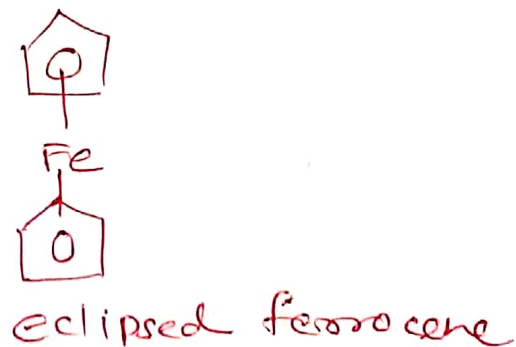
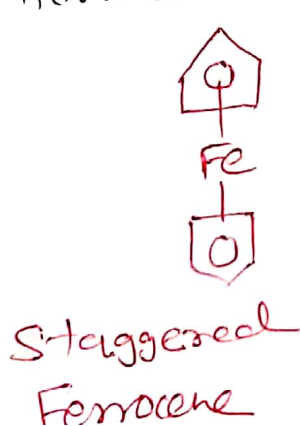
[C] Reaction with metal carbonyls.

→ The cyclopentadienyl complexes can be prepared by the reaction of cyclopentadiene with metal carbonyl.



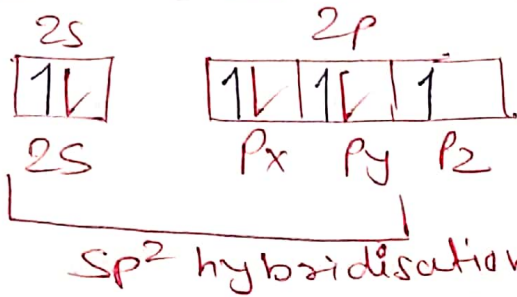
* Structure and Bonding

→ In ferrocene molecule, iron atom is sandwiched between two parallel and planar cyclopentadienyl rings. Following two conformers of ferrocene are possible.

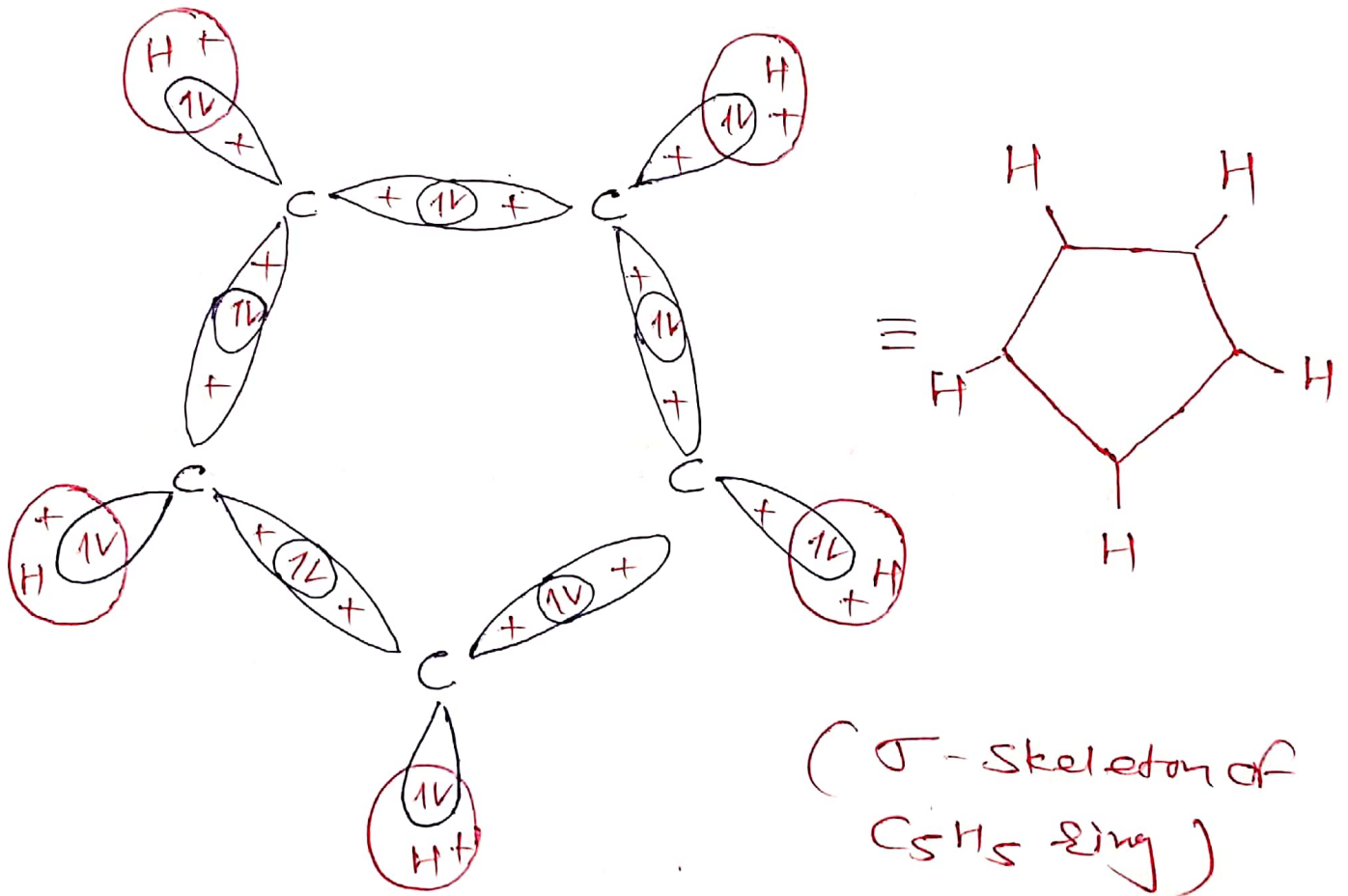


→ Each carbon atom of the cyclic and planar C_5H_5 group is sp^2 hybridised.

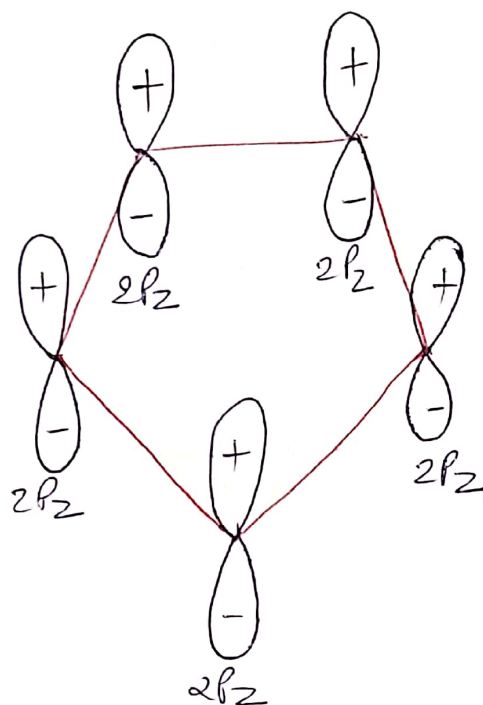
∴ VSEC of C atom in C_5H_5 ring.



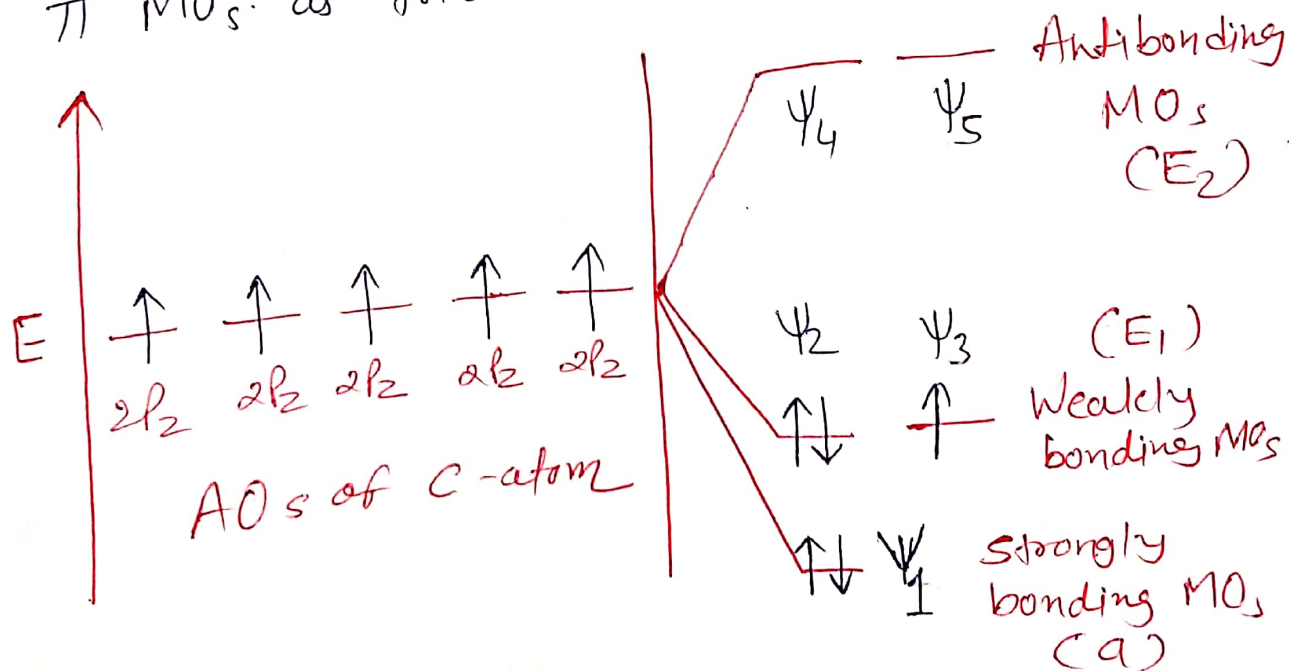
→ Each carbon atom forms three σ bonds - one with H atom and two with adjacent C-atom using its three single occupied sp^2 hybrid orbitals as follows.

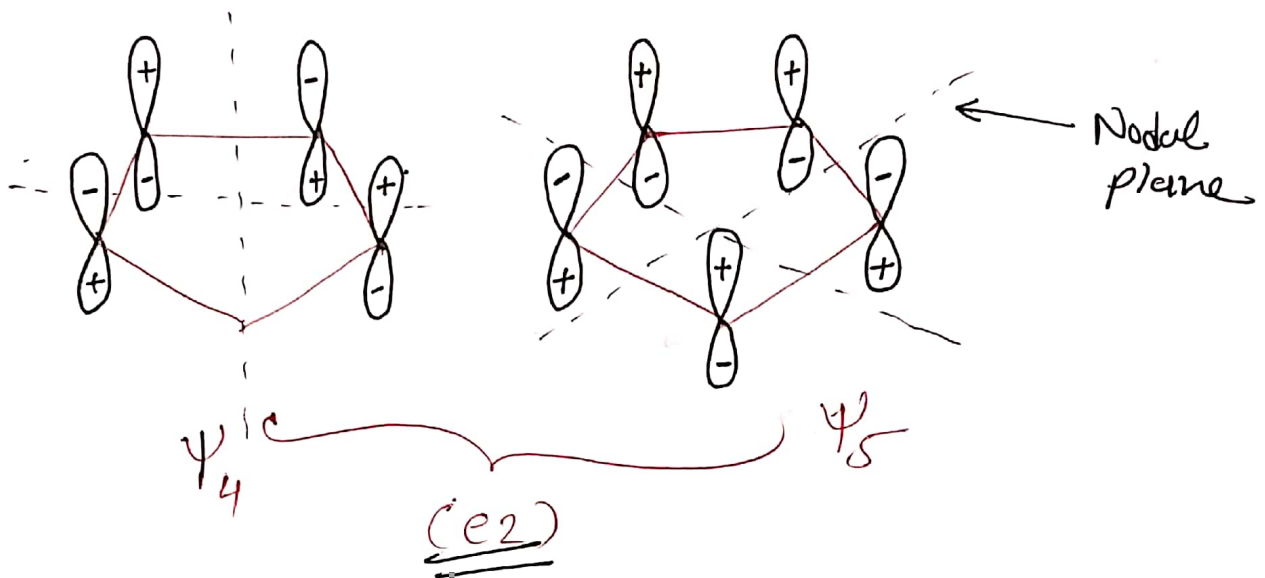
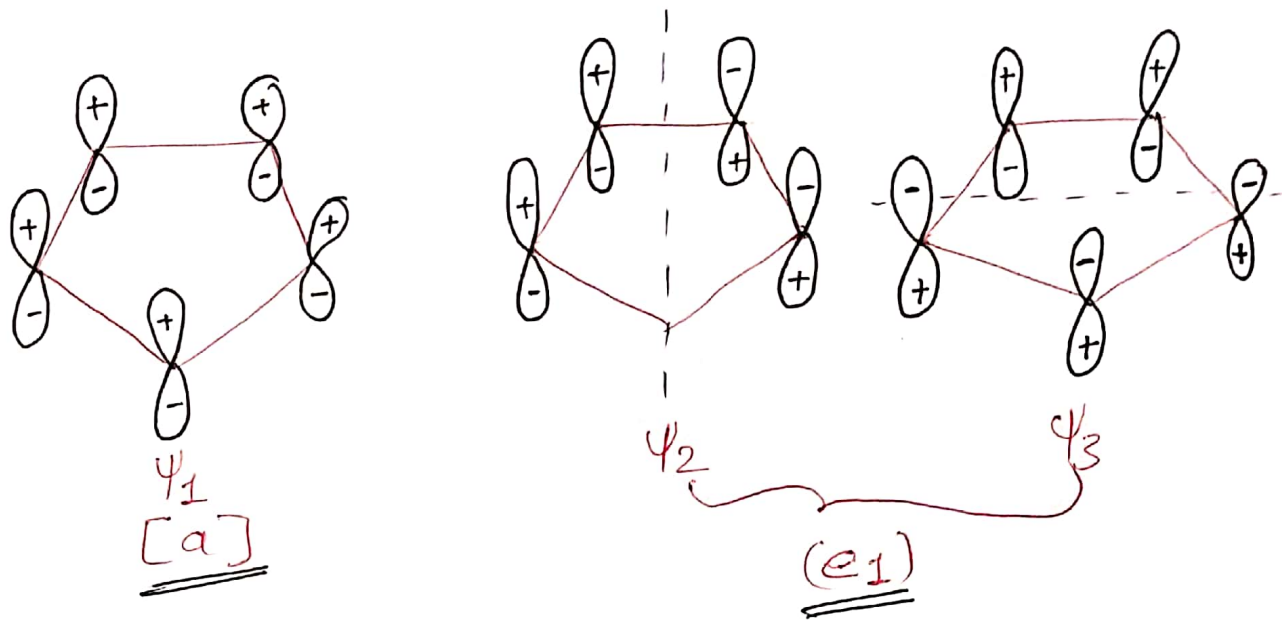


→ Thus a singly occupied $2p_z$ atomic orbitals remains unused on each carbon atom which is perpendicular to the plane of C_5H_5 ring. i.e. xy plane



→ These five singly occupied and parallel $2p_z$ atomic orbitals of C_5H_5 ring take part in linear combination producing five π MOs as follows:-





→ There is a single molecular orbital (ψ_1) of the lowest energy that has no nodal plane.

This MO is designated as "a"

→ At slightly higher energy, there is a doubly degenerate set of MOs - ψ_2 and ψ_3 which have one nodal plane containing the principal axis. They are designated as " e_1 "

→ This is followed by another doubly degenerated sets of MOs - ψ_4 and ψ_5 which have two nodal planes, perpendicular to the plane of C_{5H_5} ring. These are designated as " e_2 "

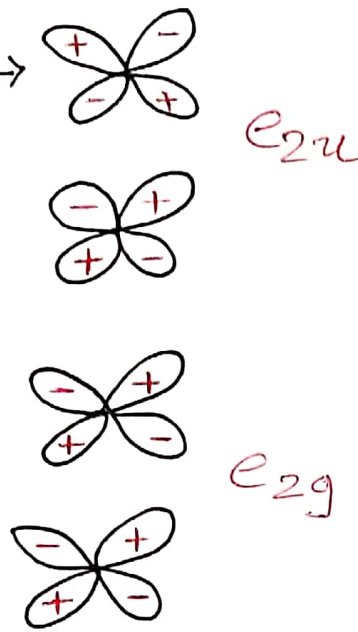
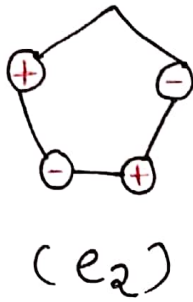
- The five π MOs of one cyclopentadienyl ring interact with the five π MOs of the other cyclopentadienyl ring of ferrocene molecule to produce 10 ligand group orbitals. (LGO)
- These combinations are labelled g (gerade) & u (ungerade).
- Let us consider the lowest energy bonding π MO., i.e. ψ_1 of a . This orbital has no nodal plane perpendicular to the plane of the ring.
- If the wave function of this orbitals on ring number 1 and on ring number 2 are written with the same sign (Addition), this produce a gerade LGO of symmetry a_{1g} .
- On the other hand, if the wave functions are written with opposite signs (Subtraction), an ungerade LGO of symmetry a_{2u} is produced.

Symmetry of π -MOs of C_5H_5

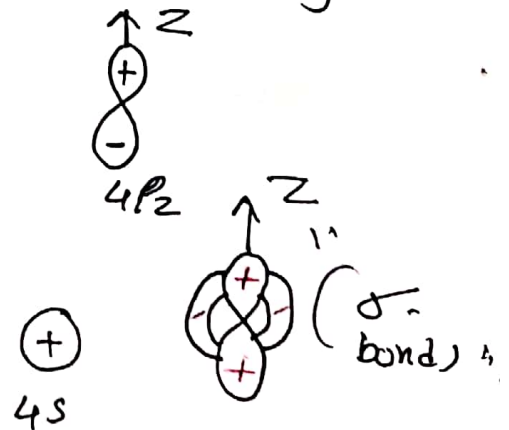
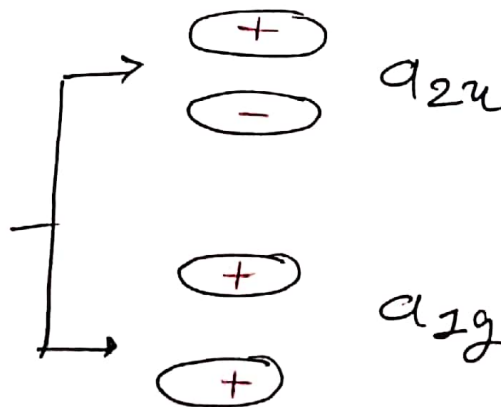
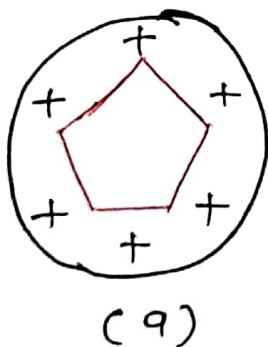
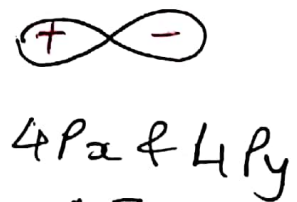
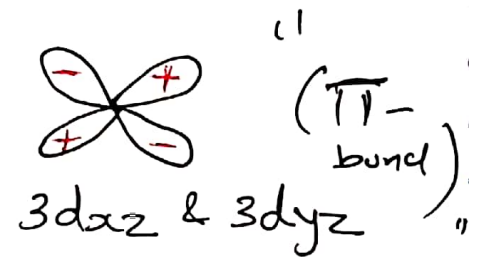
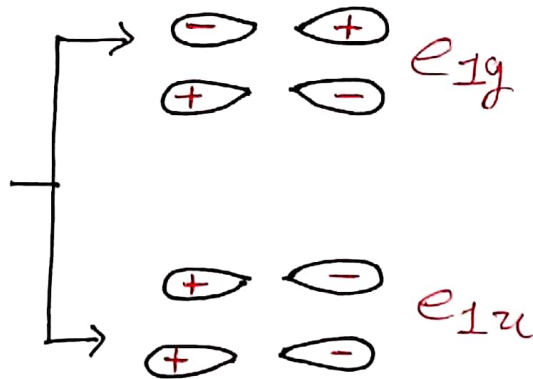
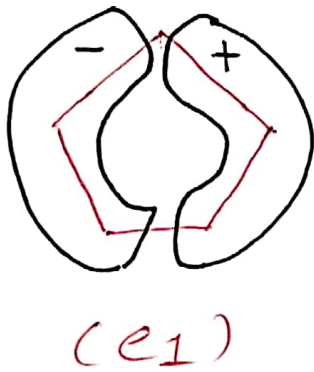
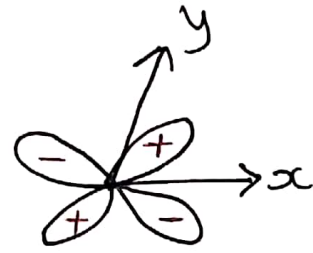
Cyclopentadienyl
LIGANDS.

AA OF
Fe.

Energy (E)



NONE



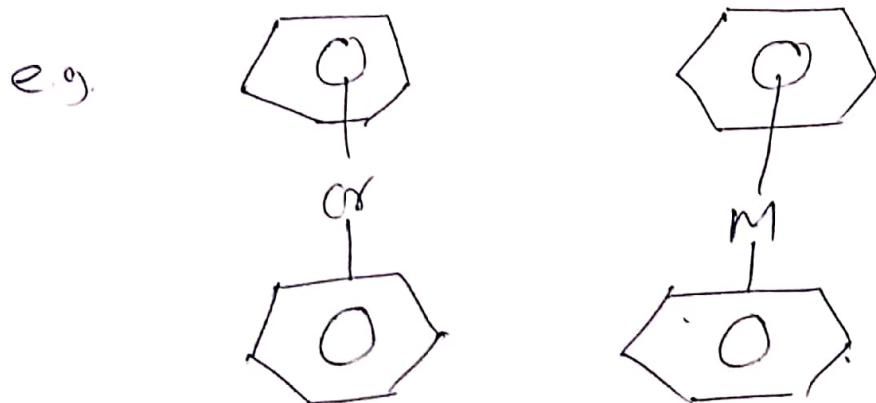
→ The a_{1g} LGO of Cp rings has very low energy and it is very stable relative to the AOs of Fe and hence it interacts very little.

→ The only well matched orbitals are e_{1g} LGO and the corresponding $3d_{xz}$ and $3d_{yz}$ AOs of Fe atom having same symmetry (e_{1g}).

→ The overlapping of these orbitals results in the formation of two strong π bonds.

η^6 - Arene Complexes [Six Electron Ligand]

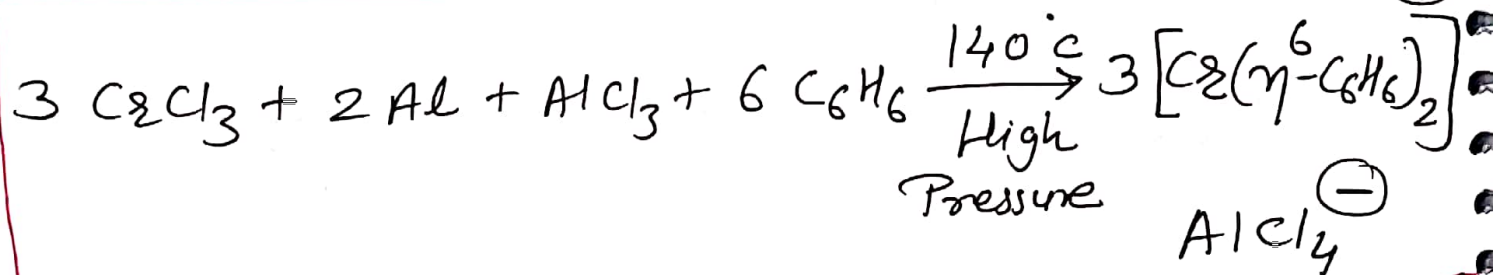
→ Benzene and substituted benzene normally acts as hexahapto (η^6) six electron donor ligand in which all the six π -electrons of benzene ring are shared with the metal atom.



(*) Methods of Preparation

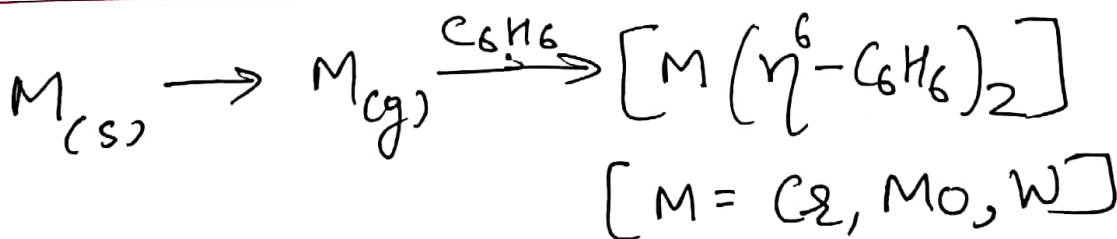
(A) From metal halides :-

- The best general method for the preparation of bis(η^6 -arene) transition metal complexes was devised by E.O. Fisher and W. Hafner.
- In this method, the transition metal halide is reduced by Al in the presence of benzene using $AlCl_3$ as catalyst.



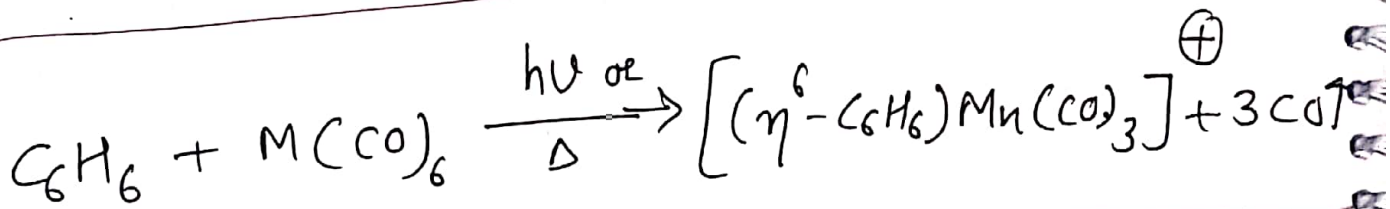
(B) Metal atom vapour phase synthesis :-

- The condensation of vapour of a metal in the presence of benzene produces η^6 -arene complexes.

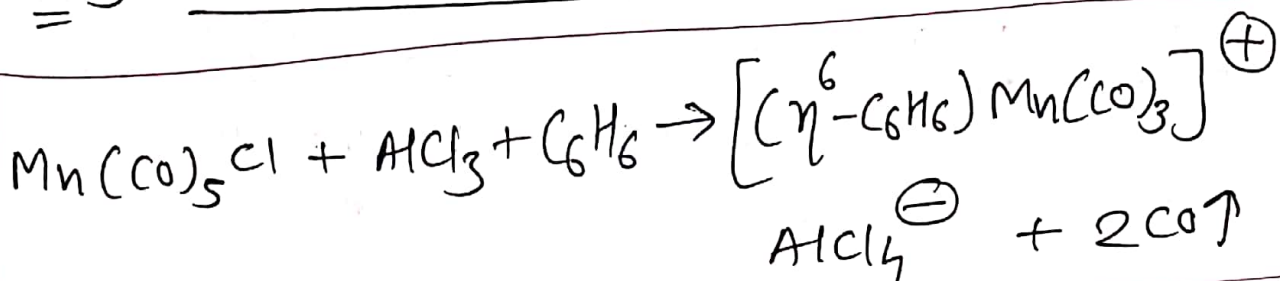


(C) From metal carbonyls :-

- The rec^h of arenes with metal carbonyls in high boiling solvents or under the influence of UV light leads to the displacement of 3 CO and the formation of arene metal carbonyl.



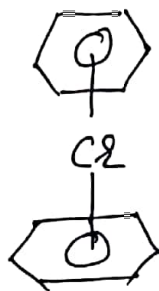
[D] Form metal carbonyl halide:-



★ Structure and Bonding

→ The various diffraction techniques such as X-ray diffraction, neutron diffraction studies on $[C_2(\eta^6-C_6H_6)_2]$ suggest that C_2 atom is sandwiched between two planes and parallel benzene rings, which are in eclipsed conformation.

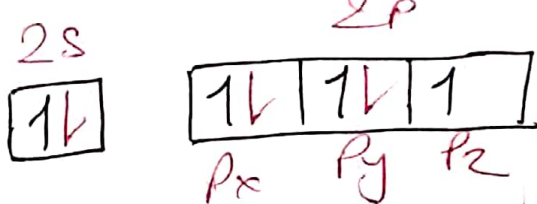
→ The structural feature of $[C_2(\eta^6-C_6H_6)_2]$ are



→ The H atoms of the benzene rings are slightly tilted towards C_2 atom.

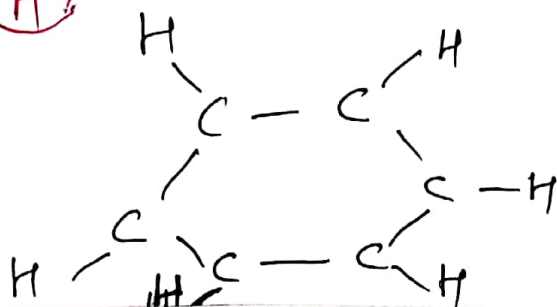
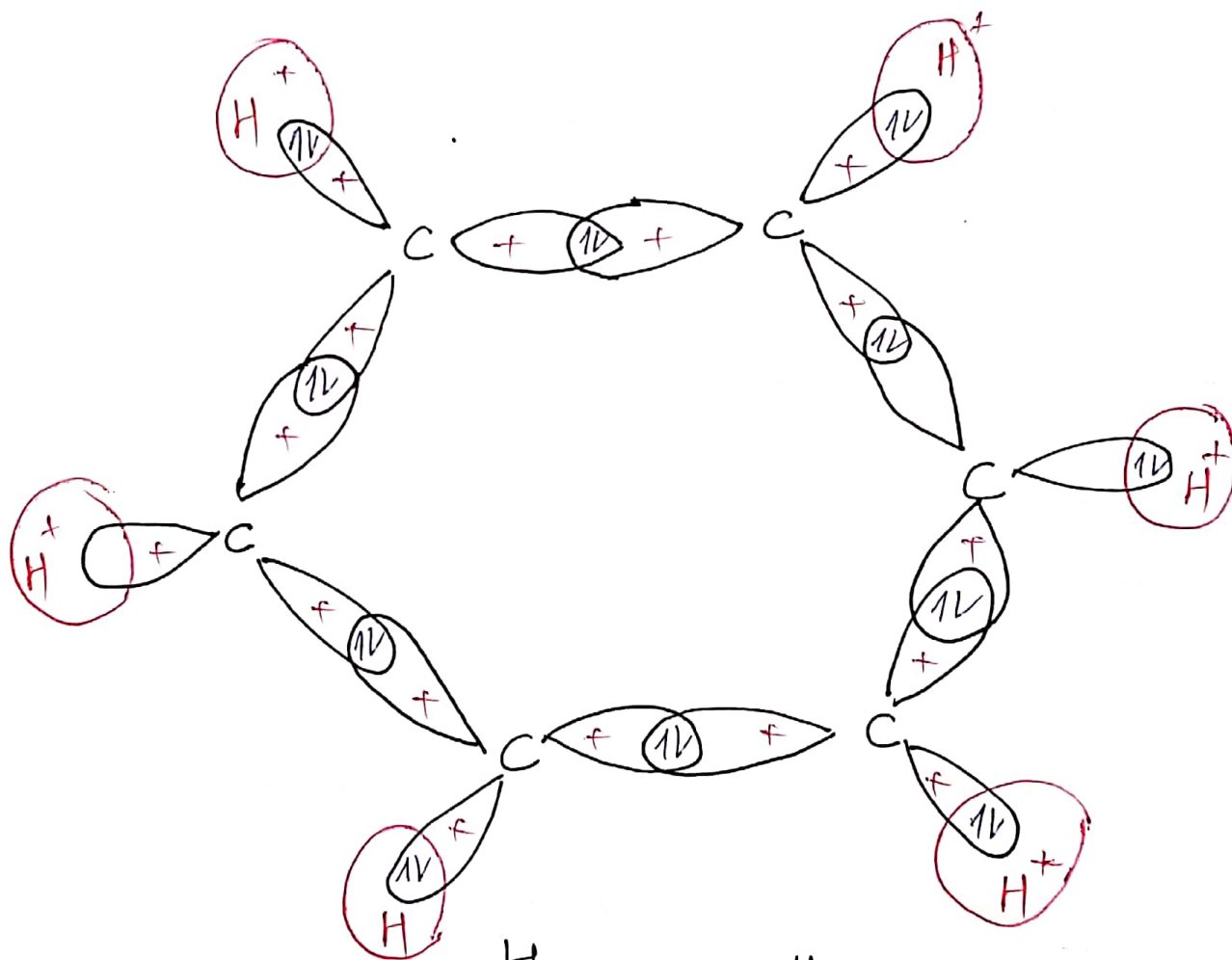
→ Let us illustrate the nature of bonding in $[C_2(\eta^6-C_6H_6)_2]$ which is isoelectronic with ferrocene.

→ VSEC of C atoms in C_6H_6 molecule.

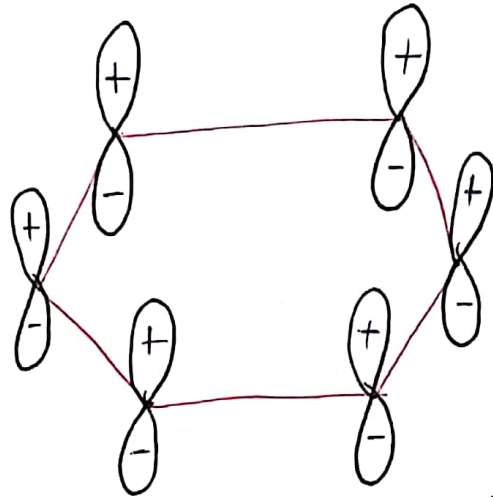


sp^2 hybridisation

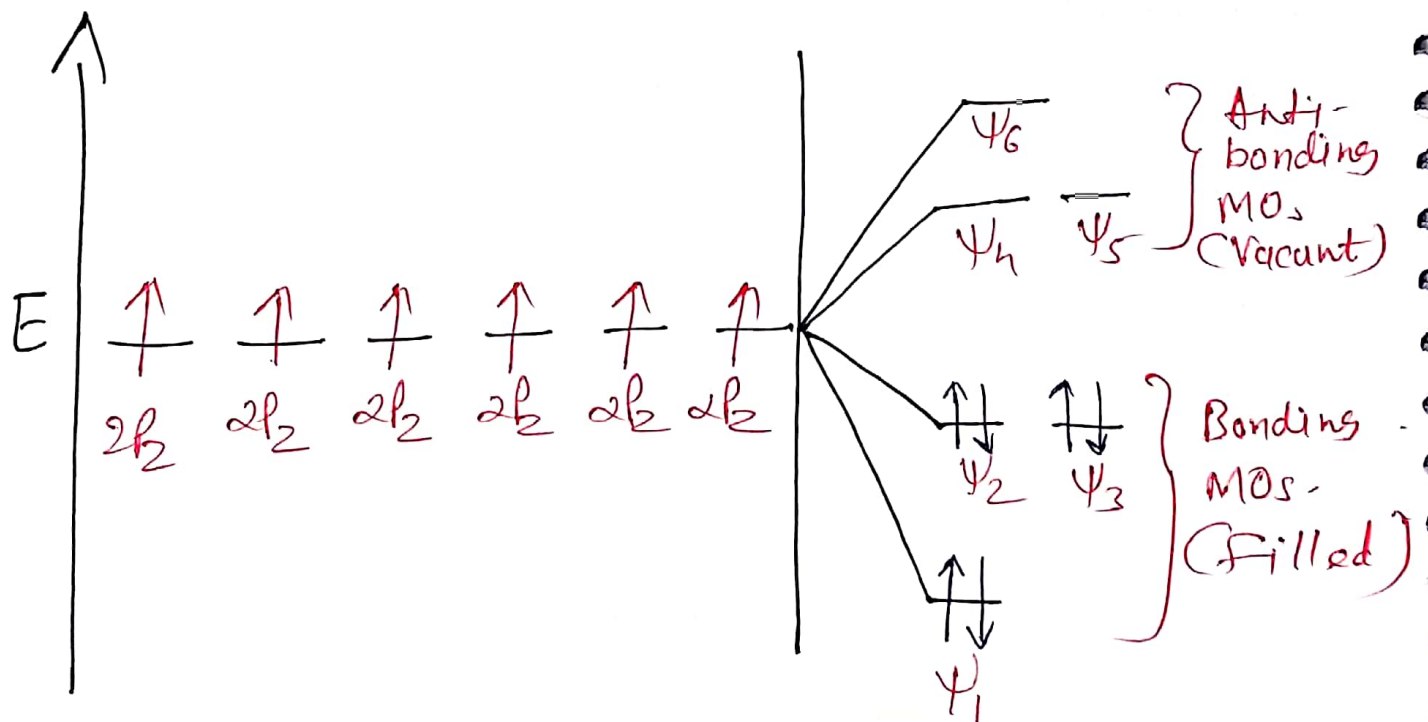
→ Each C atom forms three σ bonds - one with H atom and two with adjacent C atom using its three singly occupied sp^2 hybrid orbitals as follow.



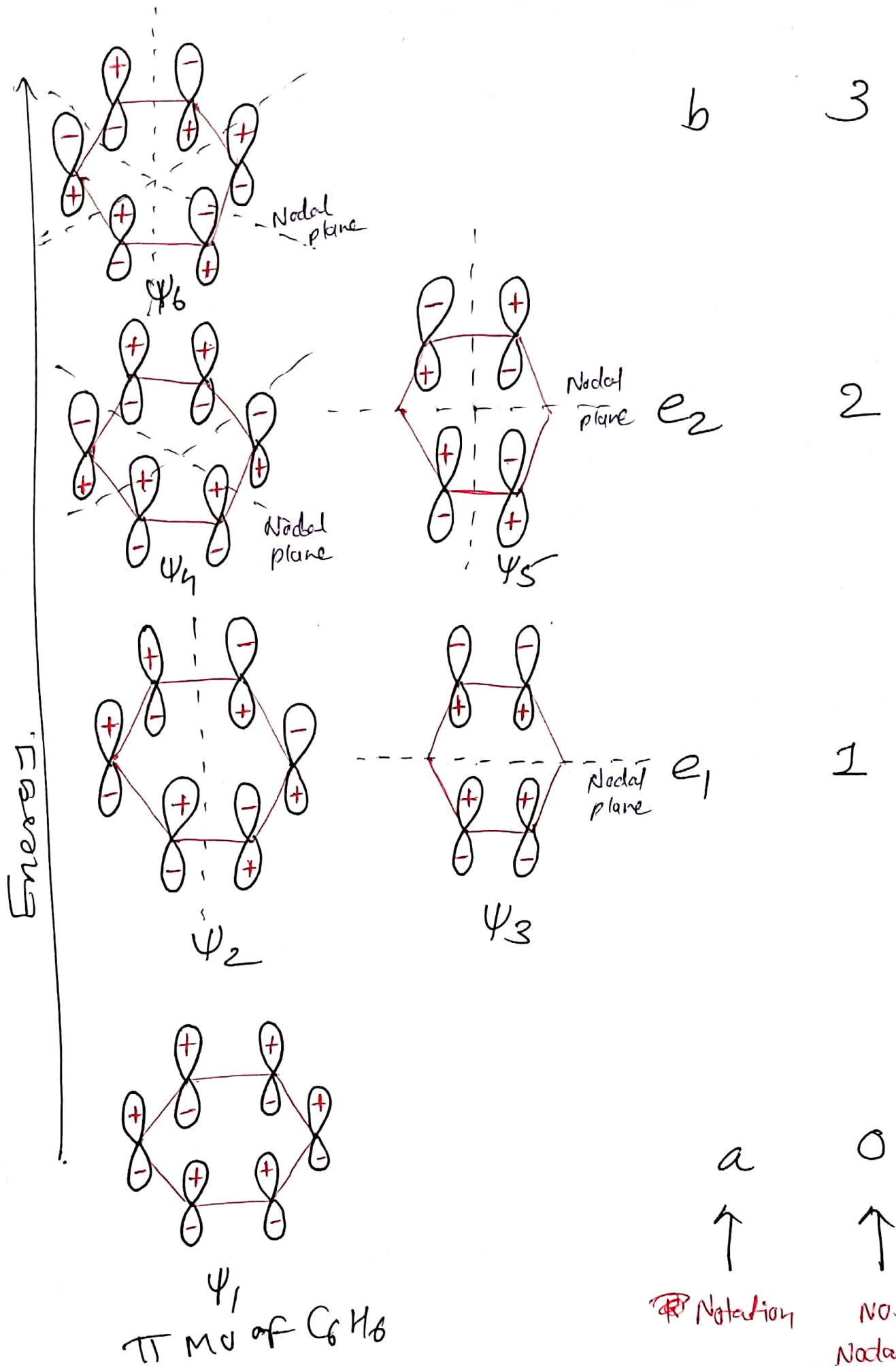
→ Thus only singly occupied $2p_z$ AO is left unused on each carbon atom which is perpendicular to the plane of benzene ring. These six parallel and singly occupied $2p_z$ AOs take part in linear combination producing six π MOs of benzene molecule.



[Six $2p_z$ AOs \perp to C_6H_6 ring]



π MOs of benzene molecule



\otimes Notation NO. of
 1st Nodal plane
 to molecule
 plane

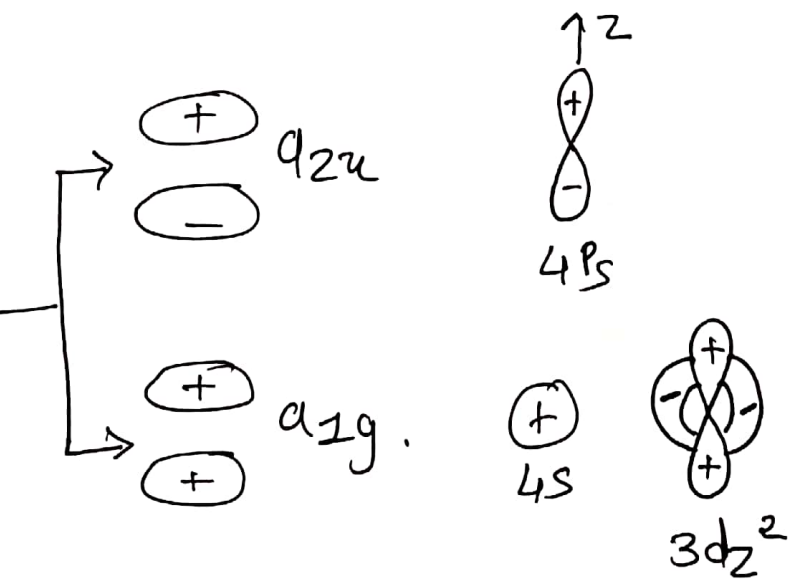
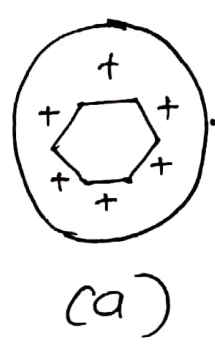
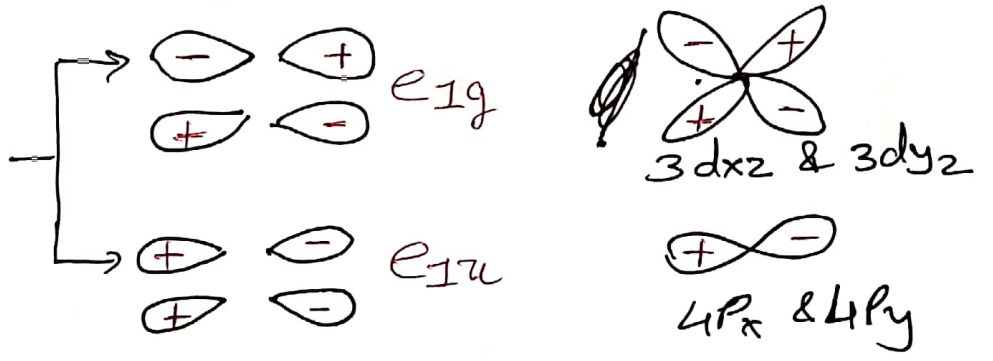
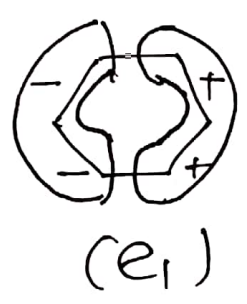
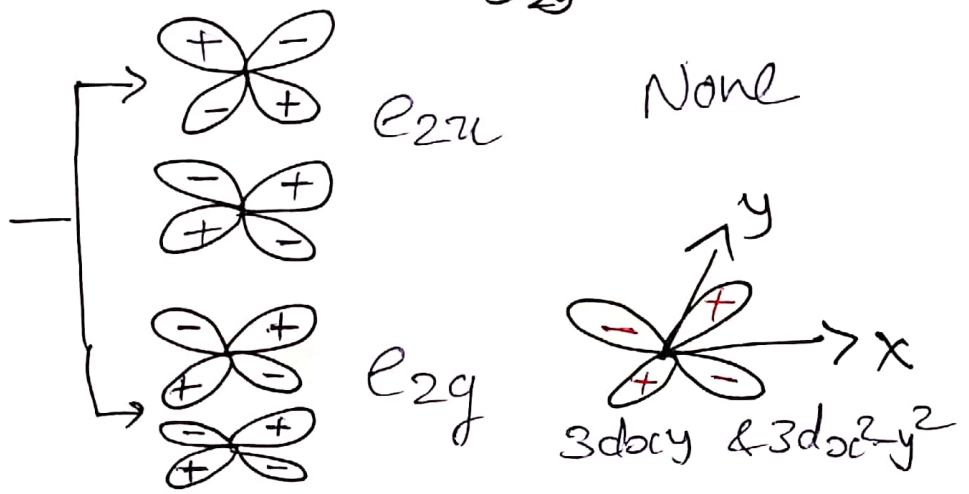
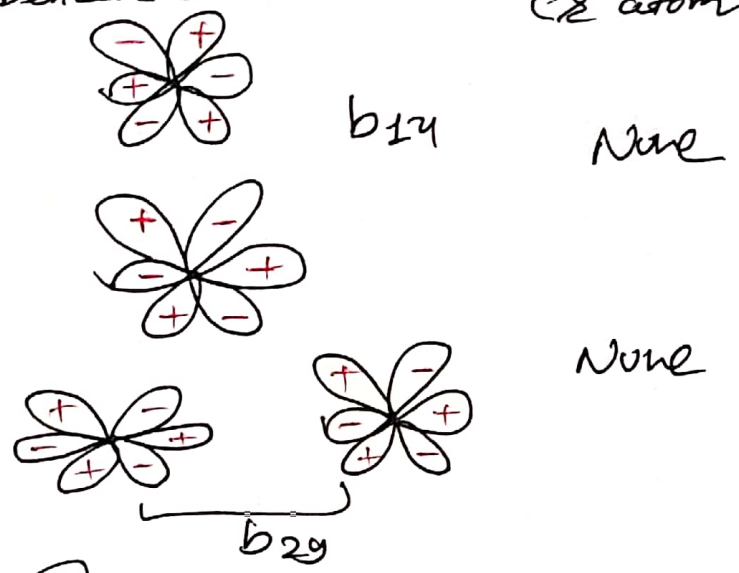
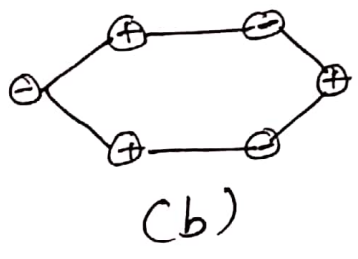
- Six π MOs of one C_6H_6 ring interact with six π MOs of another C_6H_6 ring, producing ~~6~~ ~~6~~ 12 ligand group orbitals (LGO). ~~The~~
- The LGOs are labelled g (gerade) and u (ungerade) depending upon whether they contain centre of symmetry or not.
- The LGO are produced by addition and subtraction of wave functions of π MOs of two C_6H_6 rings in the same manner as in the case of ferrocene.
- The LGOs of two C_6H_6 rings and the AOs of Cr atom with matching symmetry are given in the next page.

Symmetry of π MOs of C_6H_6

LGO of two benzene rings

AO. of C atom

Energy



- In given data, the most important bonding interaction in $[Cr(\eta^6-C_6H_6)_2]$ is between e_{1g} LGOs and $3d_{xz}$ & $3d_{yz}$ AOs of Cr with same symmetry (e_{1g}) which results in the formation of two strong π bonds.