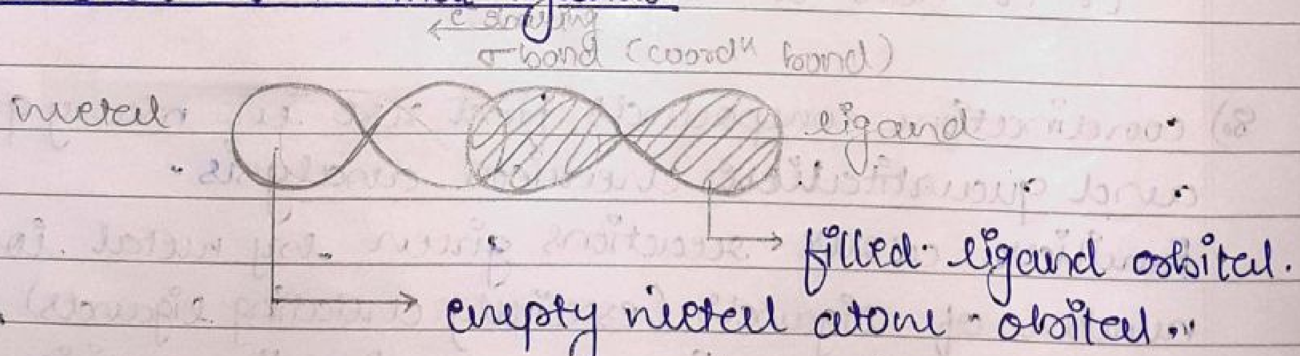
* Some other Ligand categories:

I.) Flexidentate Ligands:

- ligands which can change their denticity.
- generally, SO_4^{-2} and CO_3^{-2} acts as a monodentate ligands but in exceptional complexes, they act as a bidentate ligands.

eg:
- $[Co(NH_3)_5SO_4]Cl$ (here, SO_4^{2-} is a monodentate ligand))
- $[Co(NH_3)_4SO_4]Cl$ (here, SO_4^{2-} is a bidentate ligand)

II.) Classical or Normal ligands:



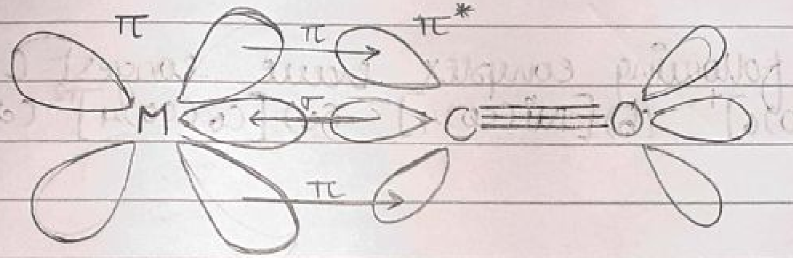
- ligand with characteristic electron donating tendency towards central metal atom and coordination bond formation, are included in these group.

eg: H_2O; OH^-; O_2^{-2}; O^{-2}; etc.

III.) <u>Non-classical or π acid or π acceptor ligand</u>: Synergic bonding

- ligands with characteristic electron pair donating tendency to central metal atom, forming a coordinate sigma bond with simultaneous electron pair acception from central metal ion through back bonding (synergic bonding) forming a partial double bond (π bond).

eg: CO; CN^-; NO^+; etc.



Synergic bonding in metal carbonyl.

- the metal-carbon bond in metal carbonyls possess both σ and π character.
- M-C σ bond is formed by the donation of lone pair of electrons on carbonyl carbon into vacant orbital of metal.
- M-C π bond is formed by the donation of pair of electrons from filled d-orbital of metal into vacant antibonding π* orbital of carbon monoxide.
- metals to ligand bonding creates a synergic effect which strengthens bond between CO and metal.

* <u>NOTE:</u>

- in blood:

$$Fe + CO \longrightarrow Fe \overset{\pi}{\underset{\sigma}{\rightleftarrows}} CO$$

carbon monoxide ∴ synergic bond

while, $Fe + O_2 \longrightarrow Fe \xleftarrow{\sigma \text{ bond}} $ (coordn bond).

✱ NOTE:

- $Fe + KCN \longrightarrow Fe \overset{\pi}{\rightleftarrows} CN$ synergic bond.

✱ NOTE:

- $\frac{e}{p} \propto$ bond length of C–O

e = no. of e^- in central metal atom
p = no. of p^+ in central metal atom

Q:1 which of following complex have longest C–O bond length:
(2016) (a) $[Mn(CO)_6]^+$ (b) $[Ni(CO)_4]$ (c) $[Co(CO)_4]^{+2}$ (d) $[Fe(CO)_4]^{+2}$

$\longrightarrow$ (a) $Mn \Rightarrow e^- = 25-1$

$e/p = \frac{24}{28}$ $\frac{6}{7}$

(b) $Ni \Longrightarrow e/p \Rightarrow \frac{28}{28}$ 1

(c) $Co \Rightarrow e = 27-2$

$e/p = \frac{25}{27}$

(d) $Fe \Rightarrow e = 26-2$

$e/p = \frac{24}{26}$

ISOMERISM

isomerism:

* Structural isomerism:

- isomers have different bonding pattern.
- structural isomers are of four types:

(I.) Linkage:

- it is shown by co-ordination compounds having ambidentate ligand.

eg: $[Co(NH_3)_5(NO_2)]Cl$ and $[Co(NH_3)_5(ONO)]Cl$.
$[Mn(CO)_5SCN]$ and $[Mn(CO)_5NCS]$.

(II.) Coordination:

- it arises from the interchange of ligands between cationic and anionic complexes of different metal ion present in the complex.

eg: $[Cr(NH_3)_6][Co(CN)_6]$ and $[Co(NH_3)_6][Cr(NH_3)_6]$.
$[Pt(NH_3)_4][PtCl_4]$ and $[PtCl(NH_3)_3][PtCl_3(NH_3)]$.

(III.) Ionisation:

- it arises due to the exchange of ionisable anion with anionic ligand.

eg: $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.
$[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$.

(IV.) Solvate:

- it is also known as hydrate isomerism.
- In this isomerism, water is taken as solvent. It has different number of water molecules is coordination sphere & outside it.

eg: $[Co(H_2O)_6]Cl_3$; $[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$; $[Co(H_2O)_3Cl_3] \cdot 3H_2O$.

* Stereoisomerism:

- they have same chemical formula and chemical bonds but they have different spatial arrangement.
- stereo isomers have two types:

(A.) Geometrical Isomerism:

- geometrical isomers are of two types CIS and TRANS.
- it is common in complexes with coordination no. 4&6.
- when two identical ligands are co-ordinated to metal ion from same side then it is CIS isomer. (latin, cis means same).
- if two identical ligands are co-ordinated to metal ion from opposite side then it is TRANS isomer. (latin, trans means across).

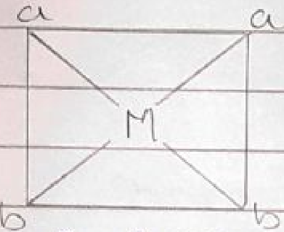
- these GIs differ in physical as well as chemical properties.
- 4-co-ordinated complex with tetrahedral geometry do not exhibit CIS-TRANS isomerism, because relative position of ligands remain same for each other.
- it is exhibited by 4-coordinated complexes with square planer geometry.

***NOTE:**

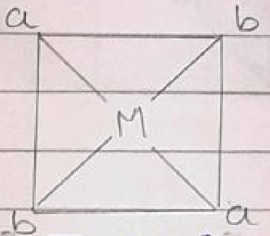
- only 5 possible cases with square planer complex. i.e. Ma_2b_2 ; Ma_2bc ; $Mabcd$; $M(AB)_2$; $M(AB)cd$. where M is metal (central metal atom).

⟹ GI with coordination number 4: (sq. planar complex).

a.) Complexes with general formula, Ma_2b_2 (where both a and b are monodentate) can have Cis and Trans isomers.

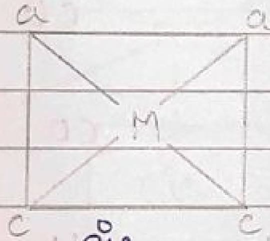


Cis-isomer

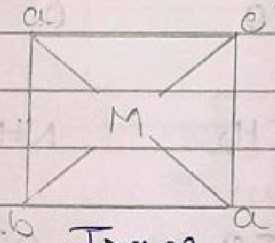


Trans-isomer

b.) Complexes with general formula, Ma_2bc can have Cis and Trans isomers.

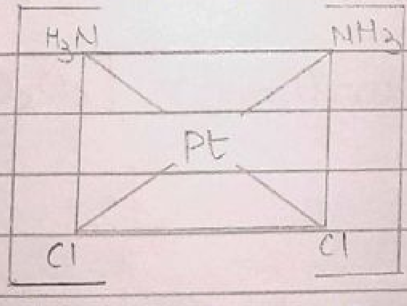


Cis

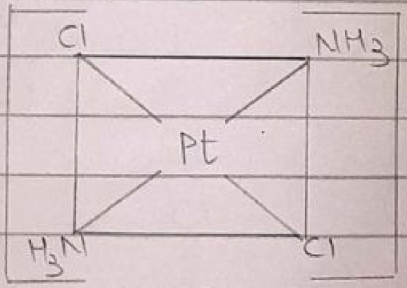


Trans

eg: (a) $[Pt(NH_3)_2Cl_2]$

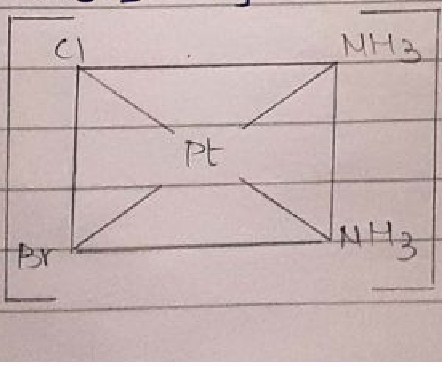


Cis-platin (anti cancer)

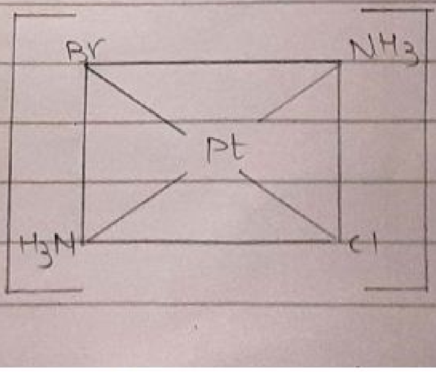


Trans

(b) $[Pt(NH_3)_2ClBr]$

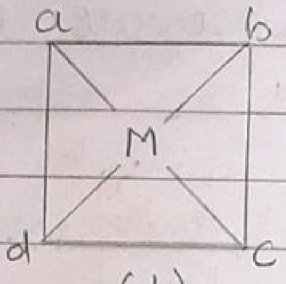


Cis

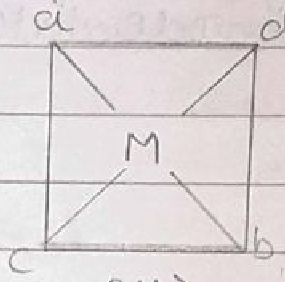


Trans

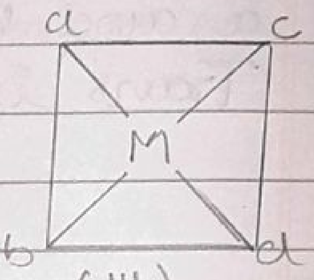
(c) Complex with general formula, Mabcd can have three isomers.



(I)

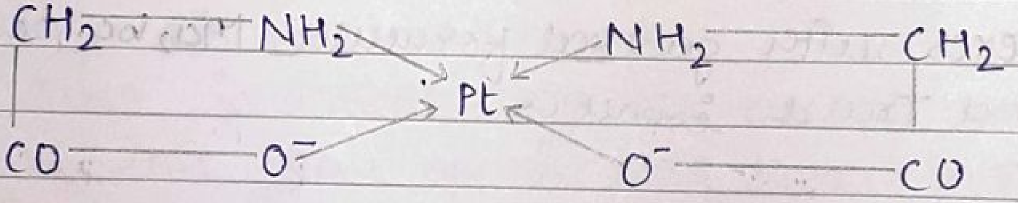


(II)

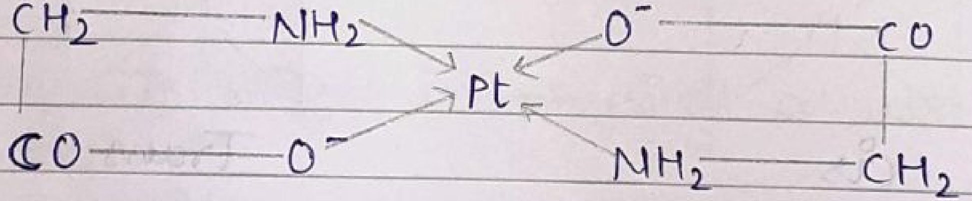


(III)

(d) Diglycinato platinum (II) complexes:

- 

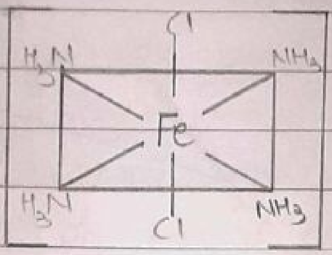
Cis

- 

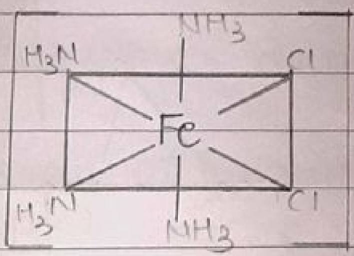
Trans

⟹ GI with coordination number 6:

a.) $[Fe(NH_3)_4Cl_2]$:

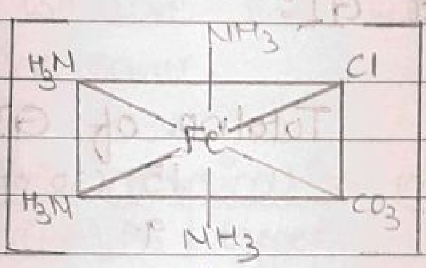


Trans

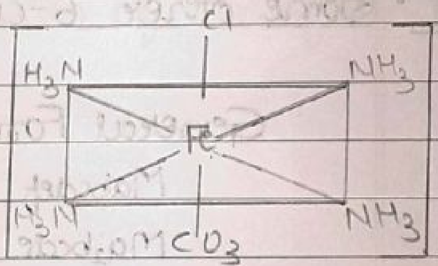


cis

b.) $[Fe(NH_3)_4ClCO_3]$



cis

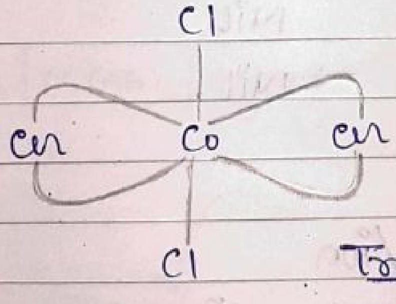


Trans.

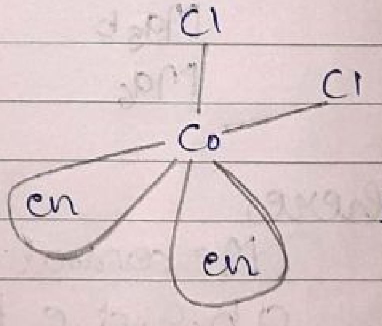
c.) $M(AA)_2B_2$ Type

- here, AA is a bidentate ligand.

eg: $[Co(en)_2Cl_2]$ (coordination no. 06)

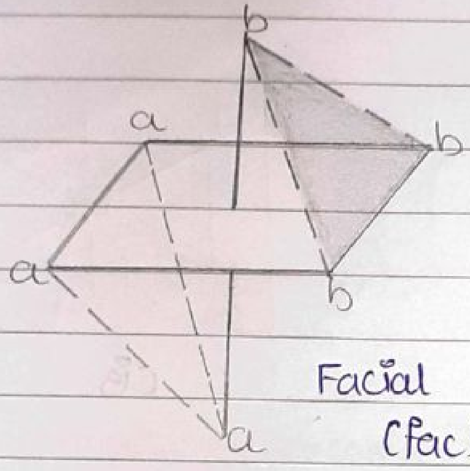


Trans

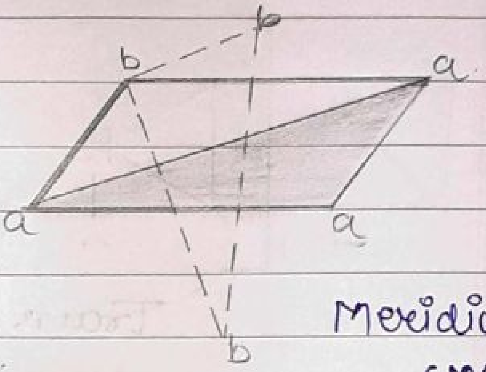


cis.

d.) Facial and Meridional isomerism (Ma_3b_3).



Facial
(fac)



Meridional
(mer)

NOTE • Some other 6-coordinated GI:

General Formula	Total no. of GI possible.
$Mabcdef$	15 (30 optical isomer)
Ma_2bcde	9
Ma_2b_2cd	6
$Ma_2b_2c_2$	5
Ma_3bcd	4
Ma_3b_2c	3
Ma_3b_3	2
Ma_4bc	2
Ma_4b_2	2
Ma_5b	Nil
Ma_6	Nil.

here,

M = central metal atom/ion

a, b, c, d, e, f = monodentate ligand.

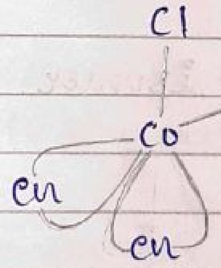
(B.) Optical Isomerism:

⟹ OI with coordination number 4:

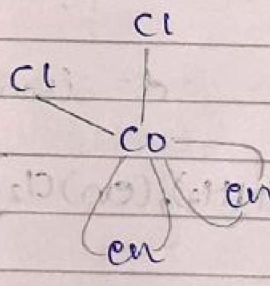
- square planer and tetrahedral complexes do not show optical isomerism.
- Square planer complex do not show OI because of the presence of plane of symmetry (POS) making it optically inactive.
- Tetrahedral complex do not show OI because of the symmetrical arrangement of ligands in a plane, this is so, because the relative position of the four ligands remains same.

⟹ OI with coordination number 6:

a.) cis $[M(AA)_2B_2]$ type:

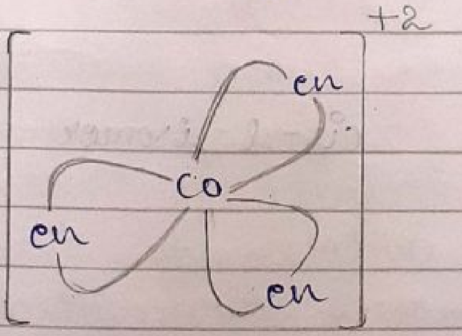


cis-dextro

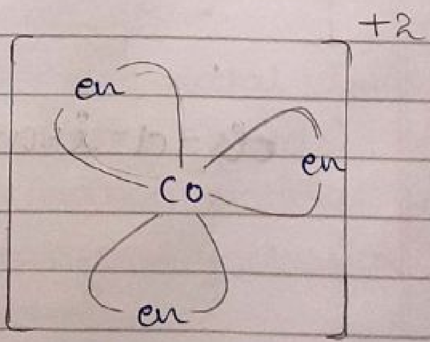


cis-laevo

b.) cis $[M(AA)_3]$ type:

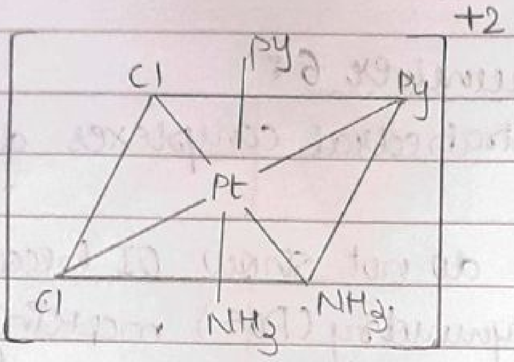


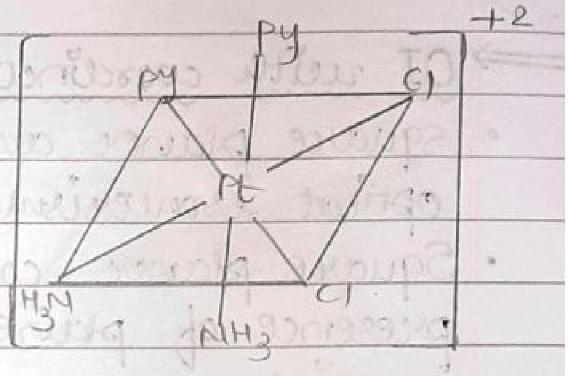
dextro



laevo.

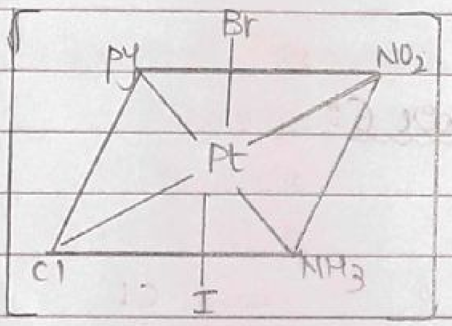
c.) $[Ma_2b_2c_2]^{n+} \longrightarrow [Pt(py)_2(NH_3)_2Cl_2]^{+2}$

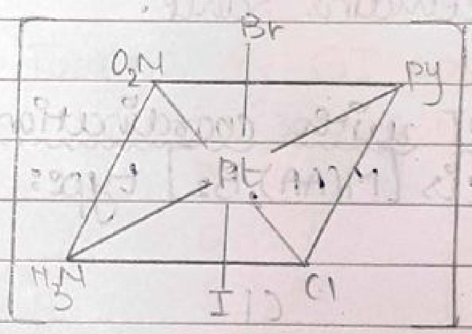




cis-d-isomer cis-l-isomer

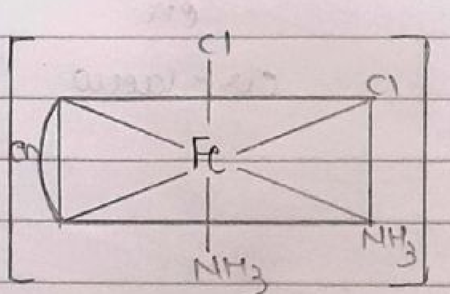
d.) $[Mabcdef] \longrightarrow [Pt(py)NH_3NO_2ClBrI]$

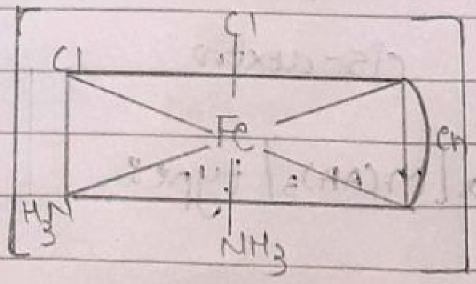




d- isomer l- isomer

e.) $[Fe(NH_3)_2(en)Cl_2]$





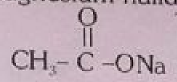
cis-d-isomer cis-l-isomer

3.6 ORGANOMETALLIC COMPOUNDS

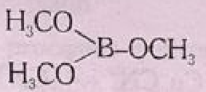
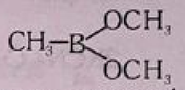
Compounds in which C-atom is directly bonded with less electronegative element.

(Ge, Sb, B, Si, P, As) Also form organometallic compounds.

Ex. $R-Zn-R$ dialkyl zinc (Frankland reagent)
$R-Mg-X$ Alkyl Magnesium halide (Grignards reagent)

(b)
Sodium acetate  $CH_3-\overset{O}{\overset{||}{C}}-ONa$
Sodium ethoxide C_2H_5-O-Na
Sodium Mercaptide H_3C-SNa

These are not organometallic compounds because in these compounds metal is not directly attached with carbon atom.

(c) $B(OCH_3)_3$ is not OMC →  and $CH_3B(OCH_3)_2$ is OMC → 

(d) Metal cyanides, carbides and carbonates are not considered OMC because in these compounds metal carbon bond has ionic nature.

Classification of Organometallic Compounds

OMC can be classified into three main categories–

σ - bonded OMC : These compounds are formed mostly by non transition and metalloid elements.

Ex.	$R-Mg-X$	(Grignard's reagent)
	$(CH_3)_2Zn$	(Dimethyl zinc or Frankland's reagent)
	R_2Cd	(dialkyl cadmium)
	$(C_2H_5)_4Pb$	(Tetra ethyl lead) – used as antiknocking agent in petrol.
	$\underset{\text{Solid}}{(CH_3)_3Al}+TiCl_4$	(Ziegler natta catalyst) – Heterogeneous catalyst, used in polymerisation of alkene.

π - bonded OMC : These are usaully formed by transition metals.

Ex.	Ferrocene	$[Fe(\eta^5-C_5H_5)_2]$	where η = No. of carbon atoms combined with metal atom.
	Zeise's salt	$K[PtCl_3(\eta^2-C_2H_4)]$	
	Dibenzene chromium	$[Cr(\eta^6-C_6H_6)_2]$	

σ and π - bonded OMC : Transition metals of gp. 6, 7, 8, 9 and 10 in their zero oxidation state form such type of OMC. The carbonyl compounds of these metals have both σ and π bonds.

Ex. $[Ni(CO)_4]$, $[Fe(CO)_5]$, $[Mn_2(CO)_{10}]$
$[M(CO)_6]$ $[M = Cr, Mo, W]$

3.7 APPLICATION OF COORDINATION CHEMISTRY

(a) Test of Ni^{+2} : Ni^{+2} ion give rosy red ppt when react with dmg in weak alkaline medium.

book

* Application of Co-ordination Chemisty

1.) cis$[Pt(NH_3)_2Cl_2]$ complex is used in chemotherapy.

2.) $[CaH_2EDTA]$ complex is used in removing lead poisoning.

3.) $[Na_2EDTA]$ complex also known as Versine solution is used for quatitative estimation of water hardness.

4.) $[RhCl(PPh_3)_3]$ complex is used in unsaturated oil's hydrogenation.

5.) Haemoglobin is a coordination complex of iron(Fe).
(∴ Fe acts as a central metal atom).

6.) Chloropyll is a coordination complex of magnesium(Mg).
(∴ Mg acts as a central metal atom).

7.) Vitamin-B12 is a coordination complex of cobalt (Co).
(∴ Co acts as a central metal atom).

8.) coordination compounds find use in many qualitative and quantitative chemical analysis.

- Familiar colour reactions given by metal ions with number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis of detection and estimation by classical and instrumental methods of analysis.
- eg: EDTA, DMG (dimethylglyoxime), α-nitroso-β-napthol, cupron, etc.