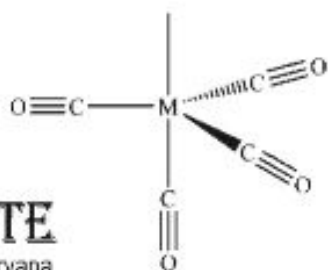


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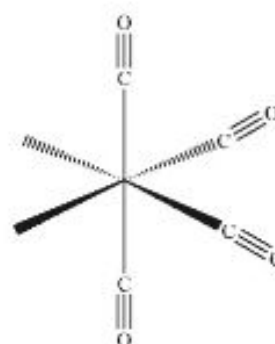
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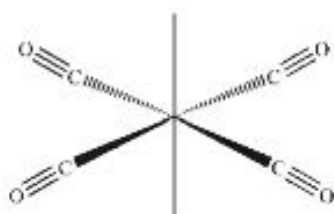
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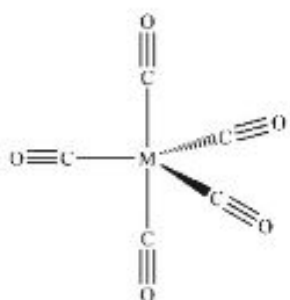


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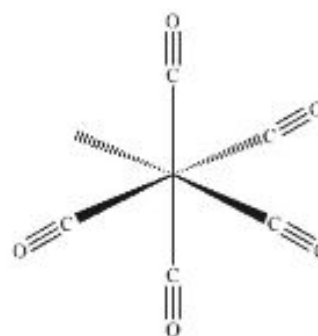


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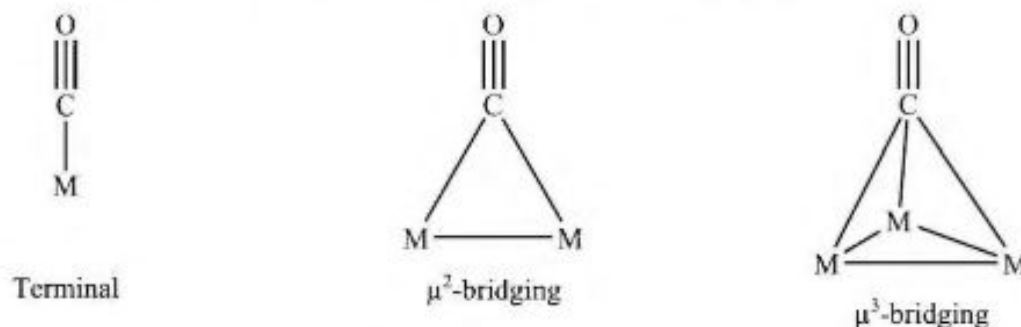
It is worthy to note that these rules apply to metal carbonyls in solution or the gas phase.

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➤ **4. Differentiation of Terminal and Bridging Carbonyl Groups**

The mode of attachment of carbonyl group to metal centre 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 centres. Three main modes of attachment of carbonyl group with metal centre 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 labelled 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:

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

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 ν_{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 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 metal carbonyl complexes. Consider the following trend in isoelectronic and isostructural metal carbonyls.

Compound	$[\text{Ni}(\text{CO})_4]$	$[\text{Co}(\text{CO})_4]^{1-}$	$[\text{Fe}(\text{CO})_4]^{2-}$
$\nu_{CO} (\text{cm}^{-1})$	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

The similar trend is observed in 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 centre, 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 centre, which in turn would support the metal-carbonyl back bonding, yielding somewhat lower carbon-oxygen bond order and lower carbonyl stretching frequency.

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

Hence, the bond order of CO in $[\text{Ni}(\text{PMe}_3)(\text{CO})_3]$ is definitely lower than in $[\text{Ni}(\text{PF}_3)(\text{CO})_4]$ because PMe_3 is a weaker π -acceptor than PF_3 ligand.

➤ **6. Study of Reaction Kinetics in Metal Carbonyls**

Infrared spectroscopy is 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:

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

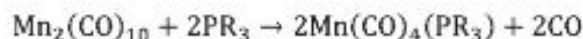
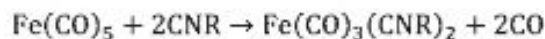
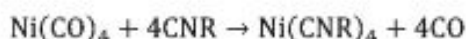
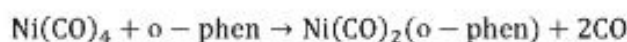
Where ϵ is the molar extinction coefficient and T is the transmittance of the solution. Therefore, the rate of disappearance or appearance of a characteristic infrared absorption band can be used to estimate the rate of change of concentration for the corresponding reactant or product. In other words, the rate intensity decrease in IR peaks of reactant, or the rate intensity increase in IR peaks of product metal carbonyl is proportional to 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 mixed carbonyl or some important organometallic complexes. Some of the main reactions shown by metal carbonyls are discussed below.

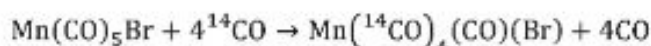
➤ 1. Ligand Displacement Reactions

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 which 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 catalysed by catalytic amounts of oxidants through the electron-transfer phenomena. The displacement in 17-electron complexes proceeds via 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:



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The displacement reactions in metal carbonyls also points toward the differences in 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}C .



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.

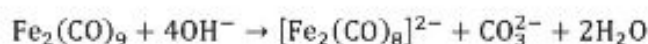
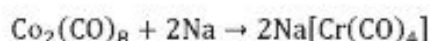
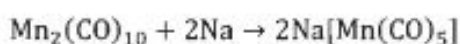
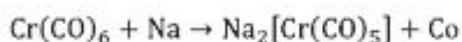


Figure 14. The structures of (a) $\text{Mn}(\text{CO})_5\text{Br}$ and (b) $\text{Mn}(\text{CO})_3(\text{Py})_3$.

Furthermore, the reaction of $\text{Mn}(\text{CO})_6$ with py always results in the formation of 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 like in the case of $\text{Ni}(\text{CO})_4$ where PF_3 ligands lead to the formation of $\text{Ni}(\text{PF}_3)_4$.

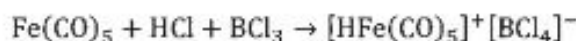
➤ 2. Formation of Carbonylate Anions

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**

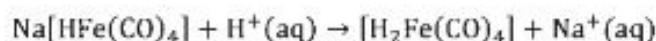
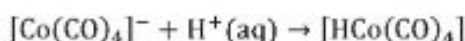
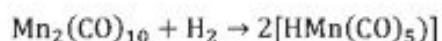
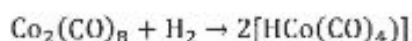
Carbonylate cations are not as common as carbonylate anions, and can be synthesized either by the protonation of metal carbonyl in strong acids or, by the reaction with carbon monoxide and some Lewis acids.



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**

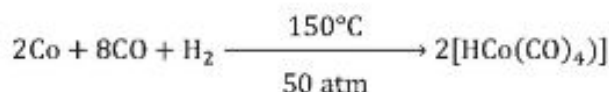
Carbonyl hydrides are generally synthesized either by the acidification of the solutions containing the corresponding carbonylate anion, or by the reactions of metal carbonyls with hydrogen. For instance:



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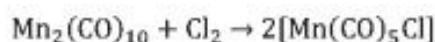
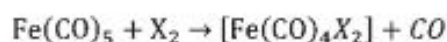
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Some of the metal carbonyl hydrides can be prepared by direct reaction of the metal with CO and H₂. For example:



➤ **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 electron-counting scheme used, this can be considered as oxidation of the metal centre.



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

