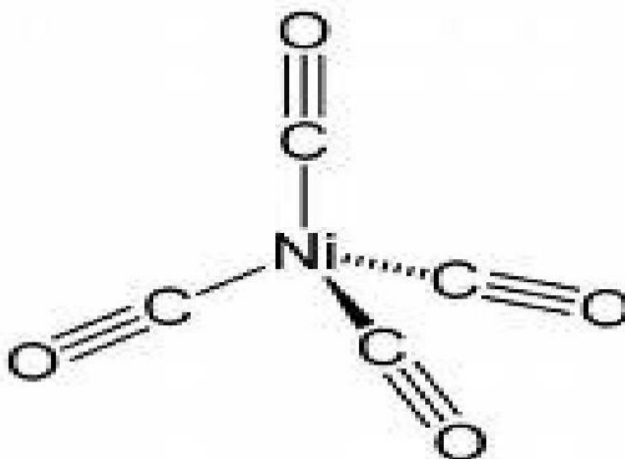


Introduction.

- In 1884 Ludwig Mond found his nickel valves were being eaten away by CO. An Experiment was designed where he deliberately heated Ni powder in a CO stream thus forming the volatile compound $\text{Ni}(\text{CO})_4$ the first metal carbonyl. ○ It was also found that further heating $\text{Ni}(\text{CO})_4$ decomposes to give pure nickel. This Ni Refining process still used today is known as the Mond process. Having no net dipole moment intermolecular forces are relatively weak allowing $\text{Ni}(\text{CO})_4$ to be liquid at room temperature. ○ Anionic charge on the complex and ion pairing of Na^+ to the carbonyl oxygen contribute to the reduced CO bond order by favoring the resonance form.
- CO also has the ability to stabilize polyanionic species by acting as a strong π Acceptor and delocalizing the negative charge over the CO oxygen. $\text{Na}_4[\text{Cr}(\text{CO})_4]$ has the extraordinarily low (CO) of 1462 cm^{-1} the extremely high.
- As the CO ligand is small and strongly bound many will usually bind as are required to achieve coordinative Saturation metal carbonyls in common with metal hydride show a strong preference for the 18e configuration.
- CO groups have a high tendency to stabilize M–M bonds not only are CO ligands Relatively small but they also leave the metal atom with a net charge similar to That in its elemental form (electro neutrality principle).

Stable complexes are those with structures such that each atom has only a small electric Charge. Stable M-L bond formation generally reduces the positive charge on the metal as well as the negative charge electron density on the ligand. The result that actual Charge on the metal is not accurately reflected in it's formal oxidation state.



Physical properties .

State:

Majority of the metallic carbonyls are liquids or volatile solids.

Color:

Most of the mononuclear carbonyls are colourless to pale yellow. $V(CO)_6$ is a bluish-black solid. Polynuclear carbonyls exhibit are dark in color.

Solubility:

Metal carbonyls are soluble in organic solvents like glacial acetic acid, acetone, benzene, carbon tetrachloride and ether.

Toxicity:

Due to low melting points and poor thermal stability, they show toxicity related to the corresponding metal and carbon monoxide. Exposure to these compounds can cause damage to lungs liver brain and kidneys. Nickel tetracarbonyl exercises.

- These compounds are carcinogenic over long-term exposure.

Magnetic Property:

All the metal carbonyls other than vanadium hexacarbonyl are diamagnetic. The metals with even atomic number form mononuclear carbonyls. Thus, all the electrons in the metal atoms are paired. In case of dinuclear metal carbonyls formed by metals with odd atomic number unpaired electrons are utilized for the formation of metal-metal bonds.

Thermal Stability:

Most of the metal carbonyls melt or decompose at low temperatures. Solid carbonyls sublime in vacuum but they undergo some degree of degradation.

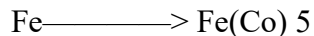
Thermodynamic Stability:

Metal carbonyls are thermodynamically unstable. They undergo aerial oxidation with different rates. $Co_2(CO)_8$ and $Fe_2(CO)_9$ are oxidized by air at room temperature while chromium and molybdenumhexacarbonyls are oxidized in air when heat

❖ Chemical properties

Synthesis of metal carbonyls.

From CO gas.



This method required the metal already reduced state because only pi basic metal can bind Co. High oxidation state metal we have we must reduced it first.

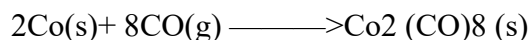
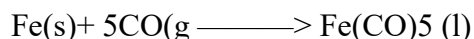
From organic carbonyl.

This can happen for aldehydes and alcohol. Reaction requires three steps. Second step is reverse of migratory insertion.

Direct Combination:

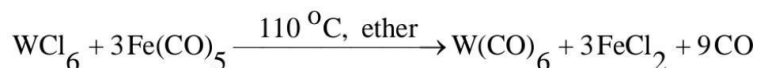
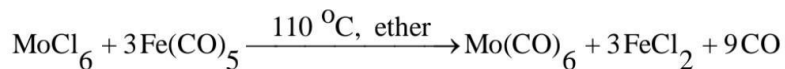
Only $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ and $\text{Co}_2(\text{CO})_8$ are normally obtained by the action of carbon.

Monoxide on the finely divided metal at suitable temperature and pressure.

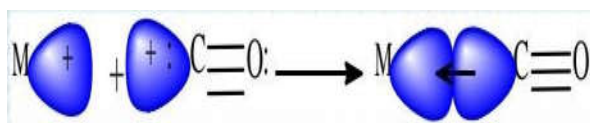


Preparation of mononuclear carbonyls for iron pentacarbonyl:

The labile carbonyl groups in iron pentacarbonyl can be replaced by chloride to give a different Metal carbonyl. These reactions are characterized by low yield which can be improved using High pressure.



Formation of sigma bond $\text{M} \rightarrow \text{CO}$.



Formation of dative σ -bond:

The overlapping of empty hybrid orbital on metal atom with the filled hybrid orbital on carbon atom of carbon monoxide molecule results into the sigma bond formation.

Formation of π -bond by back donation:

This bond is formed because of overlapping of filled $d\pi$ orbitals or hybrid $dp\pi$ orbitals of metal atom with low-lying empty orbitals on CO molecule.

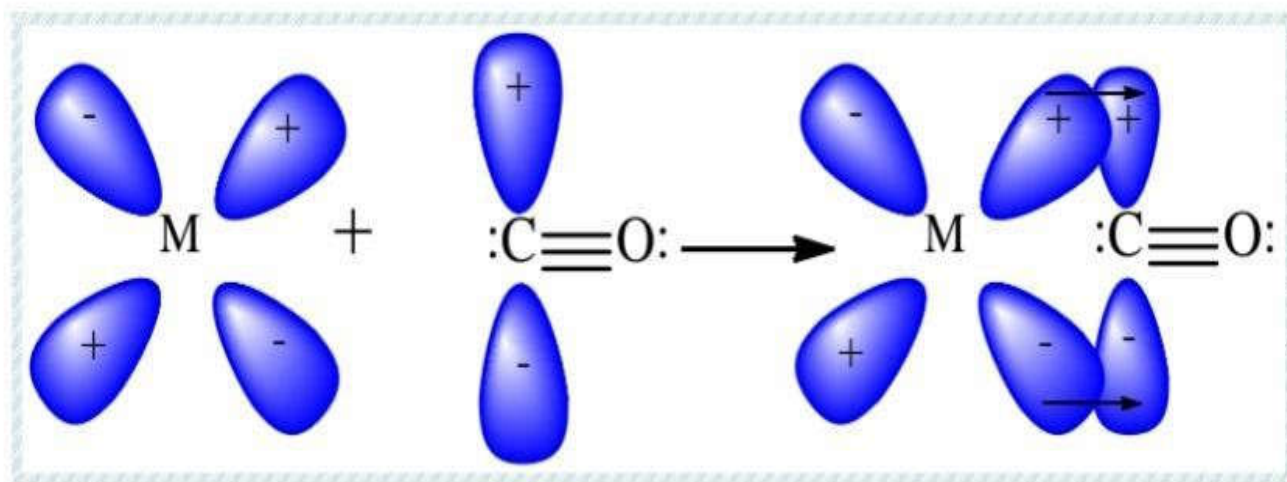
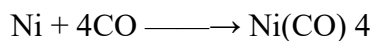


Figure: Formation of $M \xrightarrow{\pi} CO$ bond by back donation in metal carbonyls.

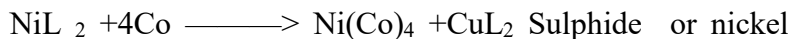
Mononuclear carbonyl.

Preparation of mononuclear carbonyl.

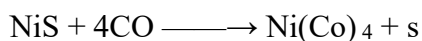
It can be prepared by passing carbon monoxide over nickel in the temperature range of 60-100°C.



It can be made by heating nickel iodide with carbon monoxide in the presence of copper which acts as a halogen acceptor.



cyanate.

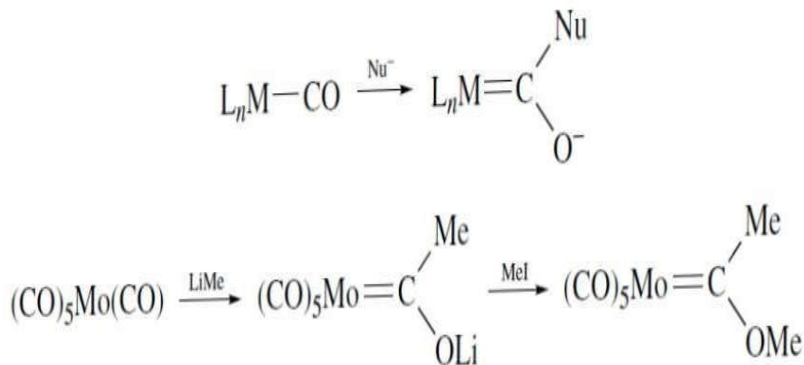


Reaction & Properties.

All reactions of the CO ligand depend on the polarization of the CO upon binding.

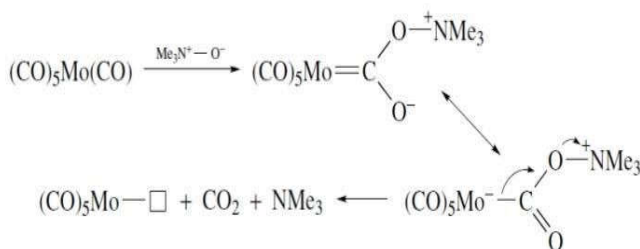
And so change in importance as the coligands and net charge change.

Nucleophilic attack at carbon:

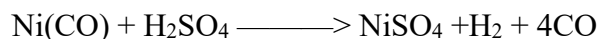


Nucleophilic attack at carbon.

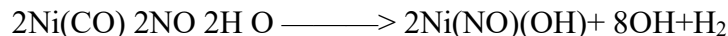
This reaction is particularly important because it is one of ligand less basic than CO itself. Hydride attack at the C atom of CO here produces the unusual formyl ligand, which is important in CO reduction to MeOH. It is stable in this case because the final 18e complex provides no empty site for rearrangement to a hydridocarbonyl complex (α -elimination)



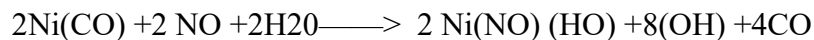
It is a colourless liquid having melting point $-25^\circ C$, boiling point $43^\circ C$ and decomposition Temperature in the range of $180-200^\circ C$. It is insoluble in water but dissolves in organic solvents. It reacts with concentrated sulphuric acid along with detonation



It reacts with moist nitric oxide to give deep blue coloured compound.



Passing gaseous hydrochloric acid in the solution of nickel tetracarbonyl results in the Decomposition.



Structure :

Nickel tetracarbonyl has a tetrahedral geometry with Ni-C bond lengths of 1.5 Å. It is also found to be diamagnetic.

Uses:

- Since $\text{Ni}(\text{CO})_4$ on heating decomposes to metallic nickel, it is used in the production of nickel Mend's process.

It is used for plating nickel on other metals.

It is used as a catalyst for synthesis of acrylic monomers in plastic industries.