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Subject: Chemistry

Class for which the note is prepared: Semester-6

Paper: C13T (Inorganic Chemistry)

Topic: Organometallic Chemistry

Part 1

Comments-Study the whole topic thoroughly.Specially application of "**applications of 18 -electron rule to metal carbonyls"** is very important.

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

Organometallics.

Definition :

An organometallic compound is generally defined as one that posses a metal carbon bond. The bonding interaction must be ionic or covalent, localised or delocalised between one or more carbon atoms of organic gr. or molecules and a transition, lanthanide, actinides or main group metal.

Thus the compound s $Fe(CO)_5$, $Ni(CO)_4$, $K[PtCl_3(C_2H_4)]$ (Zeise's Salt) etc belong to the organic metals, category, whereas the complex $[Co(en)_3]^{3+}$ which contains carbon but has no M-C bond, so it is not an organometallic compound.

Again for metal cyanide complex $[Fe(CN)_6]^{4-}$ do have M-C bond but their properties are more close to those of Werner's complexes and $CN^{\ominus}$ do not contains organic moity. Thus they are generally not consider to be organometallics. Inorganic chemicals such as NaCN although possessing a M-C bond, are not normally catagorised as organometallic compounds.

In the broad point of view organo boron, organo silicon, organo arsenic and organotelurium are included in organometallic chemistry even though B, Si As. and Te are borderline metals.

Complex-compound forms between transition metal and carbon monoxide molecules are metal carbonyls In these compounds M-C bonds exist but CO can hardly be regarded as an organo molecule. Hence strictly carbonyl complexes are included under the catagories π-acceptor complexes and are not under organometallic compounds

What do you mean by π-acid ligand ? CO is called π-acid ligand – Explain.

In the metal complex, ligand first donates non bonding electron density to the metal orbital and which ligands can accept the electron density from suitable filled metal orbital to vacant π^*_p orbital is called π-acceptor ligand. If the extent of accept 'e' density is greater than that of donation to metal orbital

thus acts as lewis acid and so it is called π-acid ligand.

In the C-M bond in carbonyl in addition to the formation of a weak σ-bond by donation of an electron pair from C to M, a stronger bond is formed by back bonding (called dative π- bonding). This arises from sidewise overlap of a filled d_{xy} orbital on metal with the empty antibonding $\pi^*_{2p_y}$ orbital of the carbon, thus forming M-C π-bond. The filling or partial filling of the antibonding orbital on carbon reduces the bond order of the C-O bond from the triple bond in CO towards a double bond. In case of CO, it acts as weak σ-donor but good π-acceptor ie, the drift (shift) of π-electron density from metal to ligand is greater than that of donation to metal. Hence CO is called π-acid ligand.

- There is a reduction of C-O bond order and an increase in C-O bond length during the formation of carbonyl with transition metal - Justify.

- In Zeise's salt, C_2H_4 is called π-ligand but for the case of ligand $(CN)_4C_2$ it is called π-acid ligand - Why?

For the case of Zeise's salt, $K[PtCl_3(C_2H_4)]$ the C_2H_4 acts as a σ-donor and π-acceptor. The electron donor and acceptor character appears to be balanced in most ethylene complex. Thus the degree of donation and back donation is nearly same. Hence it is called π-ligand but not π-acid ligand.

On the other hand, in tetracyano ethylene ligand, there are four nitrile groups which are strong electron withdrawing. Hence it satisfies* its role as a donor. That is why $(CN)_4C_2$ ligand is called π-acid ligand.

* the criteria for a π-acid ie, its role as an acceptor dominates its role

- CO and C_2H_4 for both cases in organometallics form synergic bond but CO is called π-acid ligand but not C_2H_4 — Explain.

'CO' forms weak bond with the lewis acid BF_3 but forms strong bonds with the transition metal - Justify

CO is a weak σ-donor because it has very low dipolement. Due to the presence of high electronegativity of oxygen atom, the donation of lone-pair occurs through carbon end. But it has vacant π^*_p orbital which is readily accept electron density from the suitable filled metal orbital. It acts as a good π-acceptor ligands. Therefore we can say it is a weak σ-donor and good π-acceptor ligands. For the case of metal carbonyl complex it forms weak σ-bond and strong dative π-bond with the transition metal. Hence due to the formation of synergic bond it forms strong bond with the transition metal.

When CO is allowed to react with BF_3 the adduct $BF_3B \longleftarrow :C\equiv O$ is formed. In this adduct compound there is only a weak σ-bond between the Boron and carbon atoms. Due to the electron defficiency in B atom it can not form the dative π-bond with CO molecule. Hence CO forms weak bond with lewis acid BF_3.

In metal carbonyl, CO-stabilises the unusual (low positive or, or low negative) charge on the metal atom - Explain

CO acts as a π-acid ligand. The LUMO, of 'CO' (π^*_p orbital) is vacant. At low oxidation state the electron density is relatively higher on the metal. Thus filled metal 'd'-orbital (t_{2g} orbital having π-symmetry in 'Oh' geometry) overlaps with the empty π^*_p orbital of CO and drift of π-electron density from metal to ligand takes place. Thus the ability of 'CO' to delocalise the electron density from the metal accounts for the existance of metal carbonyls with zero or low negative or low +ve oxidation state of the metal atom.

$Ni(CO)_4$ is well known but $[Zn(CO)_4]^{2+}$ is unknown though the two complexes are isoelectronic – Explain.

$Ni(CO)_4$ is a tetrahedral complex, where CO acts as a π-acid ligand. $Ni(CO)_4$ is stabilised by the involvement of synergic bond mechanism. CO donates electron density to Ni(0) through σ-bonding and simultaneously Ni(0) reduces its electron density through donating to empty πp^* orbital of CO by the overlaping with filled metal d-orbital (t_{2g} orbital having π-symmetry) with πp^* orbital of CO. Therefore due to the formation of metal carbonyl complex synergic bond formation mechanism is essential.

For the case of Zn^{+2}, Zn^{2+} is d^{10} system and isoelectronic with Ni(0) in $Ni(CO)_4$. But due to the presence of +2 oxidation on the metal atom prevents the formation of dative π-bond. This synergic bond mechanism is not operative on Zn^{+2} ion. So $[Zn(CO)_4]^{2+}$ is not formed. That is why $Ni(CO)_4$ is well known but $[Zn(CO)_4]^{2+}$ is unknown.

Different ligands in Organometallic Compound

An atom, ion or molecule which is capable of donating a pair of electrons to the metal atom is called a ligand. The no. of ligand atoms simultaneously bound to a metal centre is called ligands **hepticity**. It is written by using the symbol 'η' (eta)

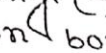
The ligands may be classified on the basis of no. of 'c'- atoms involved in bonding to the metal atom ie, hepticity. The hepticity ranges from 1-8.

1) One electron bonded ligands:

These are the molecules in this the 'c'-atom of the ligands is bonded directly to the metal atom. Such ligands are also called mono-hepto ligands (one electron donor η')

e.g ⇒ CH_3 group attached by a single M-C bond. These ligands are of the following different types —

i) Hydrocarbon ligands :

These include alkyl ($-CH_3$) anyl ($-C_6H_5$), sigma cyclopentadienyl ($-C_6H_5$) etc groups eg ⇒  one carbon bonded cyclopentadienyl compound.

ii) Acyl-ligands :

These include acyl group which involves direct bonding of the acyl gr. to a metal atom as shown below : $M-C(=O)-R$

iii) Carbene-ligands :

These involved the direct metal of carbene to a metal atom — $M \leftarrow :C(R)(R)$

2) Two carbon bonded group :

These are the molecules in which two carbon atoms of the ligands are bonded to the metal atom. These are called dihepto ligands. (η^2) or two e'-donors.

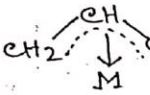
 or 

$K[Pt\text{-}Cl_3(\eta^2 C_2H_4)].H_2O$ Zeise's salt

3) Three carbon bonded ligands :

These are the molecule in which three c-atoms of the ligands bonded to the metal atom. These are called trihepto ligands (η^3)

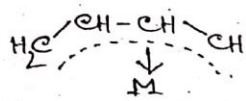
e.g ⇒ Alkyl group ($-C_3H_5$) acts as π-alkyl ligands as shown below.



(η^3-C_3H_5-M-complex)

$[Ir(\eta^3 C_3H_5)(NO)(PPh_3)_2]^{\oplus}$

4) Four carbon bonded ligands :

eg ⇒  (η^4-C_4H_6-M complex)

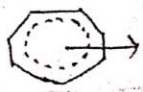
5) Five carbon bonded ligands :

(η^5-Cp-M complex) $[(\eta^5 Cp)_2 Fe]$

6) Six-carbon bonded ligands :

(η^6-C_6H_6-M complex) $[(\eta^6 C_6H_6)_2 Cr]$.

7) Seven-carbon bonded ligands :



(η^7-C_7H_7-M Complex) $[Mo(\eta^7-C_7H_7)(CO)_3]^{\oplus}$

8) Eight Carbon bonded ligands :

(η^8-C_8H_8-M complex)

[(η^8-C_8H_8), U]

Structure of CO-molecule on the basis of VBT :

According to VBT theory CO molecule is represented by the structure :C≡O:. In this structure 'C' atom and 'O' atom both are sp-hybridised.

'C' atom (g.s) — 2s: 1↓ | 2p: 1 1

sp-hybridisation

C-atom (sp-hybridised) — 1↓ 1 | 1

'O'-atom (g.s) — 1↓ | 1 1 1↓

sp-hybridisation.

'O'-atom (sp-hybridised) — 1↓ 1 | 1 1↓

The C-O bond is formed by the group overlap b/w singly filled sp-hybrid orbitals on carbon and oxygen atom while C-O π-bond results by the overlap between the singly filled 2py orbital on 'C' atom and 'O' atoms. O→C coordinate bond is obtained by the donation of one electron residing in 2pz orbital on 'O' atom to the vacant 2pz orbital of C-atom. The 'e' pair present in sp-hybrid orbital of both the atoms remains as lonepair of electrons on these atoms.

C-atom in sp hybridised state — 1↓ 1 | 1

O-atom in sp hybridised state — 1↓ 1 | 1 1↓

σ, π, ↑ Coordinate bond.

:C≡O:

↳ lonepair of 'e' in sp hybrid orbital.

formation of different bond in CO molecule on the basis of VBT.

18-electron Rule :

In nitrosyl and carbonyl complexes the valence electron of the metal ion and the 'e' donated by the ligand is equal to 18. The complexes having the 18 electrons in the valence shell of central metal ion are the stable complexes & it is called 18-e rule.

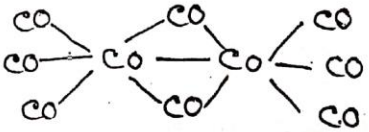
In case of $[Cr(CO)_6]$ complex the no. of e in the valence shell of $Cr = 6$, the 'e' donated by 6-CO molecules $= (6 \times 2) = 12$. Therefore the total no. of e in the valence shell of the metal ion $= (12 + 6) = 18$.
Hence $[Cr(CO)_6]$ complex obeys 18-e rule and it is a stable complex.

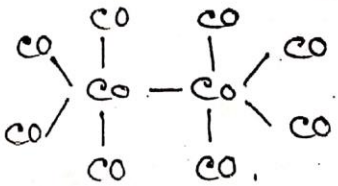
$[Fe(CO)_5]$, $[Ni(CO)_4]$, $[Mn_2(CO)_{10}]$ $[Co_2(CO)_8]$ obey 18-e rule.

" $[Fe(CO)_5] \Rightarrow [8 + (5 \times 2)] = 18$

$[Mn_2(CO)_{10}] \Rightarrow [14 + 20 + 2] = 36$.

$[Co_2(CO)_8] \Rightarrow$

In solid state :  $[9 + 6 + 2 + 1] = 18$

In solution :  $[9 + 8 + 1] = 18$.

EAN - Rule [Effective Atomic Number Rule]

On the basis of the concept of coordinate bond it is suggested that after the ligands have donated a certain no. of electron to the central metal ion to L-M bonding, the total no. of 'e' on the central atom including those gained from ligand (L) in the bonding is called the EAN. (Effective atomic no) of the central metal ion. In many cases this total no. of e (EAN) surrounding the co-ordinated metal ion is equal to the atomic no. of the inert gas. This is called EAN rule.

When the EAN is 36 (crypton), 54 (Xenon), 86 (Radon) rule is said to be followed. Therefore the EAN of the central metal ion in a given complex is given by -

$$\boxed{EAN = (x - x) + ny}$$

x = Atomic no. of metal ion.
x = Oxidation state of the central metal ion.
n = no. of ligand
y = no. of 'e' donated by one ligand.

eg: In case of $Ni(CO)_4$,

EAN = [atomic no. of Ni atom + 'e' donated by four 'CO' gr]

= [28 + 8] = 36.

Hence $[Ni(CO)_4]$ complex obeys EAN rule.

Application of EAN Rule :

With the help of this rule the magnetic property of complex ion can be predicted. It has been observed that the complex ion whose central atom obeys this rule are diamagnetic.

Since the EAN of Co^{+3} ion in $[Co(NH_3)_6]^{3+}$ ion = 36, this ion obeys EAN rule. and hence $[Co(NH_3)_6]^{3+}$ ion is diamagnetic.

The complex ion whose central metal atom does not obey EAN rule are generally paramagnetic. The no. of unpaired e' present in the complex ion

Application 18-electrons and EAN rule on some Carbonyl compounds :

i) Nutral atom method
ii) Charge distribution method.

a) $[Mn(CO)_5Cl]$ i) 1st method ⇒ 7+10+1 = 18
ii) 2nd method ⇒ 6+10+2 = 18

b) $[HCo(CO)_4]$ ⇒ 1+9+8 = 18

c) $[CH_3Re(CO)_5]$ ⇒ i) 1+7+10 = 18

d) $[Mn(\eta^2-C_2H_4)(CO)_5]$ ⇒ i) 7+2+10 = 19

e) $[Mn(\eta^3-C_3H_5)(CO)_4]$ ⇒ i) 7+3+8 = 18

f) $[Co(\eta^3-C_3H_5)(CO)_3]$ ⇒ 9+3+6 = 18

g) $[Co(\eta^5-Cp)(CO)_2]$ ⇒ 8+6+4 = 18

h) $[Fe(\eta^5-Cp)_2]$ ⇒ 8+10 = 18

i) $[Co(\eta^5-Cp)_2]^+$ ⇒ 8+10 = 18.

Calculate the no. of metal-metal atom bonds of the following compounds obeying 18-electron rule.

i) $[Os_4(CO)_{14}]$ ii) $[Os_4(CO)_{15}]$ iii) $[Os_4(CO)_{16}]$

Ans: i) $28+32+2x = 72$ x is metal metal bonds.
$x = 6$

ii) $32+30+2x = 72$
$x = 5$

iii) $32+32+2x = 72$
$x = 4$

Find the values of 'x' and 'y' assuming validity of 18-electrons rule.

i) $[Fe(\eta^5-Cp)(CO)_x(NO)_y]$ $8+5+2x+3y = 18$
if $x=1$, $y=1$

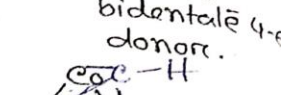
ii) $[Fe(\eta^5-Cp)(\eta^1-Cp)(CO)_x]$ $8+5+1+2x = 18$ $x=2$

iii) $[Mn(CO)_x(NO)_y]$ $7+2x+3y = 18$
$x=1$ $y=3$.

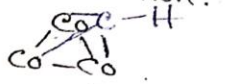
iv) $[Co_2(CO)_x(\eta^2-C_2H_4)]$ $18+2x+2=36$, $x=8$ [as here present two C

8 Find the values of n - assuming validity of the 18 electron rule.

1) $[\overset{+2}{Ru}\overset{-1}{H}(\overset{-1}{CO_2Me})(PPh_3)_n]$ $\Rightarrow 6+2+4+2n=18$, $n=3$



2) $[Co_3(CO)_nCH]$ $\Rightarrow 27+2n+3+6=54$, $n=9$



3) $[Fe_4(\eta^5-Cp)_2(CO)_n]$ $\Rightarrow 32+10+2n+12=72$, $n=9$

Classification of Carbonyl :

Metallic carbonyls have been classified into the following two ways -

1. Classification based on the no. of metallic atoms present in carbonyl

This classification gives the following two types of carbonyls -

(a) Mononuclear Carbonyls :

The molecule of these carbonyls contain only one metallic atom.

eg $\Rightarrow$ $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$ etc.

(b) Polynuclear Carbonyls :

The molecule of of these carbonyls contains two or more metallic atoms. These carbonyls may be homonuclear (eg $\Rightarrow$ $Co_2(CO)_8$, $Fe_2(CO)_4$, $Fe_3(CO)_{12}$ etc) or heteronuclear (eg $\Rightarrow$ $MnCo(CO)_9$, $MnRe(CO)_{10}$ etc)

2. Classification based on the structure of carbonyls :

This classification gives the following types of carbonyls -

(a) Non-bridge Carbonyls :

These carbonyls do not contain any bridging carbonyl group. These carbonyls may be of the following types -

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.

⑥ 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), $Fe_2(CO)_9$, $DS_2(CO)_9$ etc.

Classification of Carbonyl

- Classification based on the no. of metallic atoms present in carbonyls
  - Mononuclear: $Ni(CO)_4$, $Fe(CO)_5$
  - Polynuclear: $MnCo(CO)_9$, $MnRe(CO)_{10}$ etc.
- Classification based on the structure of carbonyls.
  - Non-bridged
    - Nonbridge 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 :

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

Solve the problems:

1. Explain the σ- π synergic effect with reference to M-L bonding aspect in metal carbonyls.

2. Calculate the no. of metal-metal bonds of the following compounds obeying 18 electron rule.

   (i) $Os_4(CO)_{16}$

   (ii) $Co_2(CO)_8$

   (iii) $Fe_2(CO)_9$

   (iv) $Fe_3(CO)_{12}$