BHU - MSC (IInd Semester)

CHM202: Inorganic Chemistry-II

Topic: Metal Carbonyls

Content Writer: Dr MD Pandey, Department of Chemistry Institute of Science, BHU

Organometallic Compounds: Organometallic compounds are those in which the central metal atoms are bonded directly to carbon atoms of hydrocarbon, radicals or molecules. **The central metal atoms are generally less electronegative than carbon**. Compounds such as carbides, cyanides and carbonyls, though they contain metal–carbon bonds, are excluded from the family of organometallic compounds.

Metalcarbonyls: Metal carbonyls are important class of organometallic compounds that have been studied for a long time. Way back in 1884, Ludwig Mond, upon observing that the nickel valves were being eating away by CO gas in a nickel refining industry, heated nickel powder in a stream of CO gas to synthesize the first known metal carbonyl compound in the form $Ni(CO)_4$. The famous Mond refining process was thus born, grounded on the premise that the volatile $Ni(CO)_4$ compound can be decomposed to pure metal at elevated temperature. Mond subsequently founded the Mond Nickel Company Limited for purifying nickel from its ore using this method.

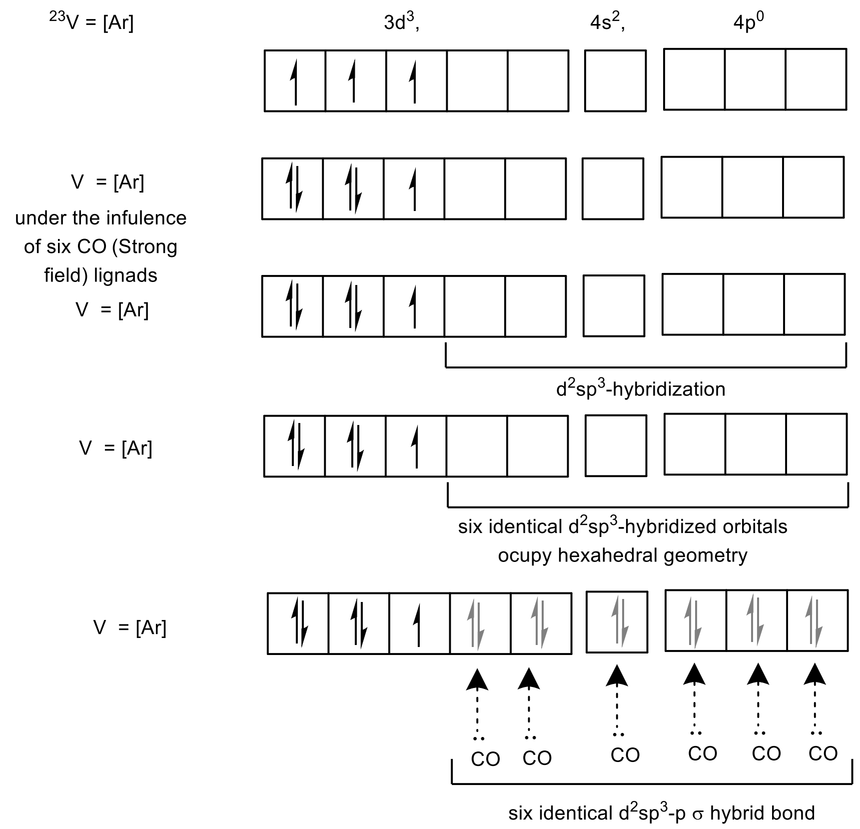
Bonding and Molecular orbital diagram:

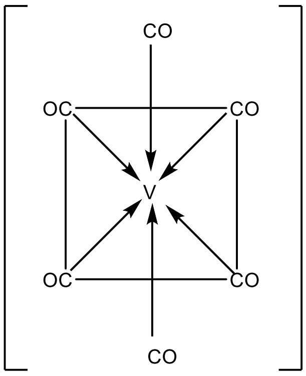
Preparation of Metal Carbonyl Complexes

Reactions of Metal Carbonyl complexes:

Structure of Metal Carbonyls

$V(CO)_6$:



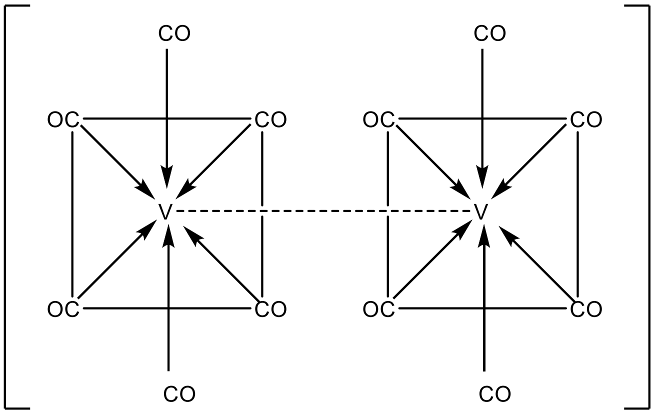


d^2sp^3-hybridized octahderal complex

$V(CO)_6$ is a paramagnetic compound due to an unpaired electron in 3d orbital. Its EAN is 35 (23+12), therefore this complex is lesser stable.

$$\begin{array}{lccc} & V(CO)_6 + V(CO)_6 & \longrightarrow & V_2(CO)_{12} \\ \text{EAN} & 35 \quad 35 & & 36 \end{array}$$

The above dimerization is generally not possible because of steric effect.



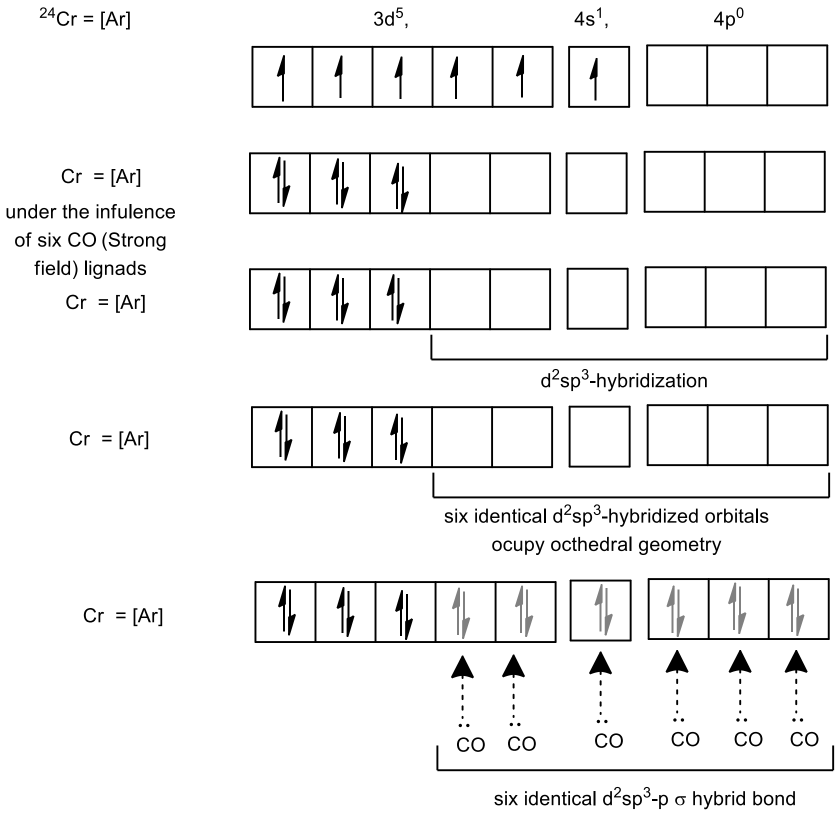
Already six CO groups were present hence incoming 7th group destabilized the system thus, $V(CO)_6$ exist only in monomeric form.

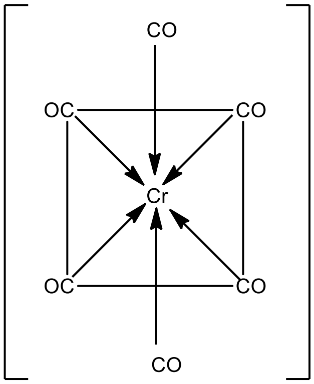
The stability of $V(CO)_6$ is very less because it does not obey EAN rule so they decomposed easily (decomposition temperature is 70°C). $V(CO)_6$ has one electron deficiency, so they reacts very fast like sodium for completing EAN 36.

$$\begin{array}{lcc} & V(CO)_6 + Na \longrightarrow & Na^+[V(CO)_6]^- \\ \text{EAN} & 35 & 36 \end{array}$$

The compound $Na[V(CO)_6]$ is negative charged hence are electrovalent in nature.

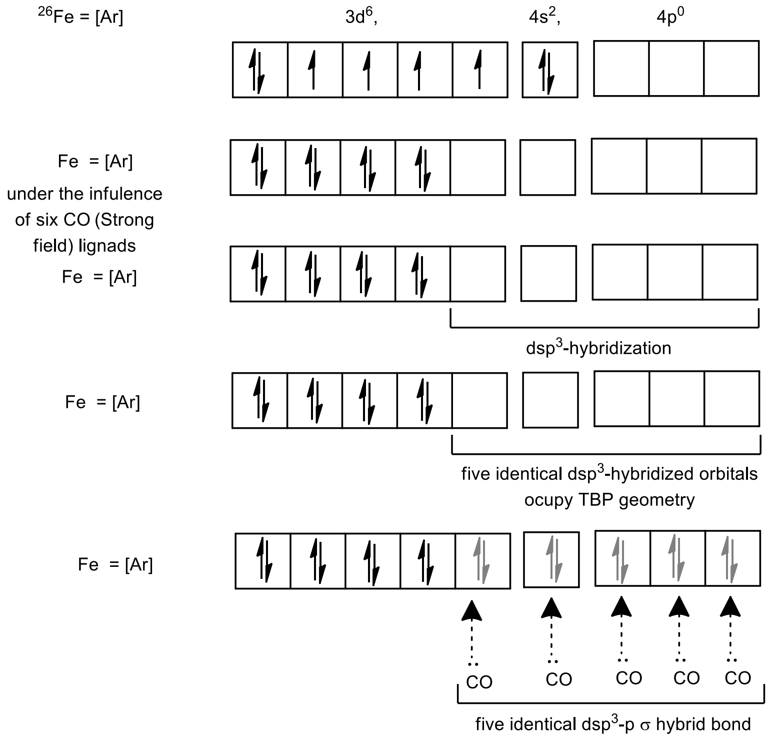
$Cr(CO)_6$: $Cr(CO)_6$ is a diamagnetic, d^2sp^3 hybridized octahedral complex having EAN is 36 (24+12).



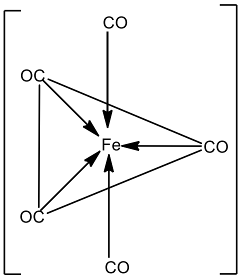


d^{2}sp^3-hybridized octahderal complex

Fe(CO)$_5$: dsp^3 hybridization may be either trigonal bipyramidal (dz^{2}sp^3 hybridization) or square pyramidal (dx^2-y^{2}sp^3 hybridization) geometry. It has been confirmed by single x-ray crystallography that Fe(CO)$_5$ is a dz^{2}sp^3 hybridized diamagnetic complex having TBP geometry.

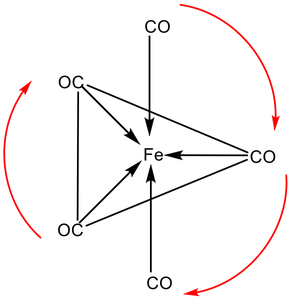


dsp^3 hybridization may be either trigonal bipyramidal (dz^{2}sp^3 hybridization) or square pyramidal (dx^2-y^{2}sp^3 hybridization) geometry. It has been confirmed by single x-ray crystallography that Fe(CO)$_5$ is a dz^{2}sp^3 hybridized diamagnetic complex having TBP geometry.



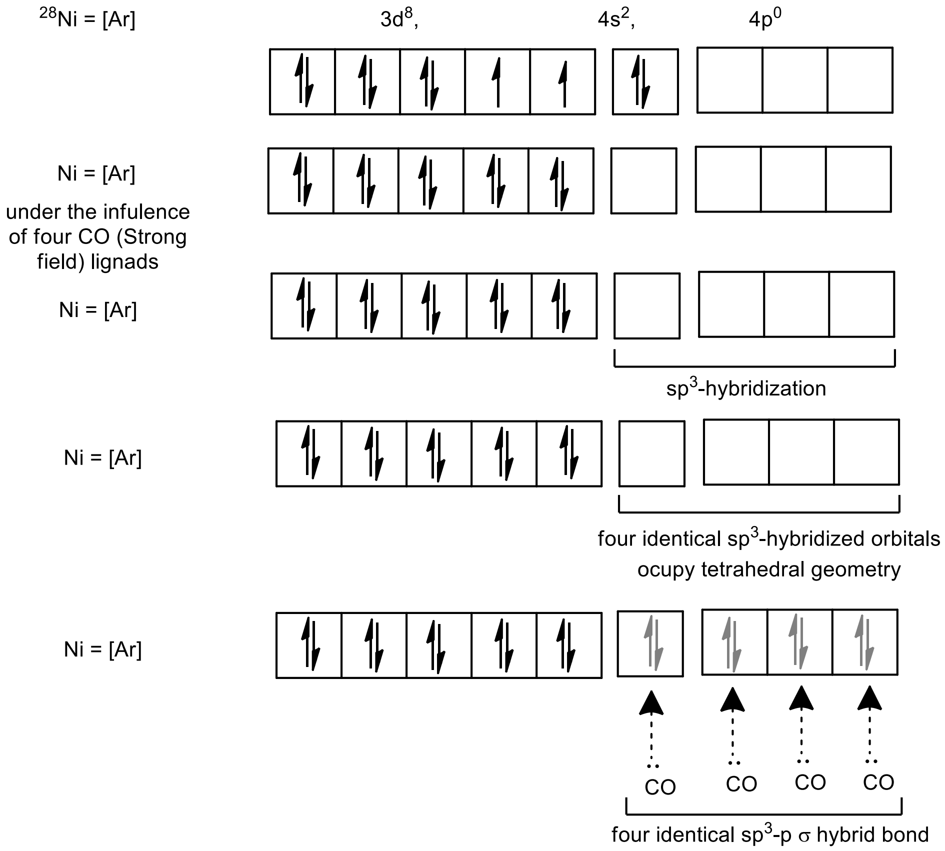
dsp^3-hybridized trigonal bipyramidal (TBP) complex

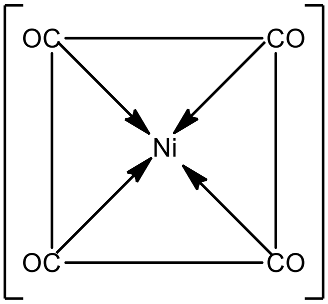
$Fe(CO)_5$ molecule have fluxional behavior, molecules shows rapid change in their structure. If any changes in its stereochemistry, is called fluxional behavior. The rapid interconversion of axial and equatorial CO groups called scrambling of CO group.



This show only one ^{13}C-NMR peak because rapid change in axial and equatorial bond so only one peak of ^{13}C-NMR.

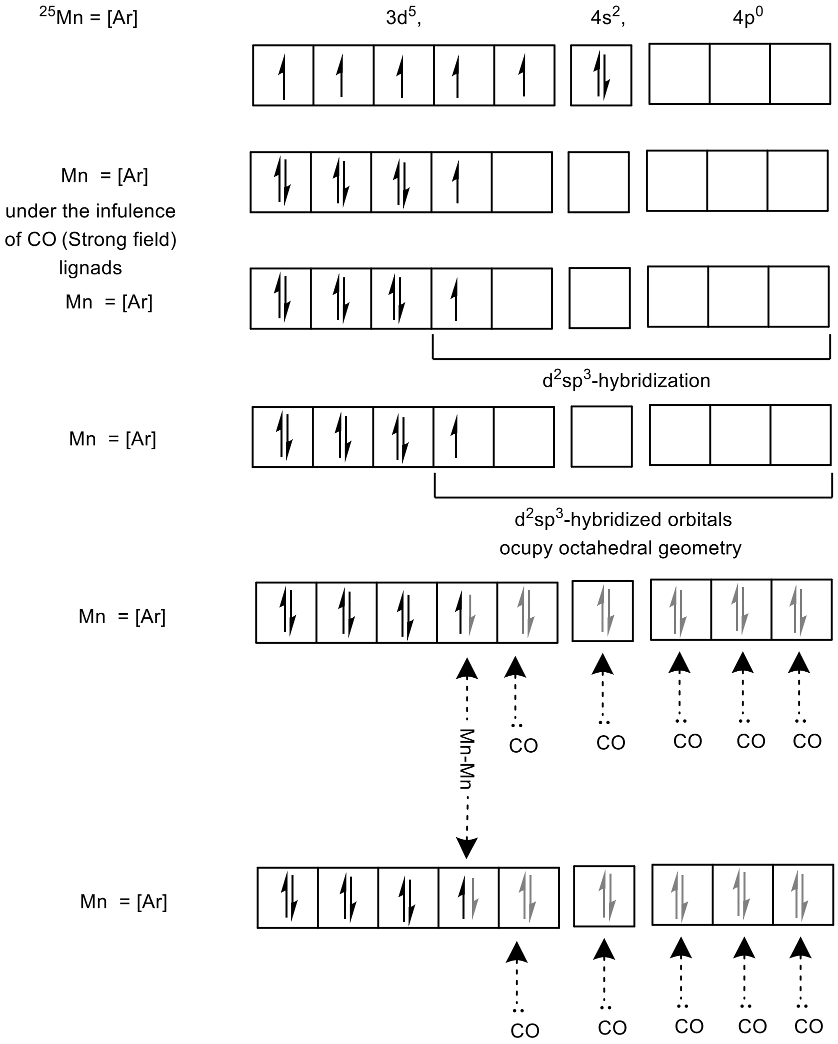
$Ni(CO)_4$: $Ni(CO)_4$ is sp^3 hybridized diamagnetic tetrahedral complex having EAN 36.

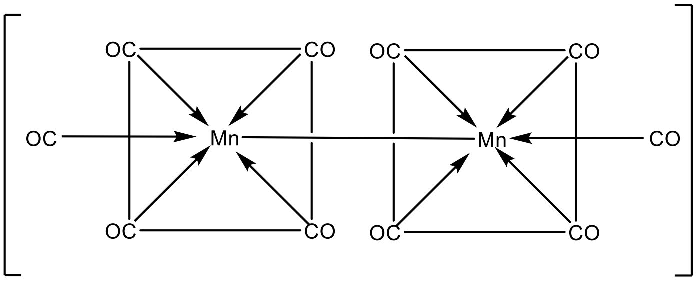




sp^3-hybridized tetrahedral complex

$Mn_2(CO)_{10}$: $Mn_2(CO)_{10}$ is a d^2sp^3 hybridized diamagnetic complex. It has ten terminal CO groups and one Mn-Mn metallic bond. Its staggered confirmation is most stable because of steric factor. EAN of $Mn_2(CO)_{10}$ is 36 [25 (Mn) +10 (five ^{t}CO) + 1 (Mn-Mn)]. Due to odd atomic number it will never fallow EAN in mono nuclear carbonyl like $Mn(CO)_5$. However it can complete EAN by the following way.





$$Mn(CO)_5 + e^- \longrightarrow [Mn(CO)_5]^-$$

$$Mn(CO)_6 - e- \longrightarrow [Mn(CO)_6]^+$$

$$Mn(CO)_5 + H \longrightarrow [HMn(CO)_5]$$

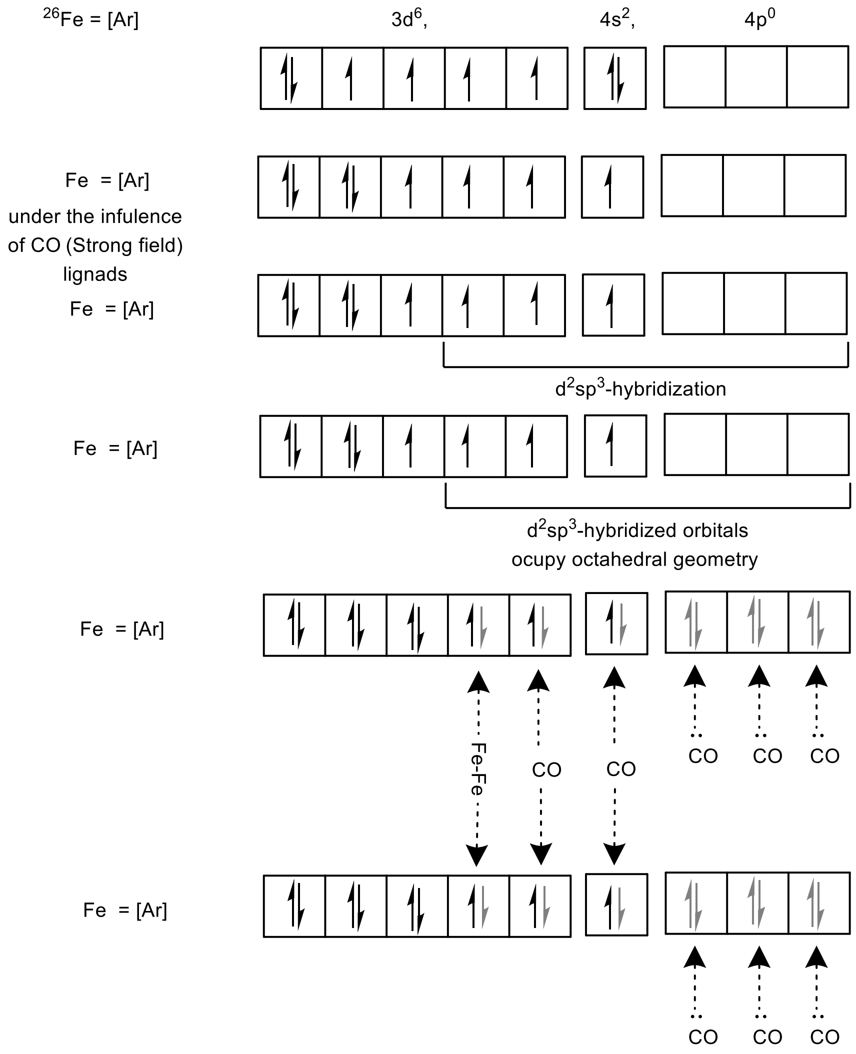
$$Mn(CO)_5 + Br^- \longrightarrow [BrMn(CO)_5]^-$$

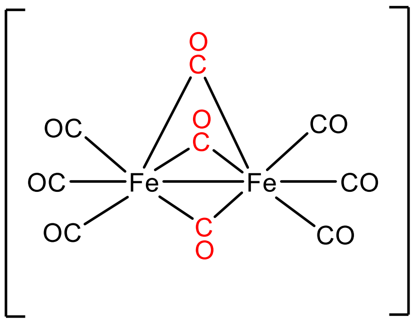
$$Mn(CO)_5 + CH_3^{\cdot} \longrightarrow [CH_3Mn(CO)_5]$$

$$2Mn(CO)_5 \longrightarrow [Mn_2(CO)_{10}]$$

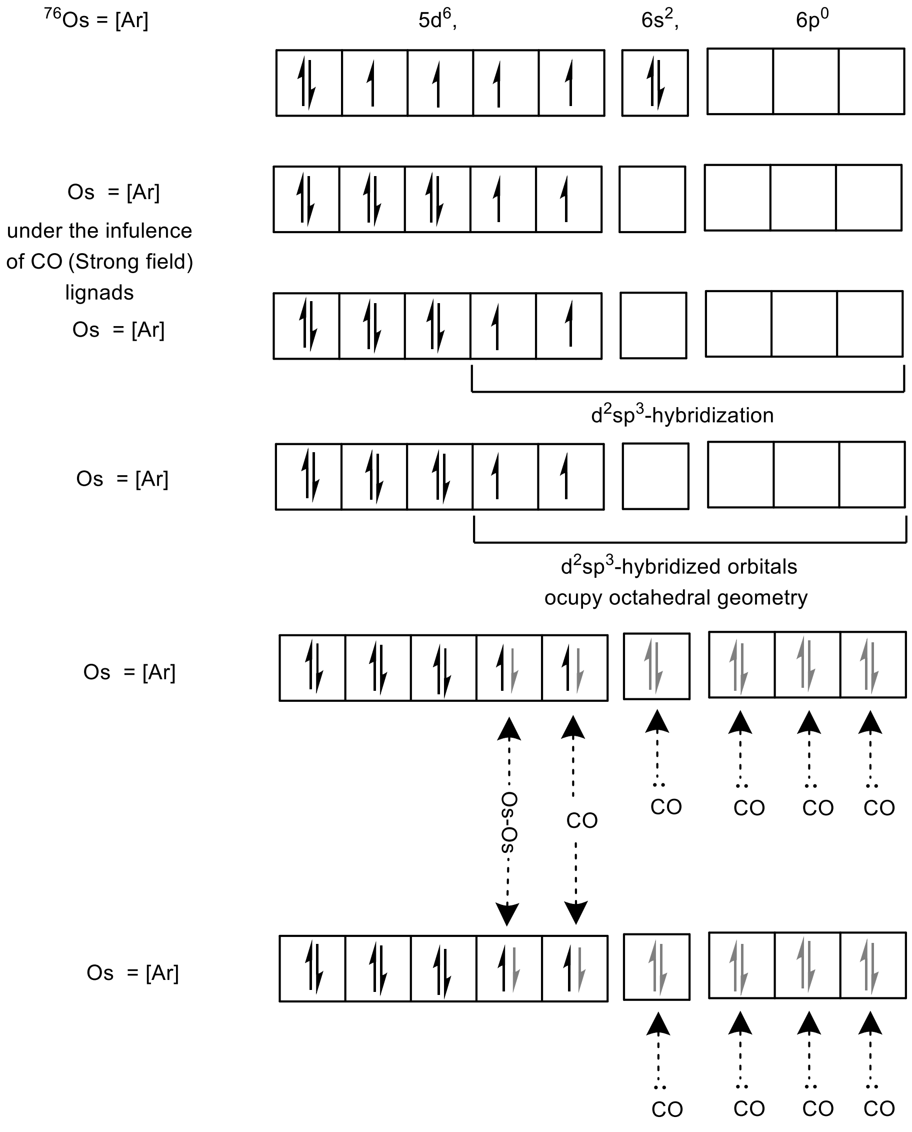
$Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$ have similar stricture and properties.

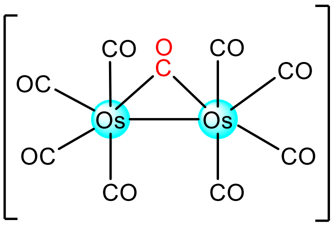
$Fe_2(CO)_9$: $Fe_2(CO)_9$ is d^2sp^3 hybridized diamagnetic complex. It contains three terminal ^{t}CO and three bridging ^{b}CO group and one Fe-Fe metallic bond. It has EAN 36 [26+ 6 (three ^{t}CO) + 3 (three ^{b}CO) + 1 (Fe-Fe)].



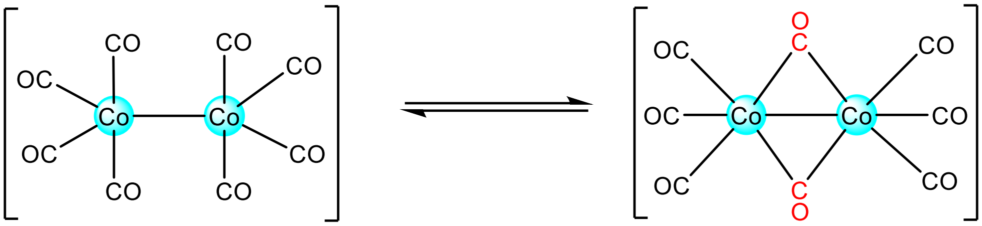


$Os_2(CO)_9$: $Os_2(CO)_9$ is diamagnetic d^2sp^3 hybridized complex having eight terminal ^{t}CO groups and one bridging ^{b}CO group and one Os-Os bond. Its EAN fallows 18 electron rule; 18 [8 (Os valence shell) + 8 (four terminal CO) + 1 (one bridged CO) + 1 (Os-Os)]. Larger the size of atom less is the chance of bridging atoms 3d > 4d > 5d.





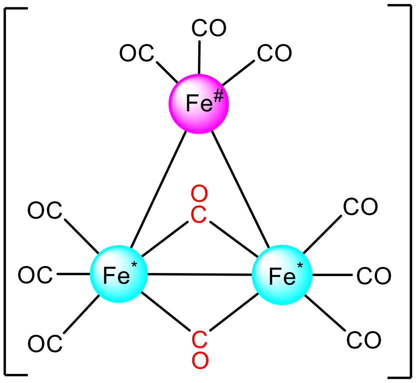
$Co_2(CO)_8$: In liquid, both bridge and non-bridge structure exists in equilibrium. While in the solid state only bridge structure exists. Increase in temperature results conversion of bridge structure into non-bridge structure. $Rh_2(CO)_8$ and $Ir_2(CO)_8$ is similar to $Co_2(CO)_8$.



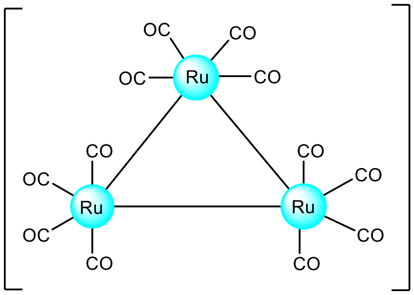
Non-bridge strucure

Bridge strucure (solid)

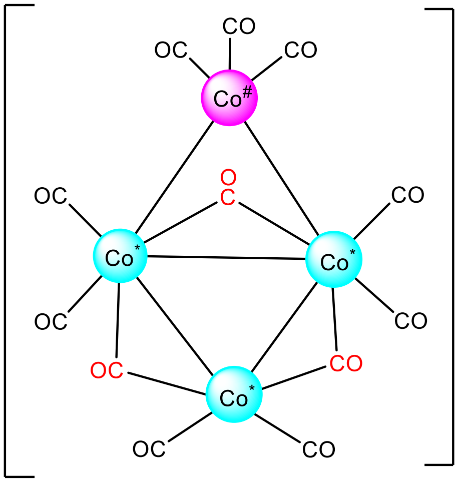
$Fe_3(CO)_{12}$: Two Fe* atoms are similar while one Fe$^{\#}$ is structurally different. EAN of both types of Fe atoms fallow 36. EAN of one Fe$^{\#}$ is 36 [(26 (Fe atom) + 8 (four terminal CO) + 2 (two M–M bond)], EAN of two Fe* is 36 [(26 (Fe atom) + 6 (three terminal CO) + 2 (two bridge CO) + 2 (two M–M bond)].



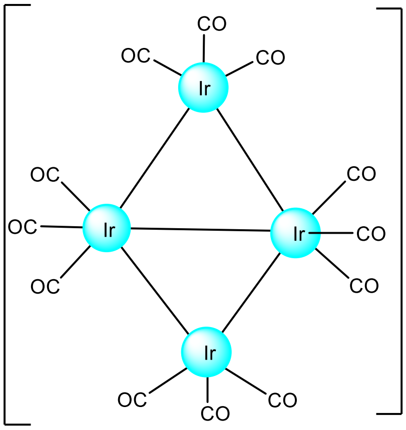
$Ru_3(CO)_{12}$: Each Ru atom has four terminal CO groups. EAN of each Ru atoms fallow 18 electron rule; 18 [8 (Ru valence shell) + 8 (four terminal CO) + 2 (two Ru-Ru bond)]. Structure of $Os_3(CO)_{12}$ is similar to $Ru_3(CO)_{12}$.



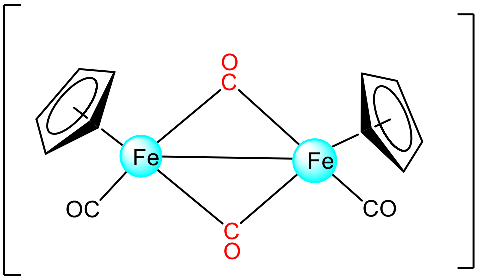
$Co_4(CO)_{12}$: Three Co^* atoms are similar while one $Co^\#$ atom is structurally different. EAN of both types of Co atoms follow 36.EAN of one $Fe^\#$ is 36 [(27 (Co atom) + 6 (three terminal CO) + 3 (three M-M bond)], EAN of three Co^* is 36 [(26 (Fe atom) + 6 (three terminal CO) + 2 (two bridge CO) + 2 (two M-M bond)]. $Rh_4(CO)_{12}$ structure is similar to $Co_4(CO)_{12}$.



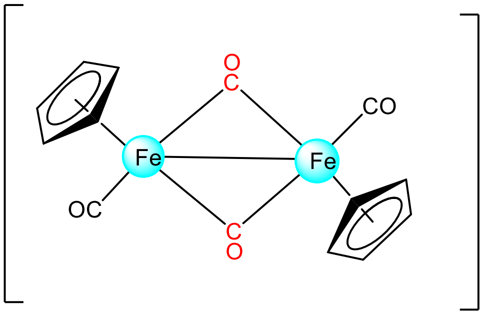
$Ir_4(CO)_{12}$: The EAN of $Ir_4(CO)_{12}$ fallow 18 electron rule; 18 [(8 (Ir valence shell) + 6 (three terminal CO) + 3 (three Ir–Ir bond)].



$(\eta^5C_5H_5)_2Fe(CO)_4$:

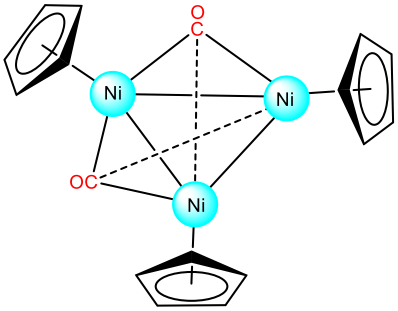


cis

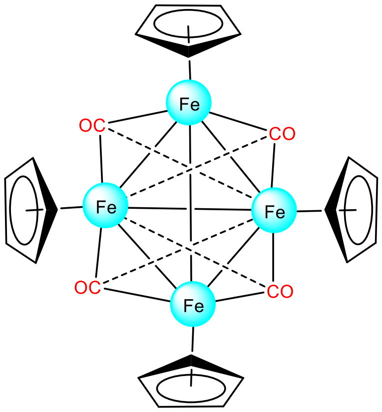


trans

$Ni_3(CO)_2(\eta^5\text{-}C_5H_5)_3$: EAN of $Ni_3(CO)2(\eta^5\text{-}C_5H_5)_3$ is 36.33; [(28 (Ni atom) + 5 (Cp Ring) + 1.33 (two triply bridged CO group; 2 x 2/3) + 2 (Ni-Ni bond)].



[$Fe(CO)(cp)_4$] and [$Fe_4(CO)_4(cp)_4$]:

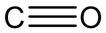


Stretching frequency: Qualitative measurement of bond strength is observed as infrared frequency (IR) (Measured for CO group and not for M-C bond because a number of bonding vibrations are observed for M-C bond). While stretching frequency for CO group is measurable at ~2000 cm^{-1}. This has strong, sharp and well differentiate unit.

Bond order and stretching frequency of CO group

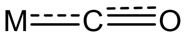
A-B

Bond order	α	Bond energy Bond strength Force constant	α	Stretching frequency (IR)



Bond Order 3

IR 2143 cm^{-1}



Bond Order 2-3

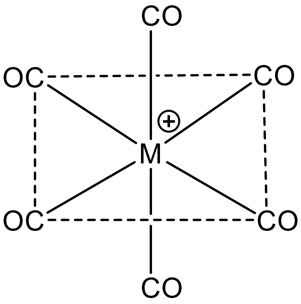
IR 2125 - 1860 cm^{-1}

Factor affecting the IR frequency

(a) Charge on metal:

$Mn(CO)_6^+$	2090 cm^{-1}
$Co(CO)_6$	2000 cm^{-1}
$V(CO)_6^-$	1868 cm^{-1}

The metal having positive charge less tendency to donate of electron.



Positive charge on metal donates fewer electrons to CO anti-bonding LUMO, so bond order will be increase consequentially stretching frequency increases and vice-versa for negative charge.

Metal has more electrons accepting tendency and lesser electron donating tendency therefore CO bond order will increase as no electron will enter anti-bonding.

Metals donate the electron and their electron inter into anti-bonding of CO, so bond order of CO will decreases and increase the energy of system and so frequency will also increase.

Negative charge on metal having high tendency to donation of electron so M-C bond order increase some useful data

$[Ni(CO)_4]$	2060 cm^{-1}
$[Co(CO)_4]^-$	1890 cm^{-1}
$[Fe(CO)_4]^{2-}$	1790 cm^{-1}

Bond order = (bonding electron – anti-bonding electron)/2

M-C bond order α 1/CO bond order

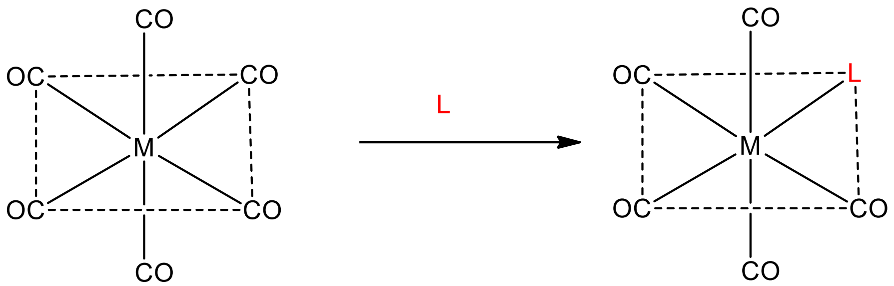
(b) Nature of CO groups

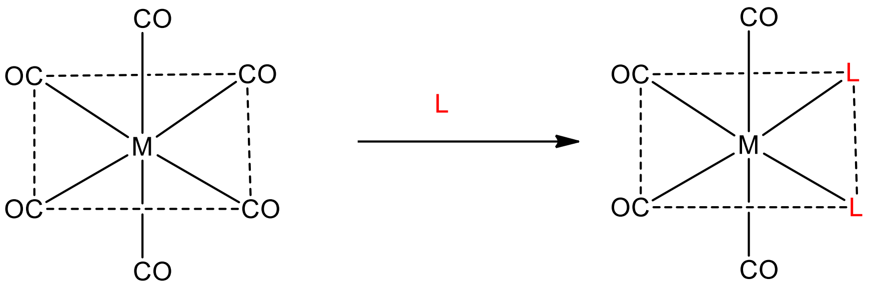
Terminal CO group – 2125-1850 cm^{-1}

Doubly bridged CO group – 1850 – 1750 cm^{-1}

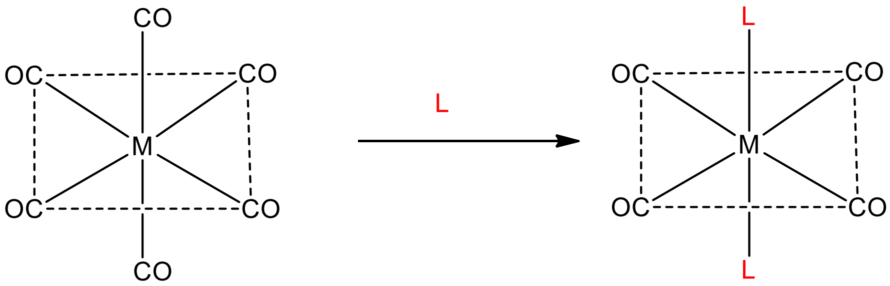
Triple birded CO group – 1730 – 1620 cm^{-1}

(c) Molecular geometry





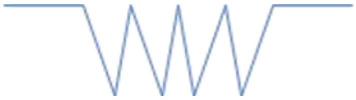
cis $M(CO)_4L_2$

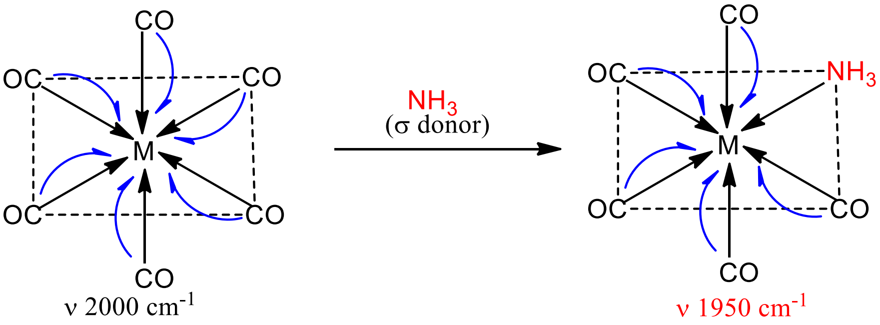


trans $M(CO)_4L_2$

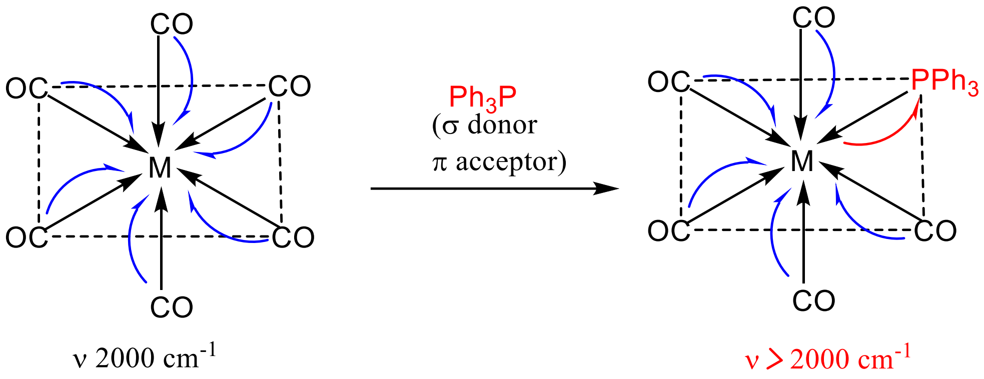
M-C frequency α 1/CO frequency

On the basis of number of bands, cis and trans can be detected. Cis isomer contains four bands while trans contain one band.

 cis $M(CO)_4L_2$	 trans $M(CO)_4L_2$



If NH_3 will attached to metal hence back donation of electron will be greater *i.e.*, now it will be at five CO group hence νCO will decrease.



If ligand has more tendency to accept back donation of electron then νCO will increase and vice-versa.

Molecular formula	**Molecular Geometry**	**No. of IR bands**
$[M(CO)_6]$	O_h	1
$[M(CO)_5L]$	C_{4v}	3
cis-$[M(CO)_4L_2]$	C_{2v}	4
trans-$[M(CO)_4L_2]$	D_{4h}	1

References:

CHM202: Inorganic Chemistry-II

Metal Carbonyls

https://epgp.inflibnet.ac.in/

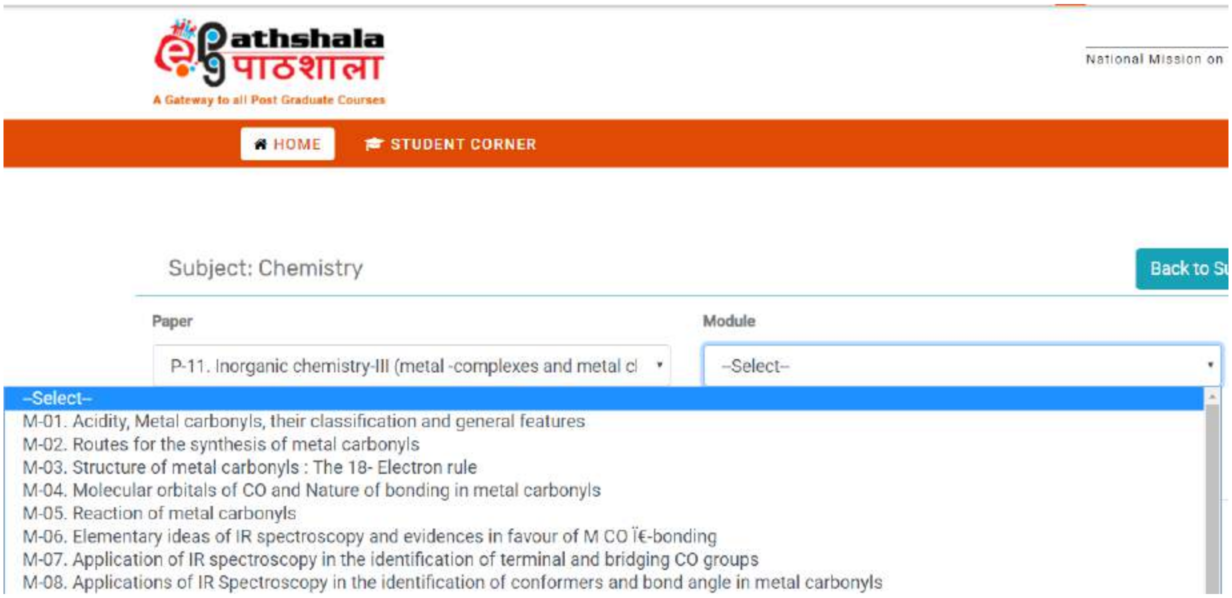
Go to chemistry

https://epgp.inflibnet.ac.in/Home/ViewSubject?catid=5

Paper 11

Module 01-08

E-Text for study materials and Self-Learning for video



Subject: Chemistry

Paper: P-11. Inorganic chemistry-III (metal -complexes and metal cl

Module: --Select--

--Select--
M-01. Acidity, Metal carbonyls, their classification and general features
M-02. Routes for the synthesis of metal carbonyls
M-03. Structure of metal carbonyls : The 18- Electron rule
M-04. Molecular orbitals of CO and Nature of bonding in metal carbonyls
M-05. Reaction of metal carbonyls
M-06. Elementary ideas of IR spectroscopy and evidences in favour of M CO Ï€-bonding
M-07. Application of IR spectroscopy in the identification of terminal and bridging CO groups
M-08. Applications of IR Spectroscopy in the identification of conformers and bond angle in metal carbonyls