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Subject: Chemistry

Class for which the note is prepared: Semester-6

Paper: C13T (Inorganic Chemistry)

Topic: Organometallic Chemistry

Part 2

Comments- Study the whole topic thoroughly.

[N.B. - Acknowledgement of indebtedness to Mr.Sibshankar Das, my respected Teacher regarding collection of study materials in Inorganic Chemistry**]**

i) Nonbridge carbonyls which contain only terminal carbonyl groups.
eg ⇒ $Ni(CO)_4$, $Fe(CO)_5$, $Ru(CO)_5$ etc.

ii) Non bridge carbonyl which contains terminal carbonyl groups as well as metal-metal bond.
eg ⇒ $Co_2(CO)_8$ (in soln) $Mn_2(CO)_{10}$, $Fe_3(CO)_{12}$ etc.

(b) Bridging Carbonyls :
These contains bridging carbonyl groups along with terminal carbonyl group and one M-M bond.
eg ⇒ $Co_2(CO)_8$ (in solid state), $Fe_2(CO)_9$, $Os_2(CO)_9$ etc.

Classification of Carbonyl

- Classification based on the no. of metallic atoms present in carbonyls
  - Mononuclear: $Ni(CO)_4$, $Fe(CO)_5$
  - Polynuclear: $Mn_2(CO)_9$, $MnRe(CO)_{10}$ etc.
- Classification based on the structure of carbonyls.
  - Non-bridged
    - Non bridge carbonyl which contain only terminal carbonyl groups. $Ni(CO)_5$, $Ru(CO)_5$ etc
    - Non-bridge carbonyl which contain terminal carbonyl gp. as well as M-M bond: $Co_2(CO)_8$ (in soln) $Mn_2(CO)_{10}$, $Fe_3(CO)_{12}$ etc.
  - Bridged: $Co_2(CO)_8$ (in solid state), $Fe_2(CO)_9$ etc.

» Important carbonyls formed by transition metals :

$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$	$Fe_2(CO)_9$	$Fe_3(CO)_{12}$	$Co_2(CO)_8$	$Ni(CO)_4$
	$Mo(CO)_6$	$Tc(CO)_{10}$	$Ru(CO)_5$			$Co_4(CO)_{12}$	
	$W(CO)_6$	$Re(CO)_{10}$	$Os(CO)_5$	$Os_2(CO)_9$,	$Os_3(CO)_{12}$		

» Vanadium Complex [$V(CO)_6$] :
Among the mononuclear complexes only exceptions of the 18-e rule is hexacarbonyl vanadium(0) which is paramagnetic and the valence shell of V contains 17 electrons.

Electron Count: $5+12=17$

It does not dimerise to form 18-e compound like $Mn_2(CO)_{10}$, $Co_2(CO)_8$. If $V(CO)_6$ dimerises to form $V_2(CO)_{12}$ it will give each metal a coordination no. of 7 which may present too much steric to hindrence to allow stability and the L-L repulsion may overcome a weak metal-metal bond.

$V(CO)_6$ is less stable than carbonyl complex obeying the 18-e rule. It decomposes at room temp and readily accept electron in presence of reducing agent to form 18-e anion.

$$Na + V(CO)_6 \longrightarrow Na^{\oplus}[V(CO)_6]^{\ominus}$$

Preparation:

When VCl_3 is allowed to react with 'CO' in presence of Na at 100°C and 150 atm pressure in the acid medium $V(CO)_6$ is obtained.

$$VCl_3 + 6CO + 3Na \xrightarrow[\text{acidifying by } H_3PO_4]{\text{100°C, 150 atm}} V(CO)_6 + 3NaCl.$$

(in diglyme solvent; solvent – Diglym)

Chromium Hexacarbonyl $[Cr(CO)_6]$

Preparation:

i) When $CrCl_3$ is allowed to react with CO in presence of $AlCl_3$ and powdered Al, at 140°C in benzene solvent. $Cr(CO)_6$ is obtained.

$$CrCl_3 + Al + 6CO \xrightarrow[\text{benzene}]{AlCl_3,\ 140°C} AlCl_3 + Cr(CO)_6$$

ii) When MCl_6 [M = Mo, W] is allowed to react with $Fe(CO)_5$ at 180°C in ether solvent $M(CO)_6$ is obtained.

$$MCl_5 + 3Fe(CO)_5 \xrightarrow[\text{ether}]{180°C} M(CO)_6 + 3FeCl_2 + 9CO.$$

Properties:

i) $Cr(CO)_6$ is reduced with alkaline metals in liq NH_3 and alkali metal borohydrides.

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

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

ii) It reacts with amines like Py, en etc to form the products in which CO groups in $Cr(CO)_6$ are replaced by molecules of the amines.

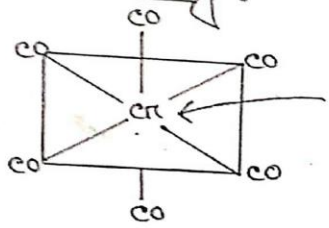
eg ⇒ $Cr(CO)_6$ (White solid) $\xrightarrow{2\,Py}$ $[Cr(CO)_4(Py)_2]$ (Yellow-brown solid) $\xrightarrow{Py}$ $[Cr_2(CO)_7(Py)_5]$ (Yellow-red solid)

$[Cr(CO)_3(Py)_3]$ ← Py

Bright red solid.

Structure and Bonding :

$Cr(CO)_6$



d^2sp^3 hybridized.

Diamagnetic

Di-manganese decacarbonyl $Mn_2(CO)_{10}$

Preparation :

When MnI_2 is allowed to react with CO in presence of Mg at 25°C at 210 atm pressure in diethylether solvent $Mn_2(CO)_{10}$ is obtained.

$$2\,MnI_2 + 10\,CO + 2\,Mg \xrightarrow{25^\circ C,\ 210\ atm} Mn_2(CO)_{10} + 2\,MgI_2$$

Property :

i) When $Mn_2(CO)_{10}$ is reduced by hydrogen under 200 atm pressure at a temp^r of 200°C carbonyl hydride is formed.

$$Mn_2(CO)_{10} + H_2 \xrightarrow[200^\circ C]{200\ atm} 2\,HMn(CO)_5.$$

ii) Mn-Mn is broken by 'Li' in presence of THF and by 'Na' in presence of liq NH_3.

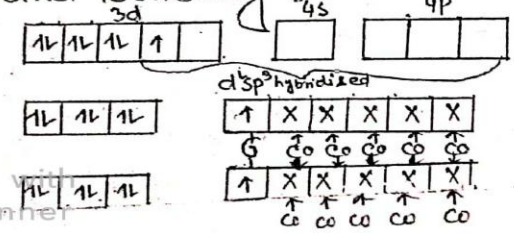
$$Mn_2(CO)_{10} + 2Li \xrightarrow{THF} 2Li^+[Mn(CO)_5]^\ominus$$

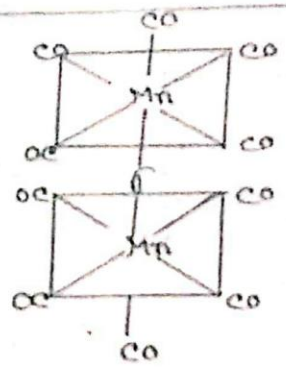
$$Mn_2(CO)_{10} + 2Na \xrightarrow{liq.NH_3} 2Na^+[Mn(CO)_5]^\ominus$$

iii) $Mn_2(CO)_{10}$ is diamagnetic substance. Diamagnetic character confirms that all the electron in $Mn_2(CO)_{10}$ are paired and Mn-Mn bond is also present in it.

Structure and Bonding :

Mn ⇒





● Ironpentacarbonyl [$Fe(CO)_5$]

Preparation :

When Fe is allowed to react with CO at 200°C and 200 atm pressure $Fe(CO)_5$ is obtained.

$$Fe + 5CO \xrightarrow[200\,atm]{200^\circ C} Fe(CO)_5$$

Property :

i) On thermal decomposition at 250°C, it gives pure 'Fe'

$$2Fe(CO)_5 \xrightarrow{250^\circ C} Fe + 5CO$$

ii) When it is irradialed with UV light $Fe_2(CO)_9$ is obtained.

$$2Fe(CO)_5 \xrightarrow{UV} Fe_2(CO)_9 + CO$$

iii) It reacts with halogen in non aquous solvent to form the stable tetra carbonyl halide

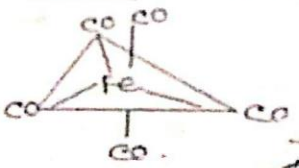
$$Fe(CO)_5 + X_2 \longrightarrow Fe(CO)_4X_2 + CO$$

iv) With NO, under pressure below 45°C it gives $Fe(NO)_4$ as the final product.

$$Fe(CO)_5 + 2NO \longrightarrow Fe(CO)_2(NO)_2 + 3CO$$

$$Fe(CO)_2(NO)_2 + 2NO \longrightarrow Fe(NO)_4 + 2CO.$$

Structure & bonding :



● $Fe_2(CO)_9$ [Di-iorron enacarbonyl]

Preparation :

It is made by the irradation of $Fe(CO)_5$ with UV light.

$$2Fe(CO)_5 \xrightarrow{UV\ light} Fe_2(CO)_9 + CO$$

● Preparation :

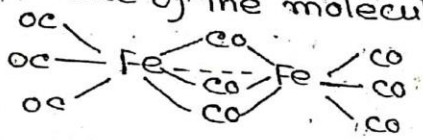
i) With NO it gives $[Fe(CO)_2(NO)_2]$ together with $Fe(CO)_5$ and $Fe_3(CO)_{12}$

$$Fe(CO)_5 \xrightarrow{NO} Fe(CO)_2(NO)_2 + Fe(CO)_5 + Fe_3(CO)_{12}$$

ii) Carbonylate anion is obtained in the reaⁿ with Na in NH_3 solⁿ

$$Fe_2(CO)_9 + 4Na \xrightarrow{NH_3} 2Na_2[Fe(CO)_4] + CO$$

The structure of the molecule is shown.

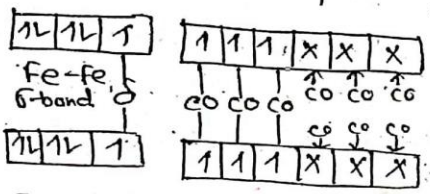


● Bonding :

Fe (GS) ⇒ 3d | 4s | 4p

Fe ⇒ d^2sp^3

Fe (d^2sp^3) ⇒



Structure of $Fe_2(CO)_9$:

IR study on $Fe(CO)_9$ shows that this molecule has two different types of carbonyl groups. X-ray crystallographic study has shown that the structure of $Fe_2(CO)_9$ molecule consist of three bridging carbonyl groups. Six terminal carbonyl groups and one single bond between two Fe atoms. Since this bond is produced by the weak coupling of the unpaired electron present in two 3d orbital of two Fe atoms, it is represented as Fe---Fe and is called δ-bond. It is diamagnetic and obeys EAN rule.

Since each Fe atom is linked with three terminal CO groups and three bridging CO groups, these atoms has co-ordination no. is equal to 6. [note that Fe-Fe bond is a fractional single bond] and hence each of Fe atom is d^2sp^3 hybridised.

Valence shell configuration of Fe atom in three state

is $3d^6 4s^2 4p^0$. When Fe atom ~~in three~~ state is $3d^6 4s^2 4$ forms $Fe_2(CO)_9$ molecule one of the two electron of 4s orbital is shifted to 3d orbital and hence the valence shell configuration of Fe atom becomes $3d^7 4s^1 4p^0$. Now two 3d orbital, one 4s orbital and all the 4p orbitals combine together and produced six d^2sp^3 hybridised orbitals. Three hybrid orbitals are vacant and three are singly filled. One of the three unhybridised 3d orbital is singly filled. Fe--Fe fractional single bond is produced by the overlap between two singly filled 3d orbitals on two Fe atoms. The attachment of bridging CO molecule with two Fe atoms is shown above.

$Fe_2(CO)_{12}$ [Tri-iron dodeca carbonyl] :

Preparation :

It is prepared by the disproportionation of $Fe_2(CO)_9$. A toluene soln of $Fe_2(CO)_9$ is heated at 70°C. On cooling green crystals of $Fe_3(CO)_{12}$ seperate, from the soln.

$$3\,Fe_2(CO)_9 \xrightarrow{70^\circ C} Fe_3(CO)_{12} + 3\,Fe(CO)_5$$

Properties :

i) When heated above 100°C, it decomposes to give metallic Fe and CO.

$$Fe_3(CO)_{12} \xrightarrow[100^\circ C]{\text{above}} 3Fe + 12\,CO$$

ii) Carbonylate anion is obtained when $Fe_3(CO)_{12}$ reacts with Na in liq NH_3.

$$Fe_3(CO)_{12} + 6\,Na \xrightarrow[NH_3]{liq} 3\,Na_2[Fe(CO)_4]$$

iii) With Py, $Fe_3(CO)_{12}$ produces $Fe_3(CO)_9(Py)_3$

$$2\,Fe_3(CO)_{12} + 3Py \longrightarrow Fe_3(CO)_9(Py)_3 + 3\,Fe(CO)_5$$

iv) At 85°C, it reacts with NO to form $Fe(CO)_2(NO)_2$

$$Fe_3(CO)_{12} + 6\,NO \longrightarrow 3\,Fe(CO)_2(NO)_2 + 6\,CO.$$

Structure and Bonding :

It has been stabilised that $Fe_3(CO)_{12}$ molecule does not contain any bridging co groups i.e, all the 12 co groups are present as terminal co groups. Each Fe atom is linked with 4-terminal carbonyl groups. The two octahedral $Fe(CO)_4$ units overlap in an angular way and bent fractional single bond between two Fe atoms is obtained. Thus in $Fe_3(CO)_{12}$ molecule 3-fractional single bond between two Fe atoms are formed. These bonds are shown as Fe---Fe. This molecule is diamagnetic. Each Fe atom obeys FAN rule.

The structure of the molecule is shown below