Metal carbonyls

1. Mononuclear metal carbonyls:

$Cr(CO)_6$; it's preparations, properties, structure and bonding

- **EAN Rule;** according to which after **'CO'** groups have donated a certain number of electron pairs to the zero valent metal atom through **OC** → **M** σ **– bonding,** the total number of electrons on the metal atom including those gained from **CO molecules** becomes equal to the number of the next inert gas.

Example; **$Cr(CO)_6$**

- ✓ ***Number of electrons on the central metal atom = atomic number of the metal atom (Z) ie., Cr(Z) = 24***
- ✓ ***Number of electrons donated by 'CO' molecules (x) ie., 6 × CO = 6 × 2 = 12***
- ✓ ***Therefore, EAN of the metal atom in carbonyl = Z + x (symbol of the next inert gas is given in parentheses) = 24 + 12 = 36 (Kr)***

- **18 – Electron Rule;** *According to this rule; in a stable metal carbonyl, total (ie; effective) number of electrons present in the valence shell (v. s.) of one metal atom is equal to 18. This number (ie; 18) is equal to* ***EN/n;*** *where* ***'n' is the number of metal (M) atoms in metal carbonyl, &***

'EN' = Number of Electrons present in the valence shell of metal in carbonyl

= Number of Electrons in the valence shell in the free State + (2 × Number of CO ligands) + (2 × Number of M – M bonds in the carbonyl)

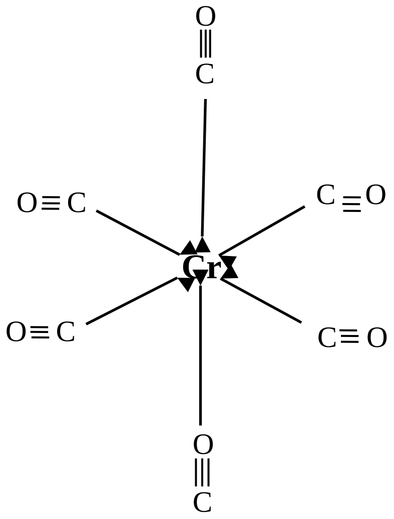
Example; $Cr(CO)_6$

$$Cr\ (3d^5\ 4s^1) = 6\ e^-$$

$$6\ CO = 6 \times 2\ e^- = 12\ e^-$$

Therefore; effective number of electrons in the valence shell of Chromium atom = 6e- + 12e- = 18e-

Structure and bonding in Chromium hexacarbonyl; $Cr(CO)_6$



Electron diffraction study of Chromium hexacarbonyl molecule in the vapour state has shown that this molecule has octahedral geometry. The **Cr – C** distance is found to be **1.92 A°** while the **C – O** bond length is **1.16 A°.** The molecule is also found to be ***diamagnetic*.**

The structure can be explained using ***d^2sp^3 hybridization*** in Chromium atom.

d^2sp^3hybridization of Cr – atom – Octahedral geometry of $Cr(CO)_6$ suggests that Cr – atom which is in zero oxidation state is ***d^2sp^3 hybridized*** as shown below:

Cr (Z=24)

Electronic configuration: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^5$ $4s^1$

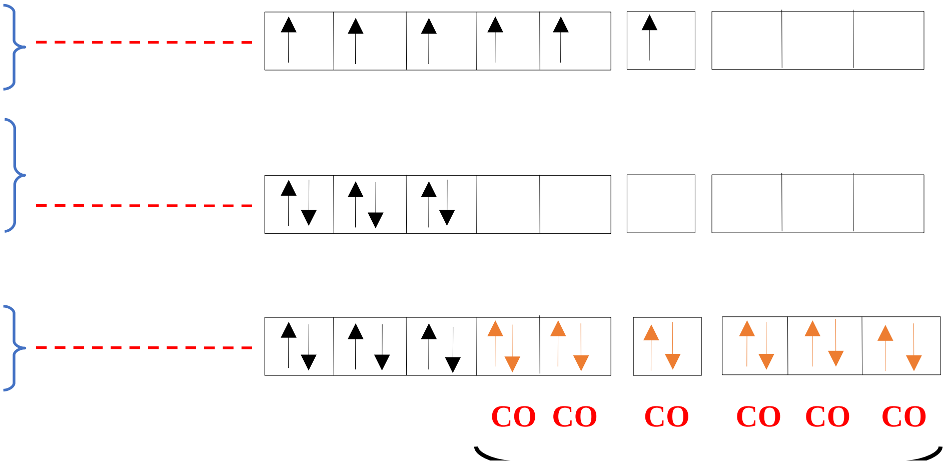
(a) Cr – atom in free state

($3d^5$ $4s^1$ $4p^0$)

(b) Cr – atom in $Cr(CO)_6$ molecule:

($3d^6$ $4s^0$ $4p^0$)

(c) $Cr(CO)_6$ molecule:



d^2sp^3 hybridisation

Octahedral shape of $Cr(CO)_6$

<u>Note:</u> d^2sp^3 hybridisation of Cr – atom in Cr(CO)6 molecule which has Octahedral geometry. Each pair of* (coloured arrows) *indicates electron pair donated by C – atom of each CO molecule (ligand).

Since $Cr(CO)_6$ is diamagnetic, all the 6 electrons present in the valence shell of Cr – atom (Cr = $3d^5\ 4s^1$) get paired in three 3d orbitals. Now ***$3d_{x^2-y^2}$, $3d_{z^2}$, 4s & three 4p*** orbitals hybridize together to form six d^2sp^3 hybrid orbitals.

$O\overset{\rightarrow}{\text{¿}}C \rightarrow Cr$ bond is formed by the overlap of the doubly – filled ***sp*** hybrid orbital on **C – atom** in CO molecule & empty d^2sp^3 hybrid on Cr – atom.

Preparations of chromium hexacarbonyl

i. ***It can be prepared by carbonylation of chromium chloride with carbon monoxide using a reducing agent like Lithium Aluminium Hydride (LAH) or $Al(C_5H_5)_3$, etc.***

$$CrCl_3 + 6CO \xrightarrow{\text{LAH, } 115^0\text{C, 70 atm}} Cr(CO)_6$$

ii. ***An indirect method of preparation involves an action of carbon monoxide on a mixture of Grignard reagent & anhydrous chromium chloride in ether which is followed by decomposition with an acid to give chromium hexacarbonyl.***

<u>OR</u>

CO (Carbon monoxide) at 50 atm pressure and at room temperature is passed into a suspension of $CrCl_3$ in ether, which has been treated with C_6H_5 – MgBr at -70°. This reaction is called <u>Job's Reaction.</u>

$$C_6H_5 - MgBr + CrCl_3 + CO \xrightarrow{\text{35 – 70 atm.}} Cr(CO)_2(C_6H_5)_4 + MgBrCl + MgBr_2$$

$$Cr(CO)_2(C_6H_5)_4 + 6H^+ \longrightarrow Cr(CO)_6 + 2Cr^{+3} + 12(C_6H_5)^- + 3H_2$$

- ***<u>By indirect synthesis involving Grignard's reagent:</u> Job prepared chromium hexacarbonyl by treating ethereal solution of Grignard's reagent with CO in presence of anhydrous $CrCl_3$. Similar relations in presence of Mo(v) & W(v) chlorides give the corresponding hexacarbonyls. According to <u>Heiber</u>, the primary reaction is as follows:***

$$4C_6H_5 - MgBr + CrCl_3 + 2CO \longrightarrow Cr(CO)_2(C_6H_5)_4 + 3MgBrCl + MgBr_2$$

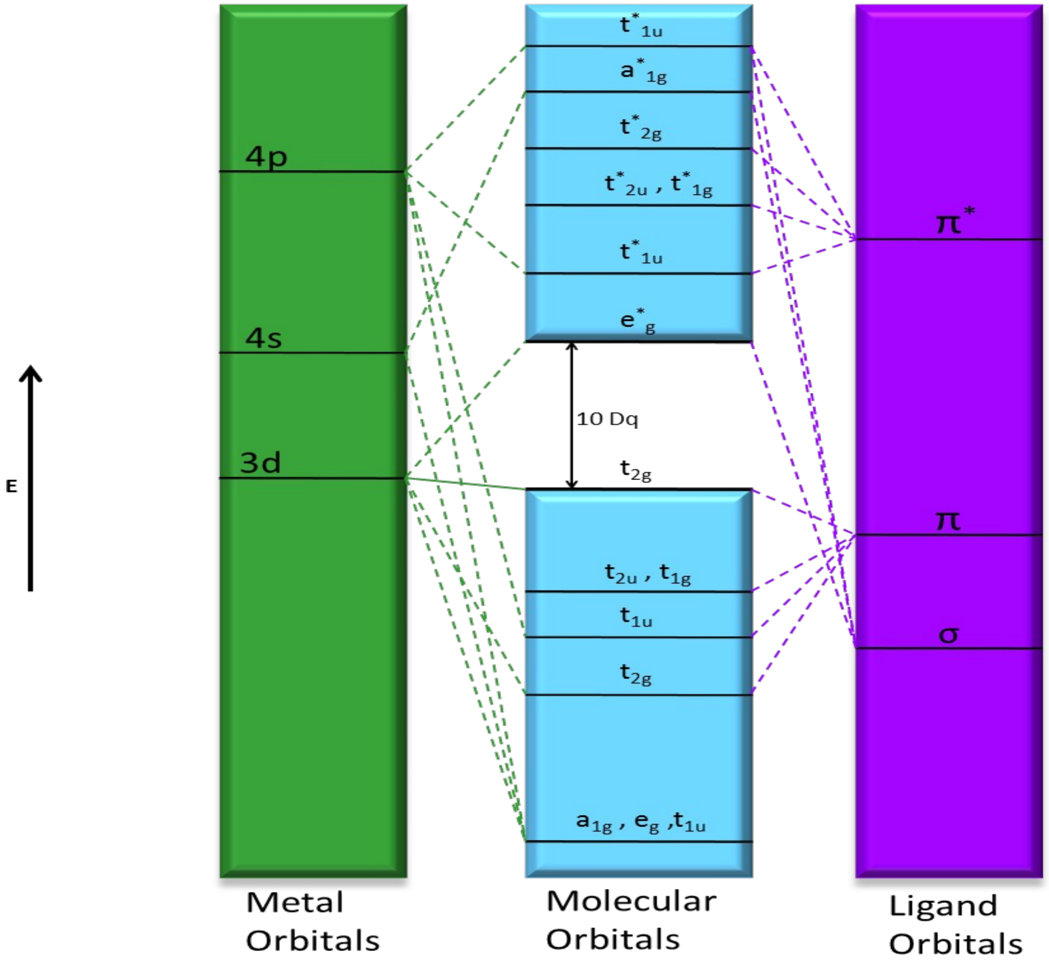
The unstable intermediate is decomposed in acid solution to give the hexacarbonyl.

$$3Cr(CO)_2(C_6H_5)_4 + 6H^+ \longrightarrow Cr(CO)_6 + 2Cr^{+3} + 12(C_6H_5)^- + 3H_2$$

The yield of the above reaction is low & can be improved by using high carbon monoxide pressure.

iii. ***$CrCl_3$ in presence of $AlCl_3$, powered aluminium and benzene is treated with CO. The yield is 88%.***

The MO energy diagram for $Cr(CO)_6$



The MO energy diagram for $Cr(CO)_6$ is shown in the figure above. For the molecular orbitals, 12 electrons are contributed from the lone pairs on the carbon atoms of the six carbon monoxide ligands. The metal contributes six electrons while 24 electrons come from the π-system of the six ligands. The MOs are occupied by these 42 electrons and the t_{2g} level becomes the highest occupied molecular orbital (HOMO) of the metal carbonyl.

The net effect of the π* orbitals is to increase the magnitude of 10.0 Dq (the splitting between the t_{2g} and e_g levels by lowering t^*_{2g} to a level lower in energy than when no π* orbitals are involved.

Consequently, the complexes are predicted to be more stable when the ligands have π and π* orbitals available for bonding. The ligand CO may be predicted to bond increasingly strongly with electron releasing metal atoms. The bond order of CO decreases progressively as the π* orbitals are increasingly populated by d → π* donation.

As discussed above, the low-lying empty π* orbitals on CO allow back bonding from the metal d - electrons to the ligand. It has a very pronounced effect on the coordinated C – O bond order.

Properties:

- ***Chromium hexacarbonyl is a white crystalline solid melting above 150°C and boiling at 220°C.***

- ***It is insoluble in water but soluble in ether, chloroform, carbon tetrachloride and benzene.***

- ***It is resistant to chemical attack. For example, it is not attacked by air, bromine, cold aqueous alkalies, dilute acids and concentrated hydrochloric acid as well as sulphuric acid (except concentrated HNO_3).***

- ***Decomposition:***
  - ✓ ***It is decomposed by chlorine gas (Cl_2) and concentrated nitric acid.***
  - ✓ ***It reacts with fluorine (F_2) at -75°C to form chromium hexafluoride.***

- ***Reduction***
  - ***i. It reacts with sodium metal in liquid ammonia to give carbonylate anion.***

$$\mathbf{Cr(CO)_6 + 2Na \longrightarrow Na_2^{+}[Cr(CO)_5] + CO}$$

  - ***ii. It is reduced with alkali metals in liquid ammonia and alkali metal borohydride: For example;***

$$\mathbf{Cr(CO)_6 \xrightarrow{Na/NH_3} Na_2[Cr(CO)_5]}$$

$$\mathbf{Cr(CO)_6 \xrightarrow{NaBH_4,\ THF} Na_2[HCr_2(CO)_{10}]}$$

$$\mathbf{Cr(CO)_6 \xrightarrow{NaBH_4,\ NH_3} Na_2[Cr_2(CO)_{10}]}$$

- ***Reaction with amines:* Chromium hexacarbonyl reacts with amines like py, phen, en to form the products in which CO groups in chromium hexacarbonyl are replaced by molecules of the amines. For example; above 140°C, py reacts with $Cr(CO)_6$ to give the following products in succession:**

$$\mathrm{Cr(CO)_6} \longrightarrow \mathrm{Cr(CO)_4(py)_2} \longrightarrow \mathrm{Cr_2(CO)(py)_5} \longrightarrow \mathrm{Cr(CO)_3(py)_3}$$

yellow brown
solid

yellow red
solid

bright red
solid

OR

- ***It gives substitution reactions with amines like 'en' & 'py'. At higher temperatures (>150°C) several pyridyl derivatives are formed.***

$$\mathrm{Cr(CO)_6 + 2py} \longrightarrow \mathrm{Cr(CO)_4(py)_2}$$

yellow brown
solid

$$\mathrm{Cr(CO)_6 + 5py} \longrightarrow \mathrm{Cr_2(CO)(py)_5}$$

yellow red
solid

$$\mathrm{Cr(CO)_6 + 3py} \longrightarrow \mathrm{Cr(CO)_3(py)_3}$$

bright red
solid