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UNIT I

ORGANO METALLIC CHEMISTRY I

*Organometallic compounds are compounds containing metal carbon bonds

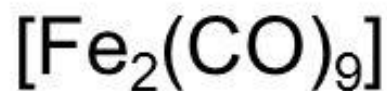
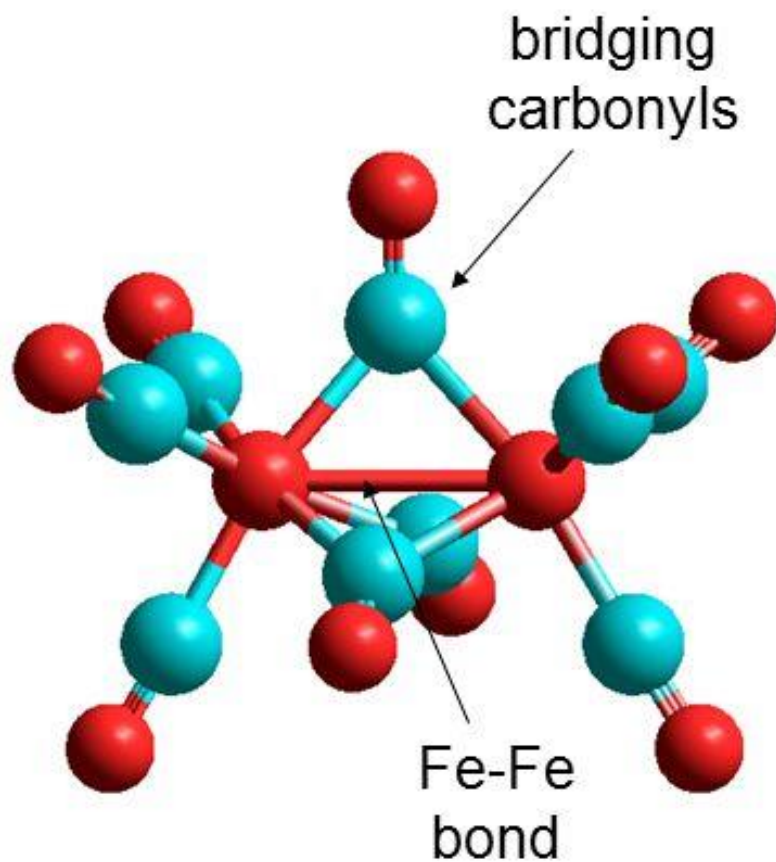
*In many complexes both σ and π bonds existing between the metal and carbon atoms.e.g., carbonyl complexes, alkyl compounds and sandwich complexes and so on.

Carbonyl complexes and the 18-electron rule

One might wonder why in the above complexes Ni(0) has four C≡O groups attached to it, Fe(0) five C≡O, and Cr(0) six C≡O. A very simple rule allows us to predict the numbers of donor groups attached to metal ions in organometallic complexes, called the **eighteen electron rule**. The latter rule states that the sum of the d-electrons possessed by the metal plus those donated by the ligands (2 per C≡O) must total eighteen:

$[\text{Ni}(\text{CO})_4]$	$[\text{Fe}(\text{CO})_5]$	$[\text{Cr}(\text{CO})_6]$
$\text{Ni}(0) = d^{10}$	$\text{Fe}(0) = d^8$	$\text{Cr}(0) = d^6$
$4 \times \text{CO} = 8$	$5 \times \text{CO} = 10$	$6 \times \text{CO} = 12$
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18 e	18e	18e

Bridging Carbonyls in $\text{Fe}_2(\text{CO})_9$



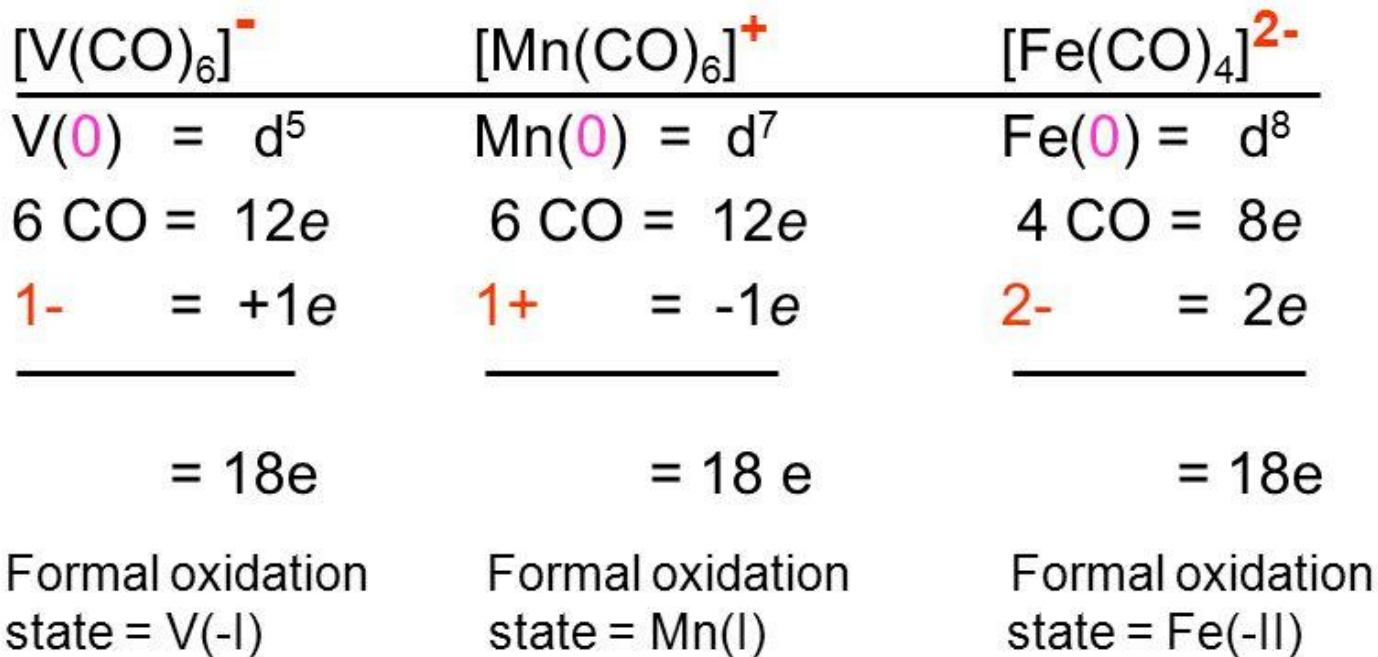
$\text{Fe}_2(\text{CO})_9$ has each Fe with three terminal CO's, three bridging CO's, and an FeFe bond. The 18 electron rule holds for each Fe atom as:

Fe(0)	=	d^8
3 CO's	=	6
3 bridge CO's	=	3
Fe-Fe bond	=	1

18 e

Carbonyl complexes and the 18-electron rule

To obey the 18-electron rule, many carbonyl complexes are anions or cations, as in:



[NOTE: In applying the 18-electron rule, metal ions are always considered to be zero-valent, not the formal oxidn. state]

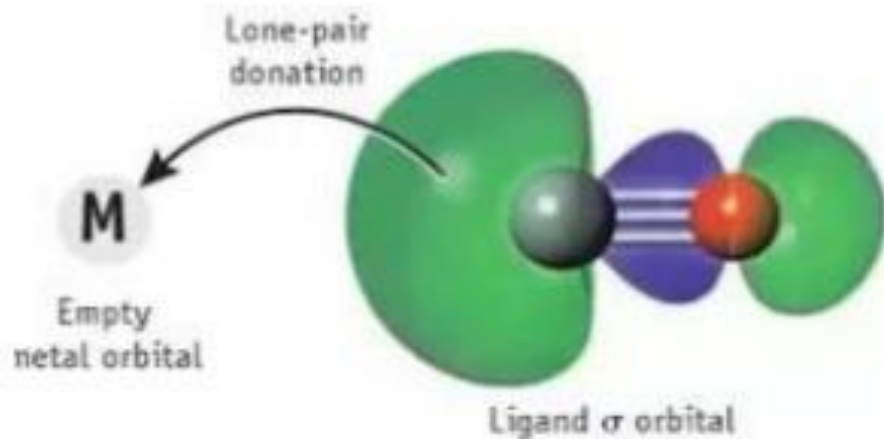
Metal-Carbon bonding in carbonyl complexes

Formation of σ -bond:

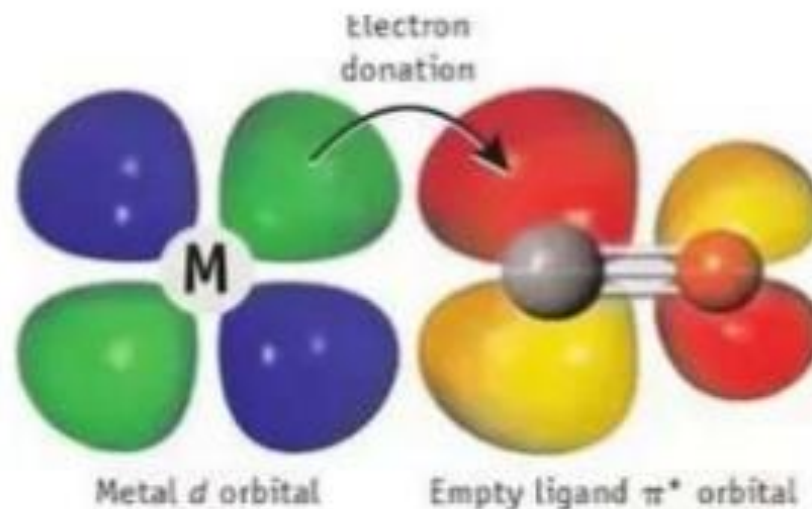
The overlapping of empty hybrid orbital on metal atom with the filled hybrid orbital on carbon atom of carbon monoxide molecule through lone pair electrons results into the formation of a $M \leftarrow CO$ σ -bond.

Formation of π -bond by back donation:

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



Ligand to metal sigma bonding.
Donation of CO lone pair to empty orbital on M.



Metal to ligand pi bonding.
Donation of electrons from filled M d orbital to empty π^* antibonding orbital on CO.

SYNERGIC EFFECT

In a metal carbonyl, the metal-carbon bond possesses both σ and π character. The bond between the carbonyl molecule and the metal is further strengthened by the synergic effect produced by the metal-ligand bond. The two types of bonding that exist in metal carbonyls are explained below:

Bridging CO groups:

- In addition to the linear M-C-O groups, the carbon monoxide ligand is also known to form bridges.
- This type of bonding is observed in some binuclear and polynuclear carbonyls.
- It is denoted by $\mu_n\text{-CO}$, where n indicates the number of metals bridged. While $n=2$ is the most common value, it reaches to be 3 or 4 in certain less common carbonyls.
- In a terminal M-C-O group, the carbon monoxide donates two electrons to an empty metal orbital, while in $\mu_2\text{-CO}$ group, the M-C bond is formed by sharing of one metal electron and one carbon electron.

M----M Bond

- In some carbonyls another bond develops between metal-metal due to weak overlap of the two singly filled appropriate hybrid orbitals.
- Also called fractional single bond and longer than normal single bond.



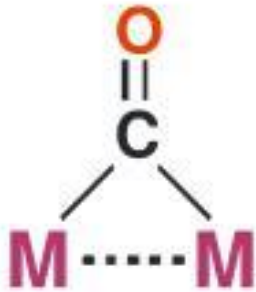
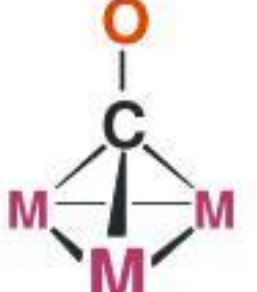
CARBONYLS & IR SPECTRA

- The C-O vibration, typically denoted ν_{CO} , occurs at 2143 cm^{-1} for CO gas. The energies of the ν_{CO} band for the metal carbonyls correlates with the strength of the carbon-oxygen bond, and inversely correlated with the strength of the π -backbonding between the metal and the carbon.
- The π basicity of the metal center depends on a lot of factors; in the isoelectronic series (Ti to Fe) at the bottom of this section, the hexacarbonyls show decreasing π -backbonding as one increases (makes more positive) the charge on the metal. π -Basic ligands increase π -electron density at the metal, and improved backbonding reduces ν_{CO} . (As the π^* orbital on CO receives electrons from the metal, the CO bond weakens and the ν decreases.)

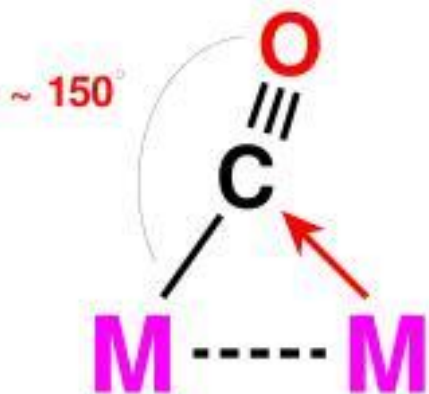
Compound	ν (cm^{-1})
$[\text{Fe}(\text{CO})_6]^{2+}$	2204
$[\text{Mn}(\text{CO})_6]^+$	2143
$\text{Cr}(\text{CO})_6$	2090
$[\text{V}(\text{CO})_6]^-$	1860
$[\text{Ti}(\text{CO})_6]^{2-}$	1750

Carbonyl Infrared (IR) Stretching Frequencies

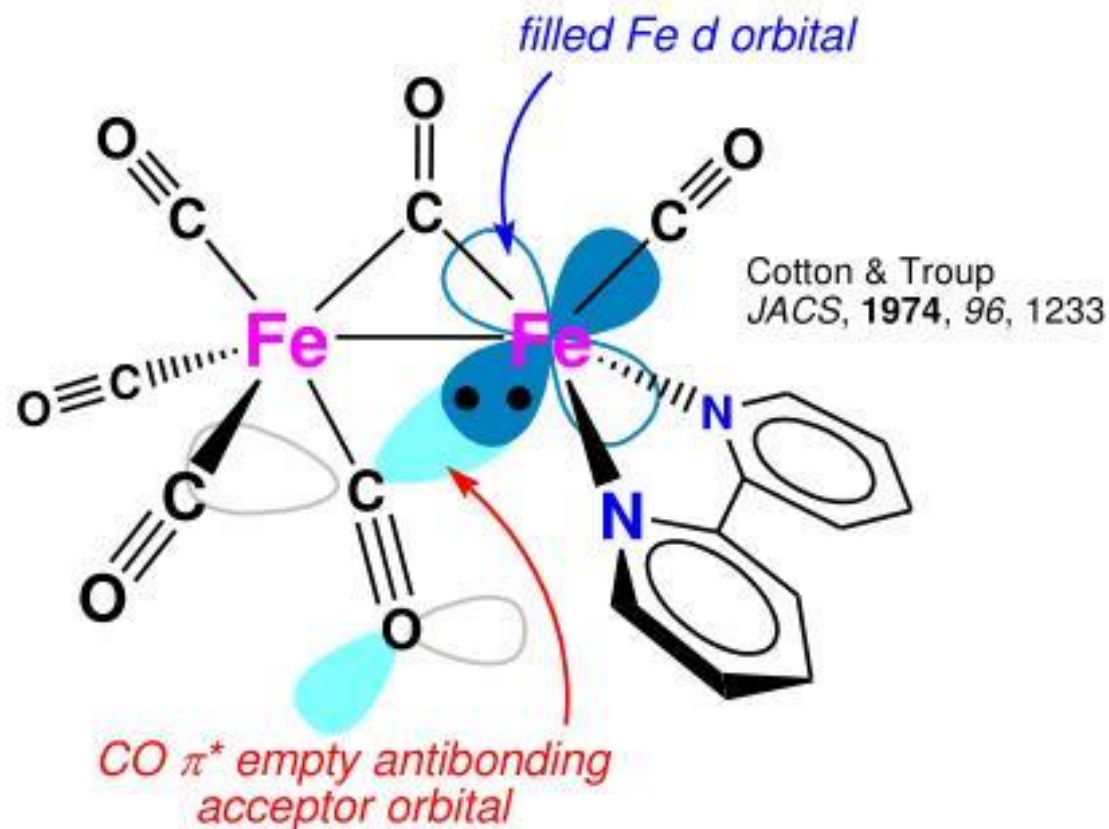
- The **position** of the carbonyl bands in the IR depends mainly on the **bonding mode** of the CO (terminal, bridging) and the **amount of electron density on the metal being π -backbonded to the CO**.
- The **number** (and intensity) of the carbonyl bands observed depends on the **number of CO ligands 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.

				
	free CO	<i>terminal mode</i>	μ_2 - <i>bridging</i>	μ_3 - <i>bridging</i>
ν_{CO} IR (cm^{-1})	2143	2120 - 1850	1850 - 1720	1730 - 1500
<i>(for neutral metal complexes)</i>				

Semi-Bridging Carbonyls



Unsymmetrical bridging form. π^* system accepts electron density from second metal center. Distortions away from a linear M-CO (180°) or a symmetrically bridging CO (120°). Typical M-CO angle around 150° (but with considerable variations).



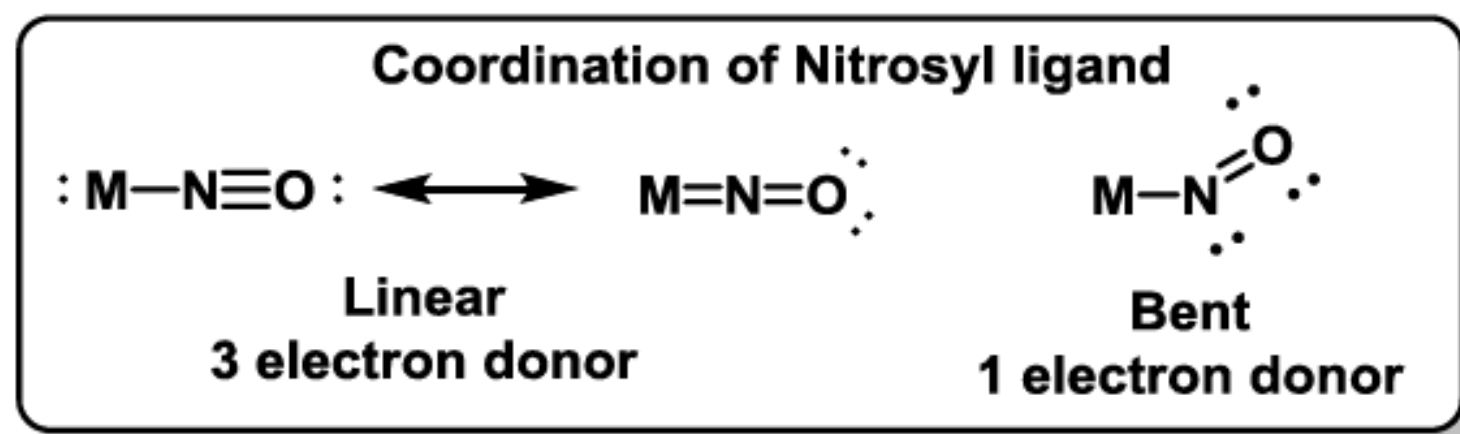
Metal nitrosyl complex

* **Metal nitrosyl complexes** are complexes that contain nitric oxide, NO, bonded to a transition metal.

Bonding and structure

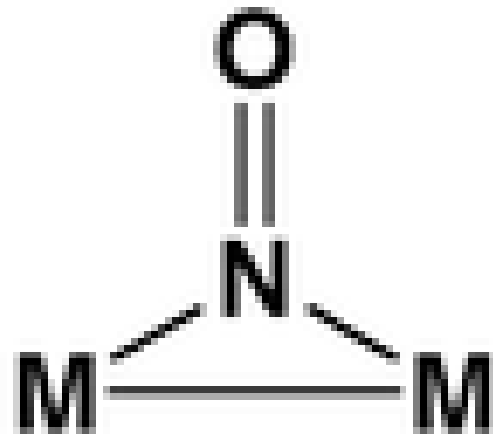
Most complexes containing the NO ligand can be viewed as derivatives of the nitrosyl cation, NO⁺. The nitrosyl cation is isoelectronic with carbon monoxide, thus the bonding between a nitrosyl ligand and a metal follows the same principles as the bonding in carbonyl complexes. The nitrosyl cation serves as a two-electron donor to the metal and accepts electrons from the metal via back-bonding.

The bonding of nitrogen monoxide (NO) resembles that of CO in coordination character. When NO coordinates to a metal center (M), it is known as a nitrosyl ligand. However, unlike CO, terminally bound NO can adopt two different bonding modes: linear or bent shown below.



When NO adopts a linear bonding mode it donates 3 electrons to the metal center while in a bent conformation donates 1 electron. (3 points)

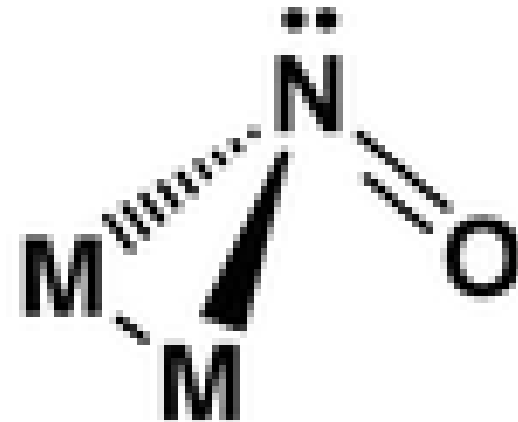
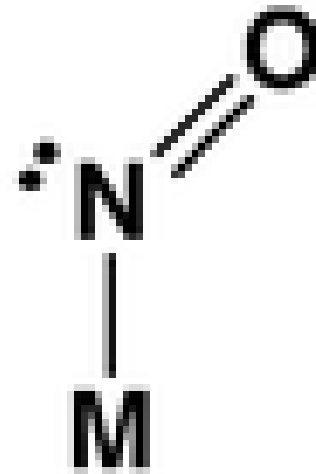
Show that $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_2(\text{NO})_2$ obey the 18 electron rule.



Linear

Planar

3-electron donor
NO groups



Bent

Pyramidal

1-electron donor
NO groups

Linear vs bent nitrosyl ligands

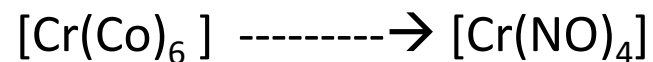
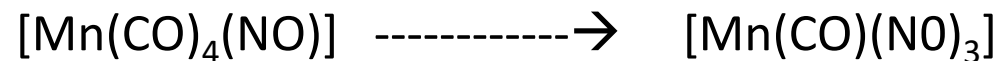
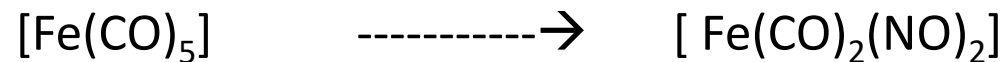
The M-N-O unit in nitrosyl complexes is usually linear, or no more than 15° from linear. Linear and bent NO ligands can be distinguished using [infrared spectroscopy](#). Linear M-N-O groups absorb in the range $1650\text{--}1900\text{ cm}^{-1}$, whereas bent nitrosyls absorb in the range $1525\text{--}1690\text{ cm}^{-1}$. The differing vibrational frequencies reflect the differing N-O [bond orders](#) for linear ([triple bond](#)) and bent NO ([double bond](#)).

ENEMARK FELTHAM NOTATION

The adoption of linear vs bent bonding can be analyzed with the **Enemark-Feltham notation**. In their framework, the factor that determines the bent vs linear NO ligands is the sum of electrons of pi-symmetry. Complexes with "pi-electrons" in excess of 6 tend to have bent NO ligands. Thus, $[\text{Co}(\text{en})_2(\text{NO})\text{Cl}]^+$, with seven electrons of pi-symmetry (six in t_{2g} orbitals and one on NO), adopts a bent NO ligand, whereas $[\text{Fe}(\text{CN})_5(\text{NO})]^{3-}$, with six electrons of pi-symmetry, adopts a linear nitrosyl.

Metal complexes possessing a linear coordination of NO

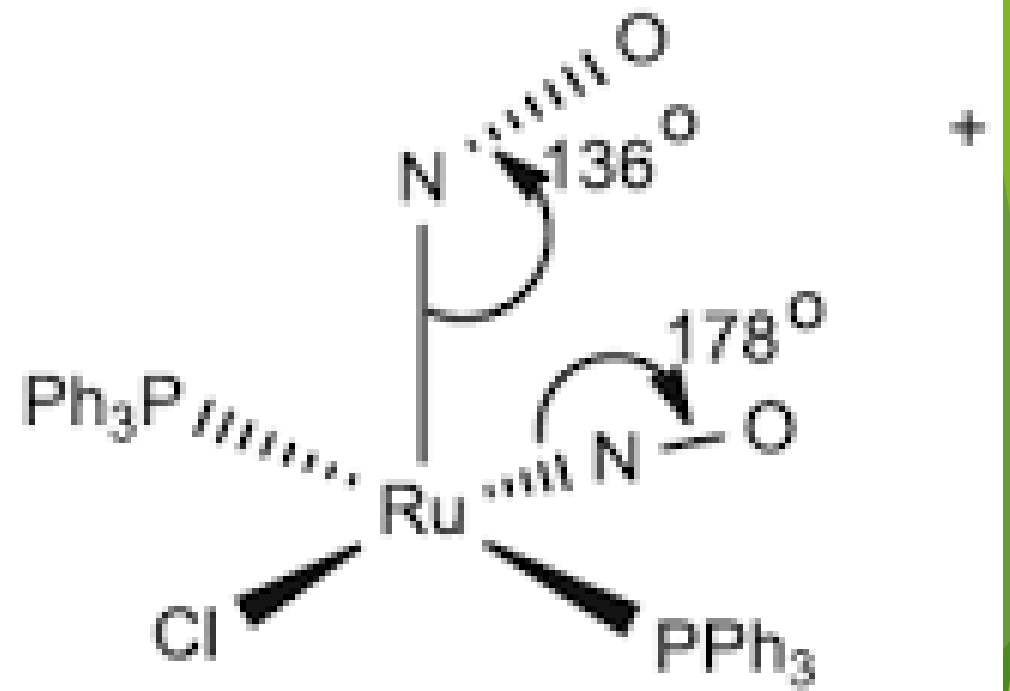
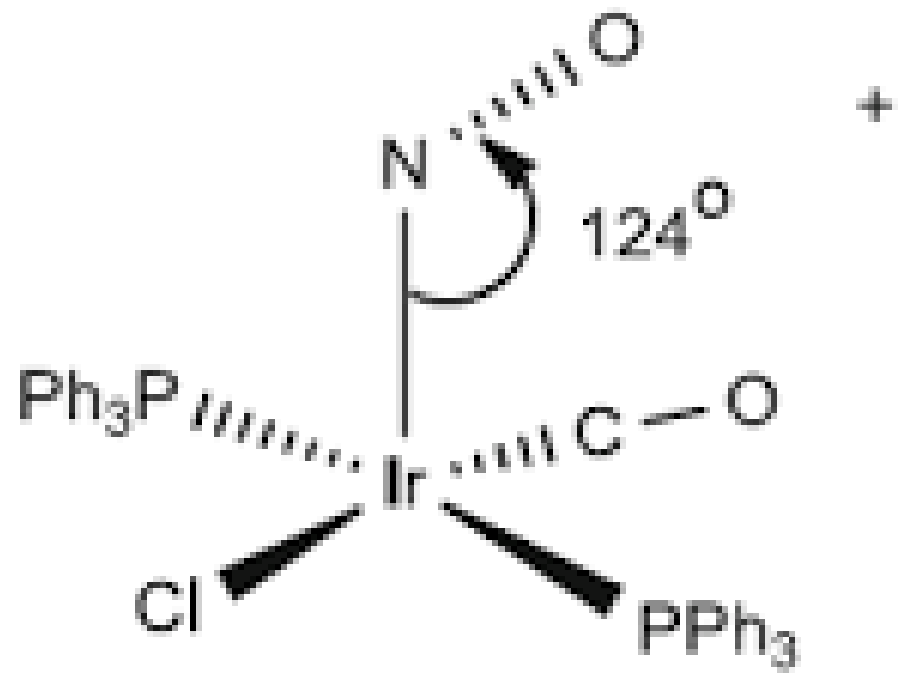
NO has one more electron than CO, hence it often acts as a three electron donor. Hence in metal carbonyl complexes, the replacement of CO by NO is compensated by a matching decrease in the atomic number of the metal centre. Therefore, 3 CO can be easily replaced by 2 NO. For example, the nitroprusside anion, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, an octahedral complex containing a "linear NO" ligand is shown as:



METAL COMPLEXES POSSESSING NON LINEAR CO-ORDINATION OF NO

There are metal complexes in which the M-N-O group features slightly bent coordination geometry where the M-N-O bond angles are in the range of 165° - 180° . For example, the cationic complex $[\text{Ir}(\text{CO})\text{Cl}(\text{NO})(\text{PPh}_3)_2]^+$ was found to have a bond angle of 124° and there are a large number of other nitrosyl complexes. On the other hand, in a related complex $[\text{RuCl}(\text{NO}_2)(\text{PPh}_3)]^+$, in which the CO ligand has been replaced by a second NO molecule, have both linear and bent M-N-O as shown in the figure below.

In this complex, the basal nitrosyl is linear Ru-N-O (178°) whereas the apical nitrosyl was found to be bent (136°). The metal-nitrogen bond lengths in the complex are in accordance with the presented structure. The Ru-N bond length in the linear system is shorter (1.73 \AA) as compared to the bent system (1.85 \AA). This indicates that there is substantial π -bonding in the linear system whereas the bent system is a σ -only metal-nitrogen bond



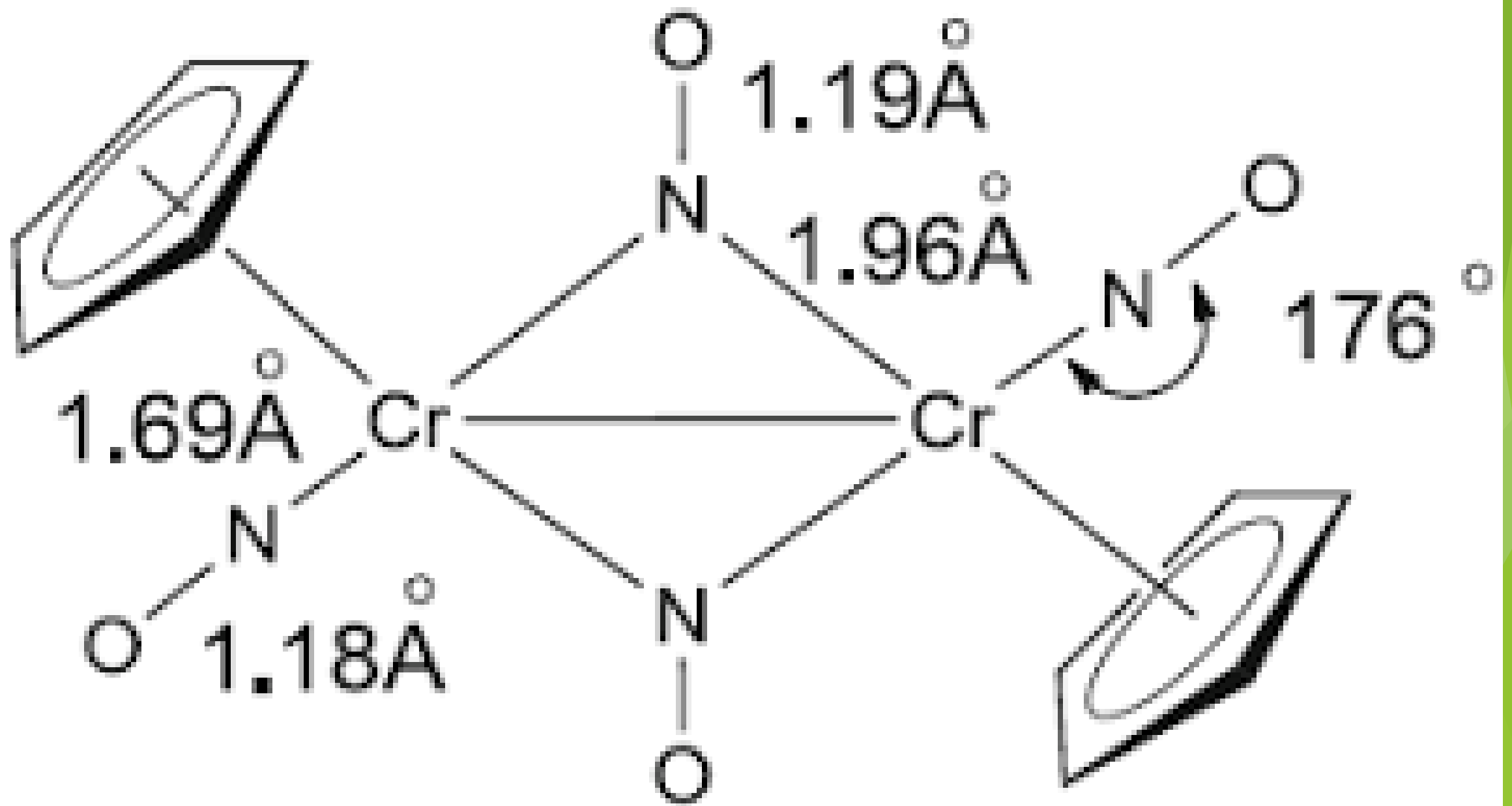
In $[\text{Co}(\text{NO})(\text{en})_2\text{Cl}]^+$ (where “en” is ethylenediamine), the NO takes a bent coordination mode. In this complex, the Co-N bond distance (1.820\AA) in Co-NO bond was found to be considerably different from Co-N bonds with the ethylenediamine ligand (1.964\AA). This indicates that the NO ligand retains significant multiple bond character because of back donation from a filled metal d-orbital to the remaining empty π^* orbital of the NO ligand. The first well-characterized example of a metal complex containing the bent nitrosyl was found in a derivative of Vaska’s complex.



The product has a square pyramidal structure with a bent nitrosyl ligand

having an Ir-N-O angle of 124° . The question of whether the nitrosyl ligand would adopt a linear or bent coordination mode can be answered by looking at the MO picture of the final complex.

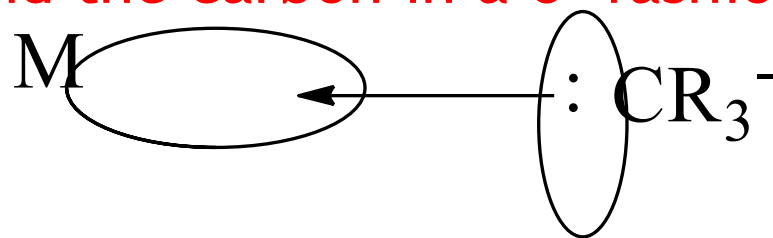
If there are available non-bonding MOs on the electron poorer metal, the electron pair on the nitrogen of NO can reside there and the nitrogen functions as a sp donor system with an associated π -back donation from the metal to the NO. Thus, NO adopts linear coordination mode in this situation. On the other hand, when the low-lying orbitals of metal are already filled (electron-rich system), the pair of electron must occupy a basically non-bonding orbital on the nitrogen of bonded NO, resulting in sp² hybridization and a bent coordination geometry of the NO.



METALATION

ALKYL AND ARYL METALATION:

An organometallic complex having σ bonds between metal atom alkyl group is alkyl metallic complex (e.g.,) Grignard Reagent .It is having Magnesium alkyl bonds. Methyl lithium is another complex . In this complex sharing of electrons between metal and the carbon in a σ fashion.



(R=H,alkyl,aryl)

Alkyl ligand may be a 2-electron donor (donor pair method) or a 1-electron donor (neutral ligand method).

Structure and Bonding

Simple alkyls are simple sigma donors, that can be considered to donate one or two electrons to the metal center depending on which electron counting formalism.



For simple metal alkyls, the M-R bond distance is typically 190 to 220 pm. This is approximately the sum of the covalent radii of carbon and metal, $r_C = 77$ pm and $r_M \sim 120$ pm. Realize that the first row transition metals are smaller, so any M-X bond distance will usually be smaller by 10-20 pm or so.

Alkyls can bridge two metal centers, something that is well known from aluminum-alkyl chemistry. For Al_2Me_6 , Bridging alkyls are also known

SYNTHESIS OF METAL-ALKYL COMPLEXES:

(1) Reaction of a transition metal halide with organolithium, organomagnesium or organoaluminium reagent.



(2) Reaction of metal carbonyl anion with alkyl halide



Methyl lithium

Methyl chloride is reacted with lithium in benzene solvent, methyl lithium result.



CH_3Li exist as a tetramer. Structure is tetrahedron. 4 H atoms constituting the corners of the tetrahedron. CH_3 group occupying spaces symmetrically in the four phases of the tetrahedron. The bonding involves electron deficient 4 centre-2-electron bond.

(e.g.,) $\text{Ti}(\text{CH}_3)_4, \text{W}(\text{CH}_3)_6$. The alkyl ligand acts as a monohapto ligand.

7) **Insertion reactions:** To form an alkyl, this usually involves an olefin insertion. The simplest generic example is the insertion of ethylene into an M-X bond, i.e.



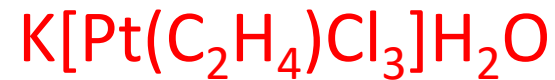
METAL ALKENE COMPLEX

Certain metal ion such as Cu^+ , Ag^+ , Hg^{2+} and Pb^{2+} forming complex with alkene. E.g., silver -alkene complex.



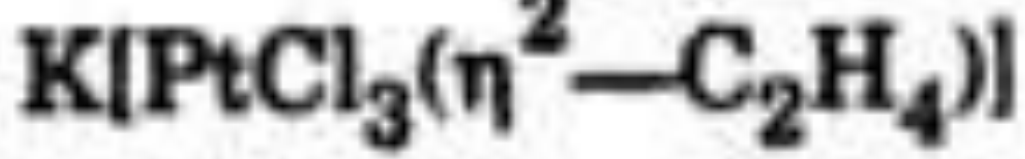
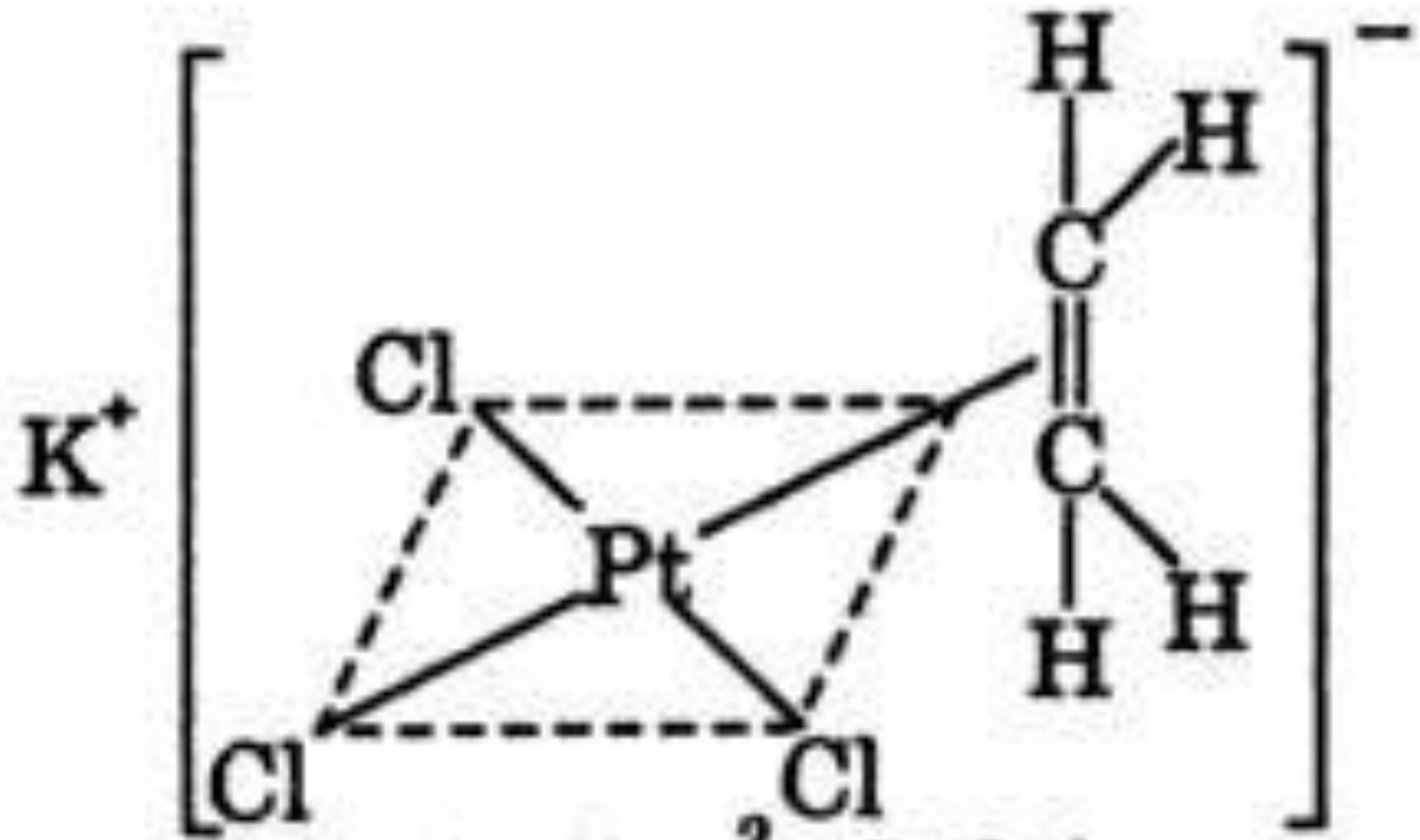
ZEISE'S SALT:

It is a Pt-alkene complex



PREPARATION:





STRUCTURAL FEATURES OF ZEISE'S SALT

1* The platinum ion in the salt is 4-coordinated, 3 sites occupied by the chloride ion and the fourth site occupied by the ethylene molecule.

2* Its geometry is square planar.

3* π electrons in ethylene are co-ordinated to the platinum metal. Overlap of π bonding orbital of the alkene with a vacant σ -type orbital of the Pt is $(5d\ 6s\ 6p^2)$ hybrid produces L \rightarrow M bond of σ type.

4* In addition to π bond originating from the overlap of a $[5dxz\ 6pz]$ filled orbital of Pt atom with empty π bonding orbital of alkene is formed.

5* Ethylene molecule is π -bonding ligand.

6* The length of the co-ordinated alkene C = C bond (1.375Å) is greater than C = C bond length (1.337) in the free ethylene molecule.

C = C bond is perpendicular to the molecular plane.

7* Planar ethylene becomes non planar on bonding to platinum.

8* The metal is located above the plane of the alkene symmetrically between the two skeletal carbon atoms.

9* The two carbon atoms are equidistant from the platinum ion.

10* Water molecule present as solvent molecule of crystallization.

11* structure is determined by X-ray, IR and raman spectra.

BONDING IN METAL- ALKENE COMPLEX:

1* In a metal alkene complex π electrons of the alkene are used to bond the ligand with the metal such a bond is called dative σ bond.

2* The primary π -electron metal bonding is strengthened by back donation from a filled metal t_{2g} orbital to a π^* orbital of the alkene ligand.

Back bonding changes hybridization of C from sp^2 to sp^3 so substituents bent back.

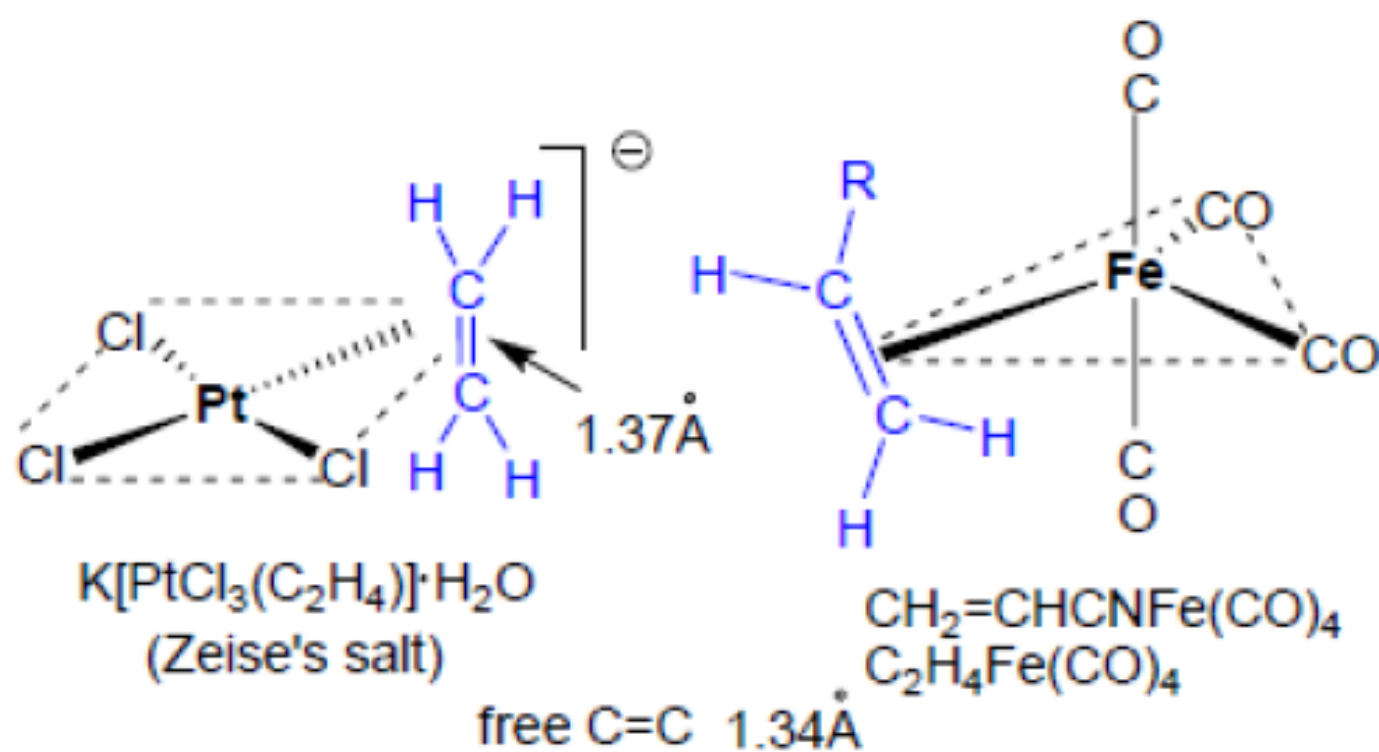
3* The complex formation and the bonding satisfy EAN rule.

4* The length of C -C coordinated olefin is greater than the C -C bond in free alkene. This is proved by decrease in the C = C stretching frequency in the complex compared to frequency in free alkene.

C = C stretch in Zeise's salt 1516cm^{-1}

C = C stretch free ethylene 1623cm^{-1}

5* Lengthening of bond can be explained by the synergistic σ donation and π acceptance of ethylene ligand.



Zeise's salt

$[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$

C-C distance = 1.37 Å

C-C distance in free ligand = 1.35 Å

Conclusion : in this complex most of bonding is ligand \rightarrow M σ -donation.

Both components *strengthen* M-C bonds and *weaken* C-C bonds, but π -donation has greatest effect in weakening C-C bond.

METAL ACETYLENE COMPLEX:

Metal acetylene complexes are similar to the metal-olefin complexes.

Structure and Bonding

- * Alkynes tend to be more electronegative and therefore tend to bind more tightly to a transition metal than alkenes. In fact, alkynes will often displace alkenes.
- * The primary difference in bonding between alkenes and alkynes is that an alkyne can act as either a 2 or 4 electron donor
- * Alkynes have **two** sets of mutually orthogonal pi bonds. We can bind one of these to the transition metal in a sigma-type fashion (**A**) as we did for alkenes, including a pi-backbond (**B**).

The orthogonal set can also bind in a pi-type fashion using an orthogonal metal d-orbital (**C**):

The back-donation to the antibonding orbital (**D**) is a delta-bond (there are two nodes in it), and the degree of overlap is quite small as the two orbitals meet side-to-side rather than engaging in direct overlap. Therefore, the contribution of **D** to the bonding of alkynes is minimal at best.

The net effect of this additional pi-donation is that alkynes are usually non-linear when coordinated to a transition metal complex. We can draw several resonance structures that depict the bonding of an alkyne. **I** is the **metallacyclopropene** resonance form. Support for this versus a simple two electron donor, **II**, can be inferred from the C-C bond distance as well the R-C-C-R angles (see below). **III** generally does not contribute to the bonding of alkyne complexes.

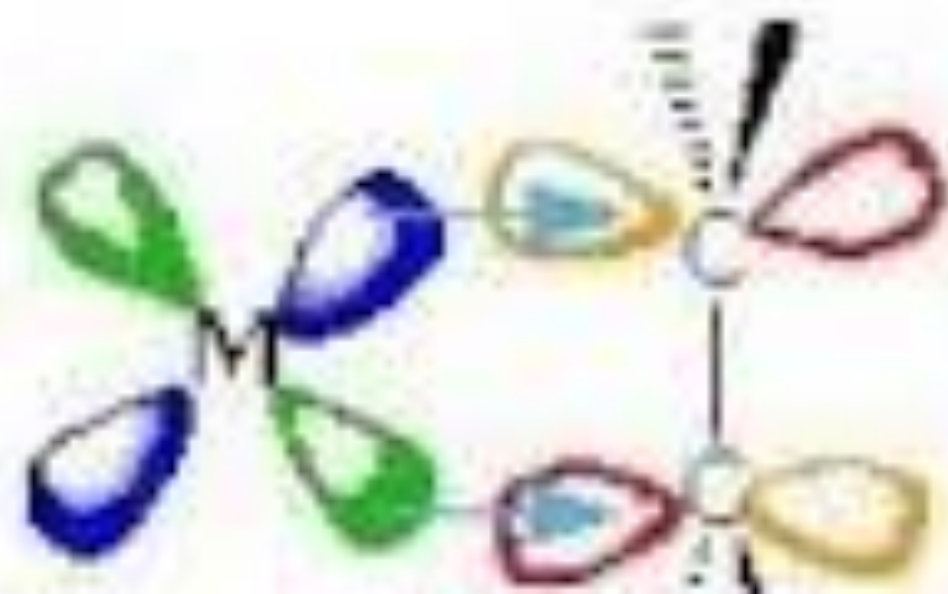
empty metal
d-orbital



filled alkene
 π -orbital

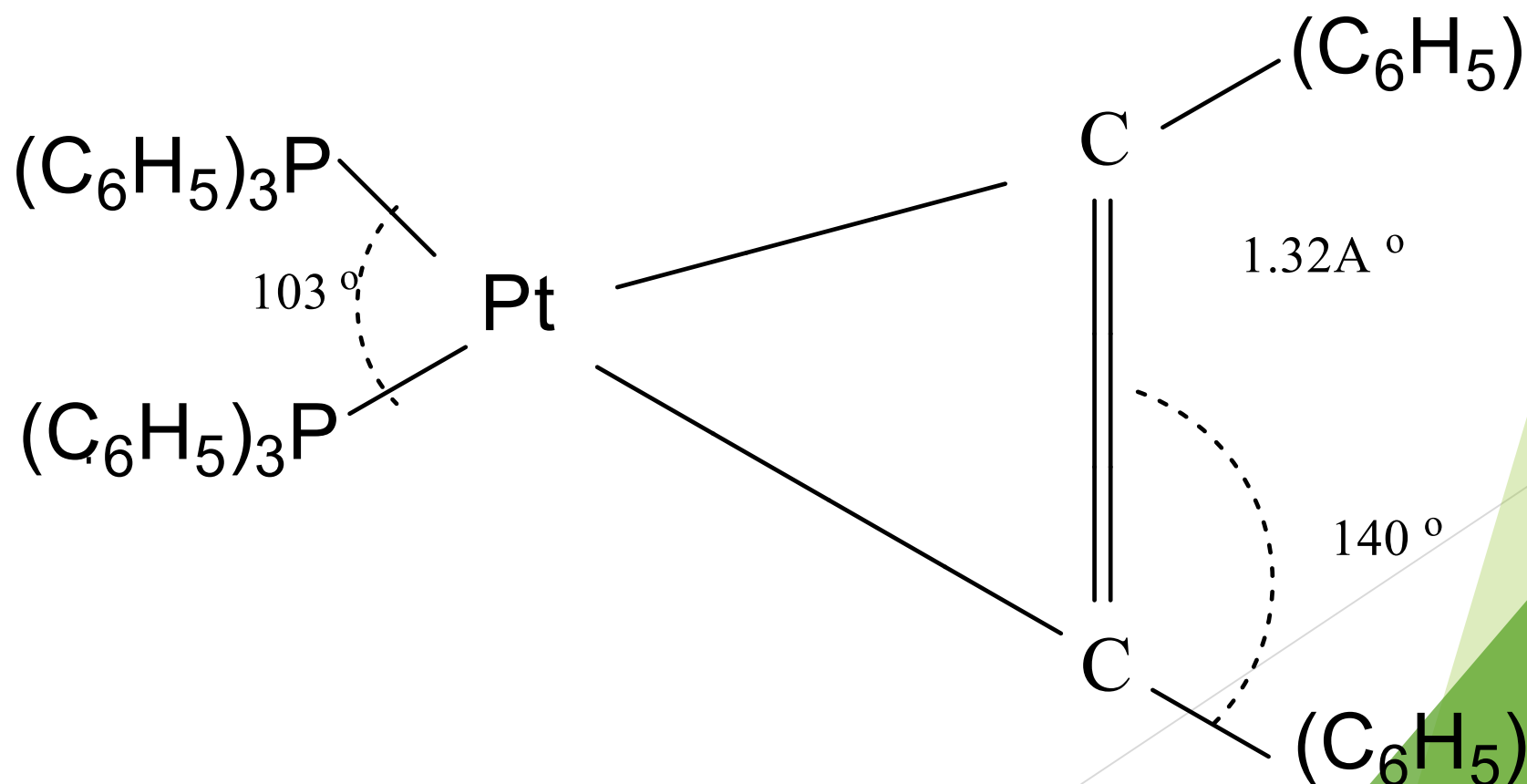
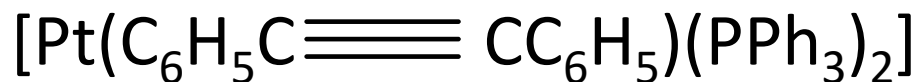
d

filled metal
d-orbital

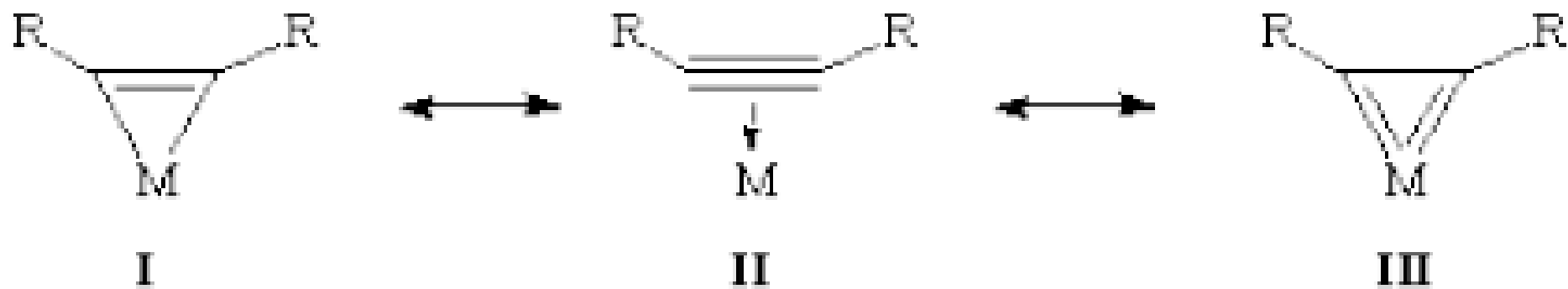


empty alkene
 π^* -orbital

There are analogues of Zeise's salt in which an acetylene molecule is bound to Pt(II) and occupies a position like that of ethylene in Zeise's salt.



RESONANCE STRUCTURE



* As expected from the reduced C-C bond order, the C-C bond distances for coordinated alkynes are typically larger (125 to 135 pm) than in the uncoordinated ligand (110 to 115 pm).

* For 4-electron donors, the R-C-C bond angles are usually in the range of 130 to 146 degrees, with M-C bond distances of 199 to 209 pm. The C-C triple bond of free alkynes are normally observed around 2200 cm^{-1} in the infrared or Raman spectrum

Coordination to a transition metal reduces the C-C bond order, leading to a lower stretching frequency in the range of 1700 to 2000 cm^{-1} . 4-electron donors reflect their reduced nature in the IR: coordinated internal alkynes are typically 1730 - 1820 cm^{-1} and coordinated terminal alkynes are typically 1675 - 1715 cm^{-1} .

METAL ARENE COMPLEX

Metallocenes:

They are also called as metal sandwich complex. It consists of metal sandwiched between two cyclic organic ligands. E.g., Ferrocene [$\text{Fe}(\eta^5\text{-}(\text{C}_5\text{H}_5)_2)$]

PREPARATION:



Ferrocene may be regarded as the Fe^{2+} derivative of cyclopentadienyl anion



(2) The reaction between FeCl_2 and C_5H_6 in presence of a strong base such as diethyl amine.



STRUCTURE OF FERROCENE:

1 * It has a sandwich structure in which the two cyclopentadienyl groups are nearly eclipsed with respect to each other. (Two planar rings are aligned in space in the same manner parallel to each other).

2* The hydrogen atoms are slightly tilted towards the iron atom.

3 * All the carbon atoms in it are equidistant from Fe, therefore the ring is assumed to have a hapticity η of 5 (i.e) $\eta^5\text{-C}_5\text{H}_5$

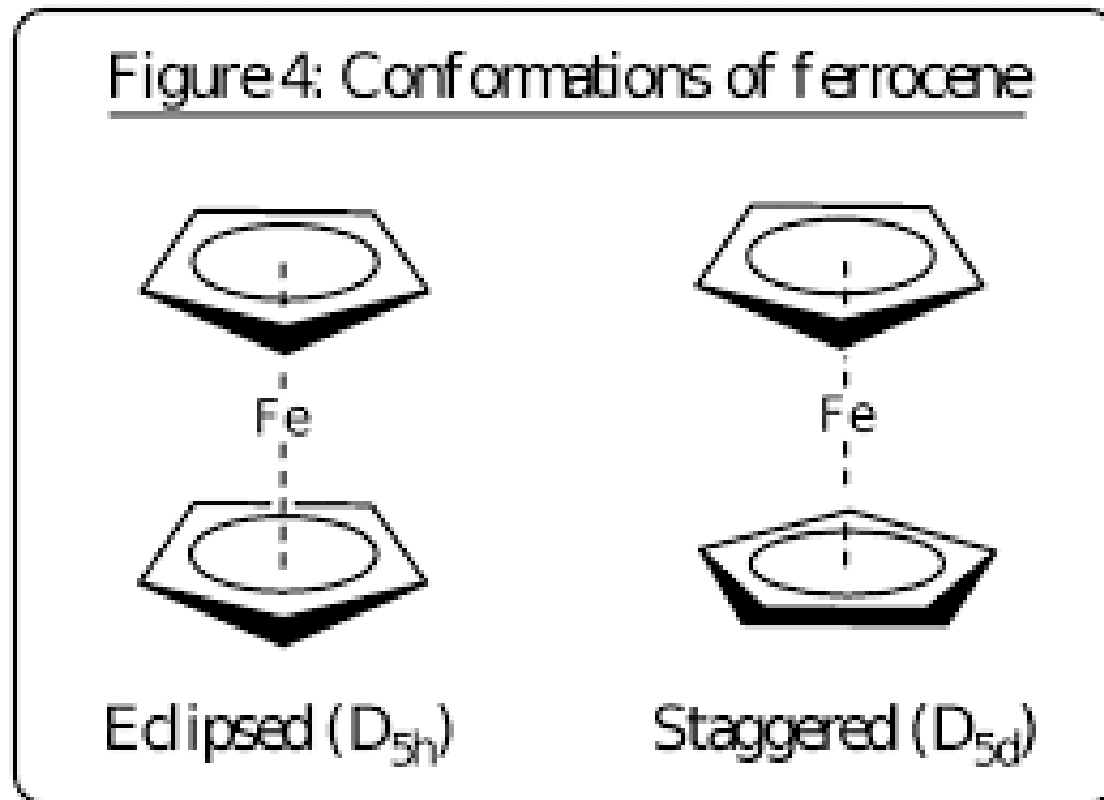
4* All the C-C distances are same (1.389Å) a value close to

1.385 Å

5* The two rings are separated by a distance of 3.25\AA

6* The Fe-C distances are all equal (2.04\AA)

7* The energy barrier for the rotation of the rings about the metal to the ring axis is very small (4KJ/mol^{-1})



BONDING IN FERROCENE:

1* The bonding in Ferrocene can be understood by considering the molecule to be a combination of a ferrous ion with two $C_5H_5^-$ anion.

2* Each $C_5H_5^-$ is planar with a symmetrical pentagonal shape.

3* The entire ring is bonded uniformly to the metal atom.

4* The bonding in it occurs by an overlap of the sextet of π electrons of the ring with the 3d orbitals of the metal thereby producing a delocalized covalent bond between the metal atom and the cyclopentadienyl ring as a whole.

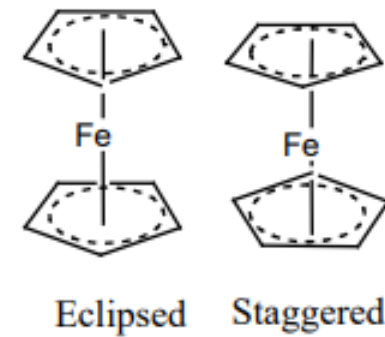
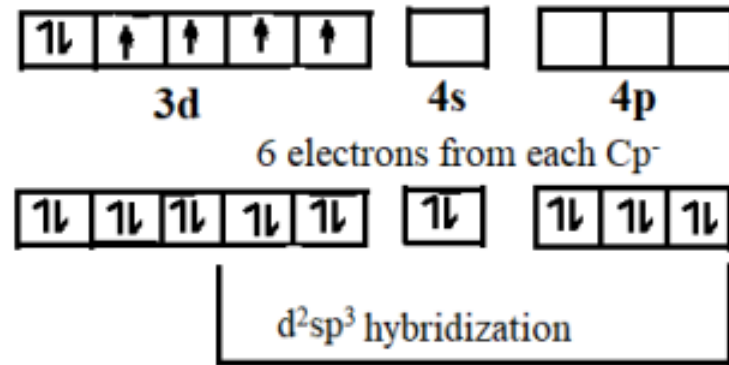
5* With reference to ferrous iron, the structure of ferrocene is pentagonal anti-prismatic.

6* Pentagonal ring of Cp (C_5H_5), analogous to hexagonal ring of benzene, is obtained by Sp^2 hybridization of carbon atoms.

7* Each p_z orbital of each carbon atom having one electron is used for formation of mobile (delocalized) π -bond

8* Total six electrons, which are placed in three of the five π -bonding orbitals (as electron pair); while remaining two π -bonding molecular orbitals remain vacant.

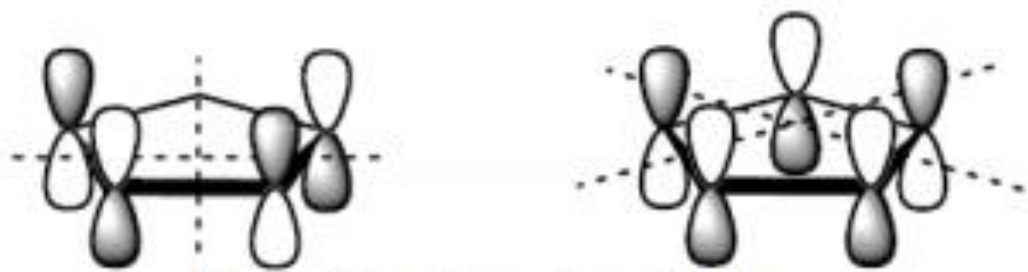
9* During combination with central Fe (II) [$d^2 sp^3$ -hybridised], each Cp coordinates giving three electron pairs. Filled orbitals (t_{2g}) of Fe (II) form back π -bond with vacant antibonding orbitals (π^* MOs) of Cp-. Thus, each Cp- links as π -donor and π -acceptor, with Fe (II).



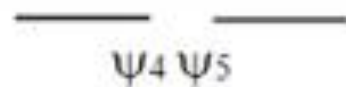
10* Linear combinations of five available p orbitals (one on each carbon atom) give rise to three bonding and two anti-bonding molecular orbitals. The most strongly bonding overlap (when all the wave functions on one side of the ring, have the same sign) is designated as 'A2'.

11* At slightly higher energy, there is a doubly degenerate set of molecular orbitals (E1), each of which has one nodal plane. This is followed by another doubly degenerate set of molecular orbitals (E2) with two nodal planes.

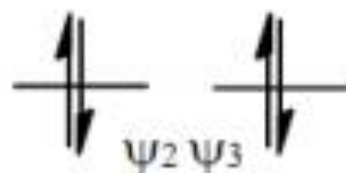
12* The A2 and E1 orbitals are both fully occupied in the electronic configuration of the Cp⁻ anion whereas the E2 orbitals are net anti-bonding and are unfilled.



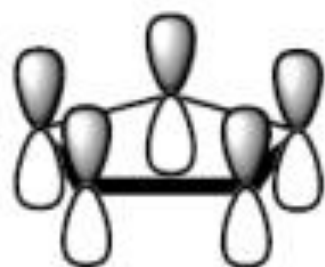
E_2 , Anti-bonding, 2 nodal plane



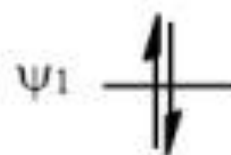
E_1 , Weakly bonding, 1 nodal plane



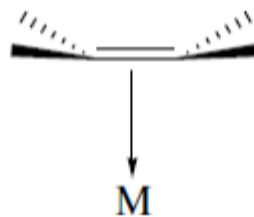
Energy ↑



A_2 , Bonding, 0 nodal plane



π bonded ligands



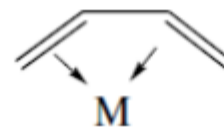
alkene complexes

alkyne complexes

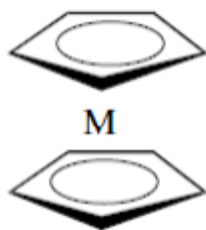


allyl complexes

diene complexes

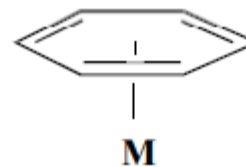
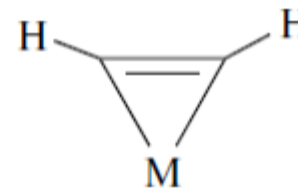


cyclopentadienyl complexes



arene complexes

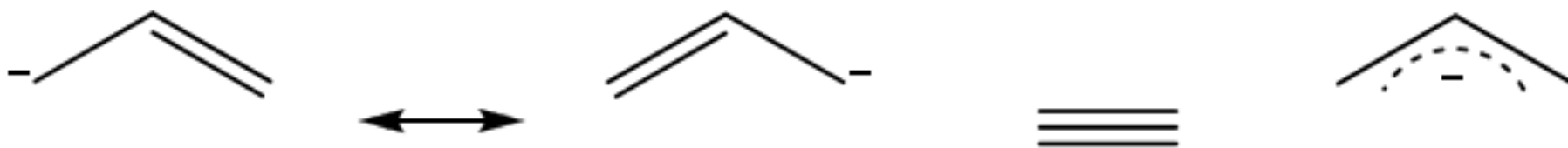
metallacycles



Transition metal allyl complexes

The allyl group, binds in one of two ways.

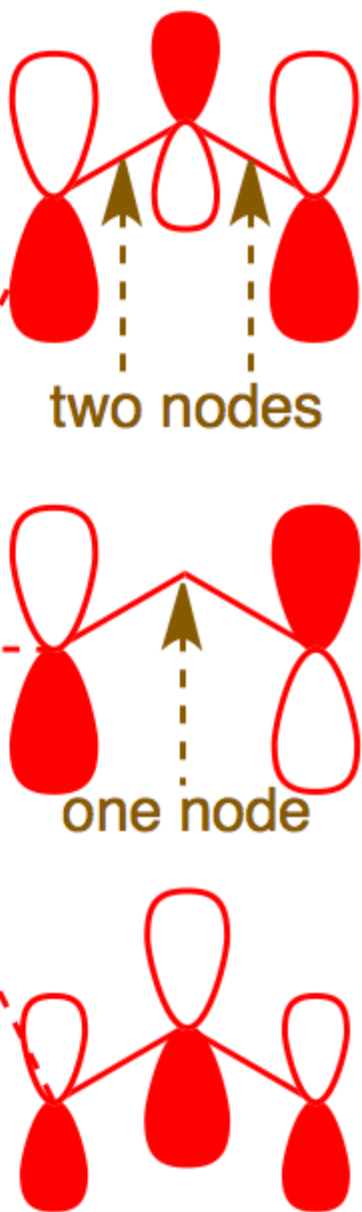
- In the η^1 - form it is a simple X-type ligand like Me and it behaves as an $2e$ -donor.
- In the η^3 - form it acts as a LX enyl ligand and it is an $4e$ -donor.
- It is often useful to think in terms of the resonance forms ($2e + 1e$ donor)



energy

3 x 2p

combine



label orbitals ψ_1 – ψ_3 in increasing energy

ψ_3

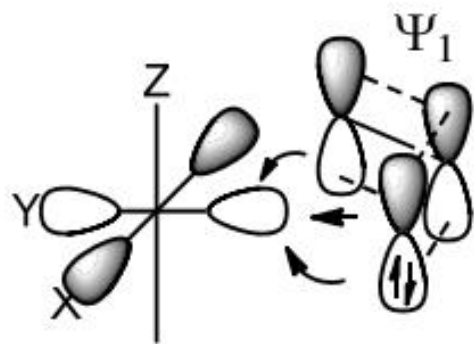
← -- this is the LUMO

ψ_2

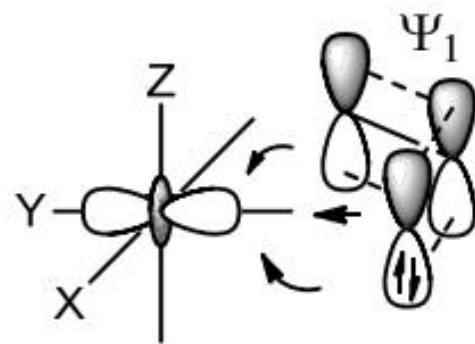
← -- this is the HOMO

put four electrons into the lowest energy orbitals

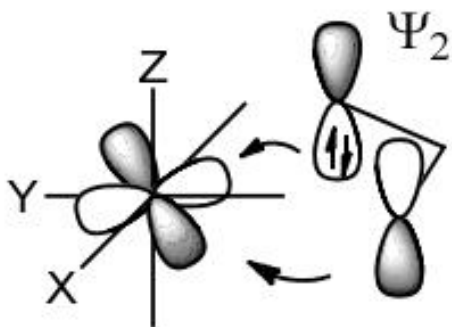
ψ_1



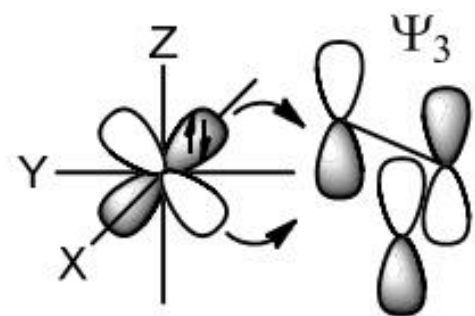
Metal dx^2-dy^2 $\xleftarrow{\sigma \text{ bond}}$ $\eta^3\text{-allyl}$



Metal dz^2 $\xleftarrow{\sigma \text{ bond}}$ $\eta^3\text{-allyl}$



Metal dxy $\xleftarrow{\pi \text{ bond}}$ $\eta^3\text{-allyl}$



Metal dyz $\xrightarrow{\pi \text{ bond}}$ $\eta^3\text{-allyl}$

Frontier molecular orbitals of the metal allyl fragment:

* Ψ_1 is occupied by 2 electrons and has appropriate symmetry, energy and orientation to overlap with a suitable metal $d\sigma$ orbital.

* Ψ_2 is also occupied by 2 electrons (ionic model) and has appropriate symmetry, energy and orientation to overlap with a suitable metal $d\pi$ orbital.

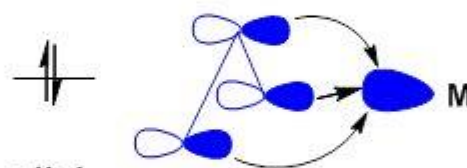
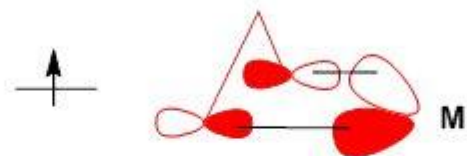
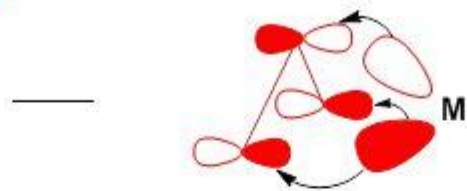
* Ψ_3 is unoccupied and has appropriate symmetry, energy and orientation to overlap with a suitable metal $d\pi$ orbital for back donation.

* The plane of the allyl is canted at an angle θ with respect to the coordination polyhedron around the metal (θ is usually $5^\circ - 10^\circ$).

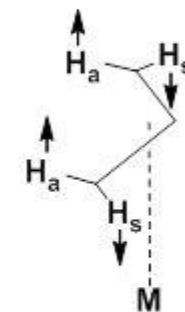
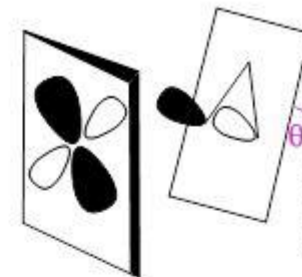
* The extent of orbital overlap between Ψ_2 and the d_{xy} orbital on the metal is improved if the allyl group moves in this way

Allyl complexes

- Two binding modes: η^1 and η^3
- The plane of the allyl is canted at an angle ($\theta = 5 - 10^\circ$) such that orbital interaction is improved.
- Fluxionality: syn and anti substituents exchange through an η^1 -intermediate.



allyl radical

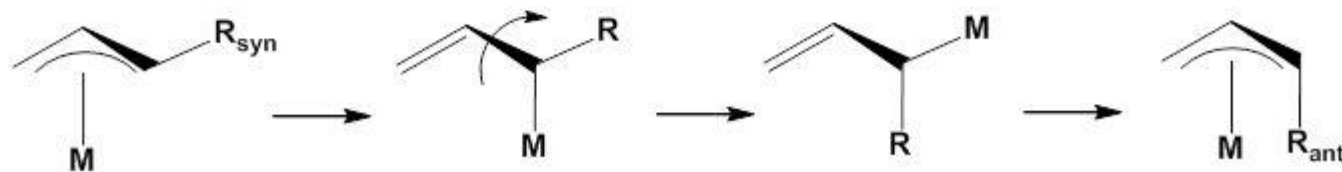


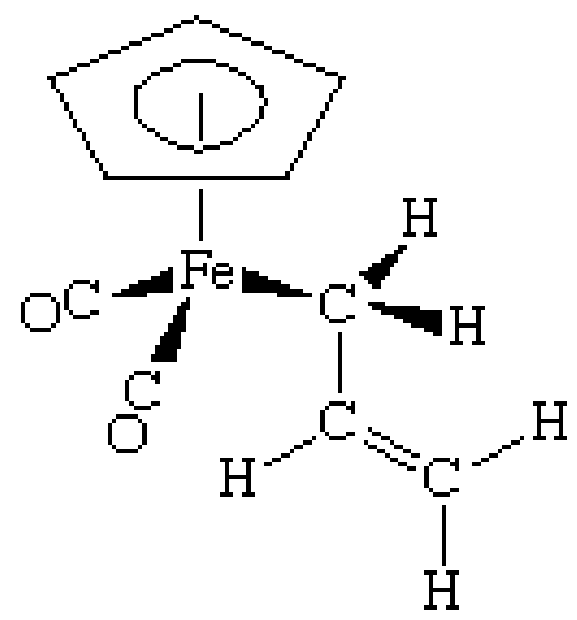
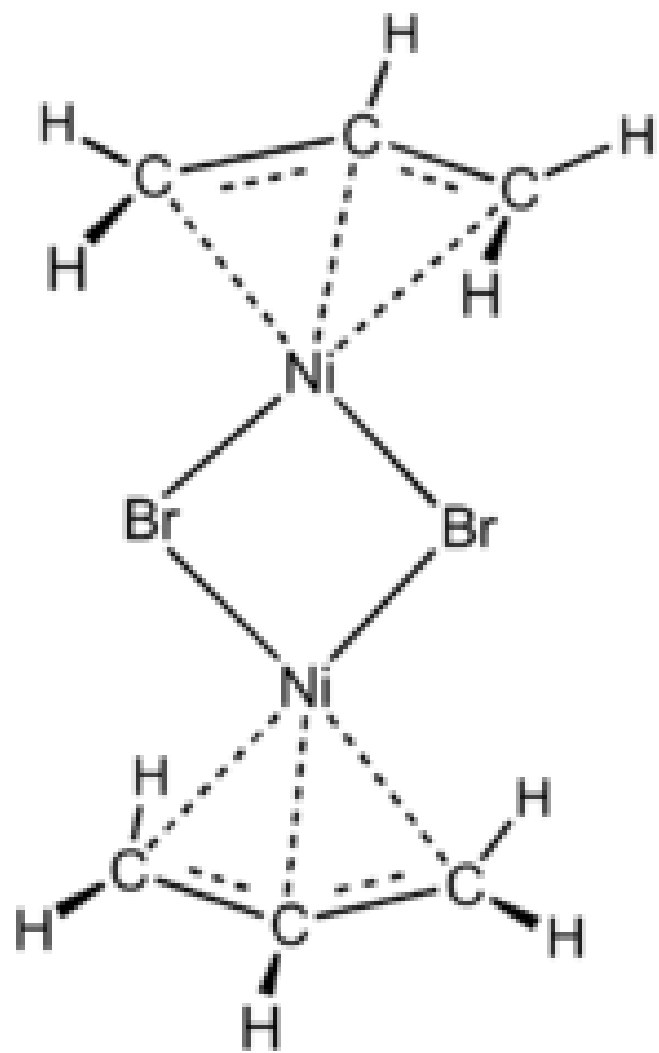
H_a - rotate away from the metal
 H_s - rotate toward the metal

$^1\text{H NMR}$: δ , 1 – 3 ppm (H_{anti}), 2 – 5 ppm (H_{syn}), 4 – 6 ppm (H_{meso})

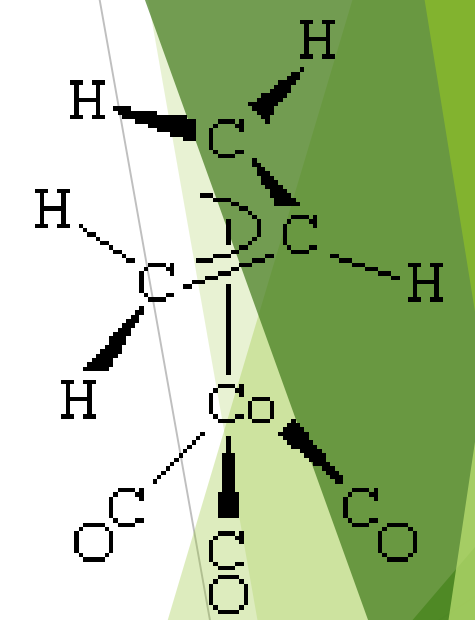
$^{13}\text{C NMR}$: δ , 80 – 90 ppm (C_{terminal}), 110 – 130 ppm (C_{terminal})

Fluxional on the NMR time scale:





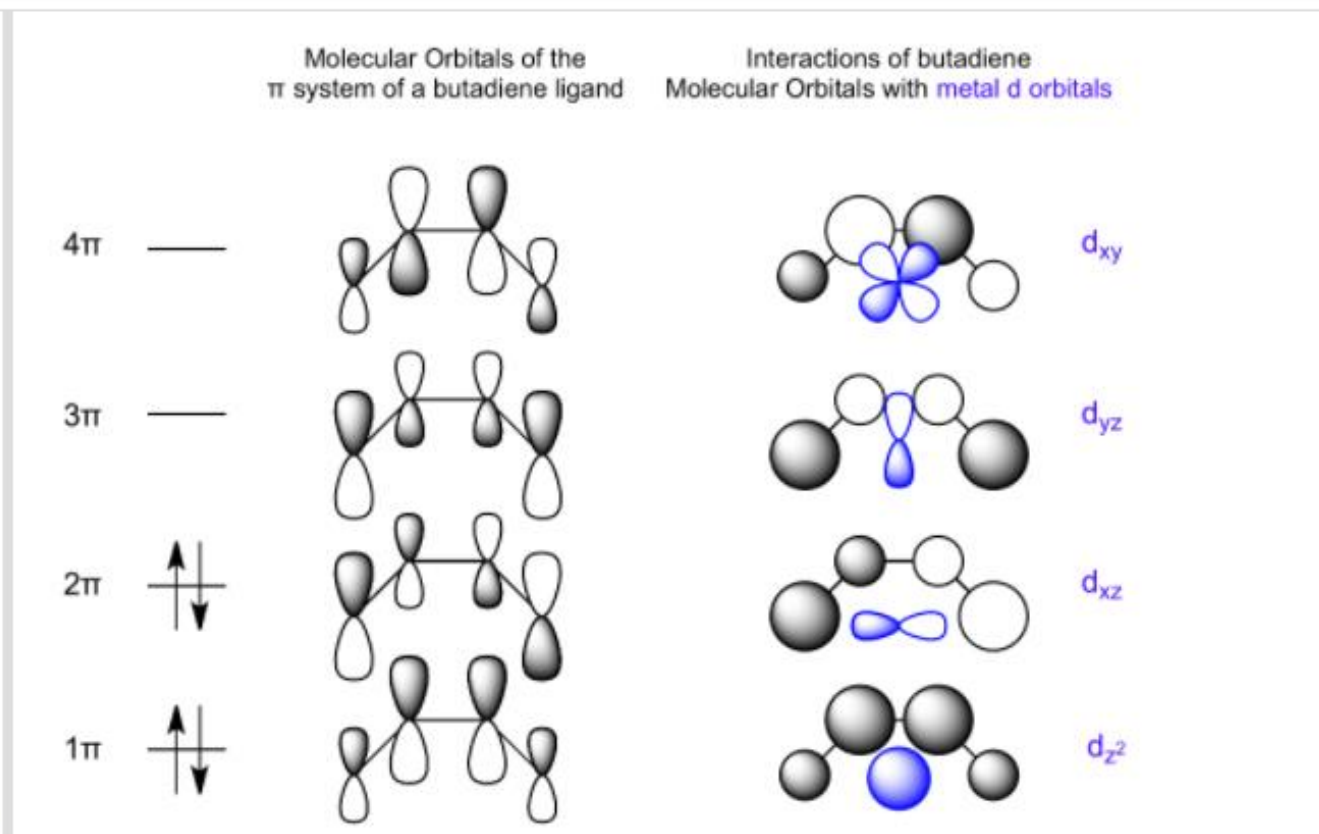
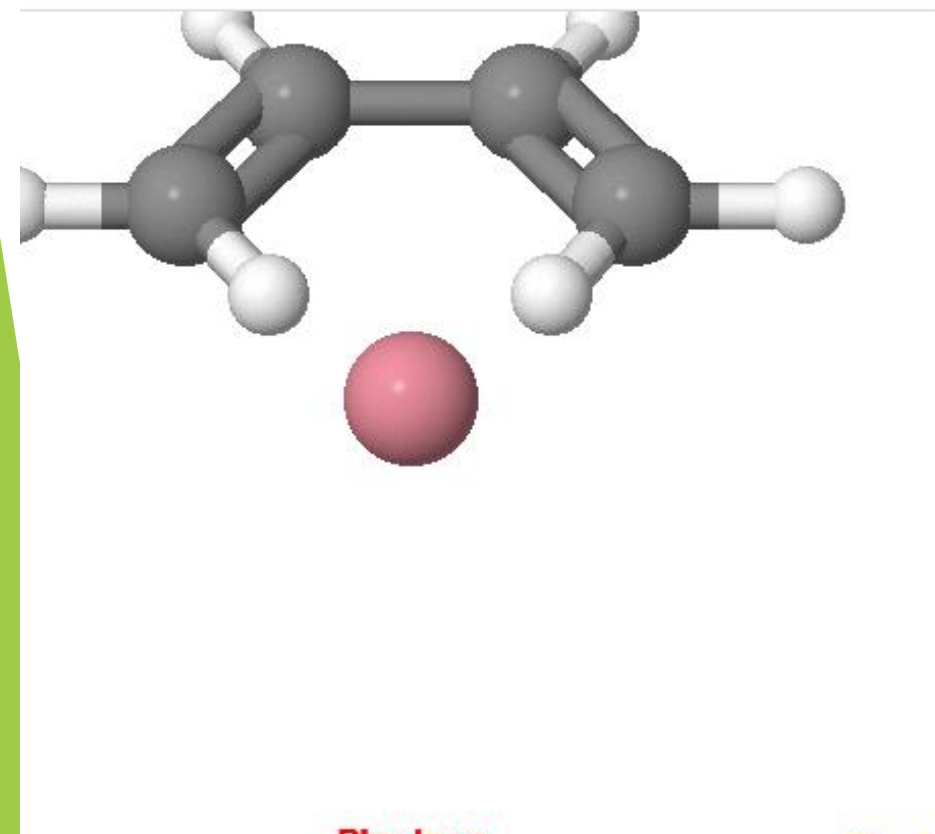
$\text{Fe}(\eta^1\text{-C}_3\text{H}_3)(\text{CO})_2(\eta^5\text{-Cp})$

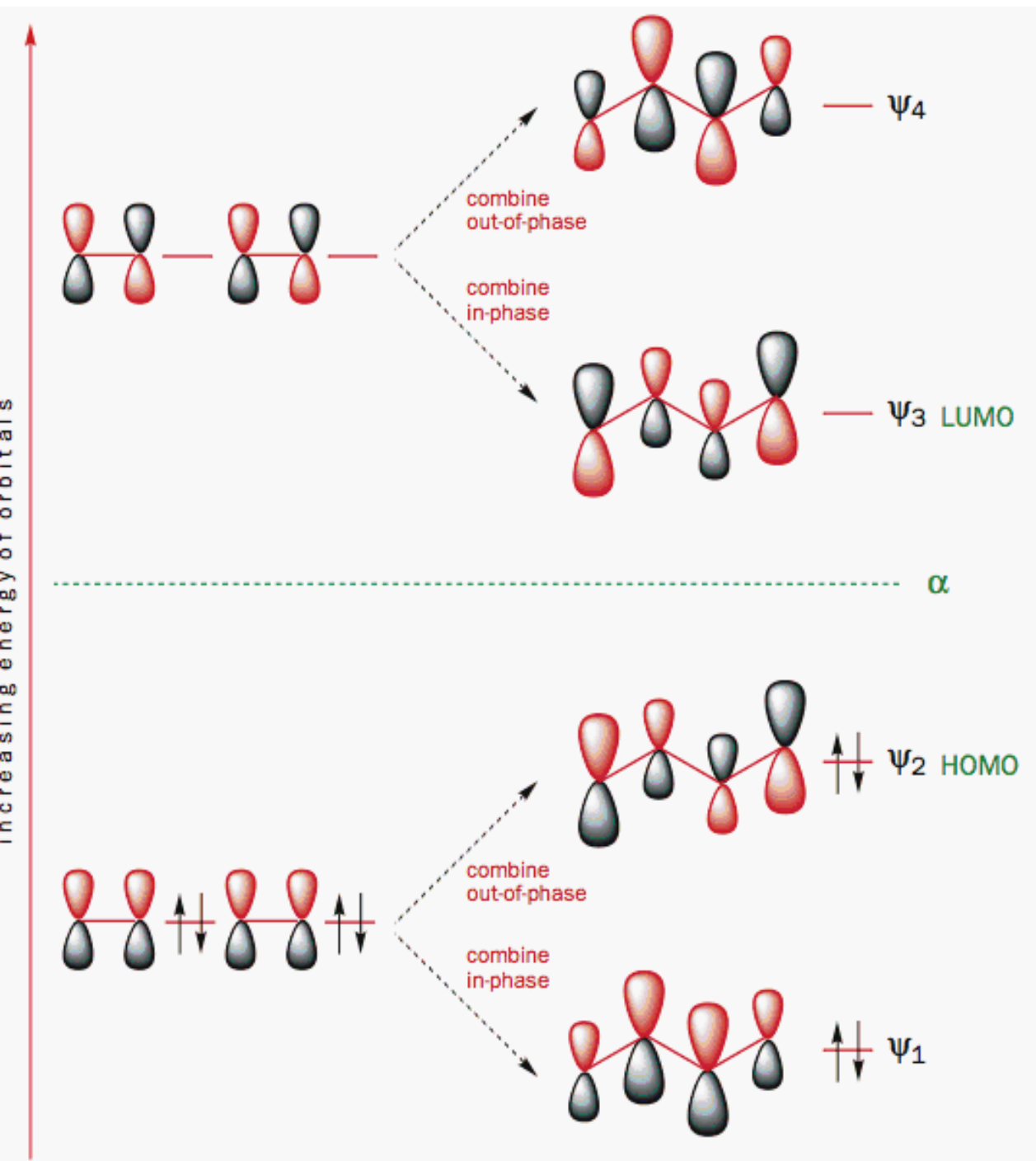


$\text{Co}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_3$

METAL BUTADIENE COMPLEX

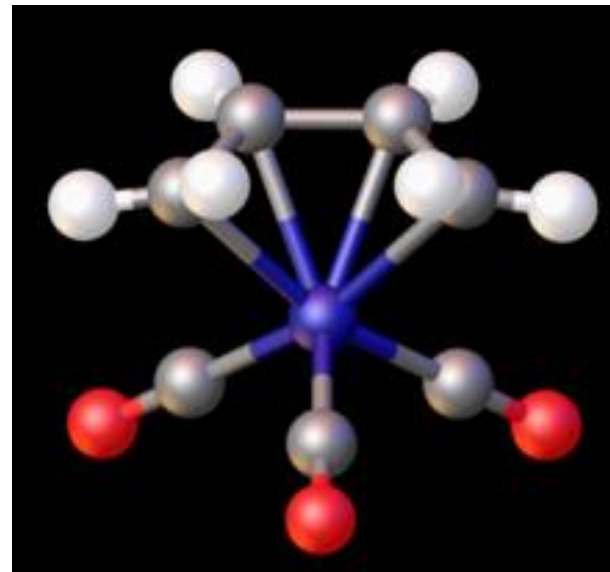
The bonding of butadiene involves matching the metal d orbitals to the π system configuration that contains the correct symmetry for bonding. The two lower energy MOs can behave as donors to the metal; the lowest a σ donor, the HOMO a π donor. The two highest MOs can accept electron density from the metal. The LUMO is a π acceptor. the highest energy MO a σ acceptor.



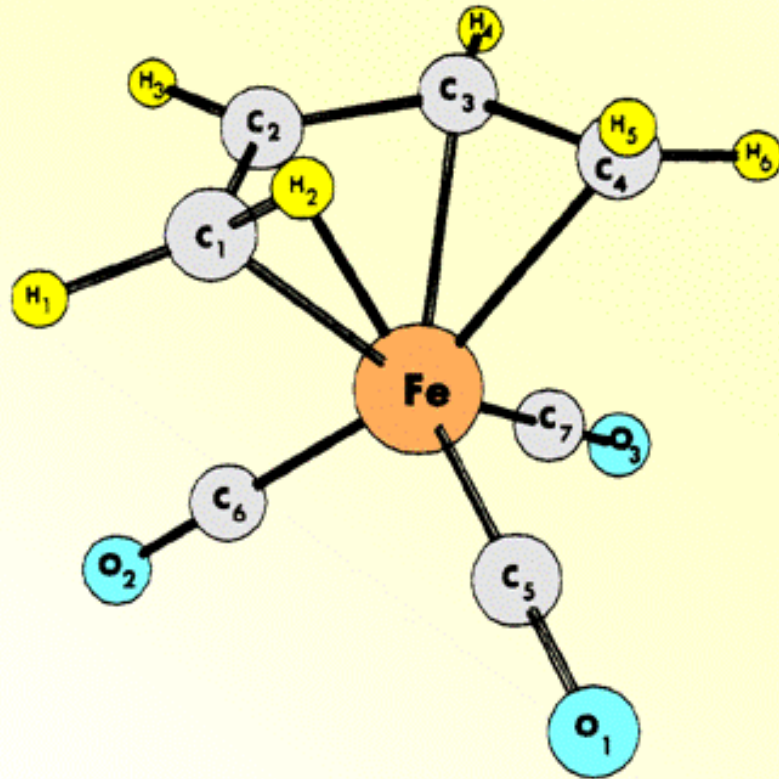


- The frontier orbitals of the butadiene, ψ_2 (HOMO) and ψ_3 (LUMO), are the most important in bonding to the metal.

- Depletion of electron density in ψ_2 by σ donation to the metal and population of ψ_3 by back donation from the metal lengthens the C1-C2 bond and shortens the C2-C3 bond because ψ_2 is C1-C2 antibonding and ψ_3 is C2-C3 bonding.



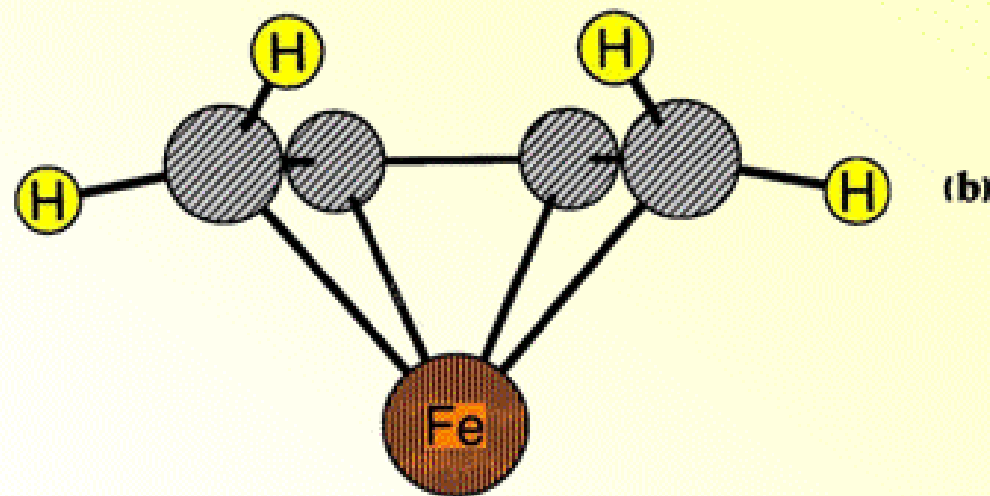
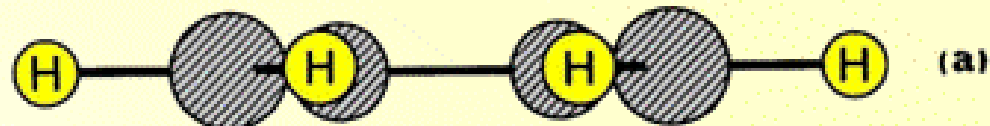
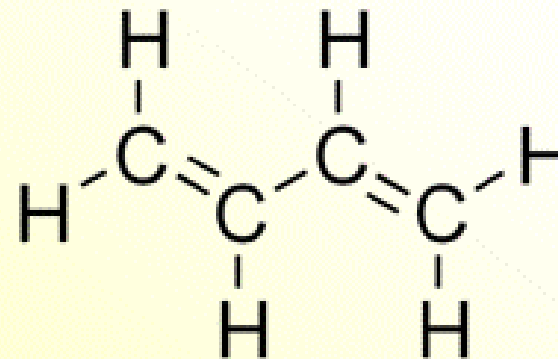
Butadiene iron tricarbonyl



- 10 isotopomers measured, including ¹³C and single and triple D substitutions
- Increase in the butadiene C₁-C₂ bond length (0.08 Å)
- Decrease in the butadiene C₂-C₃ bond length (-0.06 Å)

Substantial structure changes

→ Free butadiene in a planar-trans conformation



→ Changes to cis

→ terminal CH_2 groups are rotated by 28° out of the butadiene plane

→ CH_2 plane is folded away from the butadiene $\text{C}_1\text{-C}_2$ axis by 27°

→ HYBRIDIZATION now looks more like sp^3 than sp^2

Fluxionality

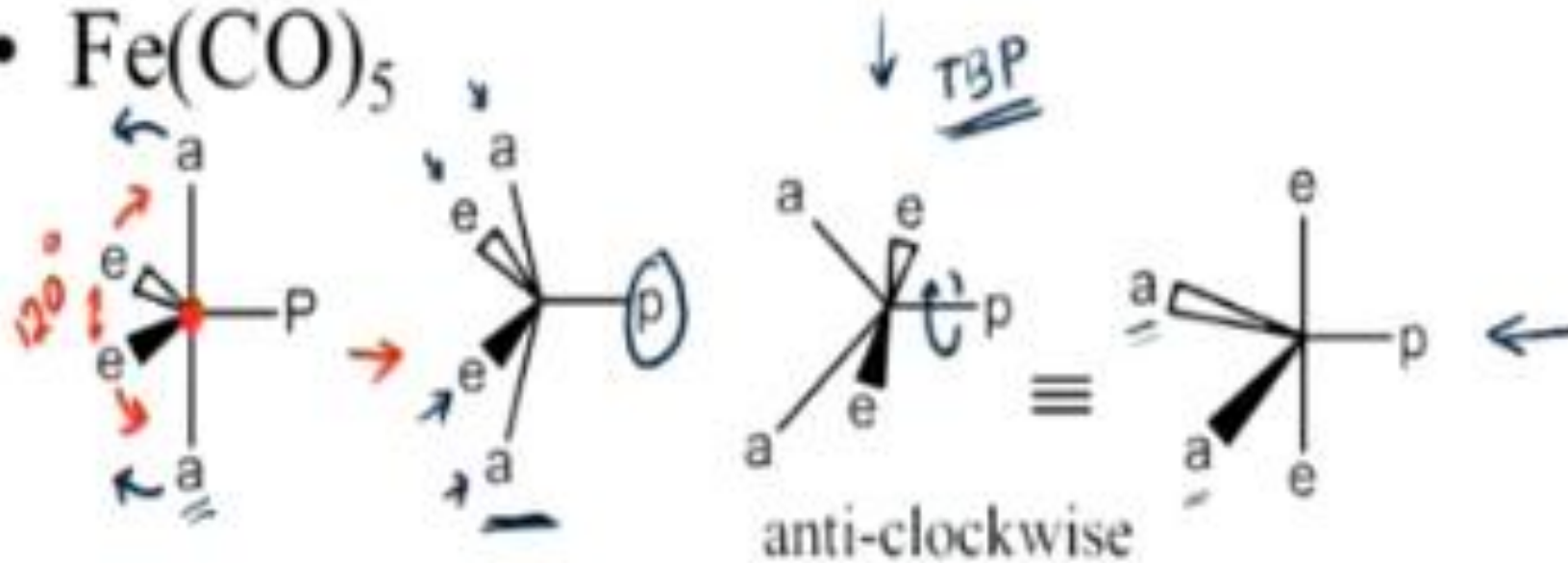
- * **Fluxional** (or **non-rigid**) molecules are molecules that undergo dynamics such that some or all of their atoms interchange between symmetry-equivalent positions.
- * We also use the term, **dynamic exchange process**, to express a molecular motion that interchanges the positions of the inequivalent groups.
- * Multinuclear NMR spectroscopy, one of the favorite tools of the organometallic chemist, is one of the most common ways of observing dynamic behavior.

Dynamic Exchange Processes

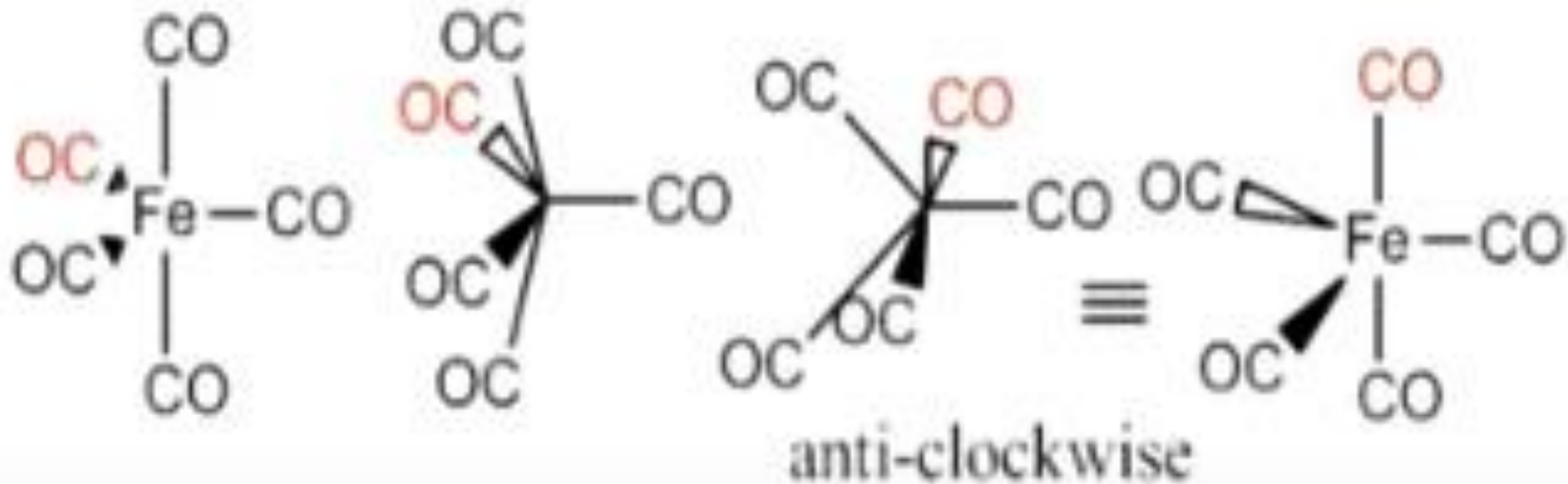
The prototypical example of such a system is the axial-equatorial interconversion of the chair form of cyclohexane

Berry Pseudorotation

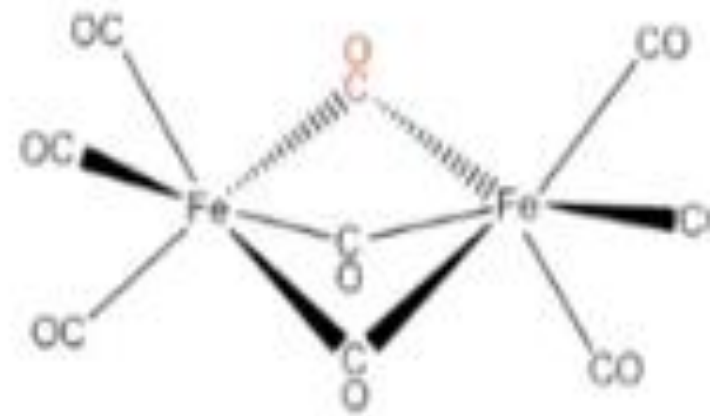
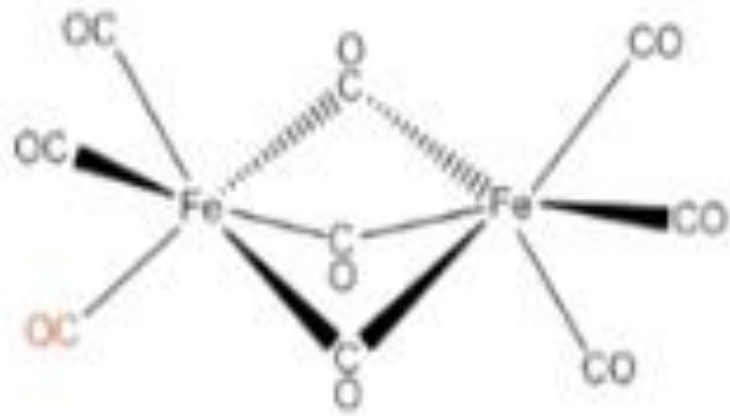
- $\text{Fe}(\text{CO})_5$



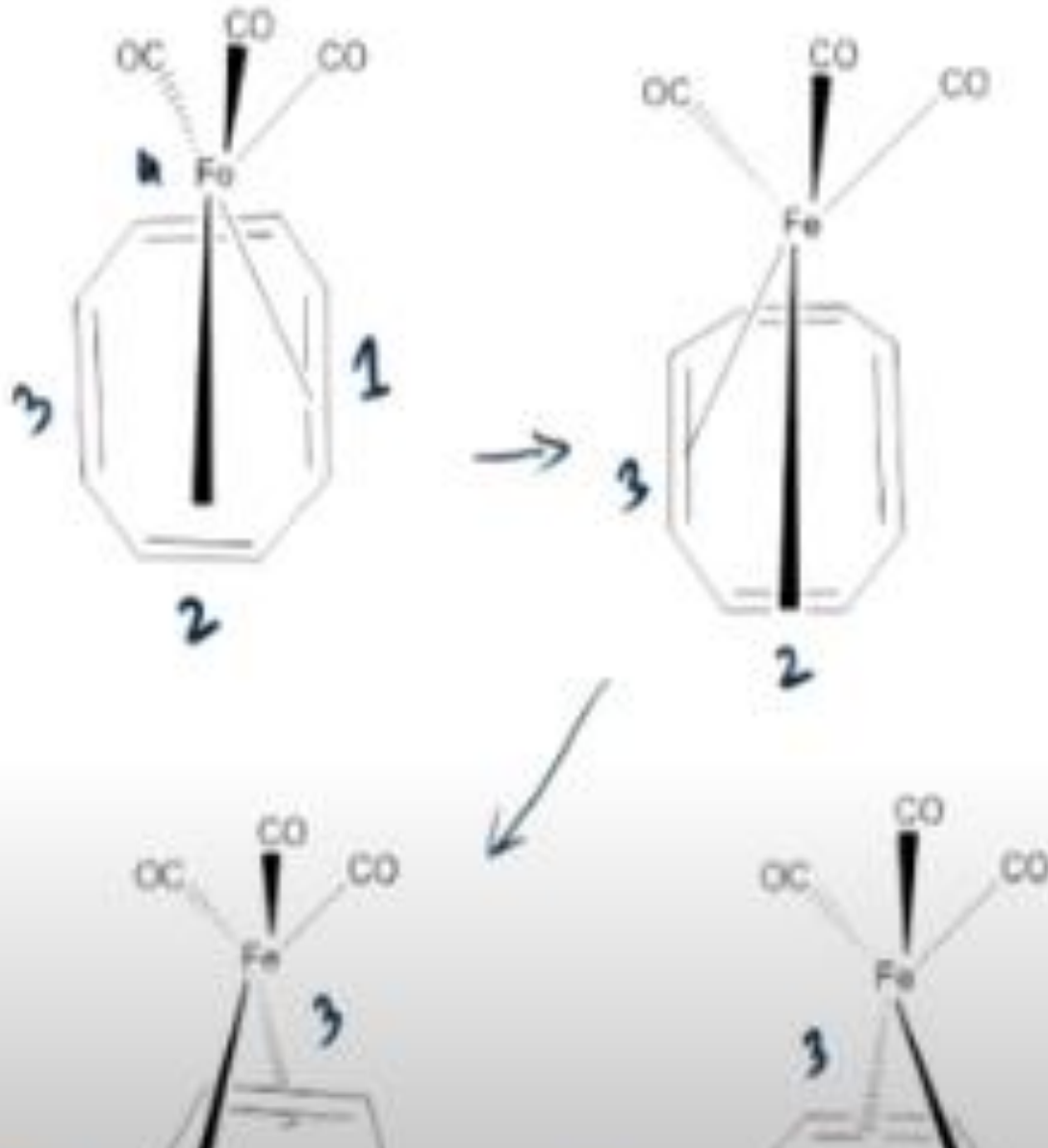
Molecular Breathing



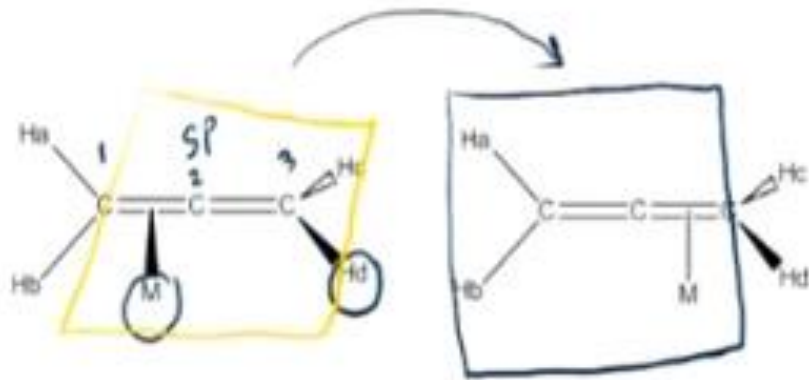
Carbonyl Hopping



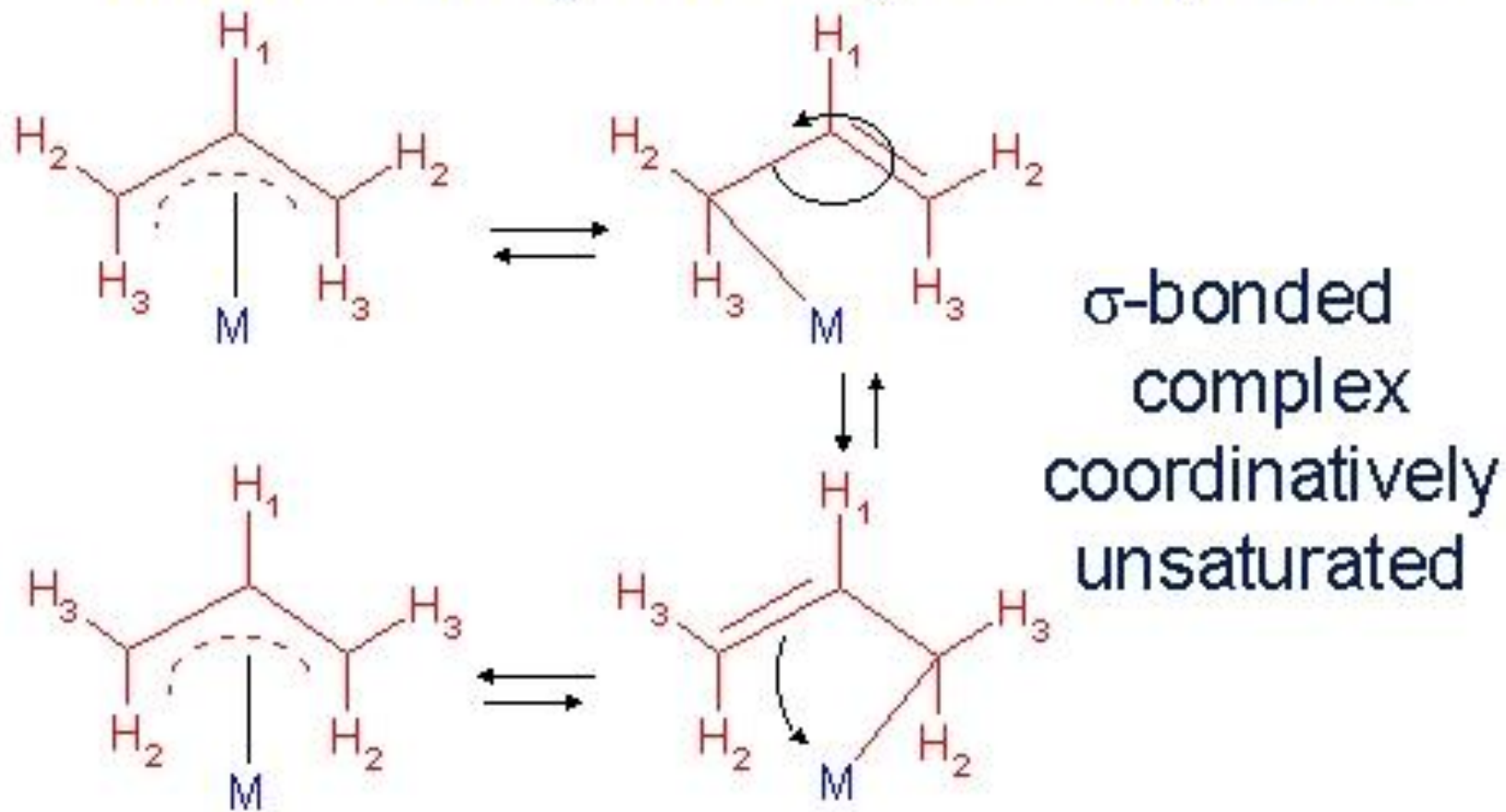
Metal Hopping



Allene complex

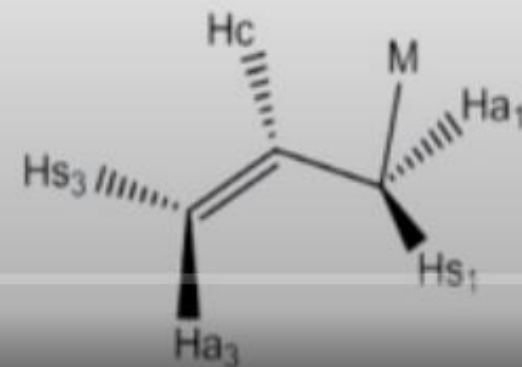
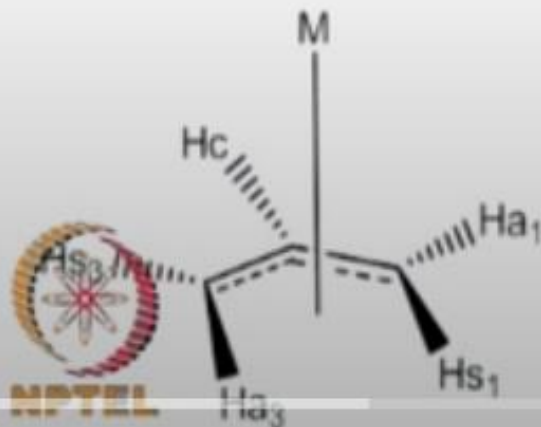
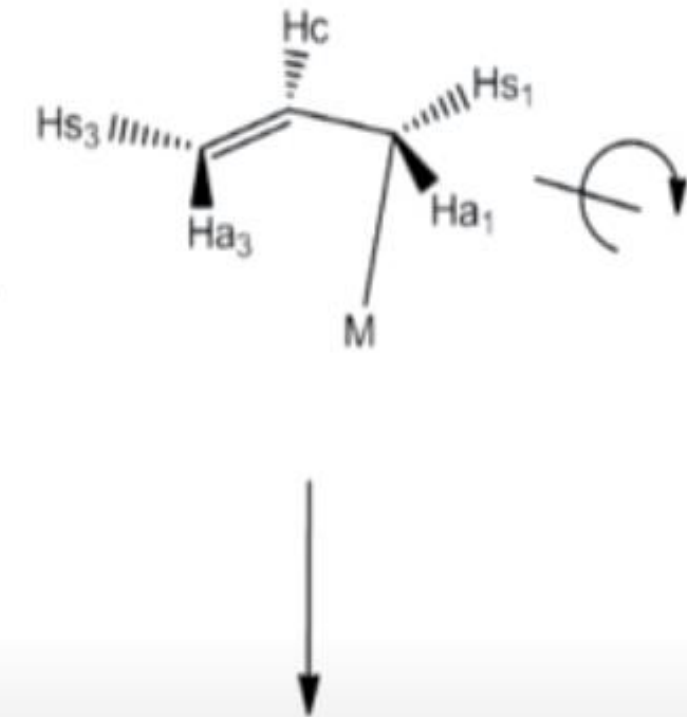
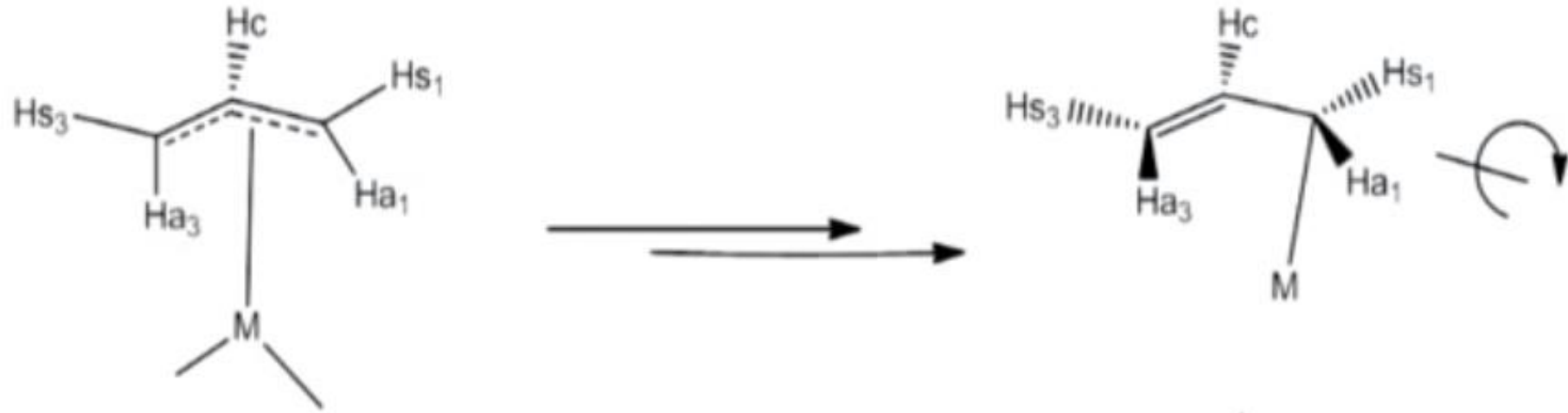


Fluxionality of Allyl Complexes

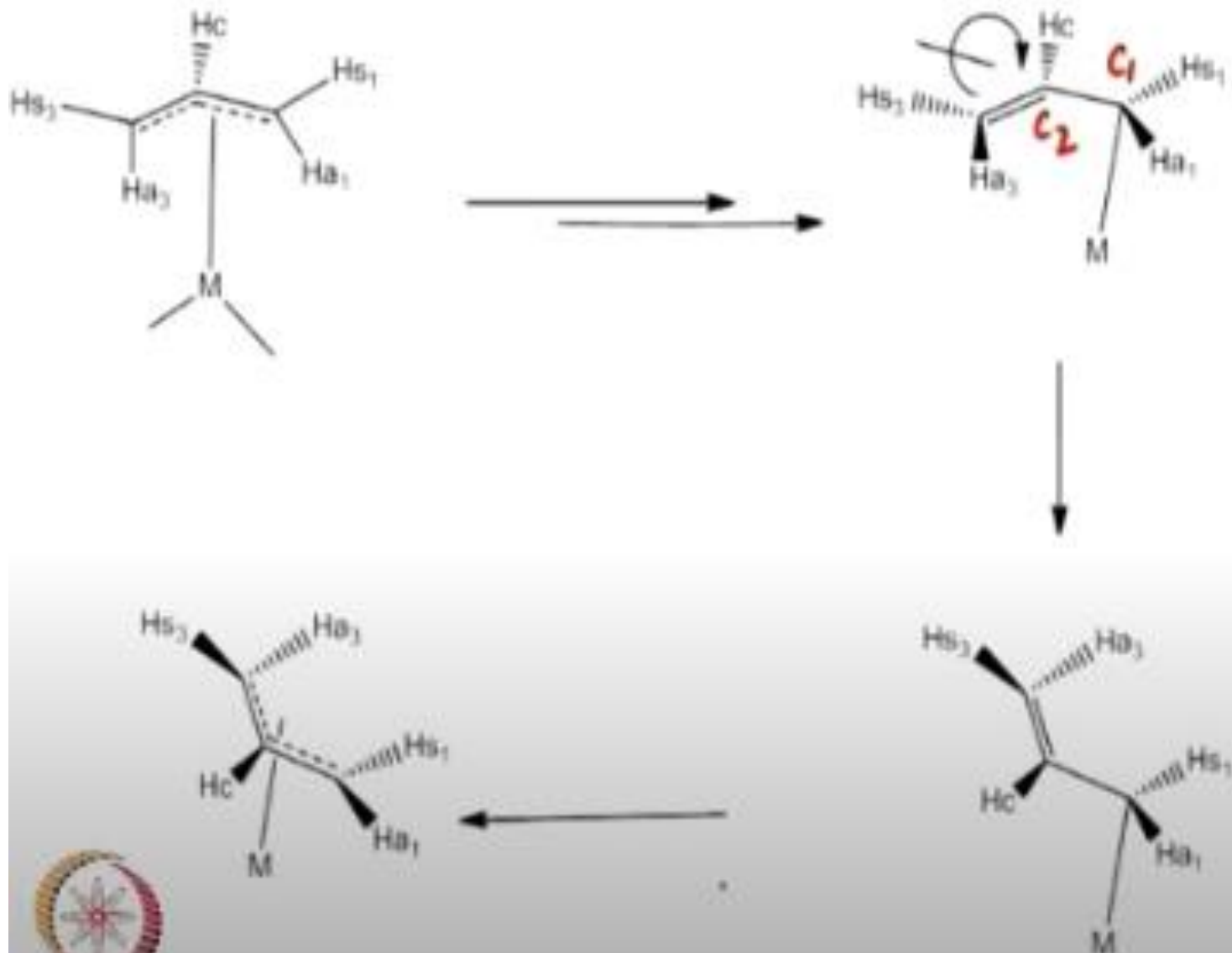


**H₂ and H₃ environment average
process slow at low temperature**

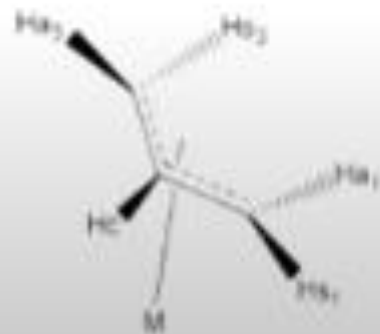
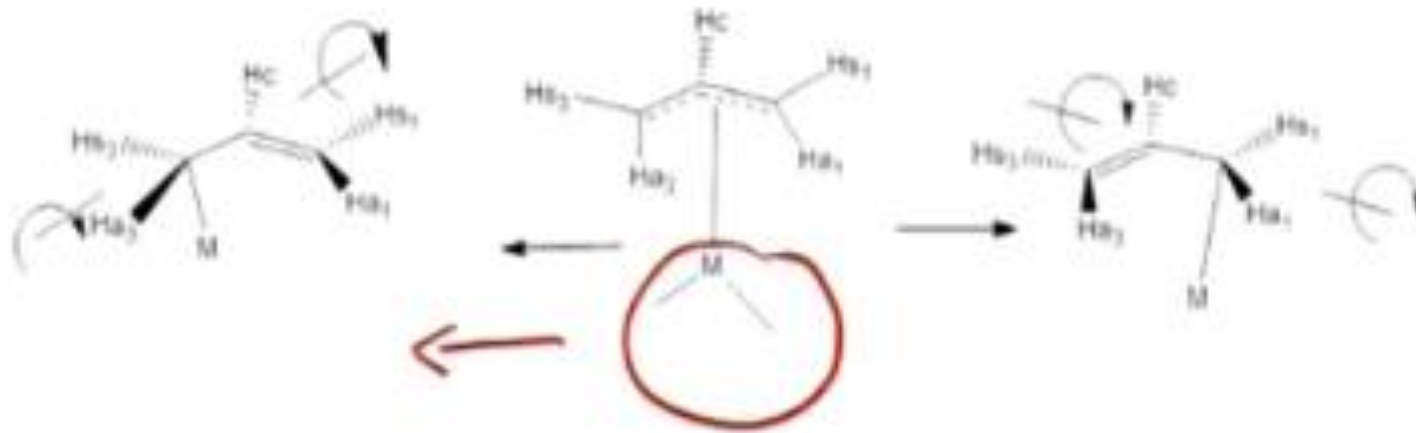
Metal Flips



Allyl Flips



Fluxional Behaviour



Allyl / Metal Flip through C3



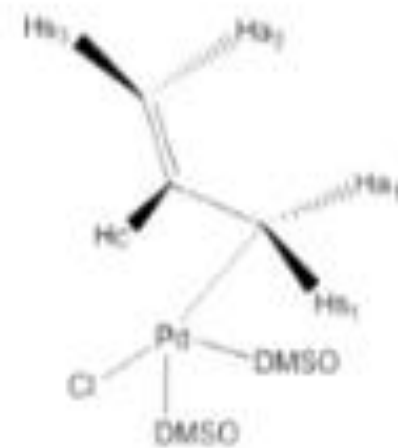
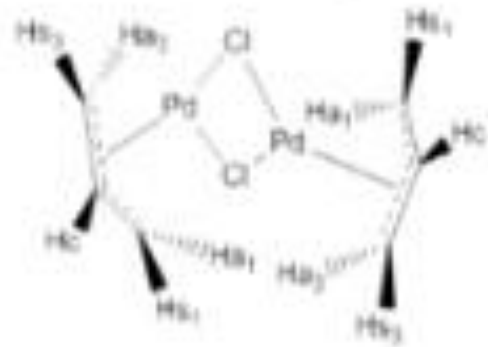
Allyl / Metal Flip through C1



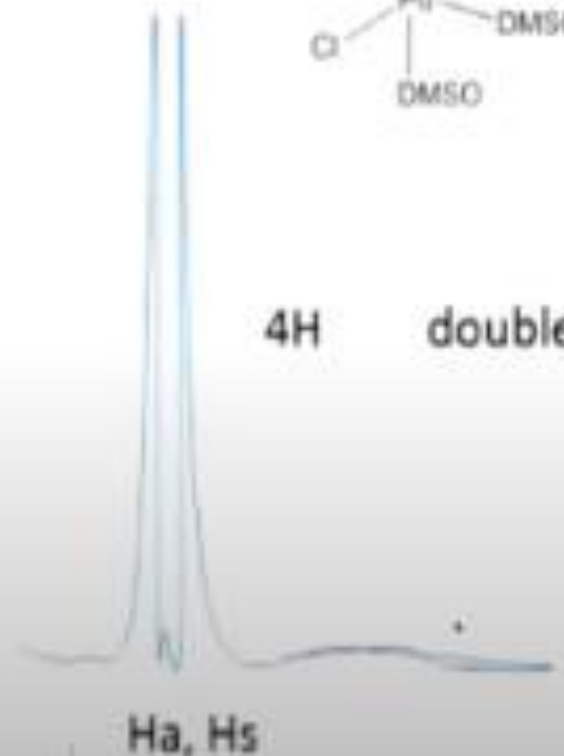
- Spectroscopic features of the allyl group reflect this fluxional behavior.
- Positions 1 and 3 are equivalent but syn and anti are rigid.
- NMR is the only spectroscopic tool! Could be complicated. Temperature dependence is to be studied.



All 4 Hydrogens become equivalent!
40 deg. DMSO as solvent

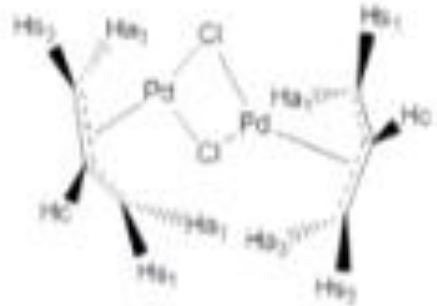


1H quintet



4H doublet!

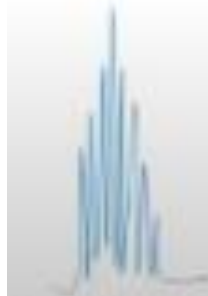
Room temperature spectrum in chloroform,



2H X2

doublet!

1H triplet of triplet



Hc



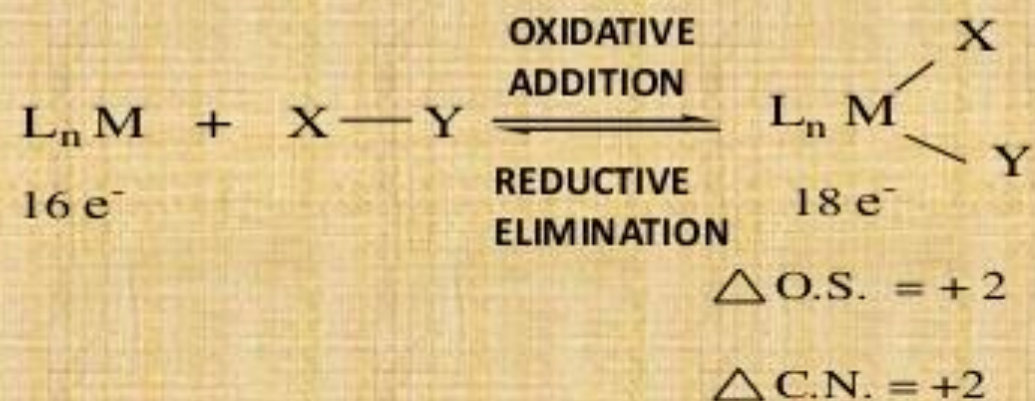
Hs



Ha

INTRODUCTION

IT IS A PROCESS BY WHICH A METAL CENTRE IN A COORDINATIVELY UNSATURATED COMPLEX INCREASES ITS OXIDATION NUMBER AS WELL AS COORDINATION NUMBER.



THE REVERSE OF THE OXIDATIVE ADDITION IS CALLED REDUCTIVE ELIMINATION.





Conditions for Oxidative Addition

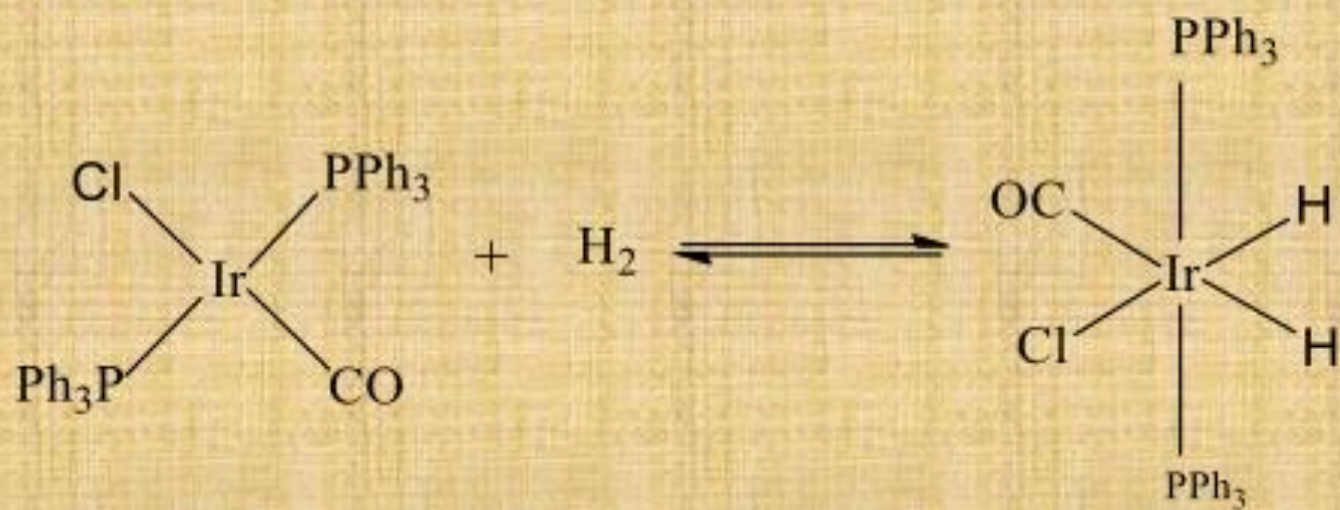
- Metal must possess non-bonding electron pair.
- The complex must be co-ordinatively unsaturated.
- Suitable orbitals should be available.
- The higher oxidation state of the metal should be energetically accessible and stable.

CHARACTERISTICS OF OXIDATIVE ADDITION

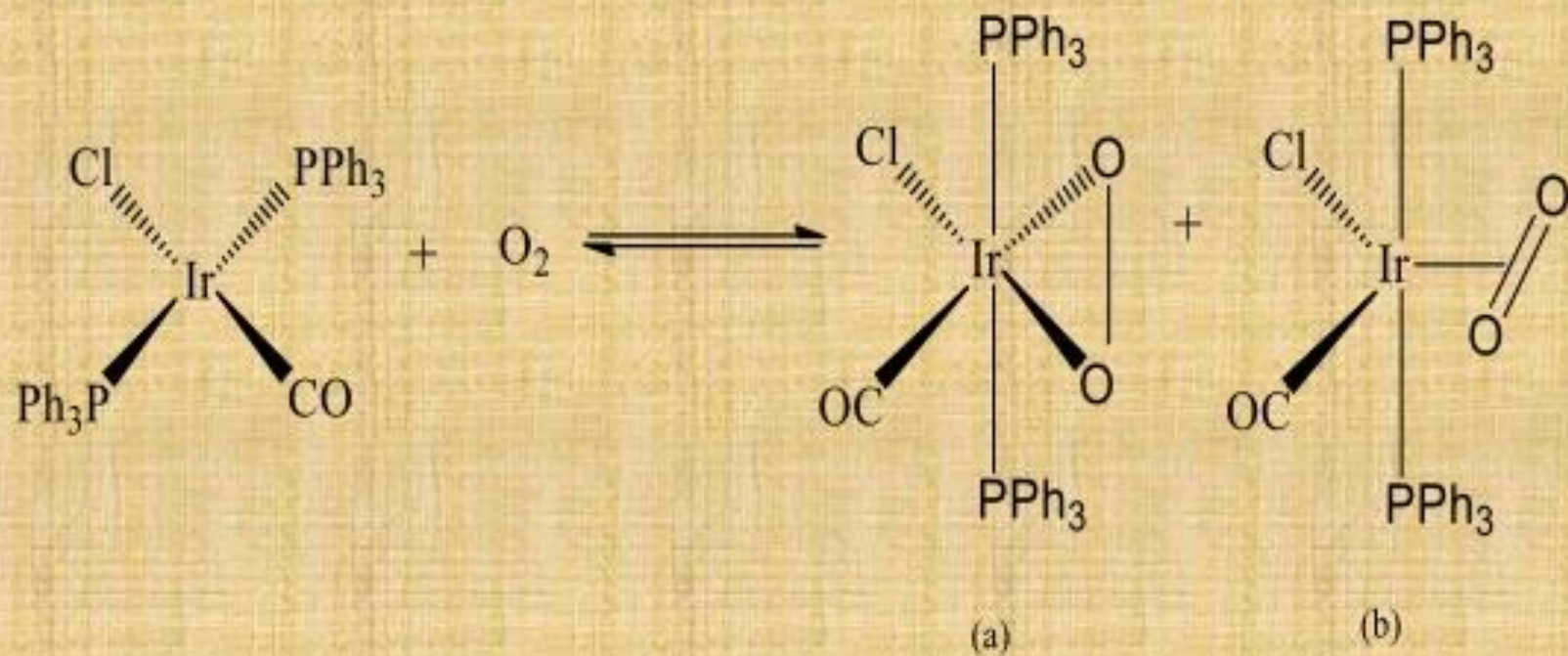
- Two new anionic ligands are added.
- Coordination number increases by two units.
- Oxidation number increases by two units.
- The oxidation state of the metal is low.
- The more electron rich the metal, the more the addition becomes easier.
- The substrate behaves both as a Lewis acid and a Lewis base.

EXAMPLE OF OXIDATIVE ADDITION

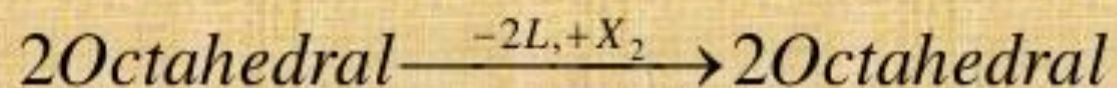
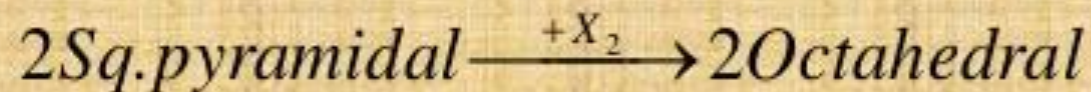
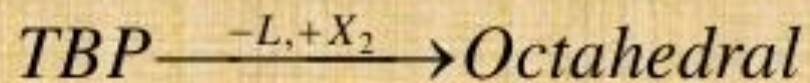
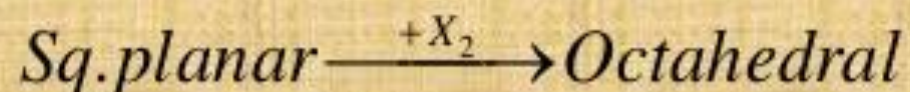
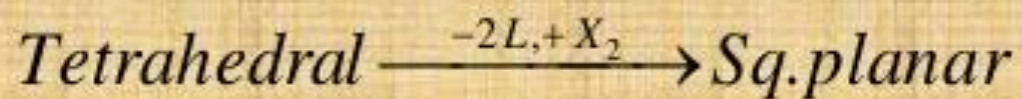
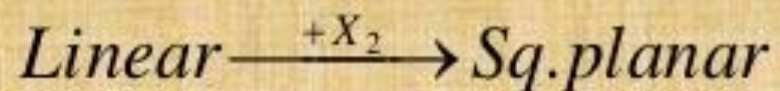
- Reaction of Vaska's complex with molecular hydrogen



- Oxidative addition without cleavage of the X-Y bond.



CHANGE IN CO-ORDINATION GEOMETRY ON OXIDATIVE ADDITION

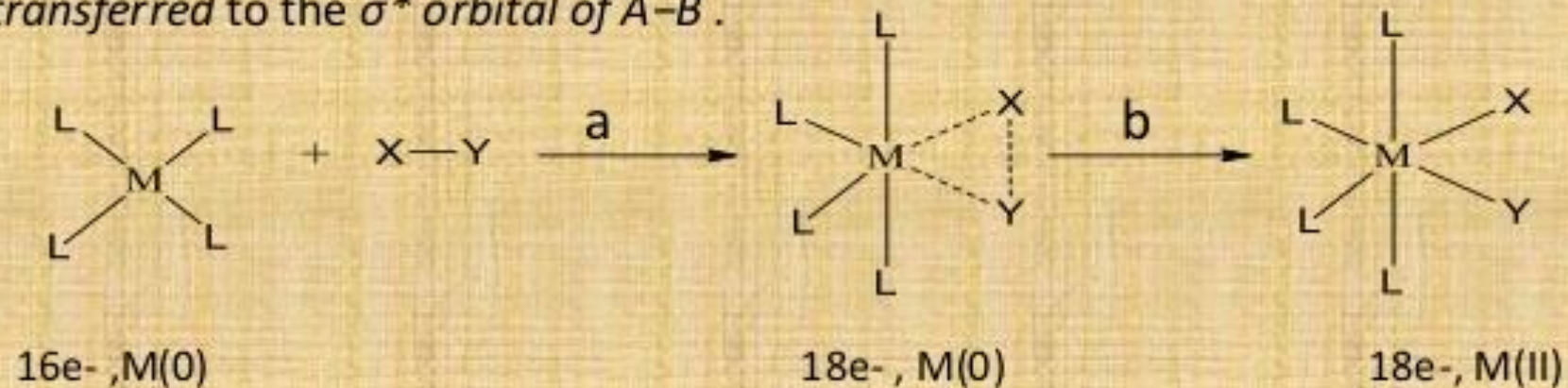


MECHANISM OF OXIDATIVE ADDITION

- *There are four mechanisms :*
 - *Concerted or three-centered*
 - *SN2*
 - *Radical*
 - *Ionic*

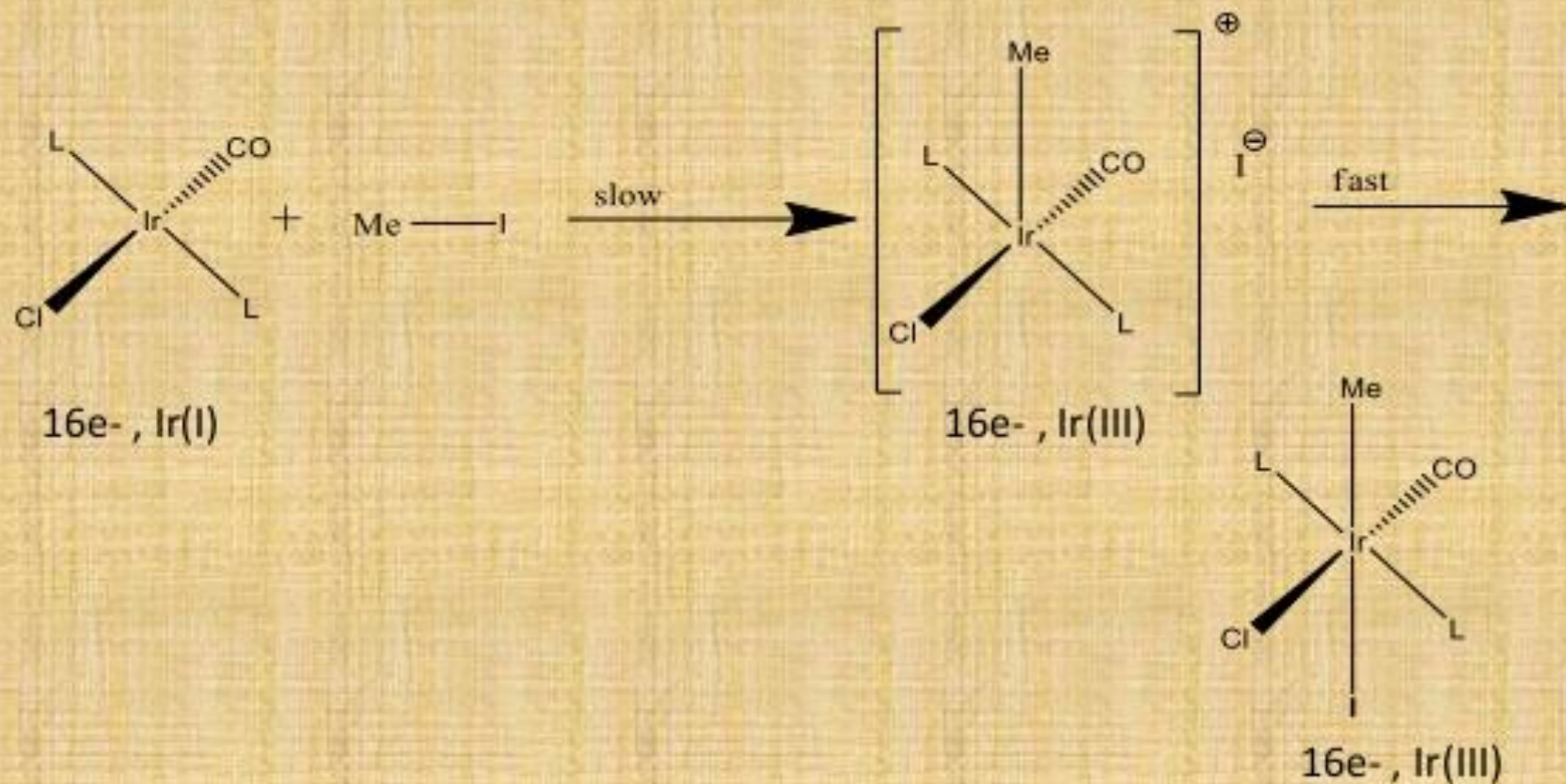
1. CONCERTED MECHANISM :

- *Follows when X-Y is non-polar.*
- *Proceeds through two steps-*
 - The associative step which involves formation of a σ - complex.*
 - Oxidative part of the reaction in which metal electrons are formally transferred to the σ^* orbital of A-B .*



2. SN2 Mechanism

- Often found in addition of polar ligands like methyl, allyl, benzyl halides.
- Proceed via a polar transition state.
- Accelerated in polar solvents.

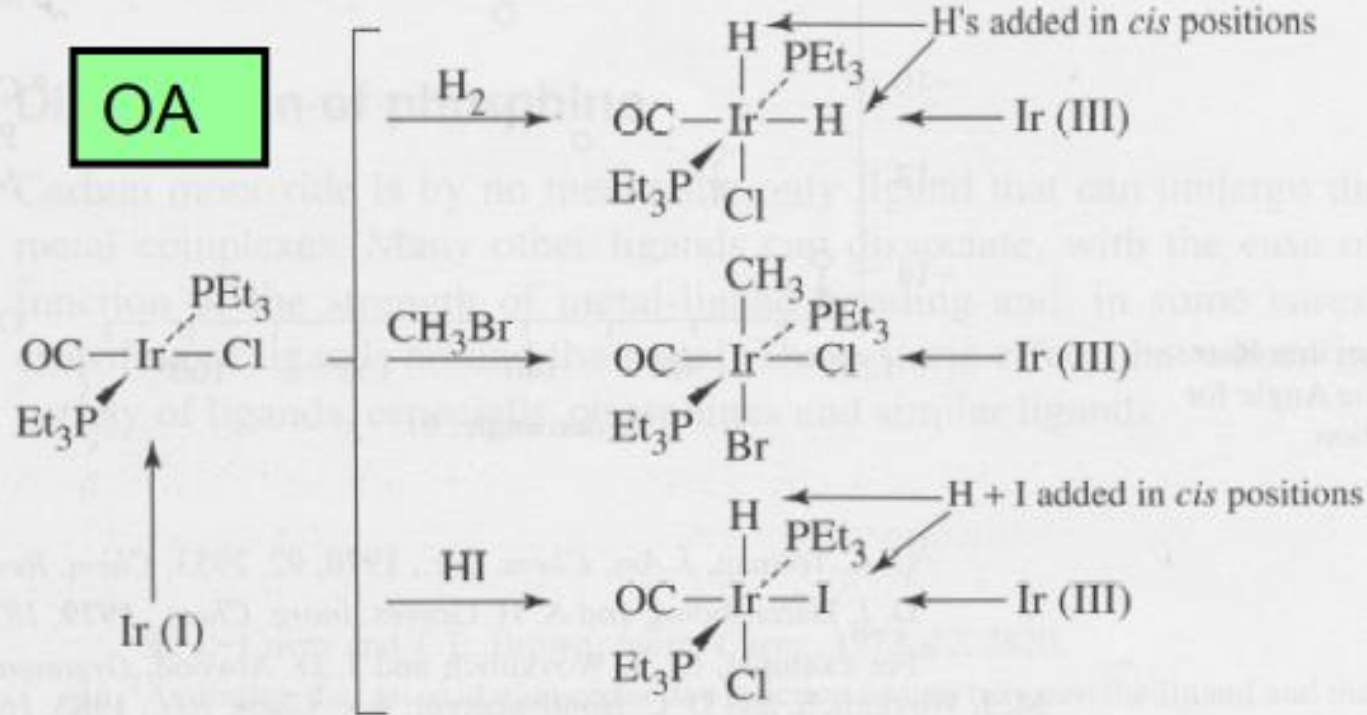


4. IONIC MECHANISM

- This mechanism for the oxidative addition reaction is common to the addition of hydrogen halides (HX) in its dissociated H^+ and X^- forms.
- There are two pathways-
 - A. the one in which the starting metal complex adds to H prior to the addition of the halide X .
 - B. the other type, in which the halide anion X^- adds to the starting metal complex first, and then the addition of proton H^+ occurs on the metal complex.

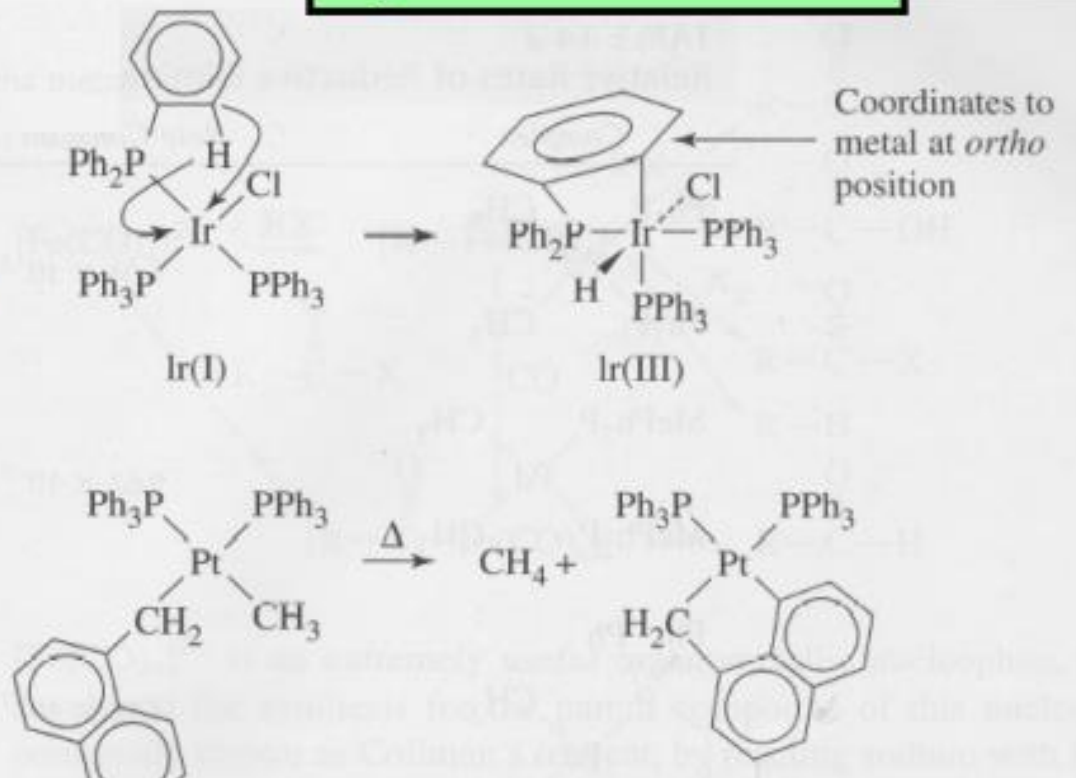


OA



cyclometallations

orthometallation



Reactions Involving Gain or Loss of Ligands

A. Ligand dissociation and substitution

B. Oxidative addition

C. Reductive elimination

D. Nucleophilic displacement

REACTIONS INVOLVING MODIFICATION OF LIGANDS

A. Insertion

B. carbonyl Insertion

C. Hydride Elimination

D. Abstraction



Addition or dissociation vs oxidative addition or reductive elimination

<i>Type of Reaction</i>	<i>Change in Coordination Number</i>	<i>Change in Formal Oxidation State of Metal</i>
Addition	Increase	None
Dissociation	Decrease	None
Oxidative addition	Increase	Increase
Reductive elimination	Decrease	Decrease

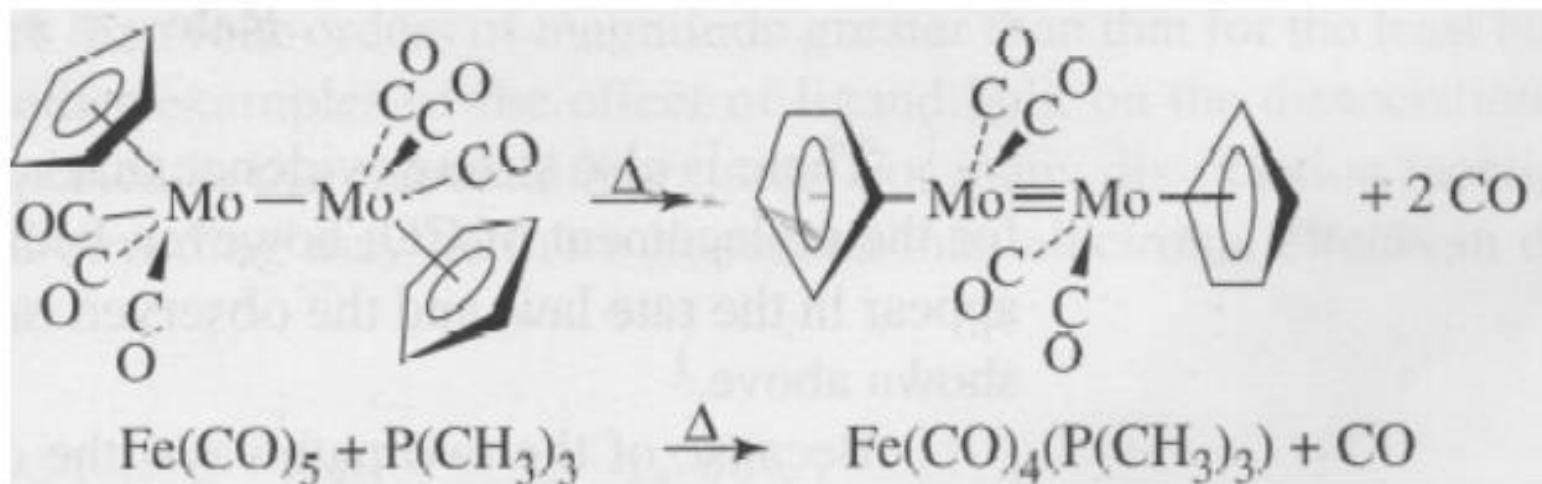
Ligand dissociation and substitution

Most of organometallic reactions involve the change in C.N of the metal by a gain or loss of ligands retaining the oxidation state of the metal. These reactions are considered as addition or dissociation.

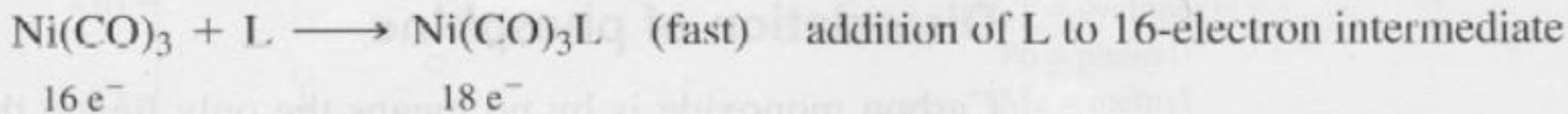
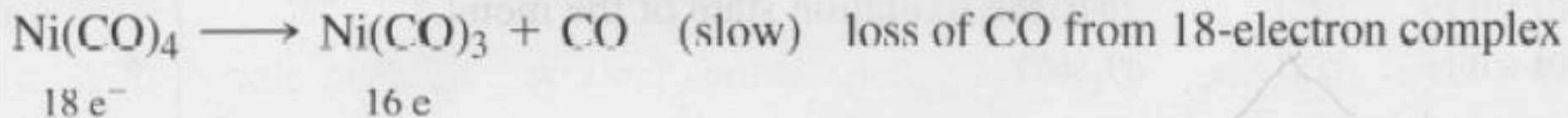
carbonyl dissociation may result in the rearrangement of remaining molecule or replacement of CO by another ligand.



CO dissociation



Independent of the concentration of L \rightarrow ???



$$\text{Rate} = k_1[\text{Ni(CO)}_4]$$

Because of the two pathways the overall rate of formation of $\text{Mo}(\text{CO})_5\text{L}$ is the sum of rate of unimolecular and bimolecular Mechanism.

Most of the CO substitution reaction proceed by a dissociative mechanism.

Associative path is for the complex of large metals (providing site for incoming ligands to attack) and for the reactions involving nucleophilic ligands.



Dissociation of phosphine

Dissociation

- The strength of M-L bonding
- The degree of crowding of ligand around metal

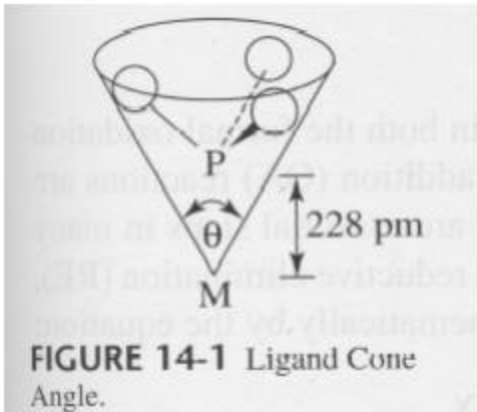


TABLE 14-1
Ligand Cone Angles

Ligand	Cone Angle θ	Ligand	Cone Angle θ
PH ₃	87°	P(CH ₃)(C ₆ H ₅) ₂	136°
PF ₃	104°	P(CF ₃) ₃	137°
P(OCH ₃) ₃	107°	P(C ₆ H ₅) ₃	145°
P(OC ₂ H ₅) ₃	109°	P(<i>cyclo</i> -C ₆ H ₁₁) ₃	170°
P(CH ₃) ₃	118°	P(<i>t</i> -C ₄ H ₉) ₃	182°
PCl ₃	124°	P(C ₆ F ₅) ₃	184°
PBr ₃	131°	P(<i>o</i> -C ₆ H ₄ CH ₃) ₃	194°
P(C ₂ H ₅) ₃	132°		

CONE ANGLE

The apex angle of a cone that encompasses the vanderwaals radius of the outermost atoms of a ligand.

The presence of bulky ligands having large cone angle lead to rapid ligand dissociation as a consequences of crowding around the metal.



Nucleophilic displacement

Nucleophilic anionic organometallic complexes

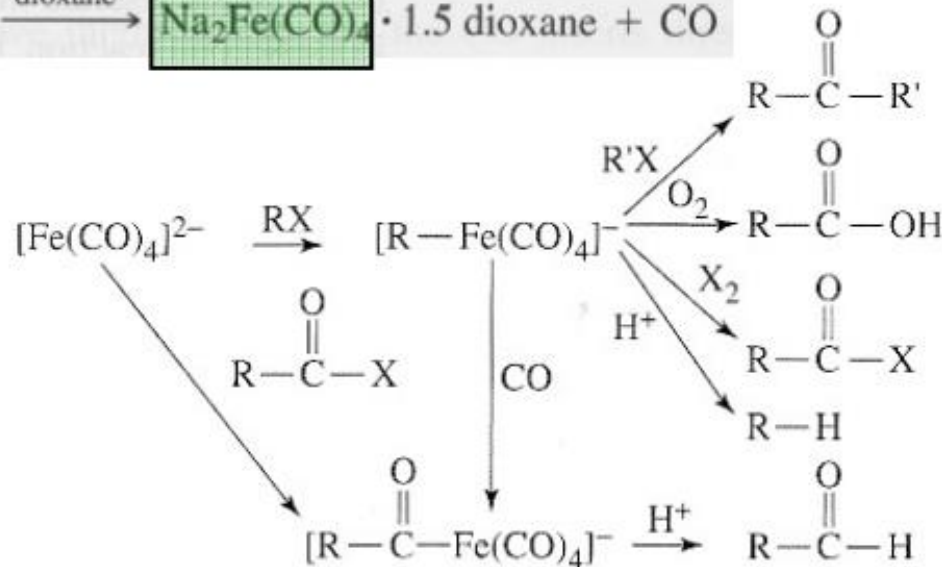
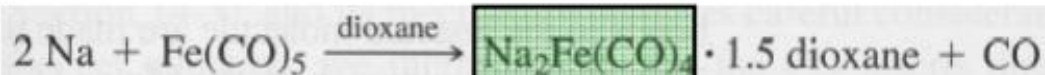
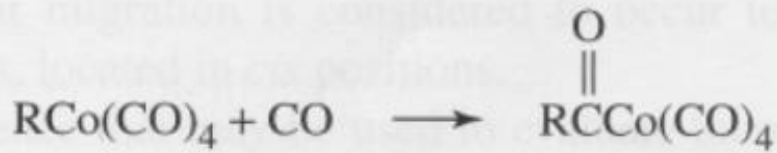


그림 14-5 $[\text{Fe}(\text{CO})_4]^{2-}$ 를 이용한 여러 가지 합성 경로.



Acyl complex

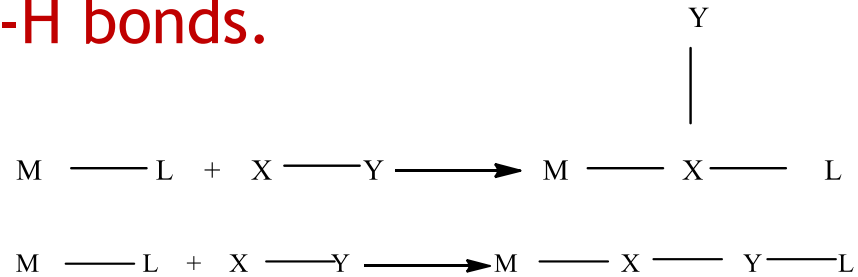


ester

Reactions Involving Modification of Ligands

INSERTION

Reaction involve the insertion of small molecules X-Y into the metal ligand bonds M-C and M-H bonds.

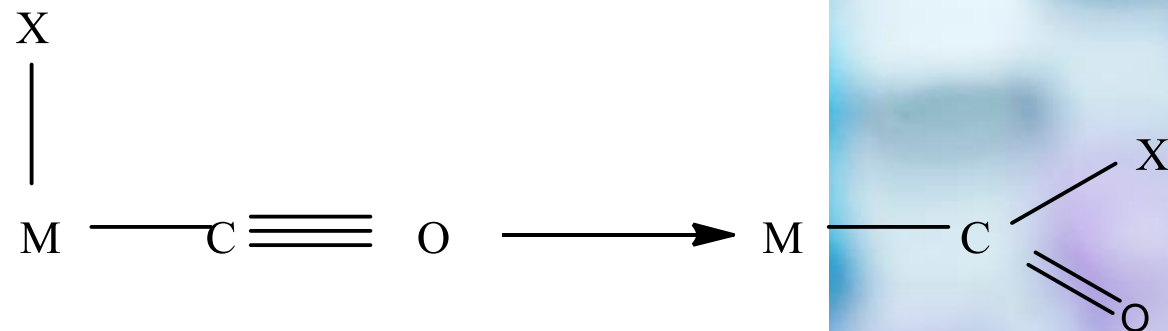


TYPES:

1,1 Insertion

1,2 Insertion

1,1 Insertion



*In this reaction the X group which is one bond away from the metal atom ends up on atom that is one bond away from the metal atom. This reaction goes via migration of X group therefore it is called migratory insertion.

*The result is decrease in the no of electrons on the metal atom by 2 with no change in the oxidation state

*In 1,1-migratory insertion we can add another species that can act as a ligand.



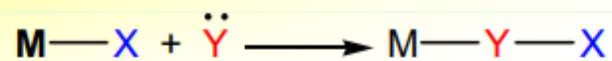
carbonyl insertion

Consider migratory insertion of CO with $[\text{Mn}(\text{CH}_3)(\text{CO})_5]$



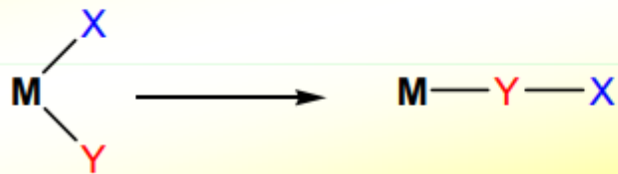
1. Question: What kind of insertion takes place – intermolecular or intramolecular?

- Intermolecular insertion:



Nucleophile Y attacks X

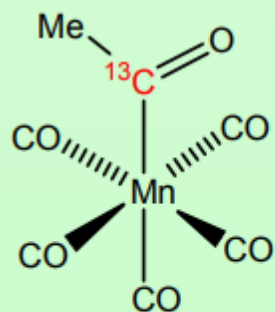
- Intramolecular insertion:



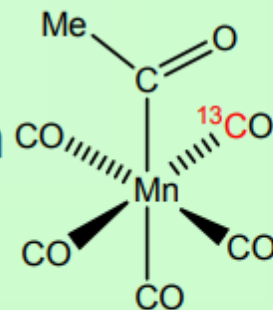
Unsaturated ligand Y insert into M-X

To answer this question ^{13}C should be used:

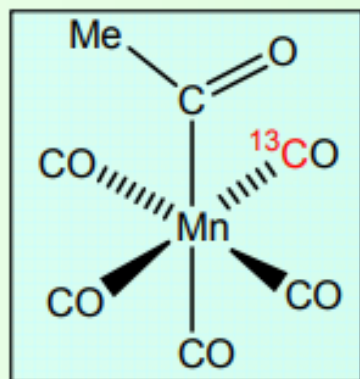
- In the case of intermolecular insertion ^{13}C will go to acyl group



- In the case of intramolecular insertion unlabeled C appears in acyl group



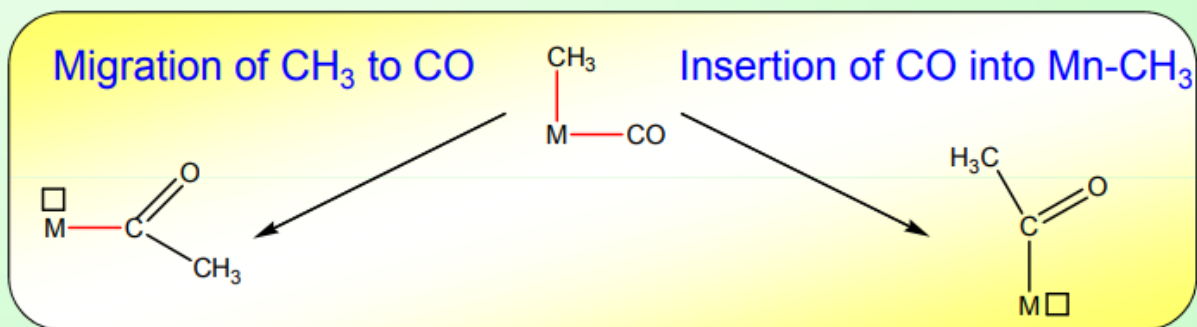
It was found that ^{13}C label exists only as a carbonyl ligand:



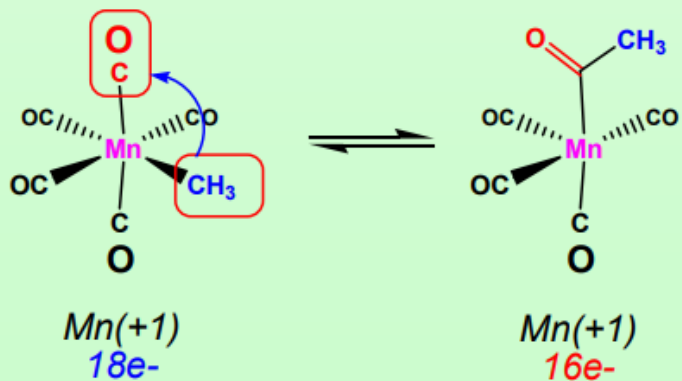
- Intramolecular insertion:



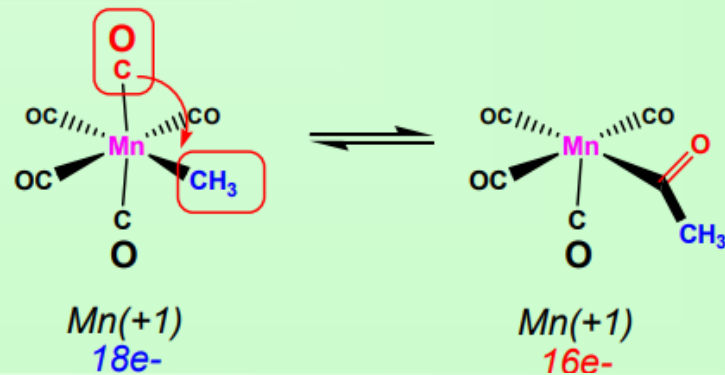
2. Question: How does insertion take place?



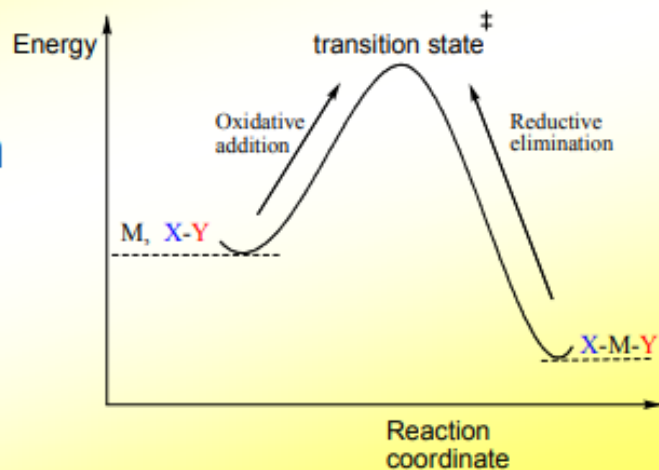
Migration



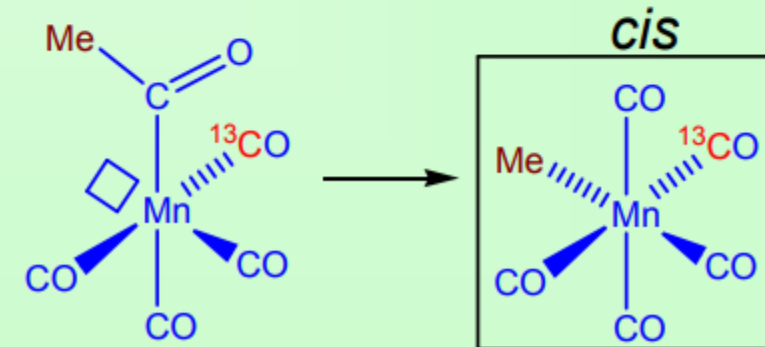
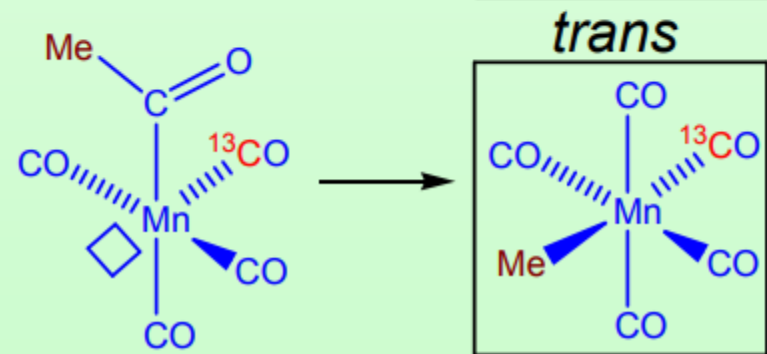
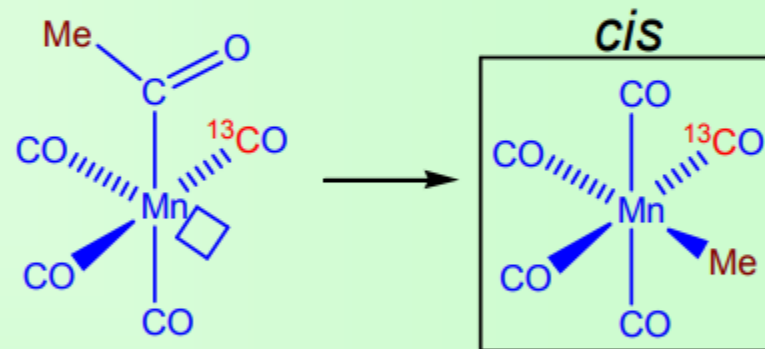
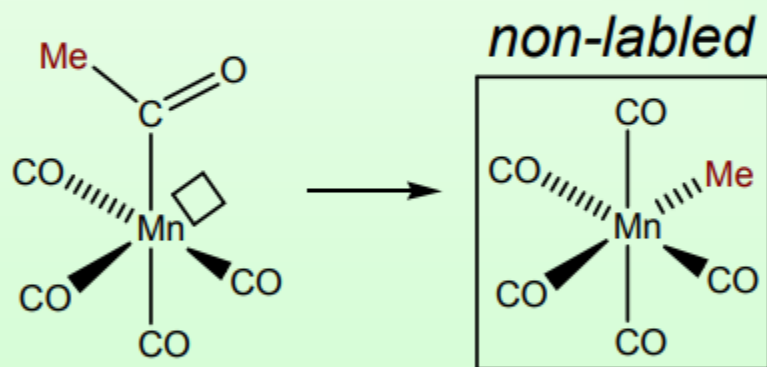
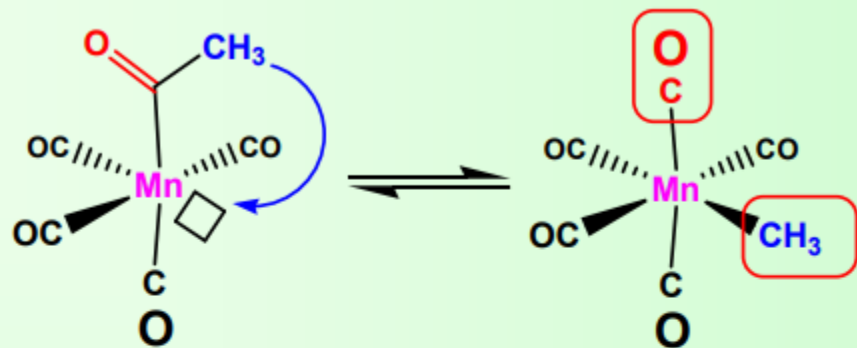
Insertion



If two opposite reactions can take place at one and the same reaction conditions – they usually proceed through the same transition state (*microscopic reversibility* principle)



a) Let's imagine that CH_3 migration takes place

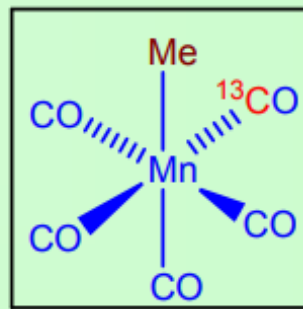
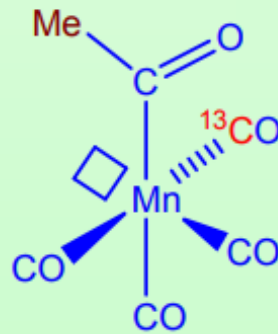
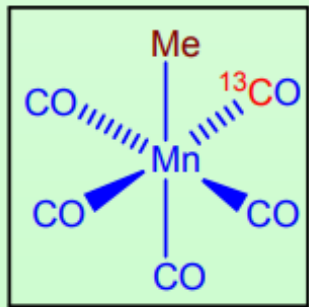
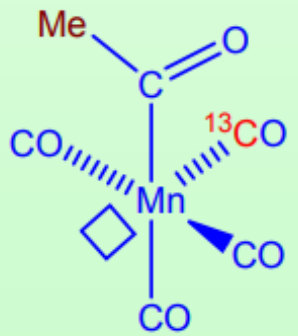
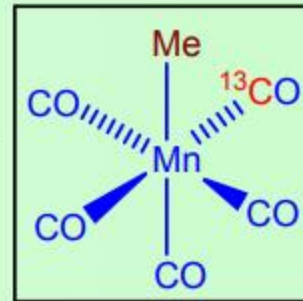
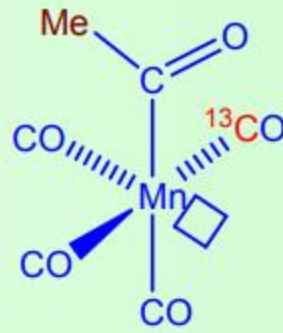
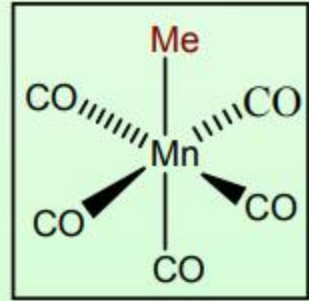
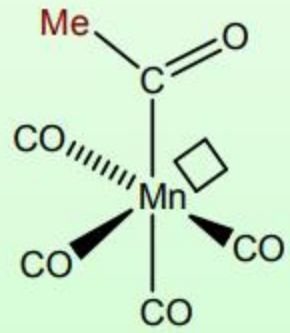
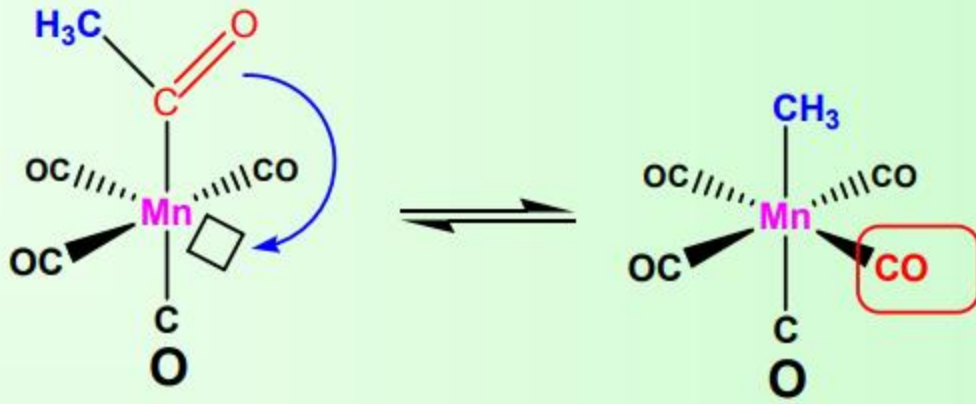


non-labeled: 25%, labeled *cis*: 50%, labeled *trans*: 25%

cis:*trans* = 2:1

b) Let's think that CO insertion takes place

2 3



non-labeled: 25%, labeled cis: 75%, labeled trans: 0%

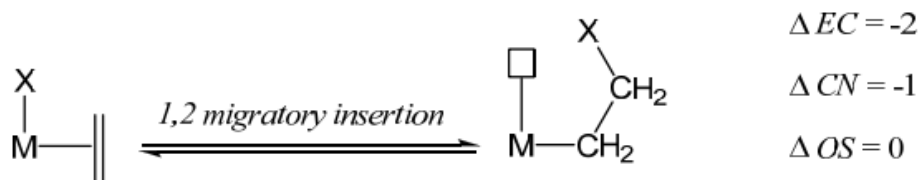
all cis



It was found that cis and trans isomer are formed in 2:1 ratio, so migration of CH₃ takes place

1,2 INSERTION

1,2 insertion in which the metal and the X ligand end up bound to adjacent (1,2) atoms of an L-type ligand with no change in O.S of the metal.



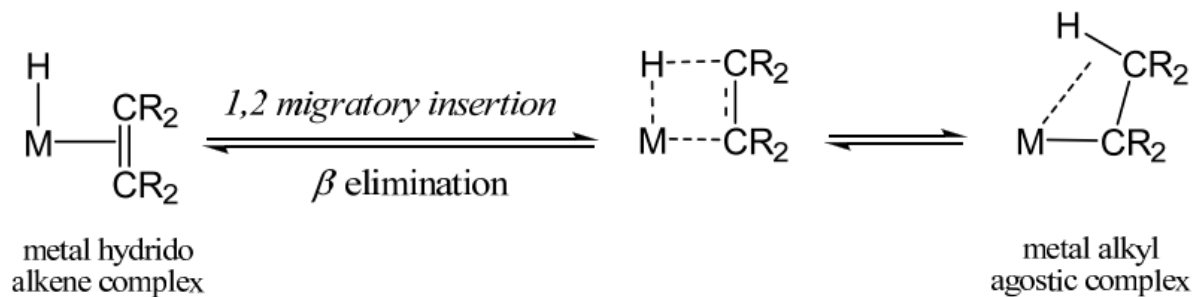
In general, η^1 ligands tend to give 1,1 insertion and η^2 ligands give 1,2 insertion

SO₂ is the only common ligand that can give both types of insertion; as a ligand, SO₂ can be η^1 (S) or η^2 (S, O).



Alkene insertions reactions

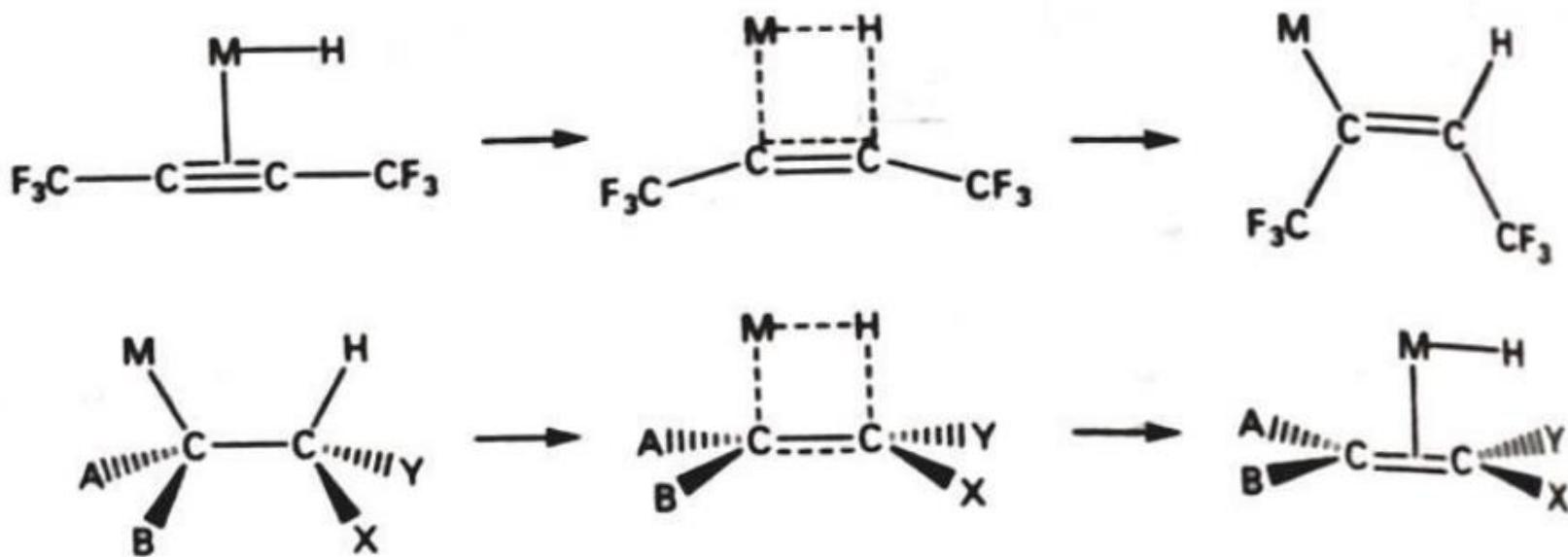
For simple alkenes, such as ethylene, the equilibrium tends to lie to the left (i.e., the alkyl β -eliminates), but for alkenes with electron-withdrawing ligands (e.g., C_2F_4) the alkyl is particularly stable, and the equilibrium lies



The X group is a hydride, alkyls, or aryls and the product is a alkyl substituted compound.

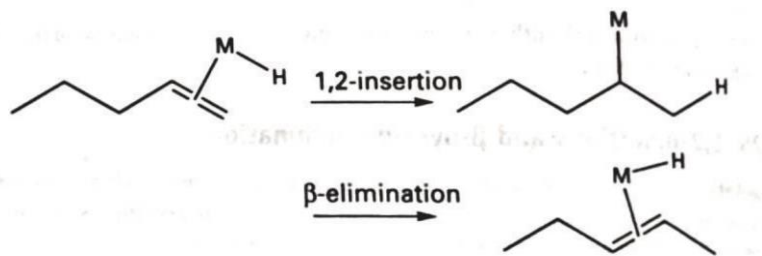


The experimental evidence shows that 1,2-insertion and β hydride elimination proceed through a syn intermediate.



β hydride elimination can provide a facile route for decomposition of alkyl containing compounds.

1,2 -insertion coupled with β -hydride elimination provide a low energy route to alkene isomerization.



Nucleophilic attack on ligand

Ligand activation by metal that leads to a direct external attack at the ligand.

Many bound ligands can be modified or removed from the metal center by nucleophilic or electrophilic reactions.

Nucleophilic attack:

Favored for metals that are weak π -bases and good σ -acids (i.e., complexes with net positive charges or π -acidic ligands).

Ligands bound to electrophilic metals will tend to be electrophilic themselves

when the complex is cationic and/or when the other metal bound ligands are electron withdrawing such that the ligand getting activated gets depleted of electron density and can undergo an external attack by a nucleophile Nu^- , like LiMe or OH^-



Carbon monoxide (CO) as a ligand can undergo nucleophilic attack when bound to a metal center of poor π -basicity, as the carbon center of the CO ligand is electron deficient owing to the ligand to metal σ -donation not being fully compensated by the metal to ligand π -back donation.

Thus, activated CO ligand undergoes nucleophilic attack by the lithium reagent to give an anionic acyl ligand, which upon alkylation generates the famous Fischer carbene complex.



Electrophilic attack:

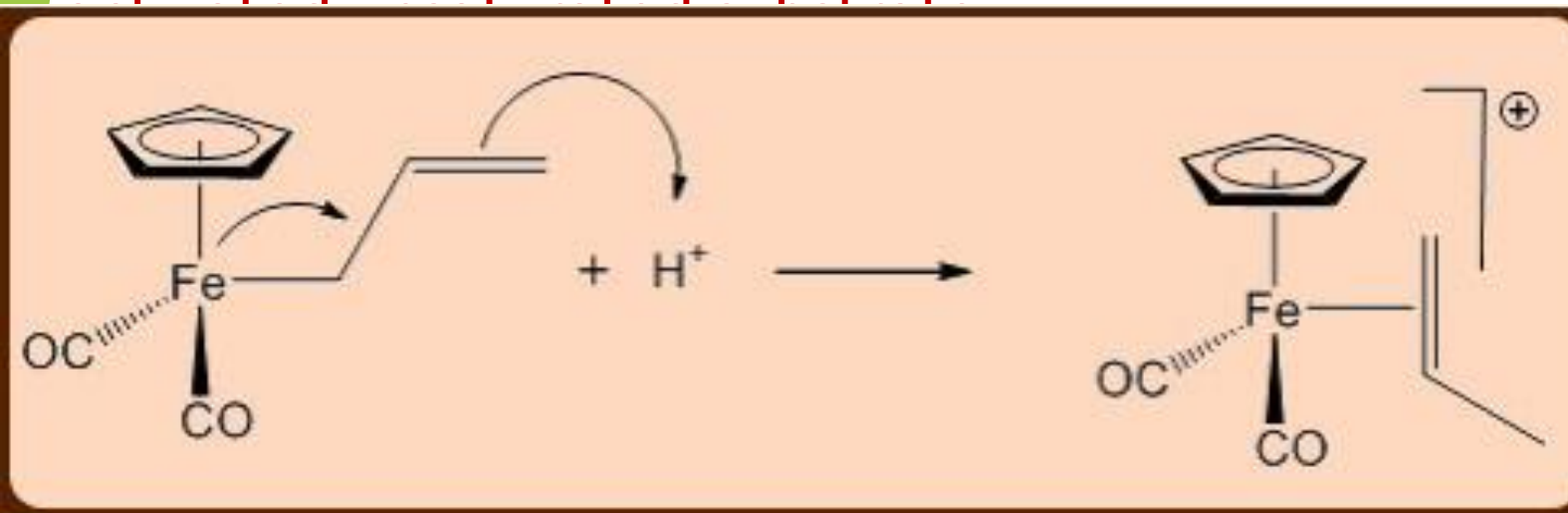
Favored for electron rich metals that act as weak σ -acids, but strong π -bases (i.e. low valent metals, or those with net negative charges and/or electron donating ligands).

Ligands bound to π -basic metals tend to be electron rich, and act as nucleophiles



when the complex is anionic with the metal center at low-oxidation state and/or when the other metal bound ligands are electron donating such that the ligand getting activated becomes electron rich from the π -back donation of the metal center and thus can undergo an external attack by an electrophile E^+ like H^+ and CH_3I .

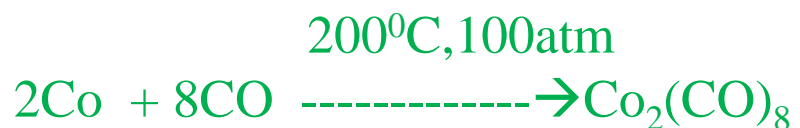
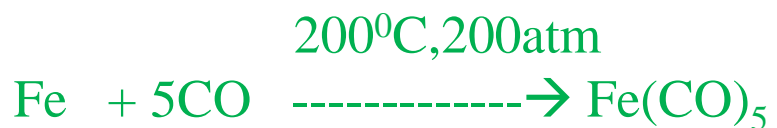
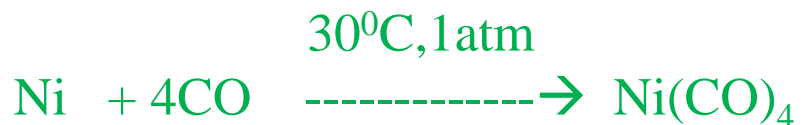
The attack of the electrophiles may result in the formation of a bond between the electrophile and the



Carbonylation

Carbonylation refers to reactions that introduce carbon monoxide into organic and inorganic substrates. so it is used as a reactant in industrial chemistry.

Direct combination of carbon monoxide and metal:



Reductive carbonylation of transition metal salts:



Reductive carbonylation by carbon monoxide:

250°C, 350atm



High press. and temp.



Reductive carbonylation by hydrogen:

150°C, 300atm



Reductive carbonylation by metals:

175°C, 250atm



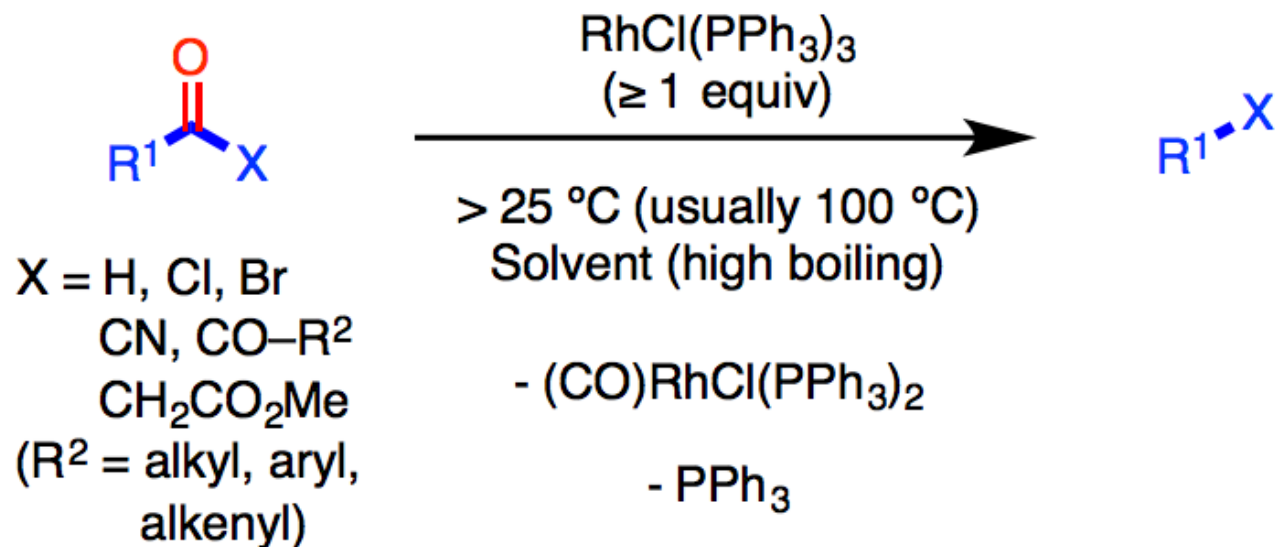
250°C, 200atm



DECARBONYLATION

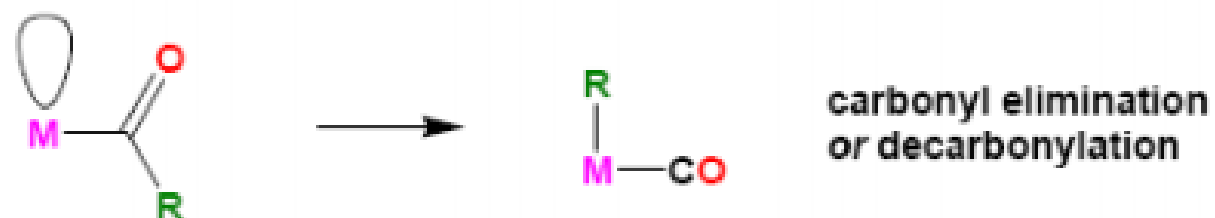
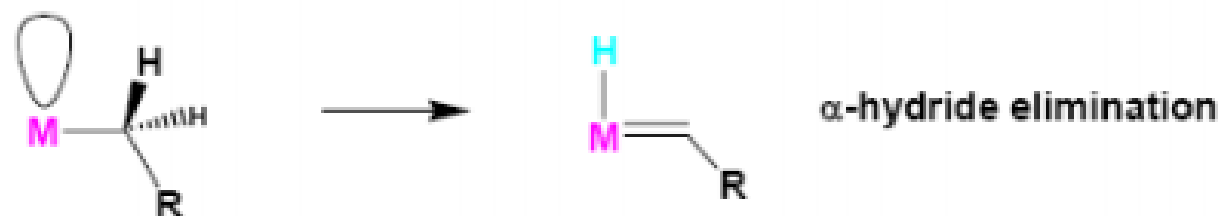
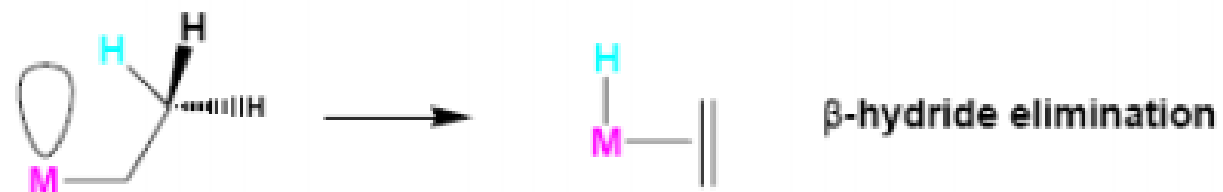
Decarbonylation is a type of organic reaction that involves loss of CO.

Overview of Tsuji-Wilkinson Decarbonylation Reaction:



Eliminations

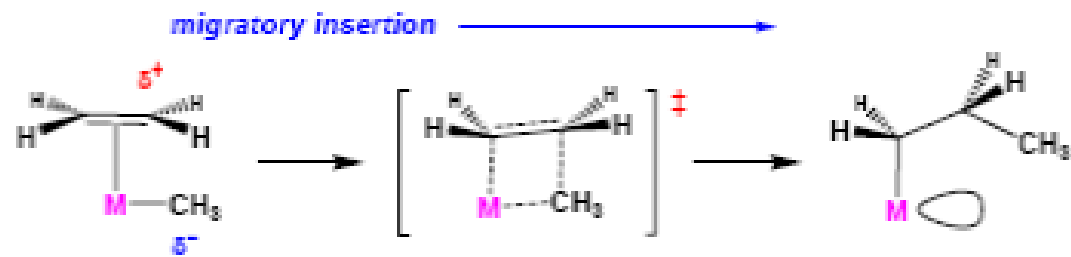
Elimination reactions are just the reverse of migratory insertion reactions. The various common elimination reactions are as follows:



The key points to remember are:

- 1) No change in formal oxidation state (exception: alkylidenes)
- 2) You must have an empty orbital that is **cisoidal** to the group that you are doing an elimination reaction on. Alternatively, a cisoidal labile ligand that can easily dissociate to open up an empty orbital.

One of the hardest elimination reactions is the breaking of a C-C bond. For example the following **migratory insertion** is quite common and plays a critical role in polymerization catalysis:



But the reverse **methyl elimination** rxn is very difficult:

