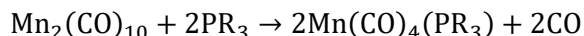
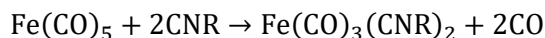
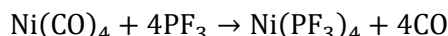
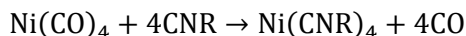


❖ Important Reactions of Metal Carbonyls

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:



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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.

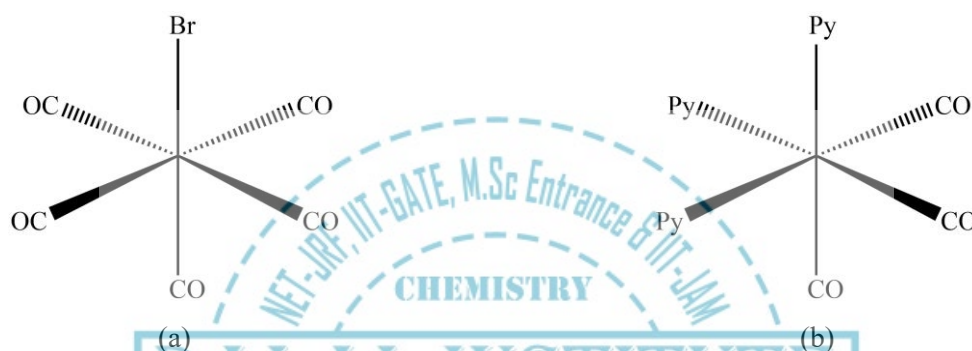
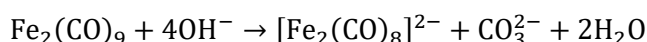
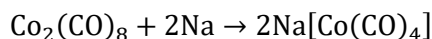
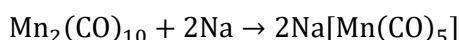
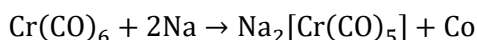


Figure 14. The structures of (a) $\text{Mn}(\text{CO})_5\text{Br}$ and (b) $\text{Mn}(\text{CO})_3(\text{Py})_3$.
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Furthermore, the reaction of $\text{Mn}(\text{CO})_6$ with py always results in the formation of a facial isomer of $\text{Mn}(\text{CO})_3(\text{py})_3$ 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 $\text{Ni}(\text{PF}_3)_4$.

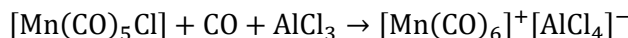
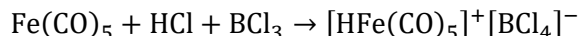
➤ 2. Formation of Carbonylate Anions

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**

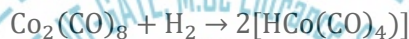
Carbonylate cations are not as common as carbonylate anions and can be synthesized either by the protonation of metal carbonyl in strong acids or, by the reaction with carbon monoxide and some Lewis acids.



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:

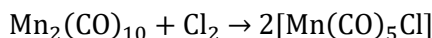
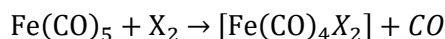


Some of the metal carbonyl hydrides can be prepared by direct reaction of the metal with CO and H₂. For example:

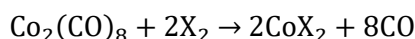
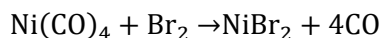


➤ **5. Synthesis of Metal Carbonyl Halides or Metal Halides**

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.

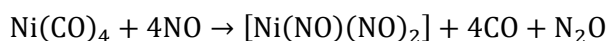
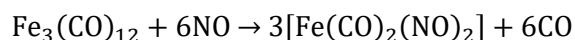
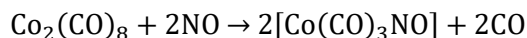


Furthermore, some metal carbonyls also get decomposed into metal halides when treated with halogens as:



➤ **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.

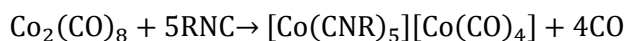
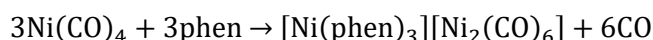
➤ **7. Disproportionation Reactions**

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.

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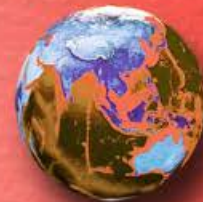
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Mandeep Dalal

(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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