

CHAPTER 11

Metal-II Complexes:

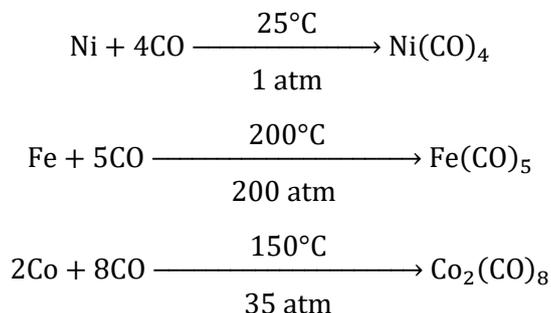
❖ Metal Carbonyls: Structure and Bonding

The bonding in coordination compounds is usually visualized as the donation of ligand electron pair to the metal center only. However, there are some ligands which not only have filled atomic orbitals (donor orbitals) but also have some empty orbitals (acceptor orbitals) of appropriate symmetry and energy to accept electron density from a central metal atom or ion. This interaction is called π -backbonding or π -backdonation; and is generally shown by CO, NO, PR_3 and alkene-alkyne type ligands. Two of the most common examples where π -backbonding occurs include $\text{Ni}(\text{CO})_4$ and Zeise's salt.

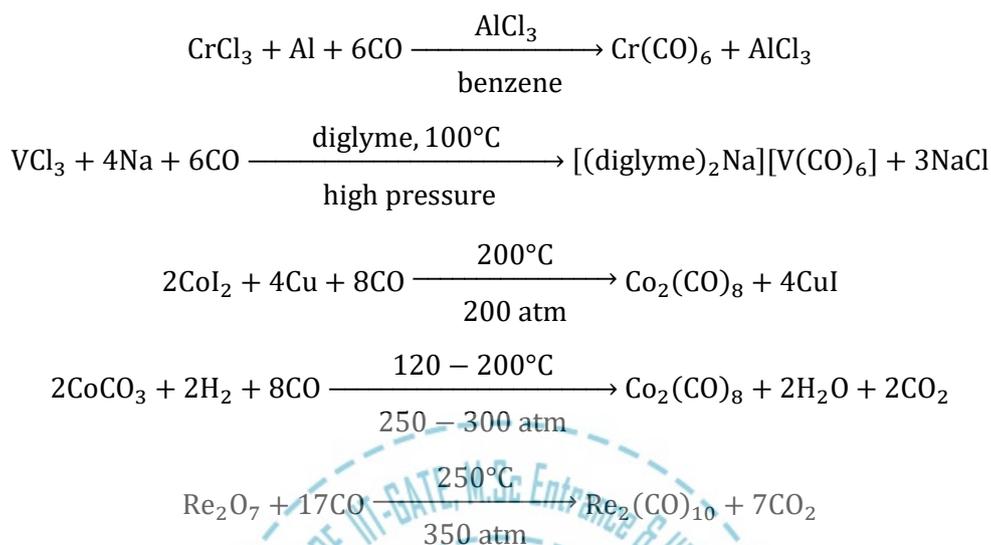
Furthermore, metal carbonyls are one of the most widely studied types of metal- π complexes, that can simply be defined as the coordination compounds of transition metals with carbon monoxide as a ligand. Metal carbonyls are very useful in synthetic organic chemistry and in homogeneous catalysis, like the process of hydroformylation. In the Mond process, nickel carbonyl is used to produce pure nickel. In organometallic chemistry, metal carbonyls act as precursors for the synthesis of many organometallic compounds. Metal carbonyls are toxic by inhalation, skin contact, or ingestion, in part due to their ability to attach to the iron of hemoglobin to give carboxyhemoglobin, which inhibits the binding of dioxygen. Metal carbonyls can be classified on the basis of the number of metal centers; mononuclear carbonyls have only one metal atom or ion such as $\text{Fe}(\text{CO})_5$, while polynuclear carbonyls contain more than one metal center like homonuclear $\text{Fe}_2(\text{CO})_9$ and heteronuclear $\text{MnRe}(\text{CO})_{10}$. One more categorization basis of metal carbonyls is the bonding profile of carbonyl ligand; non-bridging carbonyls and bridging carbonyls. Non-bridging carbonyls may or may not contain metal-metal bonds. For instance, $\text{Ru}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_{10}$ both have only terminal carbonyl groups but $\text{Mn}_2(\text{CO})_{10}$ has one metal-metal bond also. On the other hand, bridging metal carbonyls like $\text{Fe}_3(\text{CO})_{12}$, in addition to terminal CO groups, do have CO groups bridged to more than one metal center.

➤ General Methods of Preparation

1. By direct reaction: Some of the mononuclear carbonyls can be prepared by the direct reaction of carbon monoxide with metal powder.



2. By reduction: One of the most widely used methods to synthesize metal carbonyls is the reduction of corresponding metal salts in the presence of carbon monoxide.

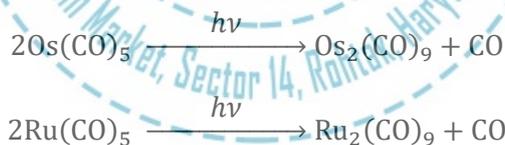


In the last reaction, carbon monoxide is the reducing agent on its own.

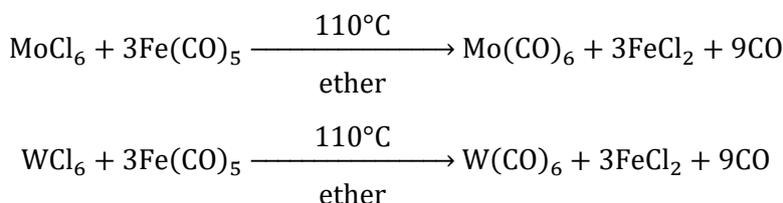
3. From mononuclear carbonyls: Iron pentacarbonyl is sensitive to light and air and can be used to synthesize $\text{Fe}_2(\text{CO})_9$ by direct photolysis.



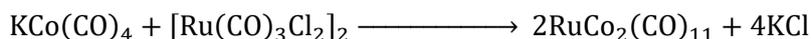
Similarly



4. From iron pentacarbonyl: Carbon monoxide ligands in $\text{Fe}(\text{CO})_5$ are labile and therefore can be used to synthesize other metal carbonyls.



5. From metathesis reaction: Mixed-metal carbonyls can successfully be prepared via a metathesis reaction route as:



➤ Structures of Metal Carbonyls

The structure of metal carbonyls can mainly be classified into three categories; first, as the mononuclear systems that contain only one metal atom, the second one as binuclear systems that may or may not contain bridging carbonyls, and the last one as the polynuclear systems which contain more than two metal centers with all terminal, all bridging, or a mixture of two types of carbonyl groups.

1. Mononuclear metal carbonyls: The structure of mononuclear metal carbonyls is pretty simple and easy to visualize. This is definitely due to the presence of only one metal center. The general examples of mononuclear metal carbonyls include tetrahedral $\text{Ni}(\text{CO})_4$ and $\text{Pd}(\text{CO})_4$; the trigonal bipyramidal case of $\text{Fe}(\text{CO})_5$, $\text{Ru}(\text{CO})_5$ and $\text{Os}(\text{CO})_5$; and the octahedral geometries of $\text{V}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$.

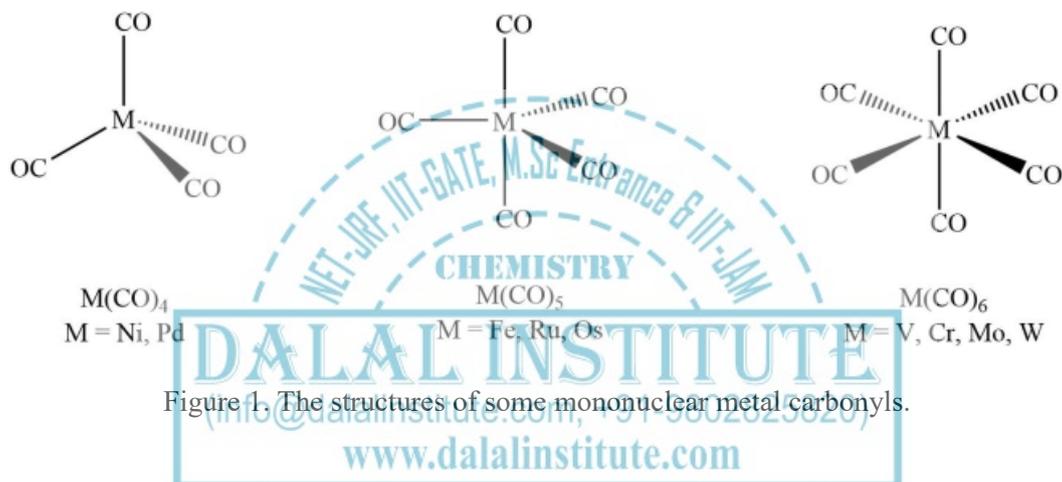


Figure 1. The structures of some mononuclear metal carbonyls.

2. Binuclear metal carbonyls: The structure of the binuclear metal carbonyls comprises of two metal centers and involve either metal-metal bonds or bridging CO groups or both. For example, the $\text{Co}_2(\text{CO})_8$ is known to exist in two isomers. The first one has a D_{3d} symmetry with one metal-metal bond with zero bridging carbonyls; the second one is of C_{2v} symmetry and has two bridging CO ligands along with one metal-metal bond. The structure of $\text{Fe}_2(\text{CO})_9$ exist with D_{3h} symmetry and contains three bridging CO ligands and six terminal CO groups attached. Furthermore, M_2CO_{10} ($\text{M} = \text{Mn, Tc, Re}$) exists with D_{4d} symmetry with one metal-metal bond and four CO ligands attached to each of the metal centers.

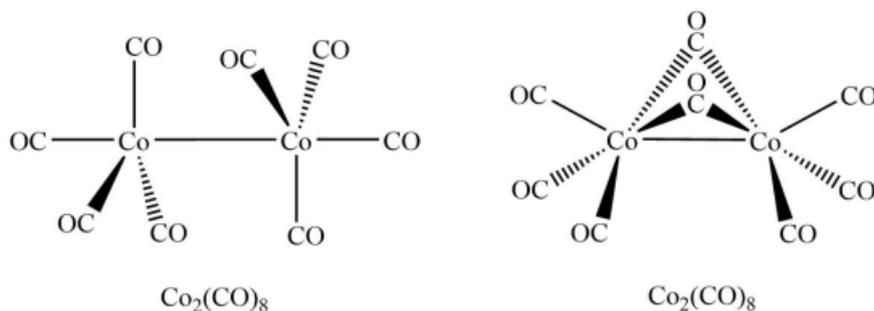


Figure 2. Continued on the next page...

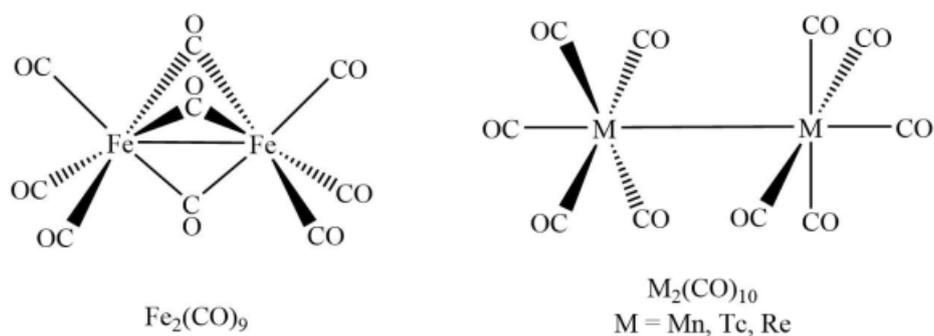


Figure 2. The structures of some binuclear metal carbonyls.

3. Polynuclear metal carbonyls: The structures of the polynuclear metal carbonyls comprises of three or more metal centers and involve all bridging, all terminal, or a mixture of two types of CO groups. For example, the $\text{Ru}_3(\text{CO})_{12}$ cluster has D_{3h} symmetry, comprises of an equilateral triangle of Ru centers, each of which has two axial and two equatorial CO ligands. $\text{Os}_3(\text{CO})_{12}$ has the same structure, whereas $\text{Fe}_3(\text{CO})_{12}$ is different, with two bridging CO ligands, resulting in C_{2v} symmetry. M_4CO_{12} ($\text{M} = \text{Co, Rh}$) is consisted of a tetrahedral M_4 core, but the molecular symmetry is C_{3v} . Three carbonyl ligands are bridging ligands and nine are terminal. However, $\text{Ir}_4(\text{CO})_{12}$ has perfect T_d symmetry with no bridging CO ligands groups. The Rh_4 and Ir_4 clusters are more thermally robust than that of the Co_4 compound, reflecting the usual trend in the strengths of metal-metal bond for second and third-row metals vs those for the first row metals. Furthermore, $[\text{Re}_4(\text{CO})_{16}]^{2-}$ has D_{2h} symmetry with no bridging carbonyl. Furthermore, the structure of $\text{Os}_4(\text{CO})_{16}$, $\text{Os}_4(\text{CO})_{15}$ and $\text{Os}_4(\text{CO})_{14}$ are somewhat more complex because of non-rigidity. The tetranuclear $\text{Os}_4(\text{CO})_{16}$ is analogs to the cyclobutane with a puckered structure. The X-ray diffraction analysis of $\text{Os}_4(\text{CO})_{14}$ unveiled an irregular tetrahedral Os_4 skeleton with four weakly semi-bridging CO groups and four different Os–Os bond lengths. The experimental structure of $\text{Os}_4(\text{CO})_{15}$ was determined to have a planar butterfly-like geometry consisting of two triangles sharing an edge. The hexanuclear $\text{M}_6(\text{CO})_{16}$ ($\text{M} = \text{Rh, Co}$) exists with an octahedral core with alternate faces participating in the bridging; i.e. with four triply bridged and twelve terminal carbonyls.

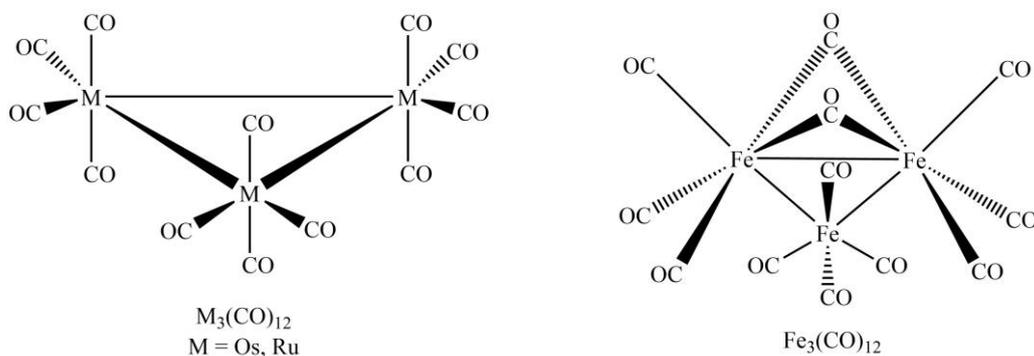


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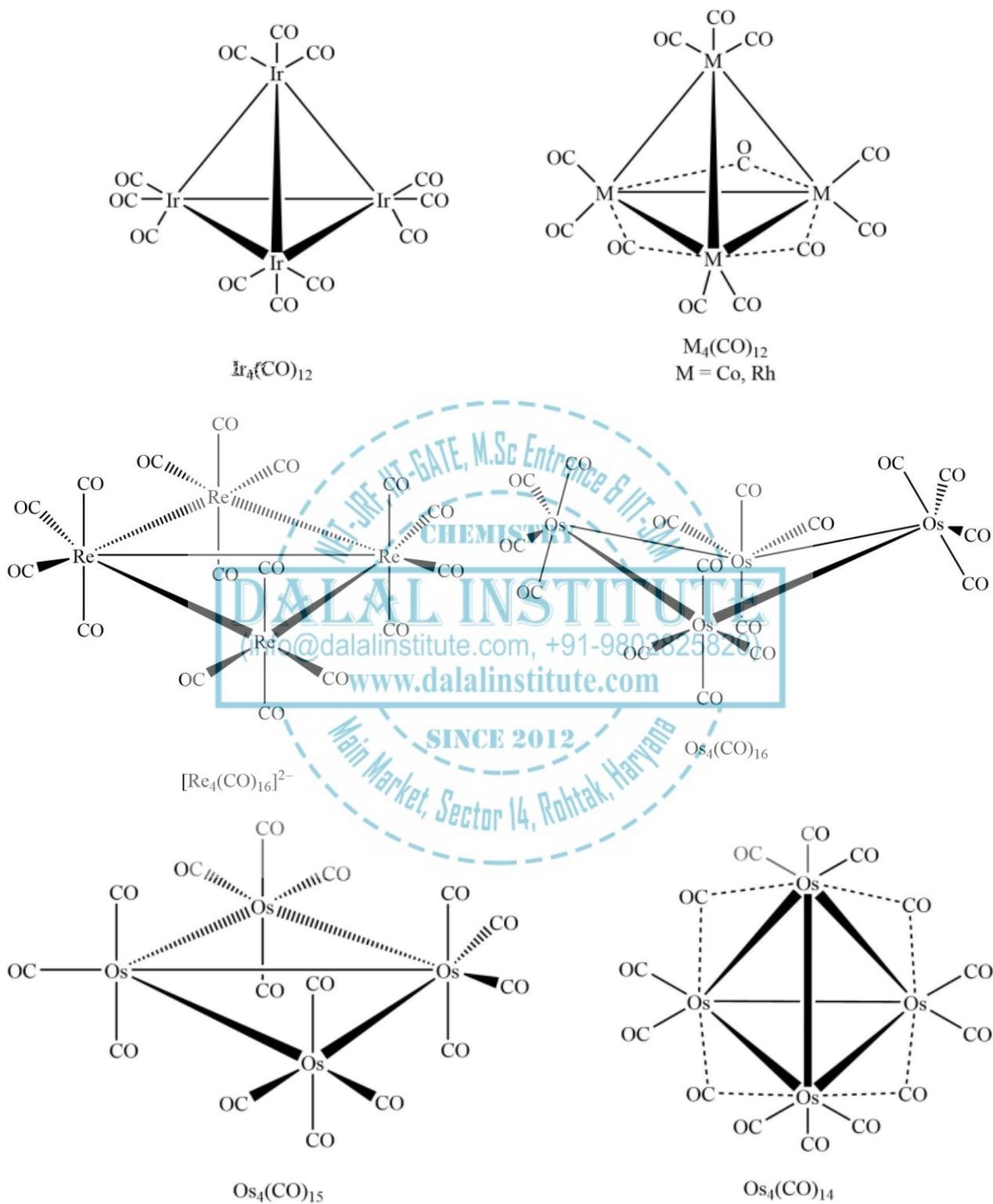


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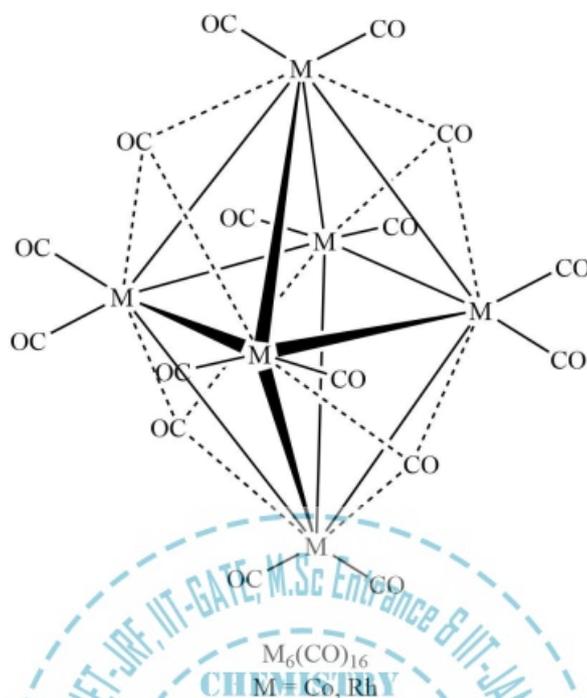


Figure 3. The structures of some polynuclear metal carbonyls.

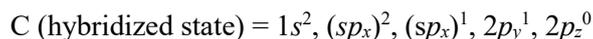
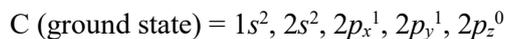
➤ **Bonding in Metal Carbonyls** www.dalalinstitute.com

In order to rationalize the nature of the bonding between the metal center and the carbonyl ligand, we must understand the bonding within the carbonyl ligand itself first. It is a quite well-known fact that the CO group acts as a good sigma donor as well as a good π -acceptor ligand. Two popular approaches to study the bonding in carbon monoxide, as well as metal carbonyls, are discussed below.

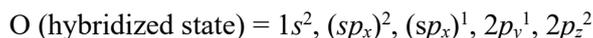
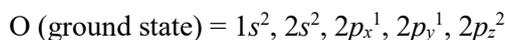
1. Valence bond theory: According to this model, the bonding within the CO molecule can be best shown as:



The carbon and oxygen atoms in CO are sp -hybridized with the following electronic configurations.



Similarly,



Now, the one half-filled sp_x -hybridized orbital of carbon atom overlap with half-filled sp_x -hybridized orbital of the oxygen atom to form a σ bond, while sp_x -hybridized lone pairs on both atoms remain non-bonding in nature. Moreover, two π bonds are formed as a result of the sidewise overlap; one between half-filled $2p_y$ orbitals, and the second one as dative or coordinative interaction of fully filled $2p_z$ orbital of oxygen with empty $2p_z$ orbital of carbon.

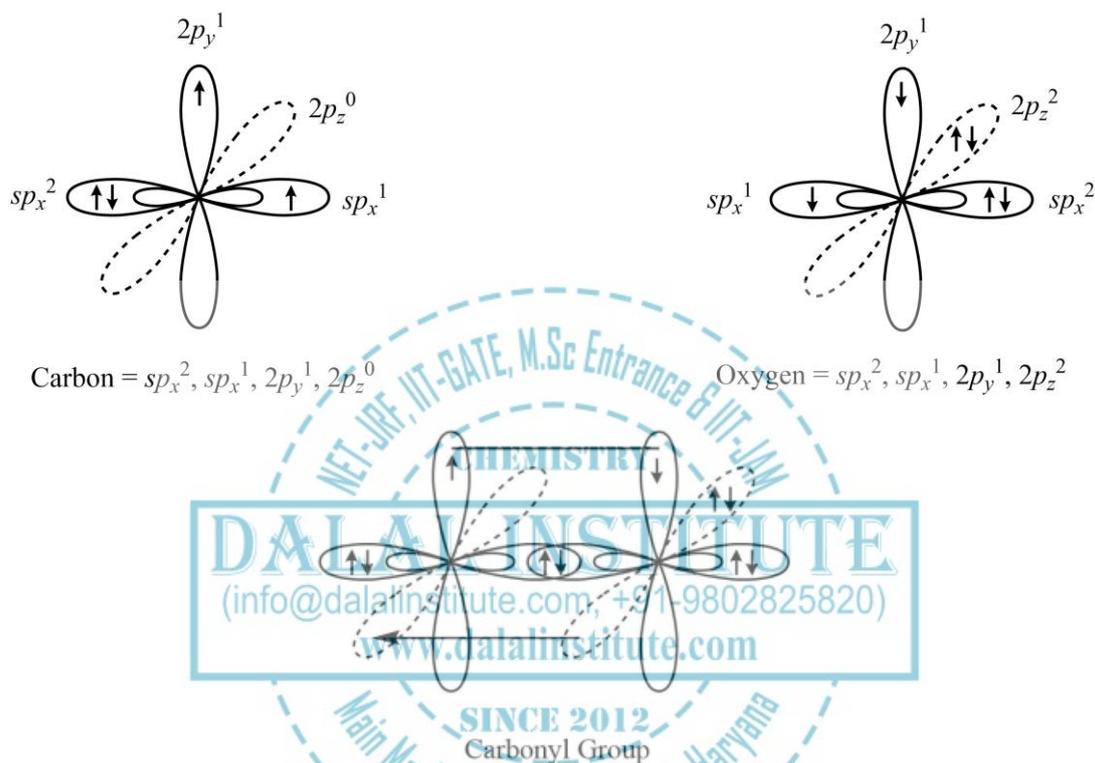


Figure 4. Bonding behavior in CO ligand according to the valence bond method.

Furthermore, the valence bond theory treats the bonding mode of the carbonyl with the metal center in terms of hybridization and resonance phenomena. The central metal atom or ion provides the required number of empty hybrid orbitals with proper orientation to accept the electron pair from surrounding ligands. For instance, in $\text{Cr}(\text{CO})_6$ the chromium atom undergoes a d^2sp^3 hybridization to generate six empty hybrid orbitals of equivalent shapes and the same energy. When one of the carbonyl ligands approaches this metal ion with its internuclear axis along x -axis, the filled hybrid lone pair of electron on carbon atom overlaps with one of the two empty hybrid orbitals oriented oppositely in x -direction. The metal-carbon multiple bond is explained in terms of various resonating structures which consequently reduces the bond strength of the carbon-oxygen bond. It should also be noted that, though there are two hybrid lone pairs (one on carbon and the other on the oxygen); the bonding of carbonyl group with metal takes place via a donation through carbon end always. This can be explained in terms of the higher energy of hybrid lone pair carbon than oxygen.

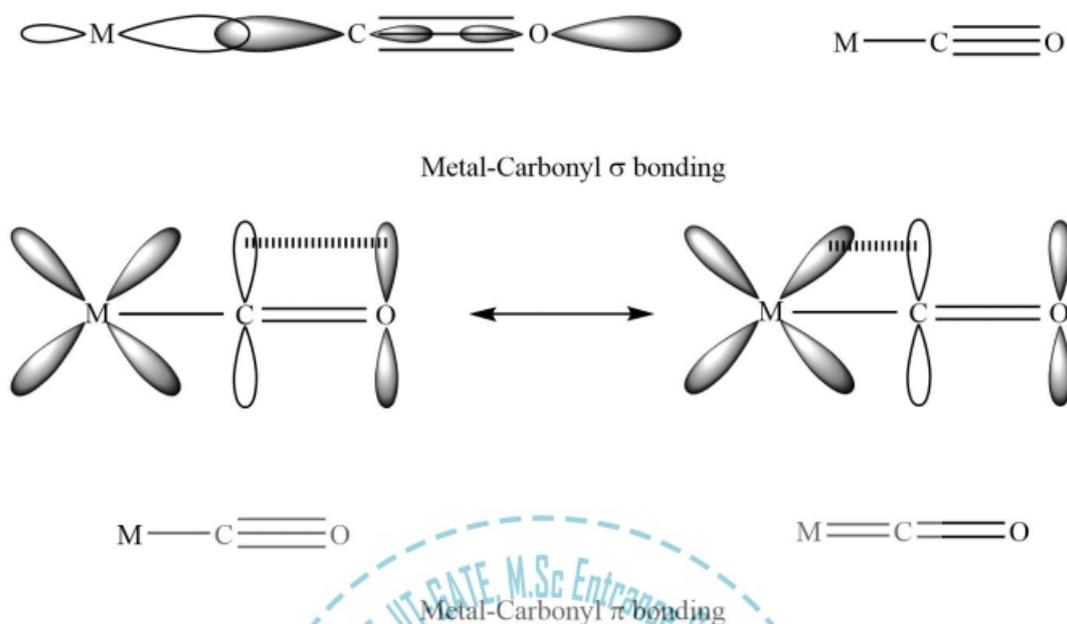
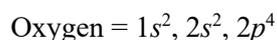
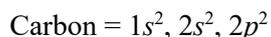


Figure 5. The valence bond nature of σ and π overlap in metal carbonyls.

2. Molecular orbital theory: This is the best model to explain the bonding within the CO ligand as well as in metal carbonyl complexes. There are total three molecular diagrams for carbonyl ligand which were proposed from time to time. Though, all three molecular orbital (MO) diagrams are able to explain the nature of metal-carbonyl π -bonding; the initial treatment was not so effective to explain the σ donation, the second one does also suffer from some minor anomalies. The third molecular orbital diagram is most widely accepted in the scientific community as it gives a logical explanation to what had been a mystery in metal carbonyl chemistry. We will study these MO diagrams in the order they were proposed.

i) The first molecular orbital diagram of carbon monoxide assumes that the atomic orbitals of carbon and oxygen interact with each other to create molecular orbitals. The electronic configurations of C and O are:



The number of outer electrons in carbon and oxygen are four and six, respectively. Thus, a total of 10 electrons are to be filled in the molecular orbitals of the carbon monoxide molecule. The higher energy of corresponding atomic orbitals of carbon is due to its lower electronegativity, which makes the bonding and antibonding molecular orbitals to receive different contributions from atomic orbitals of carbon and oxygen. The bonding molecular orbitals will be rich in atomic orbitals of oxygen while antibonding molecular orbitals, that are closer to carbon in energy, would be rich in atomic orbitals of carbon. The bonding molecular orbitals will have more characteristics of atomic orbitals of Oxygen and antibonding Molecular orbitals would have more

characteristics of carbon. The electronic configuration of CO molecule will be $\sigma 2s^2, \sigma^* 2s^2, \sigma 2p_z^2, \pi 2p_x^2, \pi 2p_y^2$ which gives a bond order three i.e. triple bond between carbon and oxygen. The molecular orbital diagram and expected bonding mode of the carbonyl ligand are given below.

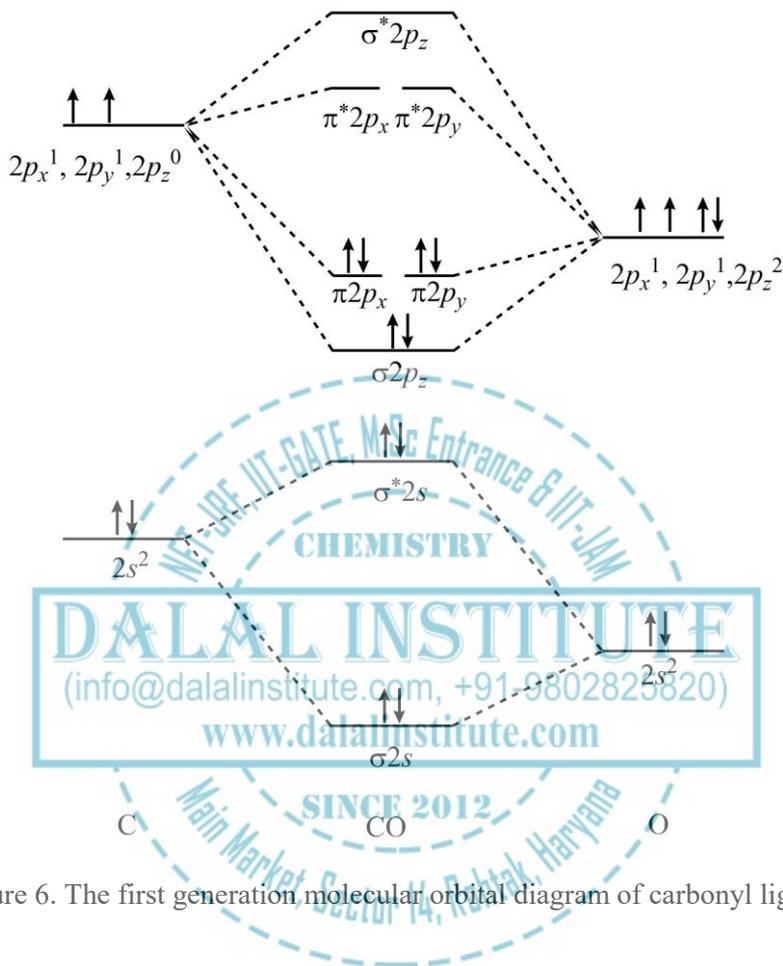


Figure 6. The first generation molecular orbital diagram of carbonyl ligand.

The formation of molecular orbitals given above is actually an oversimplification of a ticklish problem. This statement is made on the basis of two facts. The first one is that when one electron removed from CO to form CO^+ , the bond order actually increases, which is actually the opposite of what is expected if the electron is lost from the highest occupied molecular orbital (HOMO) of bonding nature. Its bond order should be decreased from the removal of an electron from $\pi 2p_x^2$ or $\pi 2p_y^2$, which suggests that the HOMO of carbon monoxide should be of antibonding nature rather bonding. The second anomaly also arises from the MO diagram of CO ligand which clearly shows that in order to donate electron density from π -bonding molecular orbital, the carbonyl ligand must approach the metal center with its carbon-oxygen internuclear axis perpendicular to x , y or z -axis assigned to the central atom. This explains how the empty $\pi^* 2p_x$ and $\pi^* 2p_y$ could be used to accept electron density from filled d -orbitals of central metal atom or ion. However, in actual practice, the carbonyl ligand binds to the metal center in linear fashion via carbon end only.

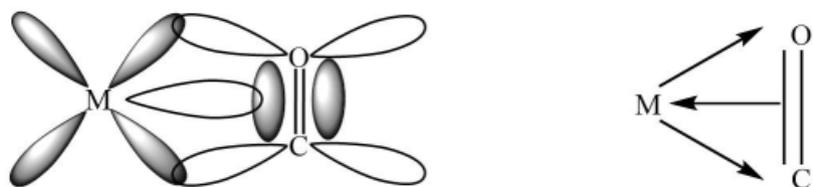
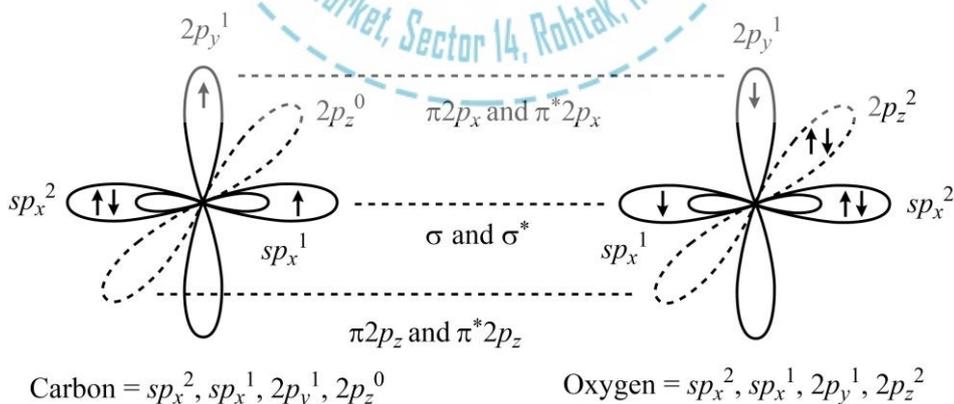
Metal-Carbonyl σ donation and π acceptance

Figure 7. The expected nature of σ and π overlap in metal carbonyls from the first MO of CO.

ii) The second molecular orbital diagram of carbon monoxide was suggested by Coulson which assumes that the first molecular orbital diagram of CO is not correct. According to Coulson, $2s$ and $2p_x$ atomic orbitals of both carbon and oxygen undergo hybridization before they create molecular orbitals. The carbon and oxygen atoms in carbon monoxide are sp -hybridized with the following electronic configurations.



The total number of valence electrons in carbon and oxygen are four and six, respectively; and thus, ten electrons are to be filled in the molecular orbitals of CO molecule. The half-filled sp_x hybrid orbitals of carbon and oxygen interact to form σ and σ^* molecular orbitals, while the fully-filled sp_x hybrid lone pair orbitals of carbon and oxygen remain non-bonding. Moreover, doubly degenerate sets of π -bonding and π -antibonding molecular orbitals are also formed due to the sidewise overlap of $2p_y$ orbitals and $2p_z$ orbitals.

Figure 8. The nature of σ and π in carbonyl ligand.

The bonding molecular orbitals will be rich in atomic orbitals of oxygen while antibonding molecular orbitals, that are closer to carbon in energy, would be rich in atomic orbitals of carbon. The bonding molecular orbitals

will have more characteristics of atomic orbitals of oxygen and antibonding molecular orbitals would have more characteristics of carbon. The molecular orbital diagram carbon monoxide proposed by Coulson is given below.

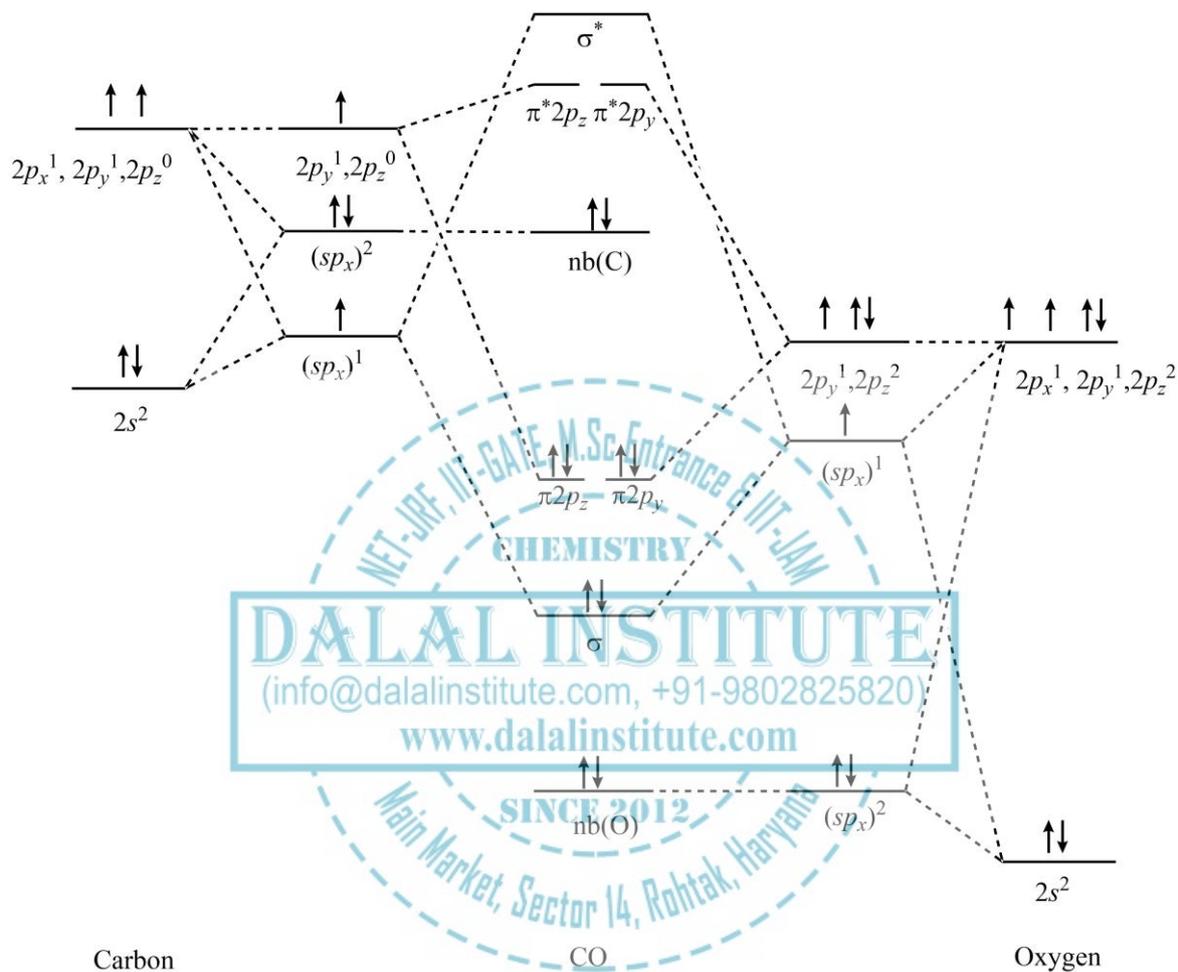


Figure 9. The second molecular orbital diagram of carbonyl ligand.

The MO diagram shown above is very useful in explaining the bonding between the metal center and carbonyl ligand. This diagram eliminates the possibility of sigma donation through bonding molecular orbital and perpendicular orientation CO ligand as the HOMO is now non-bonding hybrid lone pair rather π -bonding. This also explains why the carbonyl group prefers to bond via carbon end in a linear manner. This also explains how the lowest unoccupied molecular orbital (LUMO) π^*2p_z and π^*2p_y could be used to accept electron density from filled d -orbitals of central metal atom or ion. Moreover, the reduced CO stretching frequency of metal coordinated carbonyl can be attributed to the reduced bond order due to the transfer of d -electron density from metal to π^* orbital carbonyl ligand. However, the increase in bond order when one electron is removed from

CO to form CO^+ is still a mystery because the electron is lost from the highest occupied molecular orbital (HOMO) of nonbonding bonding nature, and the bond order should have remained the same.

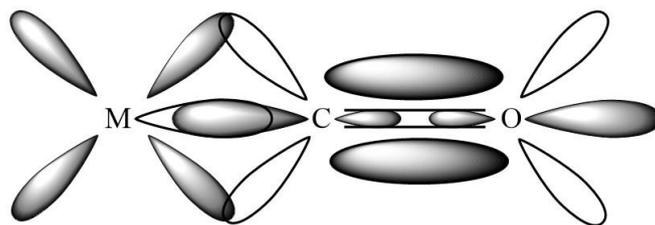


Figure 10. The nature of σ and π overlap in metal carbonyls.

iii) This molecular orbital diagram of carbon monoxide is most widely accepted to rationalize its σ -donor and π -acceptor strength. The total number of valence electrons in carbon and oxygen are four and six, respectively; and thus, ten electrons are to be filled in the molecular orbitals of CO molecule. A total of four singly degenerate σ -molecular orbitals and two doubly degenerate sets of π -molecular orbitals are formed. One doubly degenerate set of π -molecular orbitals will be bonding while the other one will be antibonding in nature. The nature of σ -molecular orbitals is more complex as three out of four are of bonding character. Initially, the σ_5 was thought to be of antibonding to justify the higher bond order of CO^+ . However, the σ_5 is slightly bonding in nature because there is some mixing with the p -atomic orbitals of the right symmetry. Out of four σ -molecular orbitals, only σ_6 possesses the antibonding character, while σ_5 goes with expected bonding characteristics. The σ_5 is essentially non-bonding and almost centered on the oxygen atom. Moreover, doubly degenerate sets of π -bonding and π -antibonding molecular orbitals are also formed due to the sidewise overlap of $2p_y$ orbitals and $2p_z$ orbitals. The π -bonding molecular orbitals set will be rich in atomic orbitals of oxygen while antibonding molecular orbitals, that are closer to carbon in energy, will be rich in atomic orbitals of carbon atom.

However, the problem that why does the bond order increases when an electron is removed from CO still persists. Because we are removing the electron from a bonding molecular orbital, its bond order must be decreased. The possible explanation for the shortening of the bond after ionization is that the ionization induces a shift of the electron-polarization in CO ligand. In other words, the ionization occurs as the loss of an electron from a σ -HOMO orbital which is mostly carbon-centered; and since the HOMO- σ orbital is only slightly bonding in nature, the loss of bonding character is quite small and could easily be compensated by the advantage in covalent character; i.e. the formation of a positive partial charge on the carbon atom increases the strength of the covalence of the bond and thus decreases the bond length. This enhanced covalent character can also be visualized in terms of better interaction of two atomic orbitals if their energies are comparable. In carbon monoxide molecule the atomic orbitals of oxygen lie energetically a lot below then the atomic orbitals of carbon; But when the CO is oxidized to CO^+ , the partial positive charge on carbon shifts the atomic orbitals of carbon down in energy, and thereby makes the energies closer to the related atomic orbitals of oxygen, which leads to a stronger interaction when bonds are made.

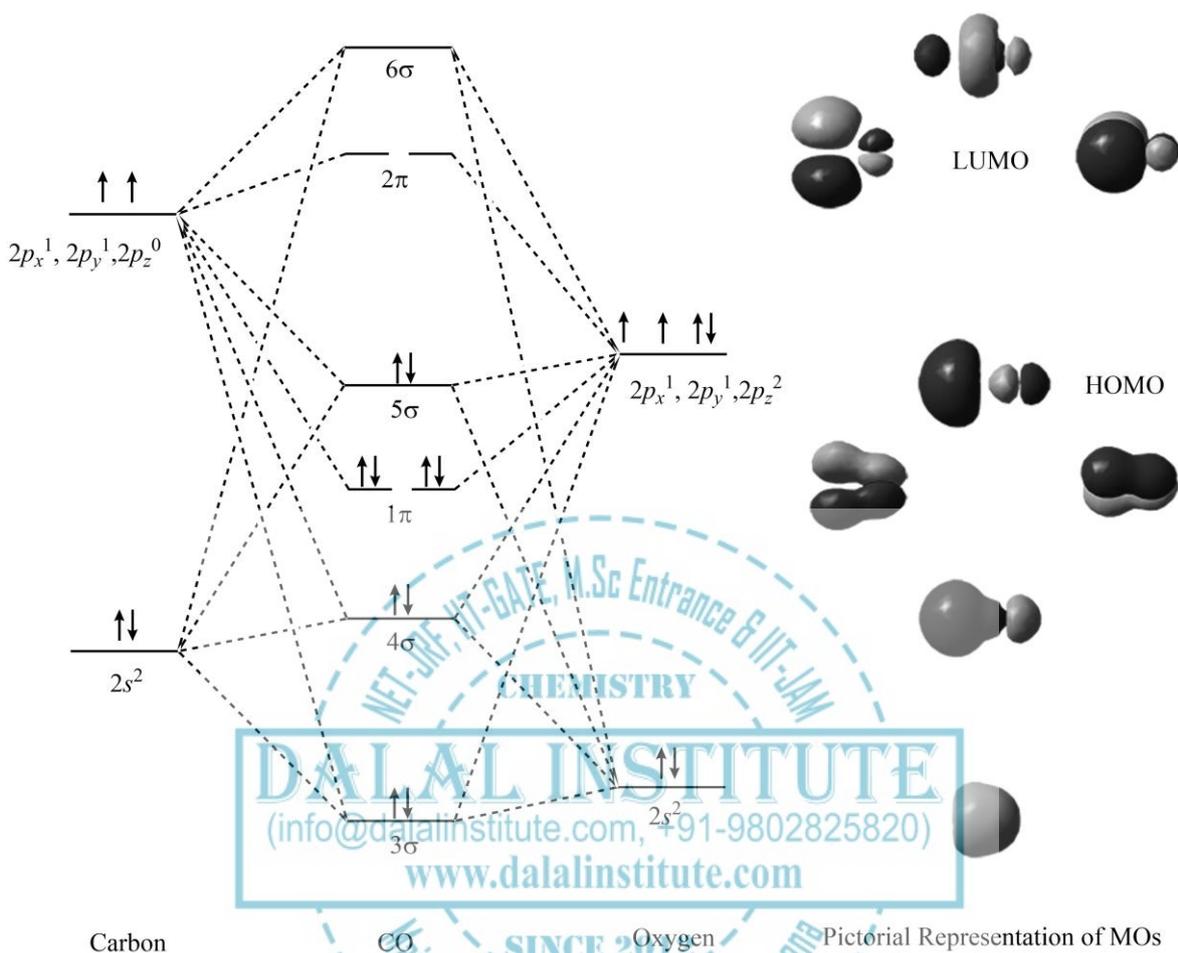


Figure 11. Third molecular orbital diagram of carbonyl ligand.

The MO diagram shown above is very useful in explaining the bonding between the metal center and carbonyl ligand. The carbonyl ligand uses its HOMO for sigma donation while simultaneously accepts electron density from filled metal d-orbital to its π^* LUMO.

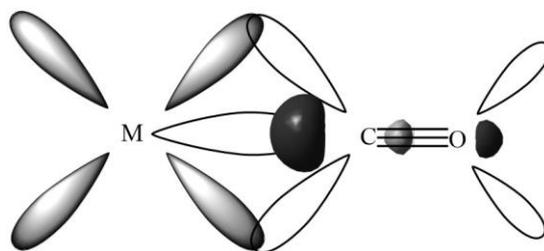


Figure 12. The nature of σ and π overlap in metal carbonyls using third MO diagram of CO.

❖ Vibrational Spectra of Metal Carbonyls for Bonding and Structure Elucidation

Vibrational spectroscopy is one of the most important methods used for the characterization of metal carbonyls. This technique provides very useful information not only about the structural prototype of different metal carbonyl compositions but also rationalizes the nature of bonding in them. Now, it is quite a well-known fact that the C–O vibration for free carbonyl group (CO gas) is typically denoted as ν_{CO} , and absorbs at 2143 cm^{-1} . However, this C–O absorption shifts downward (sometimes upward) to cover a very wide range of wavenumber as the carbonyl ligand gets attached to a metal center. This is obviously due to the fact that the energies of the ν_{CO} band for the metal carbonyls directly correlate with the strength of the carbon-oxygen bond, and are inversely correlated with the strength of the π -backbonding between the metal and the carbon. In other words, the molecular orbital diagram of carbonyl group suggests that the highest occupied molecular orbital, used for σ -donation is weakly bonding; but the lowest unoccupied molecular orbital, used for accepting d -electron density from metal center is strongly antibonding; therefore, the σ -donation does not affect the CO bond order very much but the acceptance of electron density in π^* orbital decreases the bond order and consequently the bond strength in a significant way. This effect reduces the force constant of C–O bond, while the magnitude of force constant for M–C will be increased by this backbonding. As a result, the enhancement of backbonding shifts the metal-carbon and carbon-oxygen stretching to higher and lower values, respectively. The main features about the bonding and structure of metal carbonyls which can be obtained from the vibrational spectra of metal carbonyls are discussed below:

➤ 1. π -Basicity of the Metal Centre

The π -basicity of the metal center (and thus the C–O stretching frequency) depends upon a lot of factors like the nature and magnitude of the charge on metal center, and the π -accepting tendency of ligands attached other than the carbonyl. A negative charge on the metal center, or ligands with greater σ -donation and weaker π -accepter strength, are expected to decrease the CO stretching frequency; while an accumulation of positive charge on metal center, or ligands with weaker σ -donation stronger π -accepter strength are bound to increase the CO stretching frequency. For example, in the isoelectronic series of $\text{Ti} \rightarrow \text{Fe}$, the hexacarbonyls show decreasing π -backbonding as one increases (makes more positive) the charge on the metal.

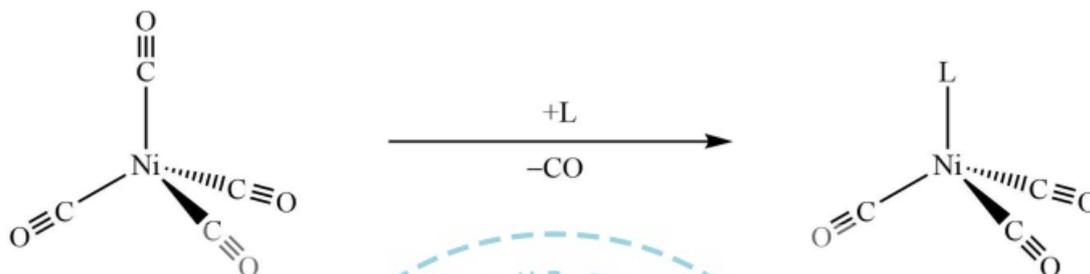
Compound	$[\text{Ti}(\text{CO})_6]^{2-}$	$[\text{V}(\text{CO})_6]^{1-}$	$[\text{Cr}(\text{CO})_6]$	$[\text{Mn}(\text{CO})_6]^{1+}$	$[\text{Fe}(\text{CO})_6]^{2+}$
$\nu_{\text{CO}} (\text{cm}^{-1})$	1748	1859	2000	2095	2204

Compound	$[\text{Hf}(\text{CO})_6]^{2-}$	$[\text{Ta}(\text{CO})_6]^{1-}$	$[\text{W}(\text{CO})_6]$	$[\text{Re}(\text{CO})_6]^{1+}$	$[\text{Os}(\text{CO})_6]^{2+}$
$\nu_{\text{CO}} (\text{cm}^{-1})$	1757	1850	1977	2085	2190

Hence, π -basic ligands increase π -electron density at the metal, and improved backbonding reduces ν_{CO} .

➤ 2. Tolman Electronic Parameter

The electron-donating or withdrawing ability of a ligand is calculated in terms of the Tolman electronic parameter (TEP), named after the inventor, Chadwick A. Tolman. It is determined by measuring the frequency of the A_1 vibrational mode of the carbonyl group in complex, $Ni(CO)_3L$ by infrared spectroscopy, where L is the ligand being studied. $Ni(CO)_3L$ was chosen as the model compound because such complexes can easily be synthesized from $Ni(CO)_4$.



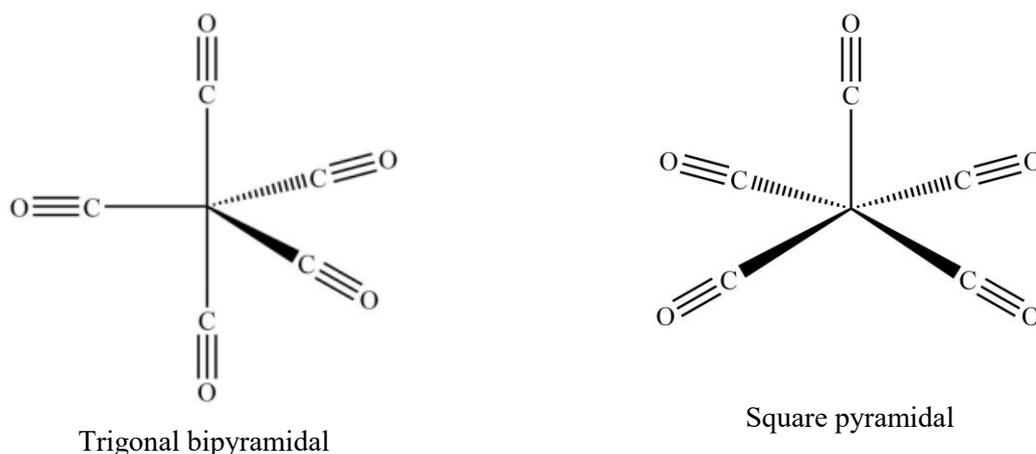
The CO band is pretty much unique and is rarely affected by other bands in the analyte's IR spectra. Moreover, owing to the small size of carbonyl ligand, steric factors do not muddle the analysis. The coordination of CO to a metal typically decreases ν_{CO} value from 2143 cm^{-1} (free CO). This can be rationalized by π -backbonding, resulting from the sidewise overlap of metal orbitals of π -symmetry with the empty anti-bonding π^* orbitals on CO ligand. This increases the strength of the metal-carbon bond, but also weakens the C–O bond. If some other ligand enhances the π -electrons-density on the metal, the CO bond strength decreases and so the ν_{CO} value. On the other hand, if other ligands present compete with CO for π -backbonding, ν_{CO} increases. TEPs for selected phosphines are given below.

L	P(t-bu) ₃	P(Me) ₃	P(Ph) ₃	P(OEt) ₃	PCl ₃	PF ₃
$\nu_{CO}\text{ (cm}^{-1}\text{)}$	2056.1	2064.1	2068.9	2076.3	2097.0	2110.8

The Tolman electronic parameter has been widely used to characterize the electronic properties of phosphine based ligands.

➤ 3. Structural Prototype of Metal Carbonyls

The symmetry behavior of different metal carbonyls can be used to determine the number of infrared active vibrational modes, which in turn enable us to comment on structural prototypes. In other words, it is well known from the group theory that only those vibrational modes will be observed which transform as the electric-dipole moment operator; therefore, the number of observable infrared transitions for a particular geometry can be predicted theoretically. These predictions are then matched with the experimentally observed infrared spectra to shortlist the various possible structural prototypes. For instance, consider the case of five-coordinated homoleptic metal carbonyl complexes. The two possible geometries are square-pyramidal and trigonal bipyramidal.

Figure 13. Two possible geometries of Iron pentacarbonyl i.e. $\text{Fe}(\text{CO})_5$ complex.

For trigonal bipyramidal geometry, a reducible representation based on five C–O bonds is:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_d$	Irreducible components
Γ_π	5	2	1	3	0	3	$2A_1' + A_2'' + E'$

Out of four irreducible representations, A_2'' transforms as z-component while E' transforms with x- and y-components of the dipole moment. Now, owing to two doubly degenerate vibrational modes (E'), only two peaks are expected in the experimental infrared spectrum. However, in the Raman infrared spectrum, three peaks are expected as only $2A_1'$ and E' irreducible components transform alongside the polarizability tensors.

For square pyramidal geometry, a reducible representation based on five C–O bonds is:

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	Irreducible components
Γ_π	5	2	1	3	3	$2A_1 + B_1 + E$

Out of four irreducible representations, $2A_1$ transforms as z-component while E transforms with x- and y-components of the dipole moment. Now, owing to two doubly degenerate vibrational modes (E), only three peaks are expected in the experimental infrared spectrum. However, in the Raman infrared spectrum, four peaks are expected as all of the irreducible components transform alongside the polarizability tensors.

Similarly, the CO ligands of octahedral complexes, e.g. $\text{Cr}(\text{CO})_6$, transform as A_{1g} , E_g , and T_{1u} , but only the T_{1u} mode (anti-symmetric stretch of the apical carbonyl ligands) is infrared-active; and therefore, only a single carbonyl stretching is observed in the IR-spectra of the octahedral metal hexacarbonyls. Spectra for complexes of lower symmetry are more complex. For example, the IR spectrum of $\text{Fe}_2(\text{CO})_9$ displays CO bands at 2082, 2019, 1829 cm^{-1} . The number of observable infrared-active vibrational modes for some metal carbonyls are listed in the following below.

Table 1. The number of IR-active vibrational modes of several prototypical metal carbonyl complexes.

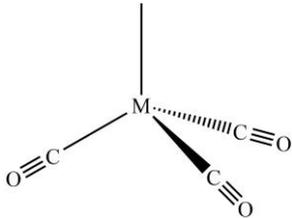
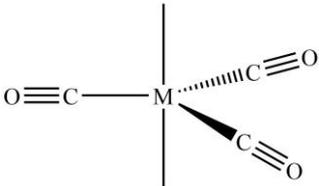
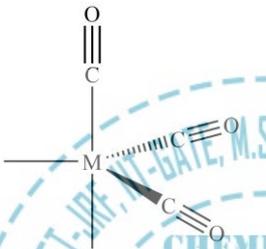
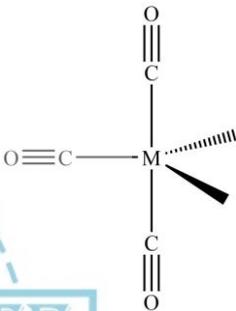
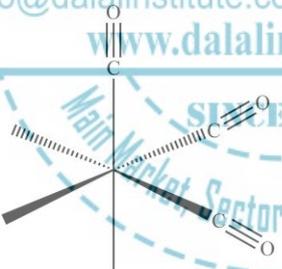
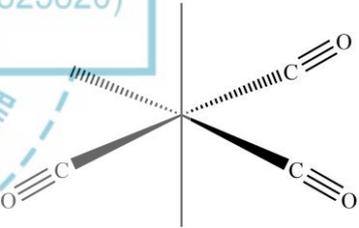
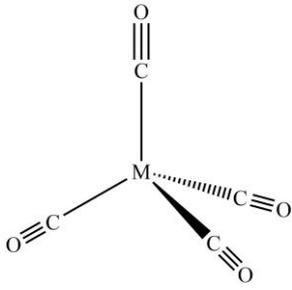
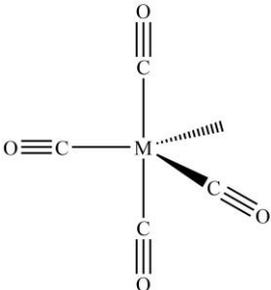
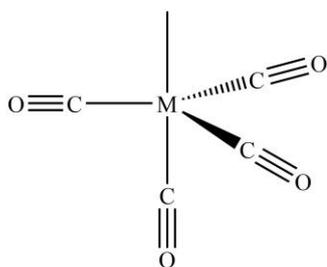
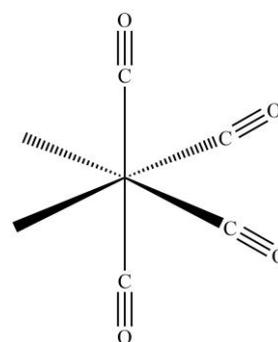
No. of carbonyls	Structural prototype (No. of IR-peaks)	Structural prototype (No. of IR-peaks)
Three		
	(2)	(1)
		
	(3)	(3)
		
	(2)	(3)
Four		
	(1)	(4)

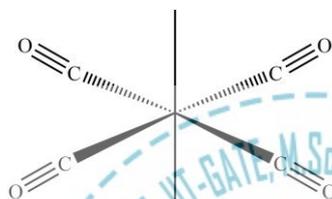
Table 1. Continued on the next page...



(3)



(4)

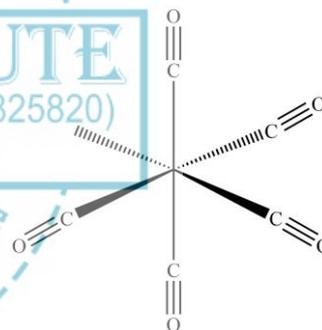


(3)

Five

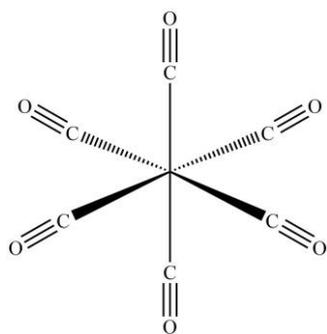


(2)



(3)

Six

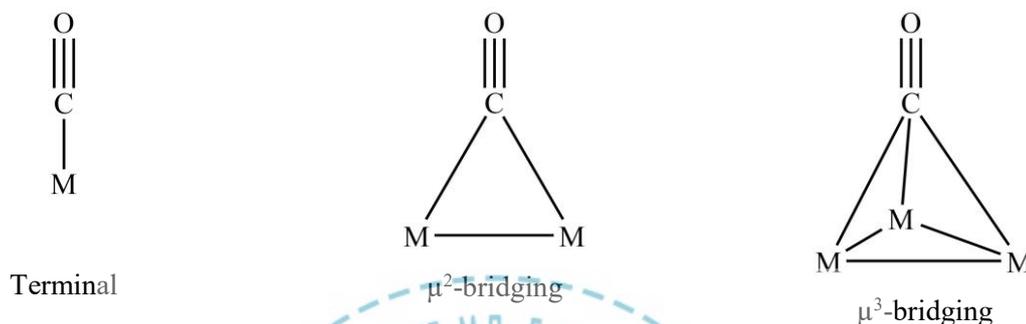


(1)

It is worthy to note that these rules apply to metal carbonyls in solution or the gas phase.

➤ 4. Differentiation of Terminal and Bridging Carbonyl Groups

The mode of attachment of the carbonyl group to the metal center can also be determined by observed CO stretching frequencies. Terminal carbonyls absorb at the higher wavenumber in comparison to the bridging ones, which is obviously due to the fact that the extent of backbonding increases with the number of metal centers. Three main modes of attachment of the carbonyl group with the metal center are:



The ν_{CO} follows the order: Terminal CO > μ^2 -bridging > μ^3 -bridging. The IR-range absorption for various types of carbonyl groups is listed below.

Table 2. The CO stretching frequencies in different metal carbonyl complexes.

Bonding mode of CO	ν_{CO} (cm^{-1})
Free CO	2143
Free CO^+	2184
Terminal CO	2120 - 1850
Symmetric μ^2 -CO	1860 - 1750
Symmetric μ^3 -CO	1730 - 1600

For instance, consider the rhodium carbonyl complexes:

Compound	μ^1 -CO, ν_{CO} (cm^{-1})	μ^2 -CO, ν_{CO} (cm^{-1})	μ^3 -CO, ν_{CO} (cm^{-1})
$\text{Rh}_2(\text{CO})_8$	2060, 2084	1846, 1862	
$\text{Rh}_4(\text{CO})_{12}$	2044, 2070, 2074	1886	
$\text{Rh}_6(\text{CO})_{16}$	2045, 2075		1819

There is also a semi-bridging mode that lies in between bridging and terminal bonding profile and is usually labeled as asymmetric bridging carbonyls.

➤ 5. Calculation of CO Bond Order

Owing to the well-known fact that the highest occupied molecular orbital (HOMO) set in carbonyl ligand is of antibonding nature, a close correlation between the magnitude of backbonding and carbon-oxygen bond order can easily be established. The vibrational frequency of a bond depends upon the strength of the bond (which is measured by its force constant), and is given as:

$$v_{CO}(\text{cm}^{-1}) = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (1)$$

Where k is the force constant and μ is the reduced mass. The physical significance of k is implied in the fact that it is proportional to the strength of the bond involved. Therefore, any factor that increases the electron density on CO group will decrease its bond order and its force constant; and the vice-versa is also true. In other words, the decrease in v_{CO} indicates a decrease in CO bond order while the increase in carbonyl stretching is associated with increasing CO bond order. For instance, the infrared absorption of free CO occurs at 2143 cm^{-1} while the metal coordinated CO absorbs generally in the range of $2120\text{-}1800 \text{ cm}^{-1}$. This clearly establishes the fact that metal to ligand back donation does occur which in turn reduces its bond order. Hence, the accumulation of positive charge or the deficiency of electron density will impart a larger CO bond order than neutral or ionic carbonyl complexes. Consider the following trend in isoelectronic-isostructural carbonyls.

Compound	$[\text{Ni}(\text{CO})_4]$	$[\text{Co}(\text{CO})_4]^{1-}$	$[\text{Fe}(\text{CO})_4]^{2-}$
$v_{CO} (\text{cm}^{-1})$	2046	1890	1730
M-C Bond order	1.33	1.89	2.16
C-O Bond order	2.64	2.14	1.85
M-C + C-O Bond order	3.97	4.03	4.01

A similar trend is observed in the case of mixed carbonyls i.e. metal carbonyls having some other ligands alongside CO group. If the other ligand is electron-withdrawing in nature, it would attract the electron density from the metal center, which in turn would oppose the metal-carbonyl back bonding, yielding somewhat higher carbon-oxygen bond order and higher carbonyl stretching frequency. On the other hand, If the other ligand is electron-donating in nature, it would donate the electron density to the metal center, which in turn would support the metal-carbonyl back bonding, yielding somewhat lower carbon-oxygen bond order and lower carbonyl stretching frequency.

Compound	$[\text{Ni}(\text{CO})_4]$	$[\text{Ni}(\text{PF}_3)(\text{CO})_3]$	$[\text{Ni}(\text{PMe}_3)(\text{CO})_3]$
$v_{CO} (\text{cm}^{-1})$	2046	1990	1980

Hence, the bond order of CO in $[\text{Ni}(\text{PMe}_3)(\text{CO})_3]$ is definitely lower than in $[\text{Ni}(\text{PF}_3)(\text{CO})_3]$ because PMe_3 is a weaker π -acceptor than PF_3 ligand.

➤ 6. Study of Reaction Kinetics in Metal Carbonyls

Infrared spectroscopy is a very useful tool in the determination of reaction kinetics of metal carbonyl complexes. From Beer's Lambert Law, we know that the absorbance (A) is related to concentration (c) and path length (l) of the sample as:

$$A = \epsilon cl = \log \frac{1}{T} \quad (1)$$

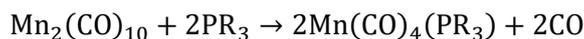
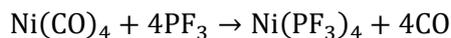
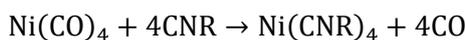
Where ϵ is the molar extinction coefficient and T is the transmittance of the solution. Therefore, the rate of disappearance or appearance of a characteristic infrared absorption band can be used to estimate the rate of change of concentration for the corresponding reactant or product. In other words, the rate of intensity decrease in IR peaks of reactant, or the rate of intensity increase in IR peaks of product metal carbonyl is proportional to the rate of change of concentration; which in turn enable us to record various kinetic parameters from reaction order to activation energy or rate constants.

❖ Important Reactions of Metal Carbonyls

Metal carbonyls are important precursors for the synthesis of a mixed carbonyl or some important organometallic complexes. Some of the main reactions shown by metal carbonyls are discussed below.

➤ 1. Ligand Displacement Reactions

The displacement or substitution of CO ligands can be induced photochemically or thermally by some other donor ligands. The ligand-domain is quite wide and comprises of cyanide (CN^-), phosphines, nitrogen donors, and ethers also. Olefins are very effective ligands that can afford synthetically useful derivatives. The displacement reaction in 18-electron complexes usually follows a dissociative pathway, via a 16-electron intermediate complex. The ligand-displacement-rate in 18-electron complexes is catalyzed by catalytic amounts of oxidants through the electron-transfer phenomena. The displacement in 17-electron complexes proceeds via an associative route with a 19-electron intermediate complex. It is worthy to note that the replacement by bidentate ligands like *o*-phenanthroline(*o*-phen) and *o*-phenylene-bis(dimethyl arsine) (diars) occurs in the multiple of two for carbonyl groups. For example:



The displacement reactions in metal carbonyls also point toward the differences in the bonding nature of the attached ligands. For instance, radiochemical tracer studies for $\text{Mn}(\text{CO})_5\text{Br}$ have unveiled that only four carbonyl groups undergo exchange with ^{14}CO .



In the structure of $\text{Mn}(\text{CO})_5\text{Br}$, four carbonyl groups undergoing exchange phenomena are present in the same plane; which means that the CO group trans to bromido is bound more firmly because the Br group is not competition for π -backbonding. On the other hand, four in-plane CO groups compete with each other all of them are good acceptors, causing a labilization of each other.

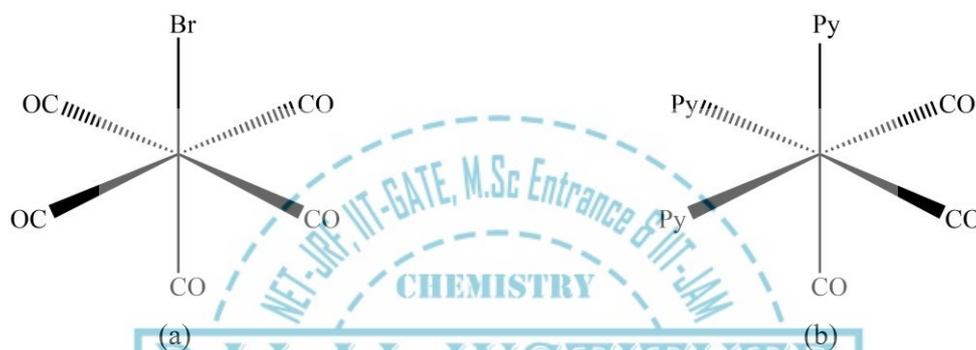
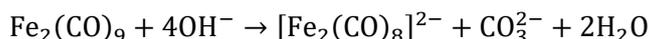
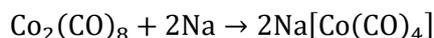
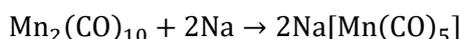
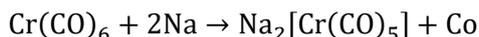


Figure 14. The structures of (a) $\text{Mn}(\text{CO})_5\text{Br}$ and (b) $\text{Mn}(\text{CO})_3(\text{Py})_3$.
 (info@dalalinstitute.com, +91-9802825820)
 www.dalalinstitute.com

Furthermore, the reaction of $\text{Mn}(\text{CO})_6$ with py always results in the formation of a facial isomer of $\text{Mn}(\text{CO})_3(\text{py})_3$ i.e. all the three carbonyl groups are located trans to the py ligands. This is obviously due to the fact that the extent of π -donation to the three CO groups is maximum in facial configuration, owing to the difference in the ability of CO and py for π -backbonding. When entering ligands are very good π -acceptors, all the carbonyl groups may be displaced, just in $\text{Ni}(\text{CO})_4$ where PF_3 ligands lead to the formation of $\text{Ni}(\text{PF}_3)_4$.

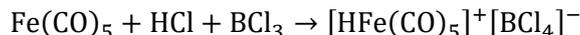
➤ 2. Formation of Carbonylate Anions

It is quite a well-known fact that many carbonylate anions like $[\text{Fe}(\text{CO})_4]^{2-}$, $[\text{Co}(\text{CO})_4]^-$, $[\text{Mn}(\text{CO})_5]^-$ and $[\text{V}(\text{CO})_6]^-$ follow the effective atomic number (EAN) rule. These ions are generally synthesized either by the reaction of metal carbonyl with a strong reducing agent or by the reaction with strong bases.



➤ **3. Formation of Carbonylate Cations**

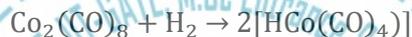
Carbonylate cations are not as common as carbonylate anions and can be synthesized either by the protonation of metal carbonyl in strong acids or, by the reaction with carbon monoxide and some Lewis acids.



The use of strong acids succeeded in preparing gold carbonyl cations such as $[\text{Au}(\text{CO})_2]^+$, which is used as a catalyst for the carbonylation of olefins. The cationic platinum carbonyl complex $[\text{Pt}(\text{CO})_4]^+$ can be prepared by working in so-called super acids such as antimony pentafluoride.

➤ **4. Synthesis of Metal Carbonyl Hydrides**

Carbonyl hydrides are generally synthesized either by the acidification of the solutions containing the corresponding carbonylate anion, or by the reactions of metal carbonyls with hydrogen. For instance:

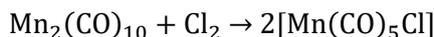
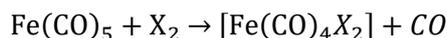


Some of the metal carbonyl hydrides can be prepared by direct reaction of the metal with CO and H₂. For example:

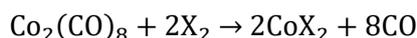
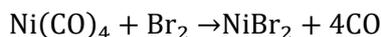


➤ **5. Synthesis of Metal Carbonyl Halides or Metal Halides**

The metal carbonyl complexes are relatively unreactive toward many electrophiles; however, most metal carbonyls do undergo halogenation. For example, Fe(CO)₅ forms ferrous carbonyl halides. In some reactions, metal-metal bonds are also broken by halogens. On the basis of the electron-counting scheme used, this can be considered as oxidation of the metal center.

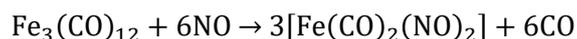
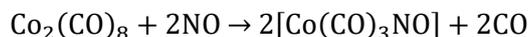


Furthermore, some metal carbonyls also get decomposed into metal halides when treated with halogens as:



➤ **6. Formation of Metal Carbonyl Nitrosyls or Metal Nitrosyls**

The metal carbonyl complexes react with nitrosyl ligand to form either metal carbonyl nitrosyls or metal nitrosyl complexes. For example:



The displacement of carbonyl by the nitrosyl cation may be achieved using $[\text{NO}][\text{BF}_4]$ i.e. nitrosyl tetrafluoroborate. On applying to the hexacarbonyls of tungsten and molybdenum, the NO binds to the metal. Some indirect methods involve the use of NO group from some other species, usually accompanied by oxidation and reduction processes. For instance, the brown ring test in which the nitric oxide ligand is actually supplied by the nitrate ion.

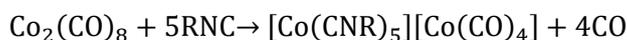
➤ **7. Disproportionation Reactions**

Many metal carbonyls show disproportionation reactions when exposed to some other coordinating ligands. For instance, $\text{Fe}(\text{CO})_5$ reacts with amines to produce hexaaminoiron(II) tetracarbonylferrate(−II); or $\text{Co}_2(\text{CO})_8$ reacts with amine to form Hexaamminecobalt(II) bis-tetracarbonylcobaltate(−I) as:



The driving force for the above two reactions can be understood in terms of the ease of formation of the carbonylate ions and the favorable coordination number for iron(II) involved. The disproportionation in both cases generates a positive metal center and a metal center with a negative oxidation state. The carbonyl ligand, being a soft base, prefers to bind to the softer acids, i.e., metal center with negative charge; on the other hand, the ligands with nitrogen as donor site are hard Lewis bases, and therefore, prefer to bind to the harder acid i.e. metal center with more positive charge on it.

A variety of carbonylate complexes can be synthesized via these disproportionation reactions which makes this type quite important as far as the practical applications are concerned. For example, the $[\text{Ni}_2(\text{CO})_6]^{2-}$ anion and $[\text{Co}(\text{CNR})_5][\text{Co}(\text{CO})_4]$ can be synthesized by the following reactions.:



It is also worthy to note that the range of coordinating agents that will cause disproportionation is rather wide.

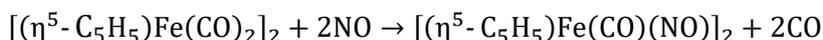
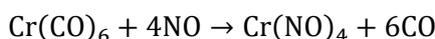
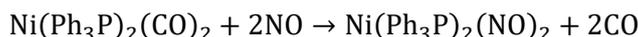
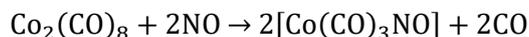
❖ Preparation, Bonding, Structure and Important Reactions of Transition Metal Nitrosyl, Dinitrogen and Dioxygen Complexes

Besides carbon monoxide, there are many other important ligands which form π -complexes with transition metal center; some of them are NO, N₂ and O₂ molecules. The methods of preparations, nature of bonding, structure and their important reactions are discussed in detail below.

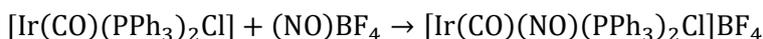
➤ 1. Metal Nitrosyl Complexes

Metal nitrosyls are the complexes that contain nitric oxide (NO) bonded to a metal center (usually transition element). There are various kinds of nitrosyl complexes known so far, which vary in respect of coligand, structure and nature of bonding. Metal complexes having nitrosyl ligands only are labeled as isoleptic nitrosyls. They are very rare, one of the special members of this class is Cr(NO)₄. On one hand, polycarbonyl complexes are very much common, even trinitrosyl complexes are rare on the other.

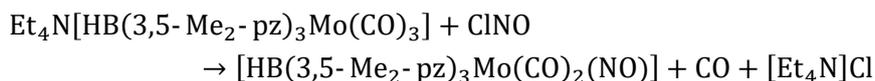
Preparation: i) Metal nitrosyl complexes can be prepared via many routes, but direct formation from nitric oxide gas is much more common. For example:



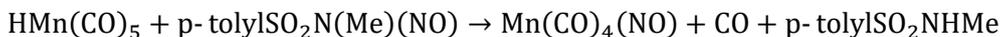
ii) From nitrosonium salts:



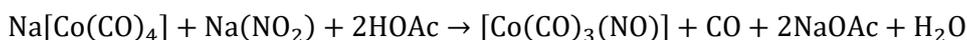
iii) From nitrosyl halides:



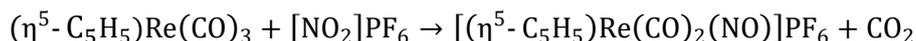
iv) From N-nitrosamides:



v) From nitrite salts:



vi) From nitronium (NO₂⁺) salts:



Bonding: Most of the metal nitrosyl complexes can be viewed as derivatives of the nitrosyl cation (NO^+) or anion (NO^-). The nitrosyl cation (with a bond order of 3) 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. However, the bond order of neutral nitrosyl and anion are 2.5 and 2, respectively; and therefore, in order to rationalize the nature of the bonding between metal center and the nitrosyl ligand, we must understand molecular orbital diagram for the nitrosyl ligand first.

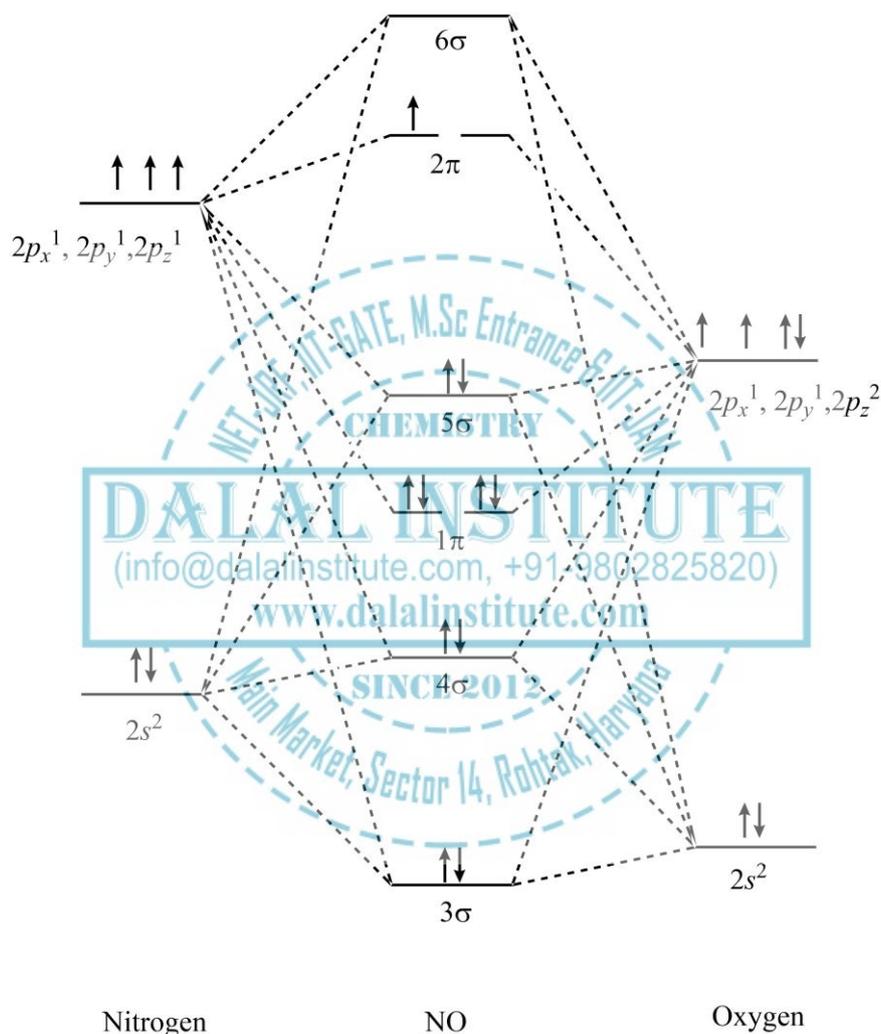


Figure 15. The molecular orbital diagram of nitric oxide (NO).

After looking at the molecular orbital diagram for NO, one can immediately recognize the difference from the carbonyl ligand that there is one extra electron in the π^* -orbital. This suggests that NO ligand can be one, two or three electron donors, depending upon the type of orbital used in bonding. If the electron present in π^* -orbital resides on NO, i.e., not transferred to the metal center, nitrosyl ligand would behave as a two-

electron donor, and the nature of metal complex should be paramagnetic. There are some nitrosyl complexes of iron and cobalt such as $[\text{Fe}(\text{NO})_2(\text{CO})_2]$ and $[\text{Co}(\text{NO})(\text{CO})_3]$, which were thought to be derived from neutral NO ligand but these compounds are diamagnetic in nature; and therefore do not contain unpaired electrons. This suggests that the nitrosyl ligand is not neutral in these complexes. This assumption is also supported by the fact that the displacement of a previously attached ligand by any other neutral ligand in metal carbonyl nitrosyl complexes is always accompanied by the release of CO group. Moreover, there are also many complexes like $[\text{Cr}(\text{NO})(\text{CN})_5]^{3-}$ and $[\text{Mn}(\text{NO})(\text{CN})_5]^{2-}$, which are actually paramagnetic and were also thought to be having neutral nitrosyl ligand. However, in the later years, it was found that the unpaired electron of the nitrosyl group is actually transferred to the metal center making NO as NO^+ ligand. Thus, we can say that the coordination of neutral nitrosyl is highly unlikely.

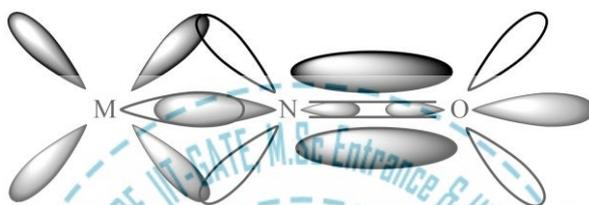
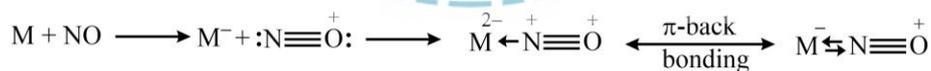


Figure 16. The nature of σ and π overlap in metal nitrosyl complexes.

i) *Complexes containing NO^+* : Nitric oxide molecule can easily release the odd electron from its antibonding molecular orbital to form a stable nitrosonium ion (NO^+). This is also very obvious from the comparison of infrared absorption wavenumbers of free NO (1880 cm^{-1}) with the nitrosonium salts ($2200 - 2300 \text{ cm}^{-1}$); and can be explained in terms of increased bond order from 2.5 to 3, and consequently the force constant value. Actually, most of the metal nitrosyls exist with nitrosyl ligand as three electron donor. For instance, the effective atomic numbers (EAN) for $[\text{Mn}(\text{CO})(\text{NO})_3]$ and $[\text{Fe}(\text{NO})_2(\text{CO})_2]$ complexes are 36 for each, which is possible only if the NO ligand act as NO^+ i.e. three electron donor.



In the initial step, the π^* electron of the NO transfers to the metal center, reducing M to M^- and itself forming NO^+ ion. Then NO^+ donates a lone pair of electron via N just like the carbon in metal carbonyls. However, the total number of electrons donated by NO, in this case, would be three while carbonyl can donate only two. The back donation of electron charge from filled d -orbital of metal to π^* -orbital of NO would result in a considerable decrease in the nitrogen-oxygen bond order. The infrared absorption peak of NO^+ in metal nitrosonium complexes lies in the range of $1900 - 1600 \text{ cm}^{-1}$ which is far less than what has been observed in nitrosonium ionic salts. Moreover, the magnitude of decrease in carbonyl stretching frequency is less than the magnitude of decrease in nitrosonium stretching frequency as we go from their corresponding free unit to metal-coordinated unit. This, therefore, confirms the better π -acceptor strength of NO^+ ligand; which is further increased by an accumulation of negative charge on nitrosonium complexes.

ii) *Complexes containing NO⁻*: Nitric oxide molecule can also accept an electron from the metal center to its antibonding molecular orbital forming a NO⁻ ion. The metal center in this process would get oxidized from Mⁿ⁺ to M⁽ⁿ⁺¹⁾⁺ ion. Then the NO⁻ ion donates a lone pair of electron via N just like the carbon in metal carbonyls. However, the total number of electrons donated by NO, in this case, would be one while the carbonyl can donate only two. The infrared absorption wavenumbers of NO⁻ in metal nitrosyl complexes are found in the range of 1100–1200 cm⁻¹ (much lower than NO), which can be explained in terms of complete transfer of one electron from *d*- π orbital of metal center to antibonding molecular orbital on nitrosyl ligand. For example, during the formation of [Co(CN)₅(NO)]³⁻ and [Co(NH₃)₅(NO)]²⁺ complexes (passing NO through amine and cyanide salts of Co²⁺), the Co(II) gets converted into low spin Co(III) with *t*_{2g}⁶ configuration. Both of these complexes, in respect of charge and magnetic moment, resemble [Co(CN)₅Br]³⁻ and [Co(NH₃)₅Cl]²⁺, respectively.

In nitrosyl complexes, the M–N–O unit is generally linear, or no more than 15° from linear. However, in some complexes, especially where back-bonding is not that much important, the M–N–O angle can largely deviate from 180°. The linear and bent NO ligands can be differentiated using infrared spectroscopy. The linear M–N–O groups absorb in the range 1650–1900 cm⁻¹ (close to metal coordinated NO⁺); whereas the bent nitrosyls absorb in the range 1525–1690 cm⁻¹ (close to metal coordinated NO⁻). The difference of vibrational frequencies reflects the difference in N–O bond orders for linear (triple bond) and bent NO (double bond). The bent NO ligand is sometimes described as the anion, NO⁻. Prototypes for such compounds are the organic nitroso compounds, such as nitrosobenzene. A complex with a bent NO ligand is trans-[Co(en)₂(NO)Cl]⁺. 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 π -symmetry.



Complexes with " π -electrons" in excess of 6 tend to have bent NO ligands. Thus, [Co(en)₂(NO)Cl]⁺, with seven electrons of π -symmetry (six in *t*_{2g} orbitals and one on NO), adopts a bent NO ligand, whereas [Fe(CN)₅(NO)]³⁻, with six electrons of π -symmetry, adopts a linear nitrosyl. In a further illustration, the M–N–O *d*-electron count of the [Cr(CN)₅NO]³⁻ anion is shown. In this example, the cyanide ligands are "innocent", i.e., they have a charge of -1 each, -5 total. To balance the fragment's overall charge, the charge on Cr–N–O is thus +2 (-3 = -5 + 2). Using the neutral electron counting scheme, Cr has 6 *d*-electrons and NO has one odd electron for a total of 7. Two electrons are subtracted to take into account that fragment's overall charge of +2, to give 5. Written in the Enemark-Feltham notation, the *d*-electron count in Cr–N–O unit is five. The results are the same if the nitrosyl ligand were considered NO⁺ or NO⁻.

Structure: The structure of metal nitrosyls can mainly be classified into three categories; first as the metal-complex systems that contain NO as a terminal ligand only, the second one as having only bridging nitrosyl group, and the third one with nitrosyl groups with the terminal as well as bridging profile.

i) *Metal complexes with terminal nitrosyl:* The NO group as a monodentate ligand in metal complexes acts either as a 12-electron unit (when NO^- forms a single bond with the metal center and M–N–O unit is linear), or as a 10-electron unit (when NO^+ forms a multiple bonds with the metal center and M–N–O unit is bent).

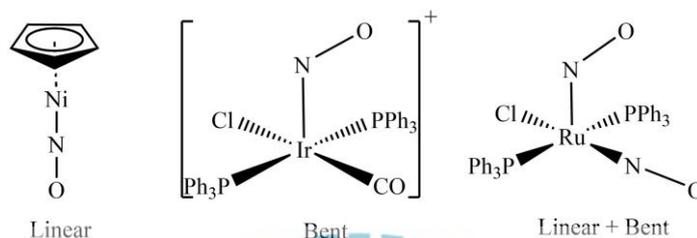


Figure 17. Metal complexes with terminal nitrosyls.

ii) *Metal complexes with bridging nitrosyl:* In some of the metal nitrosyl complexes, all NO groups are present in bridging mode. One of the common examples is given below.

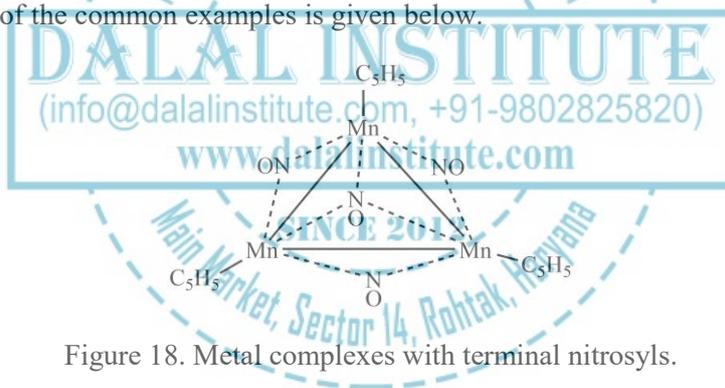


Figure 18. Metal complexes with terminal nitrosyls.

iii) *Metal complexes with the terminal as well as bridging nitrosyl:* In some of the metal nitrosyl complexes, NO groups are present in the terminal as well as in bridging mode. Some of the common examples are:

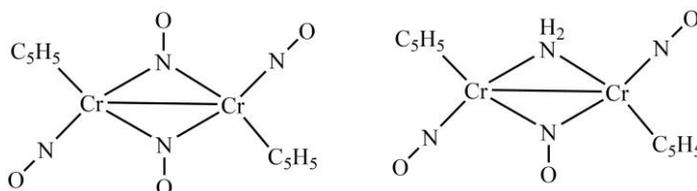
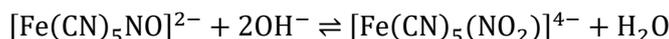
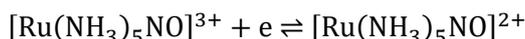
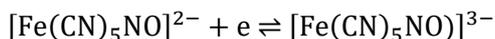


Figure 19. Metal complexes with terminal nitrosyls.

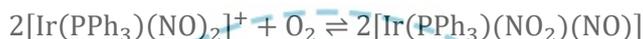
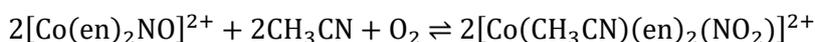
Reactions: i) The nucleophilic attack:



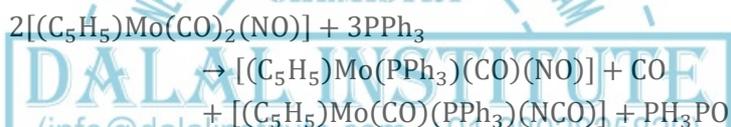
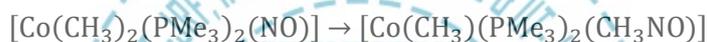
ii) Reduction of metal nitrosyls:



iii) Reactions of nitrosyls with electrophiles:



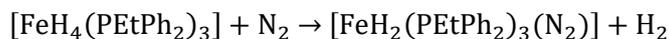
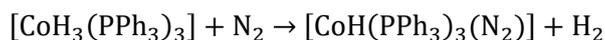
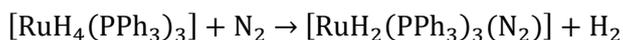
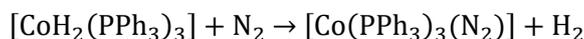
iv) Formation of carbon-nitrogen bonds:



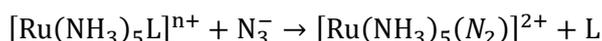
➤ 2. Metal Dinitrogen Complexes

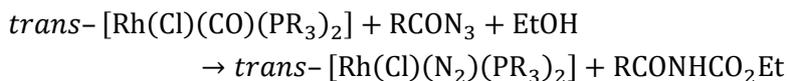
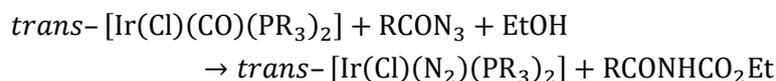
Metal dinitrogen complexes are the coordination compounds that contain the dinitrogen ligand (N_2) attached to a metal center. The first complex of dinitrogen, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ was reported by Allen and Senoff in 1965, which is consisted of a 16e- $[\text{Ru}(\text{NH}_3)_5]^{2+}$ center attached to one end of N_2 . The interest in such complexes arises because N_2 comprises the majority of the atmosphere and there are many useful compounds containing nitrogen atoms.

Preparation: i) Metal dinitrogen complexes can be prepared via many routes, but direct formation from dinitrogen is very common. For example:

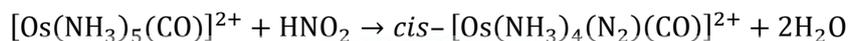


ii) From compounds containing chains of nitrogen atoms:





iii) Preparations in which two nitrogen atoms are combined to give a dinitrogen group:



Bonding: In order to rationalize the nature of the bonding between the metal center and the N_2 , we must understand the bonding within the dinitrogen ligand first. The molecular orbital diagram for N_2 is given below.

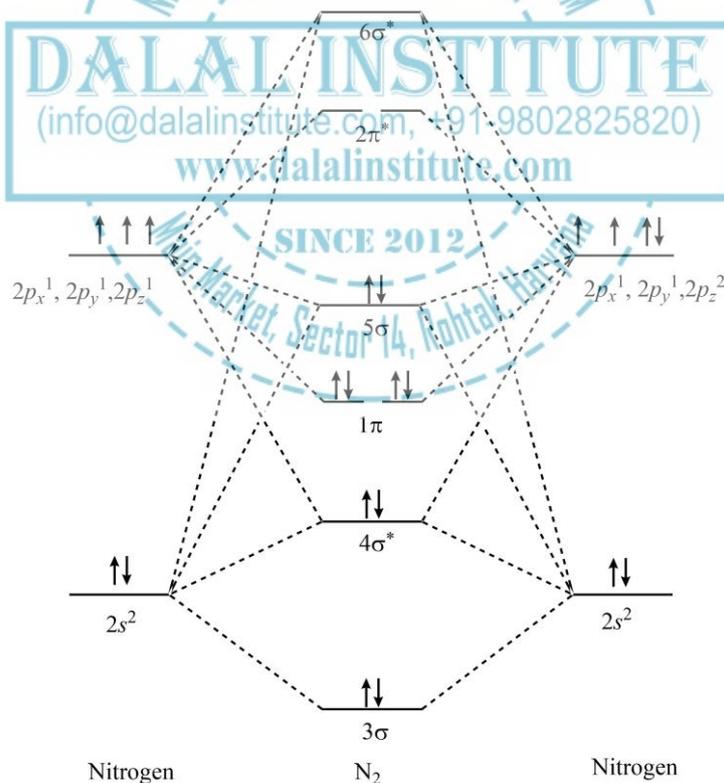


Figure 20. The molecular orbital diagram of dinitrogen molecule.

Though the N_2 molecule is isoelectronic with CO and NO^+ , it does not form a large number of metal complexes like the two. This is obviously due to the fact that it is a poor ligand and cannot act as a strong π -acceptor due to the lack of polarity. In other words, N_2 ligand is neither a good σ -donor nor good π -acceptor as there is no polarity in N–O bond. The different bridging modes of dinitrogen ligand are given below.

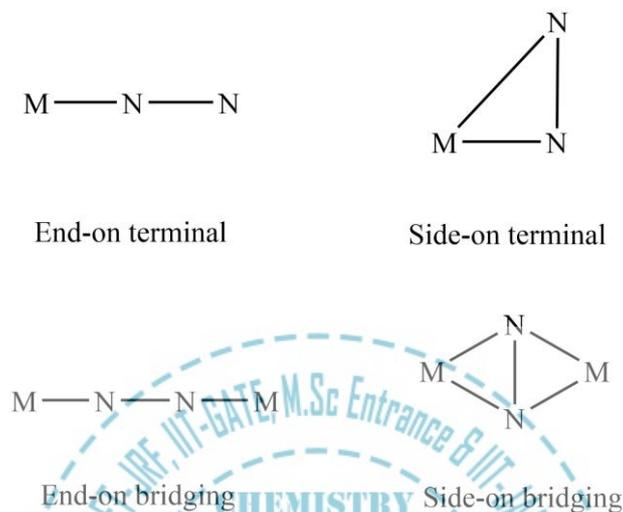


Figure 21. Bonding modes of N_2 ligand in metal-dinitrogen complexes.

The most common binding mode of dinitrogen ligand with transition metal center is end-on i.e. just like in the case of isocyanides, carbon monoxide and nitric oxide. These observations are also supported by the theoretical treatment of some dinitrogen complexes which indicated that end-on bonding is more beneficial than side on as far as the stability of the complex is concerned. The end-on bonding involves the donation of the lone pair of N_2 to the empty metal orbital and, the back-donation from filled metal d -orbital to the empty π^* orbitals of N_2 ligand. In contrast, the side-on bonding comprises of electron donation from the π and σ bonding molecular orbital of the dinitrogen to the empty orbitals of the metal and the back-donation of electron density from filled orbitals of the metal to the π^* molecular orbital of the N_2 ligand. Though the side-on bonding mode is quite common in metal-acetylenes and metal-olefin complexes, there are very few reports of side-on bonded dinitrogen complexes. Consider the example of $[Ru(NH_3)_5(N_2)]^{2+}$ complex, Ru–N bond length in Ru–N–N unit is shorter than Ru–N bond length in Ru– NH_3 unit. This shows that there is some extent of backbonding from filled d -orbital the metal center to the empty π^* molecular orbital of dinitrogen. This is also very obvious from the vibrational Raman stretching frequency of free N_2 (2331 cm^{-1}) and infrared active stretching frequency of metal coordinated ligand (2105 cm^{-1}) in $[Ru(NH_3)_5(N_2)]Cl_2$ complex. However, it is also worthy to note that metal-carbon bond in carbonyl complexes is stronger than the metal-nitrogen bond in dinitrogen complexes, which shows that CO is definitely a stronger σ -donor a better π -acceptor as highest occupied molecular orbital (HOMO) is predominantly concentrated on carbon due to high polarity.

Structure: The structures of metal-dinitrogen complexes can mainly be classified into two categories; metal-complex that contains N_2 as an end-on ligand and with N_2 group as a side-on ligand.

i) *Metal complexes with end-on dinitrogen:* As a ligand, N_2 usually binds to metals as an end-on ligand, as illustrated by Allen and Senoff's complex. Such complexes are usually analogous to related CO derivatives.

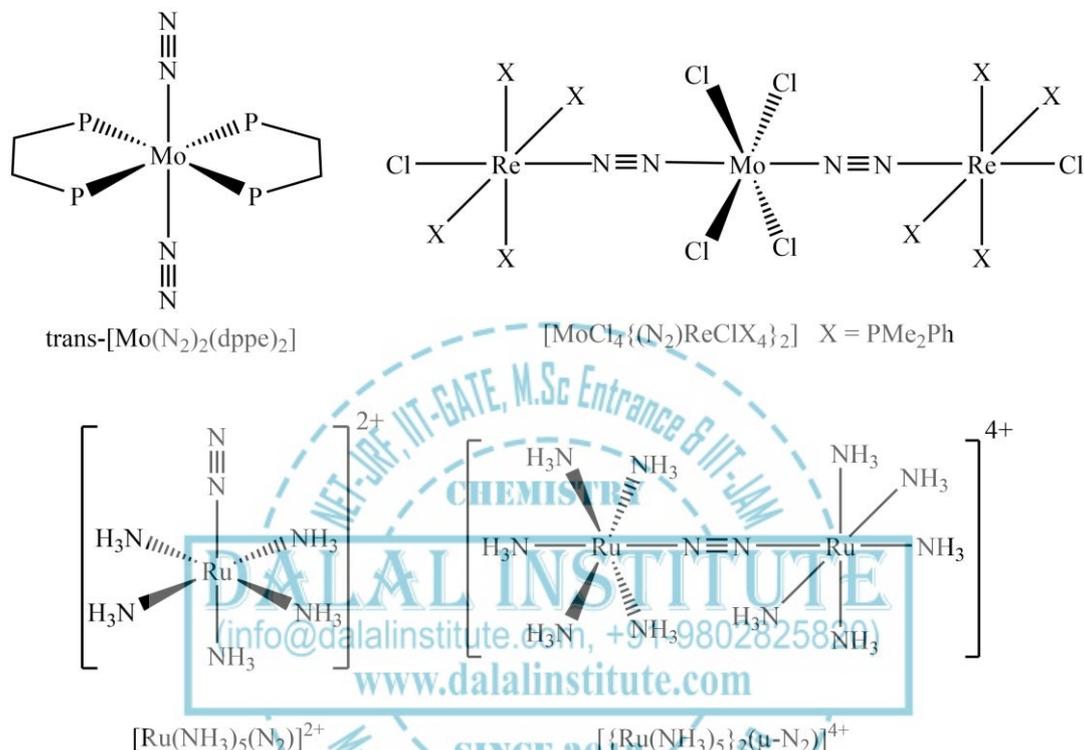


Figure 22. Metal-dinitrogen complexes with end-on N_2 ligand.

ii) *Metal complexes with side-on dinitrogen:* In some of the metal-dinitrogen complexes, the N–N vector is perpendicular to the M–M vector. Some of the most common examples are given below.

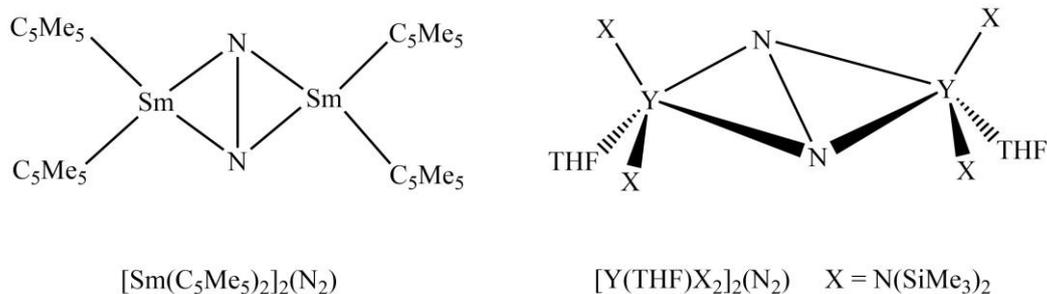
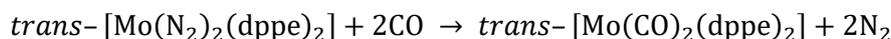
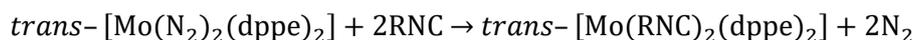
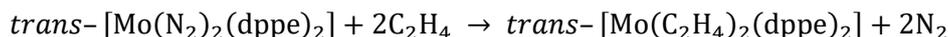
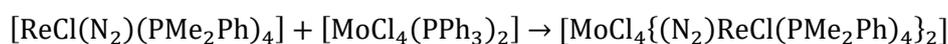
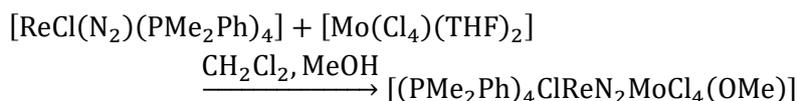


Figure 23. Metal-dinitrogen complexes with side-on N_2 ligand.

Reactions: i) The displacement of dinitrogen ligand by some other groups:



ii) Reactions of Ligating N_2 with Lewis Acids:



iii) Formation of metal-hydrazido complexes from ligating N_2 :



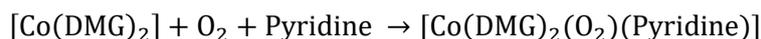
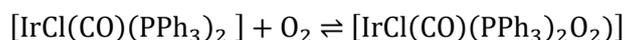
iv) Formation of carbon-nitrogen bonds:



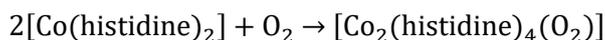
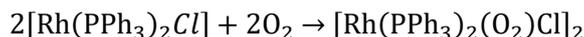
➤ 3. Metal Dioxygen Complexes

Metal dioxygen complexes are the coordination compounds which contain O_2 ligand attached to a metal center. The principal driving force behind the analysis of these compounds are oxygen-carrying proteins such as myoglobin, hemoglobin, hemocyanin, and hemerythrin. Many transition metals form complexes with O_2 , and many of these complexes form reversibly. The binding of O_2 is the first step in many important phenomena, such as cellular corrosion, respiration and in industrial chemistry. The first synthetic oxygen complex was demonstrated in 1938 with Co^{2+} complex reversibly bound O_2 . Most of the organometallic metal-dioxygen complexes are synthesized by the reaction of gaseous molecular oxygen with complexes (having d^7 , d^8 , or d^{10} electronic configuration) solution.

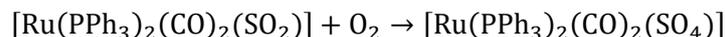
Preparation: i) Formation of a mononuclear dioxygen adduct with or without displacement of ligands



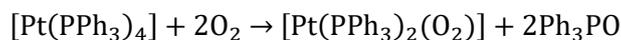
ii) Formation of a dimer or a binuclear dioxygen adduct:



iii) Oxidation of ligands with the oxidized ligand remaining coordinated:



iv) Displacement of free oxidized ligand:



Bonding: The nature of bonding in metal-dioxygen complexes is usually evaluated by single-crystal X-ray crystallography, focusing both on the overall geometry as well as the O–O distances, which reveals the bond order of the O₂ ligand. However, in order to rationalize the initial idea of the metal-ligand bonding, we must understand the bonding within the dioxygen ligand first. The molecular orbital diagram for O₂ is given below.

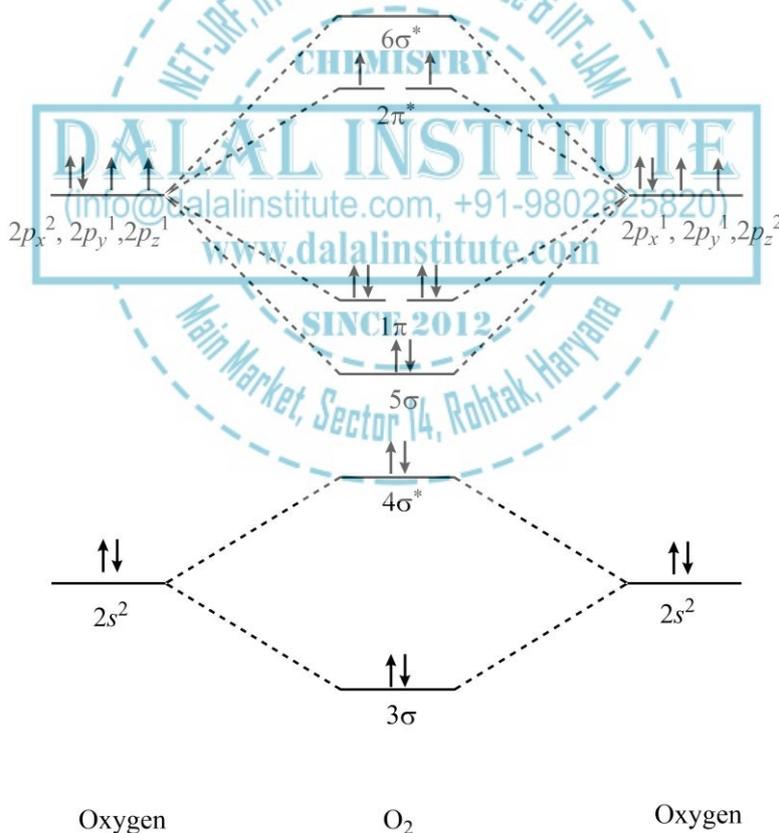


Figure 24. The molecular orbital diagram of the dioxygen molecule.

The experimental results show that the bent structure of the dioxygen unit in oxyhemoglobin is actually diamagnetic in nature; which suggests that π^*2p_x and π^*2p_y orbitals are not completely degenerate in the complex as they are in free dioxygen. A linear M–O–O structure would result in a degenerate set of π^*2p_x and π^*2p_y orbitals with a triplet state. In addition to the σ -bonding, there are two types of interactions between the d -orbitals of the metal and the π^* orbitals of the dioxygen. One is through an overlap of the $3d_{xz}$ of the metal with the π^* orbitals perpendicular to the Fe–O–O plane; while the other is through the overlap of the $3d$ orbital of the metal with the π_y^* orbital in the Fe–O–O plane. The different bridging modes of dinitrogen ligand are given below.

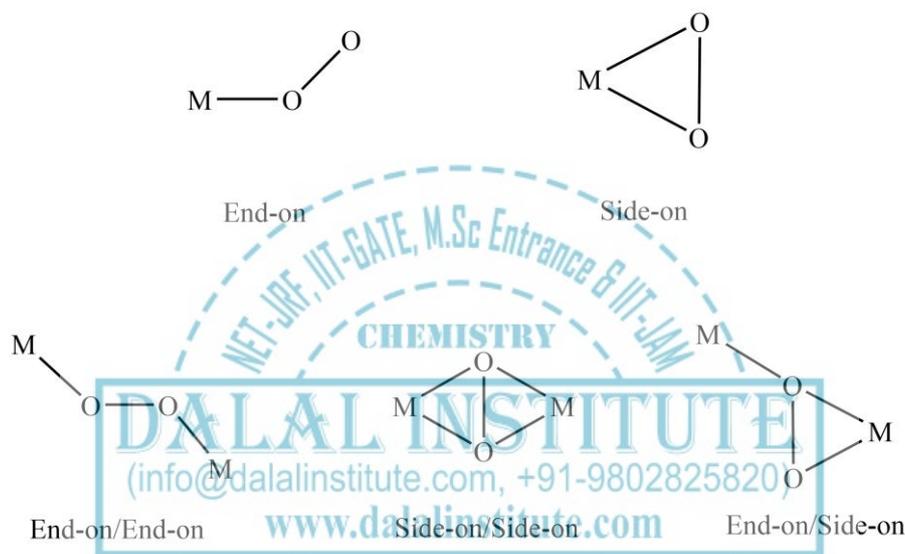


Figure 25. Bonding modes of O_2 ligand in metal-dioxygen complexes.

The O_2 ligand binds to a single metal center either end-on (η^1 -) or in a side-on (η^2 -) manner. Dioxygen adducts derived from Co^{2+} and Fe^{2+} complexes of porphyrin (and related anionic macrocyclic ligands) exhibit this bonding mode. The hemoglobin and myoglobin are two famous examples, and many other synthetic analogs have been reported which behave in a similar manner. Binding of O_2 is usually described as proceeding by electron transfer from the metal(II) center to give superoxide (O_2^-) complexes of metal(III) centers. The η^2 -bonding is the most common motif seen in the coordination chemistry of dioxygen. Since O_2 has a triplet ground state and Vaska's complex is a singlet, the reaction is slower than when singlet oxygen is used. Complexes containing η^2 - O_2 ligands are fairly common, but most are generated using hydrogen peroxide, not O_2 . The O_2 can bind to one metal of a bimetallic unit via the same modes discussed above for mononuclear complexes. A well-known example in nature is hemerythrin, which features a diiron carboxylate that binds O_2 at one Fe center. The dinuclear complexes can also cooperate in the binding, although the initial attack of O_2 probably occurs at a single metal. These binding modes include μ^2 - η^2 , η^2 -, μ^2 - η^1 , η^1 -, and μ^2 - η^1 , η^2 -. Depending on the degree of electron-transfer from the dimetal unit, these O_2 ligands can again be described as peroxo or superoxo. In nature, such dinuclear dioxygen complexes often feature copper.

Structure: The structures of metal-dioxygen complexes can mainly be classified into two categories; the first one as the metal-complex that contains dioxygen (O_2) ligand attached to one metal center and the second one with O_2 group connected to two or more metal centers. A brief discussion on both of the categories is given below with suitable examples.

i) *Mononuclear metal-dioxygen complexes:* As a ligand, O_2 can bind to a single metal-center either as an end-on ligand or as a side-on ligand. The structures of some representative metal-dioxygen complexes of such type are given below.

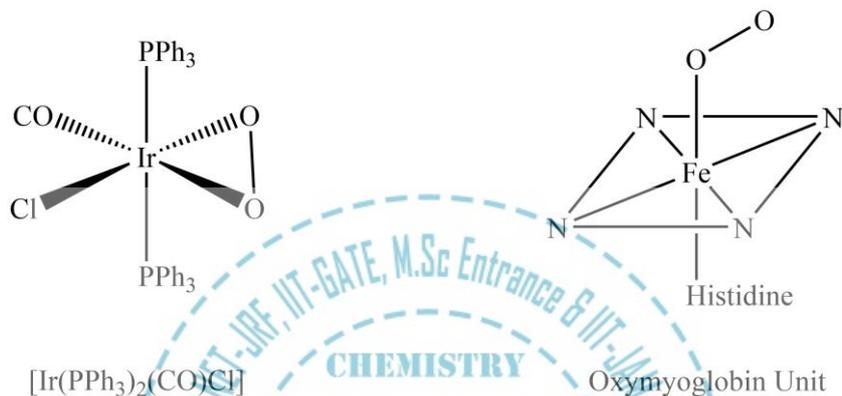


Figure 26. Mononuclear metal- O_2 complexes.

ii) *Binuclear metal-dioxygen complexes:* In binuclear metal-dioxygen complexes, the O_2 molecule can bind either to one or both metals center as an end-on/end-on, end-on/side-on and side-on/side-on ligand. The structures of some representative metal-dioxygen complexes of such type are given below.

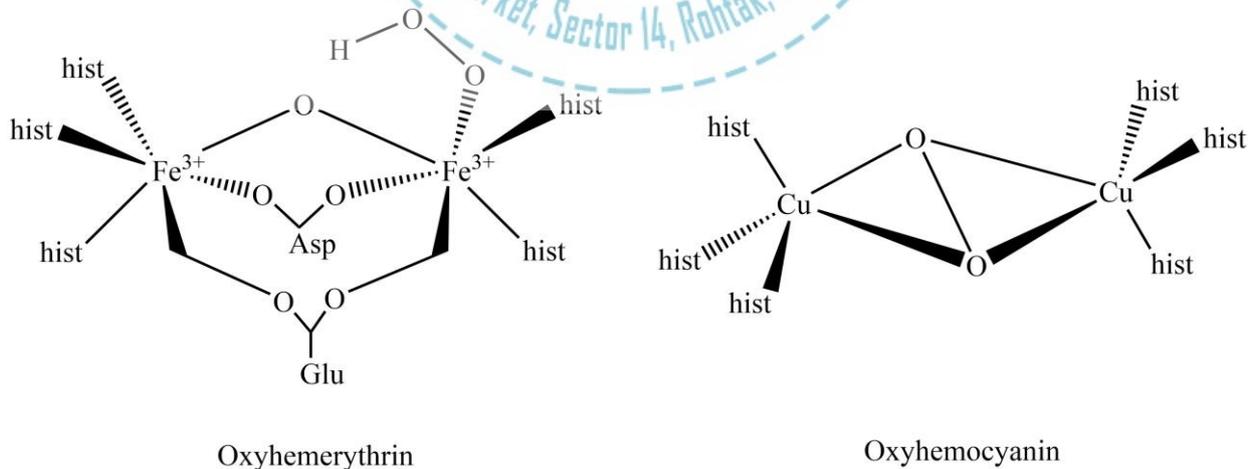
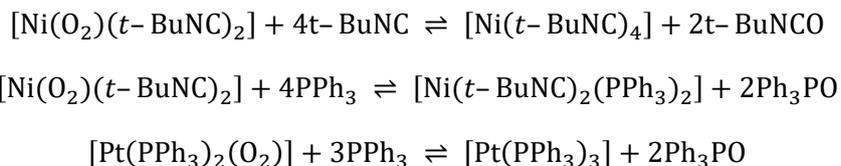
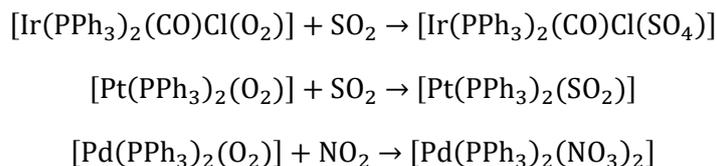


Figure 27. Metal-dioxygen complexes with side-on O_2 ligand.

Reactions: i) The displacement of molecular oxygen by some other ligand:



ii) The formation of complexes of oxidized substrates:

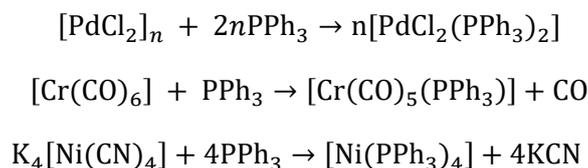


❖ Tertiary Phosphine as Ligand

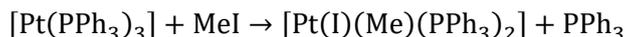
The compound phosphine (PH_3) is extremely important in coordination chemistry due to its large number of derivatives which can be used as L-type ligands (2 electron donor neutral ligands) for many metal complexes. These phosphine based ligands are the compounds with the formula $\text{PR}_n\text{H}_{3-n}$, and are often classified according to the value of n ; the values 1, 2, 3 correspond to primary, secondary and tertiary phosphines, respectively. For instance, the most popular phosphine ligand used in organometallic chemistry is triphenylphosphine, which is obviously a tertiary phosphine. All of these phosphine ligands adopt pyramidal structures that are quite favorable for the metal center to be approached. Unlike most metal ammine complexes, metal phosphine complexes tend to be lipophilic, showing very good solubility in organic solvents. They also are compatible with metals in multiple oxidation states. Therefore, owing to these two features, metal phosphine complexes are quite useful in homogeneous catalysis.

➤ General Methods of Preparation and Reactivity

The first phosphine complexes were *cis*- and *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$, reported by Cahours and Gal in 1870. Being a L-type ligand, the phosphines do not change the overall charge of the metal complex. These complexes may simply be prepared by the addition of phosphines to a coordinatively unsaturated metal precursor, or by ligand displacement of another L-type complex, such as a solvent molecule acting as a ligand. However, it should also be noted that the replacement of X-type ligand (1-electron donor neutral ligand) can also yield such complexes.



As far as the reactivity is concerned, the nature of phosphine ligands is a spectator rather than the actor. Coordinated phosphines generally do not participate in chemical reactions, except their dissociation from the metal center. However, in some high-temperature hydroformylation processes, the scission of phosphorus–carbon bonds is also observed. The thermal stability of phosphine ligands is enhanced when they are incorporated into pincer complexes. Some complexes dissociate in solutions to yield a product with a lower coordination number.



➤ **Structure and Bonding in of Tertiary Phosphine Complexes**

The metal-phosphine complexes are not considered as the organometallic compounds because of the lack of metal-carbon bonds. However, many good inorganic textbooks discuss them in their organometallic section due to their excellent bonding similarities with the carbonyl ligand. For instance, phosphines can act as very good σ -donors as well as respectable π acceptors just like CO ligand. The σ -donation occurs via a hybrid lone pair on phosphorus and the π -acceptance in orbitals that are a mixture of empty d -orbital on phosphorus and σ^* of the phosphorus-carbon bond. For a long time in coordination chemistry, the pure empty d -orbitals of phosphorus were thought to be used for the acceptance of π -electron density; and this theory was also affirmed by the fact that as the R groups attached to phosphorus become more electronegative, phosphine becomes stronger π -acceptor and vice-versa. The concept of mixing of σ^* of the phosphorus-carbon bond into empty d -orbitals of phosphorus was developed later on.

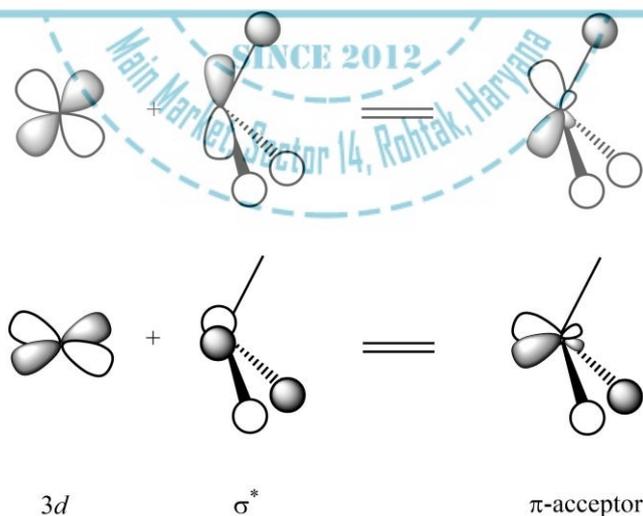


Figure 28. The π -acceptor orbitals of phosphines in metal-phosphine complexes.

Therefore, the nature of R groups in tertiary phosphines governs the relative donor-acceptor strength of the corresponding ligand. For instance, PMe_3 acts as a stronger σ donor than PF_3 due to the large electron-donating effect of the three methyl groups. However, it is a relatively weaker π -acceptor in comparison to PF_3 , which easily be explained in terms of a larger electron-withdrawing effect of 3 fluorines. Hence, the σ -donor and π -acceptor strength of tertiary phosphines can be fine-tuned just by changing the R groups.

➤ **Steric and Electronic Properties**

The most valuable thing about tertiary phosphines as ligands is that their steric and electronic properties can easily be manipulated just by changes in one or more of the three organic substituents. This fine-tuning of the electronic and steric profile of phosphine ligands is of great importance in the manipulation of catalytic properties transition metals. The ligand cone angle and Tolman electronic parameter are used to categorize various phosphines on the basis of their steric and electronic behavior, respectively. However, these parameters are not just limited to phosphines but have been extended to other ligand types also.

1. Ligand cone angle: The ligand cone angle is a measure of the size of a ligand. It is defined as the solid angle formed with the metal at the vertex and the other atoms at the perimeter of the cone. Tertiary phosphine ligands are commonly classified using this parameter, but the method can be applied to any ligand. The term cone angle was introduced by the American chemist, Chadwick A. Tolman. Originally applied to phosphines (called Tolman cone angle), the cone angles were originally determined by taking measurements from accurate physical models of them. The concept of the cone angle is most easily visualized with symmetrical ligands, e.g. PR_3 . Nevertheless, this approach has been refined to include less symmetrical ligands of the type $\text{PRR}'\text{R}''$ as well as diphosphines by using equation (1).

$$\theta = \frac{2}{3} \sum_i \frac{\theta_i}{2} \quad (1)$$

Where $\theta_i/2$ are the half of individual angles made by R, R' and R'' on M-P bond. In the case of diphosphines, the $\theta_i/2$ of the backbone is estimated as half of the bite angle of chelate, taking a bite angle of 90° , 85° and 74° , for propylene, ethylene and diphosphines with methylene backbones, respectively.

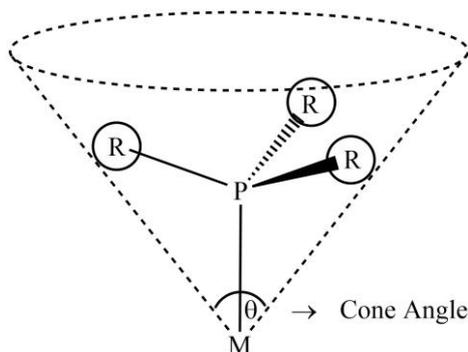


Figure 29. The ligand cone angle in metal-phosphine complexes.

The ligand-cone-angle method accepts empirical bond data and considers the perimeter as the maximum possible circumscription of a substituent which spins freely. The concept of solid-angle derives the bond length and the perimeter from the empirical crystal structure profile obtained from X-ray diffraction of solid sample. Each system has its own advantages. The exact cone angle (θ) can be found if the geometry of a ligand is known from either crystallography or computational studies. Unlike the Tolman route, no assumptions regarding the geometry are made. The cone-angle-concept is practically important in homogeneous catalysis due to the affected reactivity of the metal center from the ligand size. In a famous example, the selectivity of hydroformylation catalysts is strongly affected by the size of the coligands attached. Now though phosphines are monovalent, some are large enough to fill more than half of the coordination sphere around the metal center. The values of the cone angles of selected ligands are given below.

Table 3. The cone angle values of selected ligands.

Ligand	Cone angle	Ligand	Cone angle
PH ₃	87°	P(Me)(PPh) ₂	136°
PF ₃	104°	P(CF ₃) ₃	137°
P(OMe) ₃	107°	P(O-o-C ₆ H ₄ CH ₃) ₃	141°
P(OEt) ₃	109°	PPh ₃	145°
PMe ₃	118°	P(cyclo-C ₆ H ₁₁) ₃	170°
PCl ₃	124°	P(t-C ₄ H ₉) ₃	182°
P(Me) ₃ Ph	127°	P(C ₆ F ₅) ₃	184°
PBr ₃	131°	P(o-C ₆ H ₄ CH ₃) ₃	194°
PEt ₃	132°	P(mesityl) ₃	212°

The presence of bulky ligands (ligands with large cone angles) is found to enhance the rate of dissociation; which can be explained in terms of increased steric repulsion due to crowding around the metal center.

2. Tolman electronic parameter: The Tolman electronic parameter (TEP) is named after its inventor, Chadwick A. Tolman, and is a measure of the electron-donating or withdrawing strength of a ligand. It is determined by measuring the frequency of the A₁ vibrational mode of carbonyl stretching frequency of Ni(CO)₃L complex by infrared spectroscopy, where L is the ligand being studied. The Ni(CO)₃L is chosen as the model compound because such complexes can easily be prepared from Ni(CO)₄. Moreover, the carbonyl band is quite distinctive, and is rarely obscured by other bands in the observed infrared spectrum; and being a small ligand, steric factors are unable to complicate the analysis.

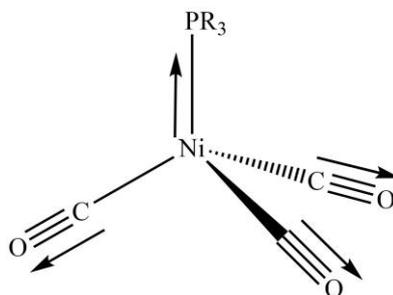


Figure 30. The A_1 stretch of $\text{Ni}(\text{CO})_3\text{L}$ used to determine the TEP in metal-phosphine complexes.

Upon coordination to a metal, $\nu(\text{CO})$ typically decreases from 2143 cm^{-1} of free CO. This can be explained by π backbonding i.e. the metal is able to form a π -bond with the carbonyl ligand by donating electrons through its d -orbitals into the empty antibonding π^* orbitals on CO. This increases the strength of metal-carbon bond, but also weakens the bond between carbon and oxygen. Moreover, the C-O bond is further weakened if other ligands present increase the π -electrons-density on the metal center, and ν_{CO} decreases. However, if other ligands compete with CO for π backbonding, ν_{CO} would increase. Tolman analyzed a series of seventy ligands in reference to $\text{P}(\text{t-Bu})_3$, because three t-butyl groups make it as the strongest donor ligand. Consequently, the A_1 band of carbonyl ligands in $\text{Ni}(\text{CO})_3[\text{P}(\text{t-Bu})_3]$ complex appears at the lowest wavenumber (2056.1 cm^{-1}), which is obviously due to the largest magnitude of back-bonding among all phosphines. Based on these observations, Tolman proposed a parameter χ_i to show the effect of individual substituents (R, R', R'') on this band as accorded by equation (2):

$$\nu_{\text{CO}} = 2056.1 \text{ cm}^{-1} + \sum_{i=1}^3 \chi_i \text{ cm}^{-1} \quad (2)$$

Now the calculation of the value of χ_i for each individual substituent in symmetrical phosphines can be done just by putting their observed spectral band. Let's say, we want to calculate the Tolman electronic parameter for PCl_3 . The infrared absorption of A_1 symmetry for $\text{Ni}(\text{CO})_3(\text{PF}_3)$ is observed at 2097.0 cm^{-1} . On putting this value for ν_{CO} in the equation (2), we get:

$$2097.0 \text{ cm}^{-1} = 2056.1 \text{ cm}^{-1} + \sum_{i=1}^3 \chi_i \text{ cm}^{-1} \quad (3)$$

$$2097.0 \text{ cm}^{-1} = 2056.1 \text{ cm}^{-1} + 3 \times \chi_i(\text{Cl}) \text{ cm}^{-1} \quad (4)$$

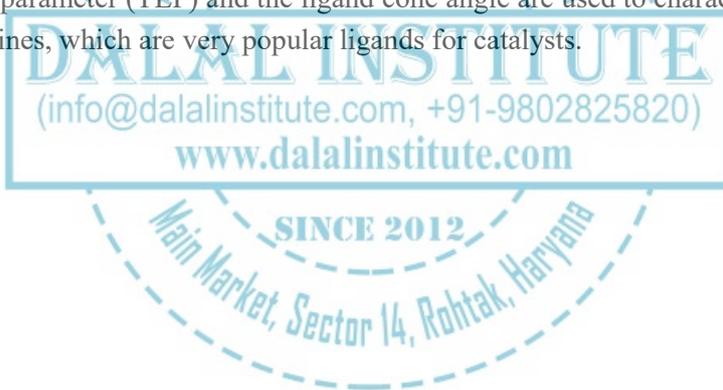
$$\chi_i = 14.8 \text{ cm}^{-1} \quad (5)$$

The values of χ for different substituents are listed in 'Table 4'; which in turn can easily be used to calculate the theoretical position of A_1 absorption band in case of tertiary phosphine ligands in which R, R', and R'' are not the same anymore.

Table 4. Substituent χ Factors for Phosphine and Related Ligands.

Substituent	χ_i (cm ⁻¹)	Substituent	χ_i (cm ⁻¹)
- <i>t</i> Bu	0.0	-OEt	6.8
-Cyclohexyl	0.1	-OMe	7.7
- <i>i</i> Pr	1.0	-H	8.3
-Et	1.8	-OPh	9.7
-Me	2.6	-C ₆ H ₅	11.2
-Ph	4.3	-Cl	14.8
- <i>p</i> -C ₆ H ₄ F	5.0	-F	18.2
- <i>m</i> -C ₆ H ₄ F	6.0	-CF ₃	19.6

The Tolman electronic parameter (TEP) and the ligand cone angle are used to characterize the electronic and steric profile of phosphines, which are very popular ligands for catalysts.



❖ Problems

- Q 1. Give the principal routes to synthesize metal carbonyl complexes.
- Q 2. Discuss the nature of bonding for transition metal complexes in the framework of the molecular orbital theory.
- Q 3. Draw and discuss the structure of $\text{Fe}_3(\text{CO})_{12}$ and $\text{Ir}_4(\text{CO})_{16}$.
- Q 4. Write a short note on the structure of osmium-carbonyl complexes with special emphasis on $\text{Os}_4(\text{CO})_{14}$, $\text{Os}_4(\text{CO})_{15}$ and $\text{Os}_4(\text{CO})_{16}$.
- Q 5. How many metal-metal bonds and terminal carbonyls are present in $\text{Rh}_6(\text{CO})_{16}$?
- Q 6. How would you distinguish between square-pyramidal and trigonal bipyramidal geometries of $\text{Fe}(\text{CO})_5$ using their vibration spectra?
- Q 7. Discuss the effect of backbonding on the carbonyl stretching frequency in hexacarbonyl complexes of the first transition series.
- Q 8. How would you calculate the reaction rate for metal carbonyls using infrared spectroscopy?
- Q 9. Discuss the points of difference between linear and bent mode of bonding for nitrosyl ligand.
- Q 10. Explain the structure and bonding of metal-dioxygen complexes in detail.
- Q 11. How does the end-on bonding mode differ from side-on bonding mode in dinitrogen complexes of transition metals?
- Q 12. Give important reactions of coordinated ligands with reference to N_2 , O_2 and NO complexes.
- Q 13. Why is tertiary phosphine so important in organometallic chemistry?
- Q 14. What kind of orbitals do the tertiary phosphine use for backbonding? Explain in detail.
- Q 15. Define the ligand cone angle and the Tolman electronic parameter.

❖ Bibliography

- [1] J. E. House, *Inorganic Chemistry*, Academic Press, California, USA, 2008.
- [2] B. R. Puri, L. R. Sharma, K. C. Kalia, *Principals of Inorganic Chemistry*, Milestone Publishers, Delhi, India, 2012.
- [3] J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry: Principals of Structure and Reactivity*, HarperCollins College Publishers, New York, USA, 1993.
- [4] B. Xu, Q. S. Li, Y. Xie, R. B. King, H. F. Schaefer, *Homoleptic Tetranuclear Osmium Carbonyls: From the Rhombus via the Butterfly to the Tetrahedron*, Dalton Trans., 2008, 1366.
- [5] T. T. Shi, Q. S. Li, Y. Xie, R. B. King, H. F. Schaefer, *Neutral Homoleptic Tetranuclear Iron Carbonyls: Why Haven't They Been Synthesized as Stable Molecules?*, New J. Chem., 34, 2010, 208.
- [6] V. J. Johnston, F. W. B. Einstein, R. K. Pomeroy, *Structures of the New Binary Metal Carbonyl $Os_4(CO)_{15}$ and $(\eta^5-C_5Me_5)(OC)IrOs_3(CO)_{11}$. Clusters with Three-Center-Two-Electron Metal-Metal Bonds?*, J. Am. Chem. Soc., 109, 1987, 7220.
- [7] P. S. Braterman, *Reactions of Coordinated Ligands: Volume 2*, Plenum Press, New York, USA, 1989.
- [8] L. L. Ingraham, D. L. Meyer, *Biochemistry of Dioxygen*, Plenum Press, New York, USA, 1985.
- [9] M. Merce, R. H. Crabtree, R. L. Richar, *A μ -Dinitrogen Complex with a Long N-N Bond. X-Ray Crystal Structure of $[(PMe_2Ph)_4CReN_2MoCl_4(OMe)]$* , J.C.S. Chem. Comm., 1973, 808.
- [10] P. L. Holland, *Metal-Dioxygen and Metal-Dinitrogen Complexes: Where Are the Electrons?*, Dalton Trans., 39, 2010, 5415.
- [11] A. D. Allen, R. O. Harris, B. R. Loescher, J. R. Stevens, R. N. Whiteley, *Dinitrogen Complexes of the Transition Metals*, Chemical Reviews, 73, 1973, 11.
- [12] J. S. Valentine, *The Dioxygen Ligand in Mononuclear Group VIII Transition Metal Complexes*, Chemical Reviews, 73, 1973, 235.
- [13] G. O. Spessard, G. L. Miessler, *Organometallic Chemistry*, Oxford University Press, New York, USA, 2010.
- [14] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Butterworth-Heinemann, Oxford, Britain, 1998.
- [15] B. W. Pfennig, *Principles of Inorganic Chemistry*, John Wiley & Sons, New Jersey, USA, 2015.

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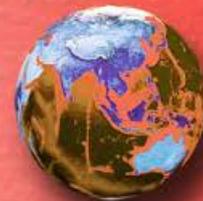
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Mandeep Dalal

(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)

Founder & Director, Dalal Institute

Contact No: +91-9802825820

Homepage: www.mandeepdalal.com

E-Mail: dr.mandeep.dalal@gmail.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands) .

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