February 2018

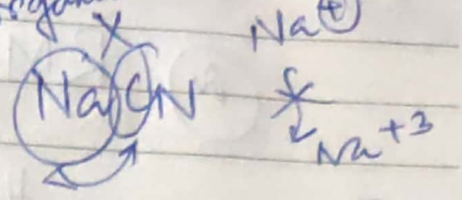
S	M	T	W	T	F	S
				01	02	03
04	05	06	07	08	09	10
11	12	13	14	15	16	17
18	19	20	21	22	23	24
25	26	27	28			

Arnab Mallick
Email:- arnabmallick344@gmail.com
Mob :- 8001874415

ORGANOMETALLIC CHEMISTRY

$\left\{ \begin{array}{c} RMgX \\ R_2CuLi \end{array} \right\}$

organometallic ✗



Willkinsonson Reagent

$[Rh(PPh_3)_3Cl]$

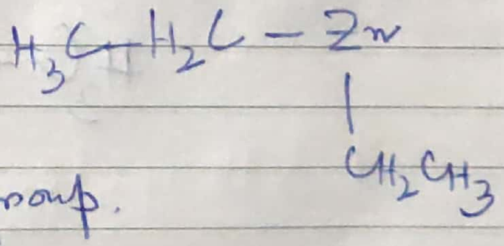
$$R-CH=CH_2 \xrightarrow[H_2]{\text{Willkinson reagent}} RCH_2CH_3$$

FATHER

↓

Edward Frankland

(Et_2Zn)



$H_3C-H_2C-Zn-CH_2CH_3$

$C-\text{M}$ → Main group.
→ Transition metal
→ Lanthanide Actinide

Notes

Types of organometallic Compound on the basis of metal

① Main Group ON Organometallic

ⓐ RMgX (Grignard Reagent)

H_3C-MgX (1,2)

ⓑ Gilman Reagent

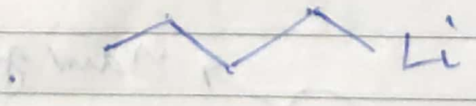
(1,4) R_2CuLi

ⓒ Ziegler Natta Catalyst

$Al(C_2H_5)_3$

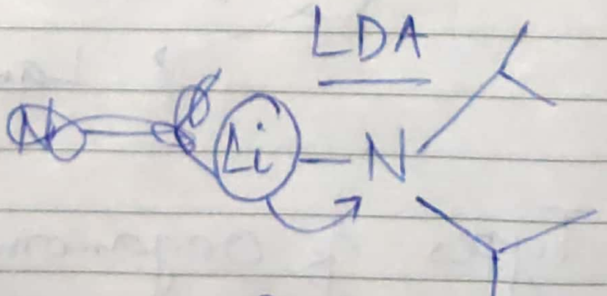
ⓓ alkyl Lithium (RLi)

H_3C-Li



ⓔ

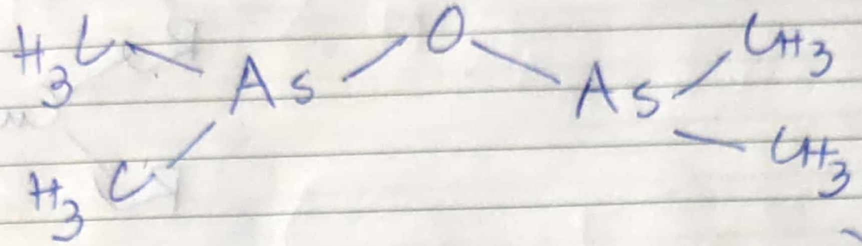
LDA



not organometallic Compound
Li attached to N not C

Notes

First Main group organometallic Comp:-



(Cacodyl oxide)

② Transition metal organometallic Compounds :-

1st :- Zeise's Salt

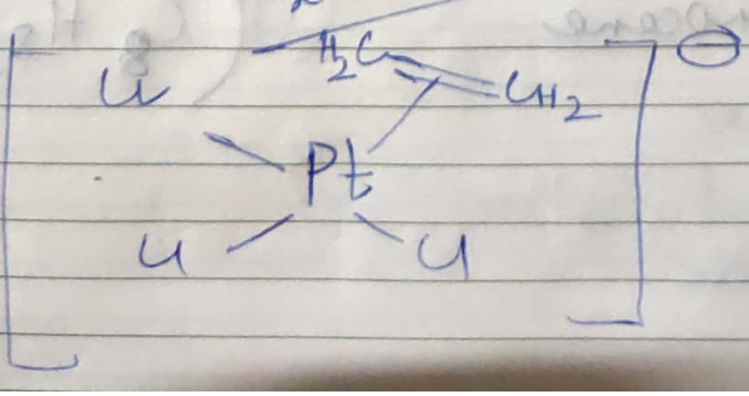
$K^{\oplus}[PtCl_3(C_2H_4)]^{\ominus}$

$Pt^{+2} \rightarrow$ Square Planar Complex

x

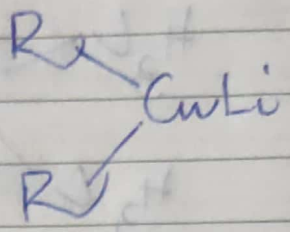
$x-3=-1$

$x=+2$



(b) Gilman Reagent :-

R_2CuLi



(c) $[Fe(CO)_4]^{2-}$

Collman's Reagent

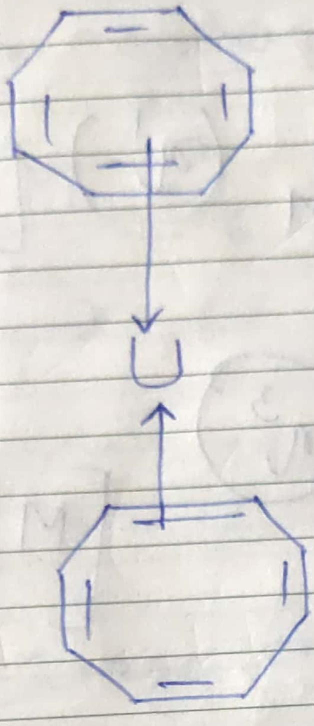
(d) $[Rh(PPh_3)_3Cl]$ Wilkinson's Reagent.

14 Sunday

(3) Lanthanides / Actinides Organometallic

Uranocene $(C_8H_8)_2U$

Notes



Uranocene

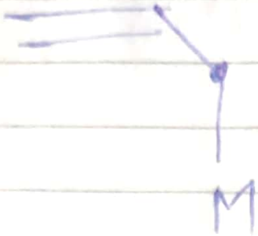
\# Hepticity :- (η)

⇒ no of donor atoms of a ligand attached to metal.

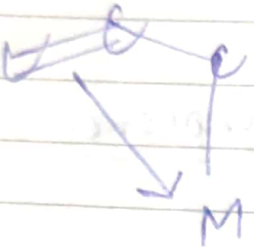
\# H_3C-MgX (η^1) $(\eta^x - L)$

x no. of donor atoms of ligand L are directly attached to metal M

#



(η^1) $[M(\eta^1-C_3H_5)]$



$\boxed{\eta^3}$

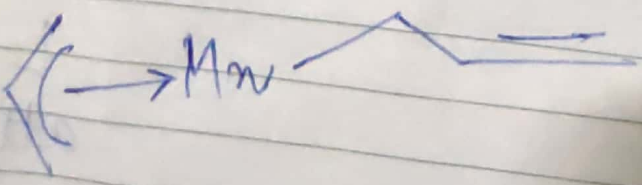
$[M\{\eta^3-C_3H_5)]$

$[M(C_3H_5)]$

If nothing is given maximum hepticity should be considered.

$Mn(\eta^1-C_3H_5)(\eta^3-C_3H_5)$

Notes



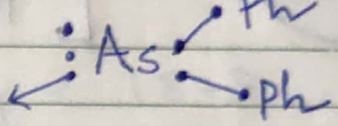
Which of the following Complex follow 18e⁻ rule?

(26) $[IrCl_3(PPh_3)_2(AsPh_2)]^{\ominus}$

$= 9 + (3\times1) + (2\times2) + 1 + 1$

$= 9 + 3 + 4 + 2$

$= 18e^-$



(27) ** $[Os(N)Br_2(PMe_3)(NMe_2)]^-$

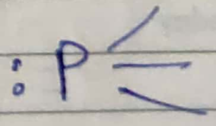
$= 8 + 3 + (2\times1) + 2 + 1 + 1$

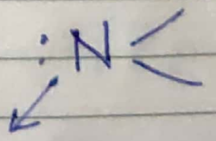
$= 17e^-$

does not follow 18e⁻ rule.

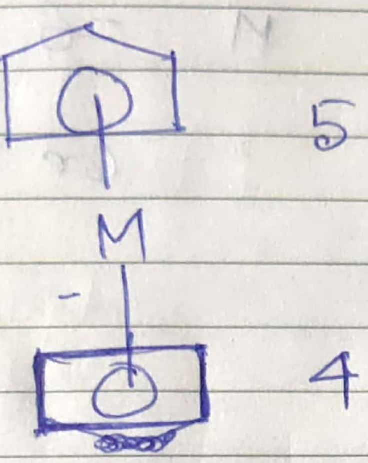
(BARC EXAM)

$Os \equiv N$





* Consider 18 e^- rule as a guide, determine the unknown quantity in the following complexes :-
(M: first row transition metal)

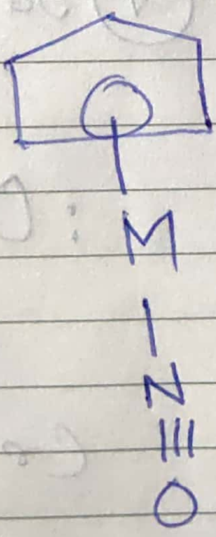


$5 + M + 4 = 18$

$M = 18 - 9$
$= 9$

Co : $4s^2 3d^7$.

*



$5 + M + 3 = 18$

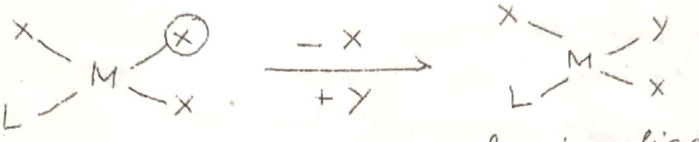
$M = 10$

Ni $4s^2 3d^8$

TRANS EFFECT :

Chernyaev (1926) observed that during substitution reactions of square planar Pt(II) complexes certain spectator ligands facilitate the substitution of the ligand that is in a position trans to them. The tendency the spectator ligand to direct an incoming ligand to occupy the position trans to it is known as trans effect

This is very important for a better understanding of the kinetic behaviour of the planar complexes. It deals with the kinetics and mechanism of the substitution reactions of Pt (II) planar complexes.



L = spectator ligand ; X = leaving ligand ; Y = incoming ligand.

Here trans-directing L ligand labilising the X ligand lying trans to it and facilitating its substitution by incoming ligand Y.

By comparing a large no. of reactions the ligands can be arranged in order of increasing trans-effect.

$H_2O < OH^- < NH_3 \sim RNH_2 < Py < Cl^- < Br^- < I^- < NO_2^- < CH_3^- < H^-, PR_3$

$< NO \sim CO \sim CN^-, C_2H_4$

The trans directing effect increases with increasing π-acidity of the ligands. The trans effect of the ligands which donot form π-bond increases with increasing polarisability

$Cl^- < Br^- < I^- < H^-$

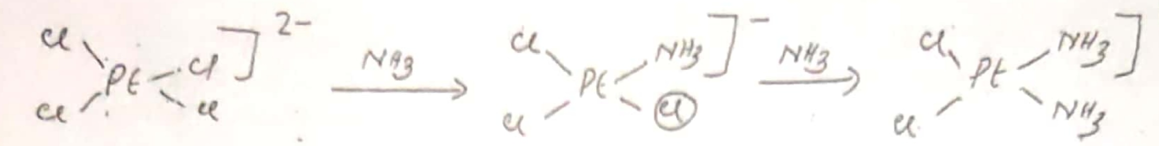
$H_2O < NH_3$

USES OF TRANS EFFECT :

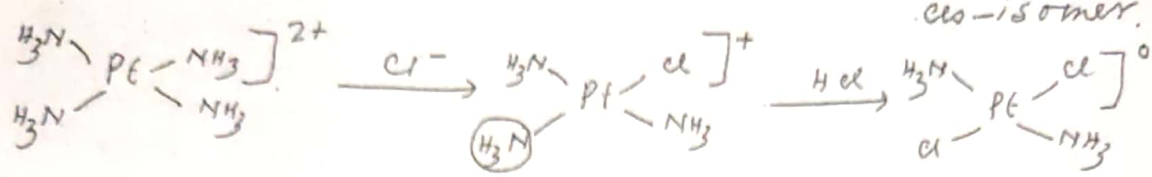
IN SYNTHESIS : By planning the sequence of addition of substituents, the synthesis of different isomers of a complex can be attained.

a) Synthesis of cis- and trans-isomers of $[Pt(NH_3)_2Cl_2]$

As trans effect of Cl^- is higher than that of NH_3, addition of NH_3 to $PtCl_4^{2-}$ gives the cis-isomer while addition of HCl to $[Pt(NH_3)_4]^{2+}$ gives the trans-isomer.



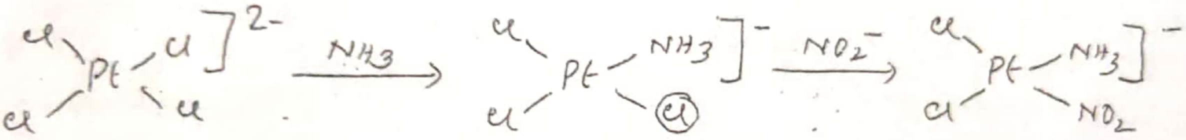
cis-isomer.



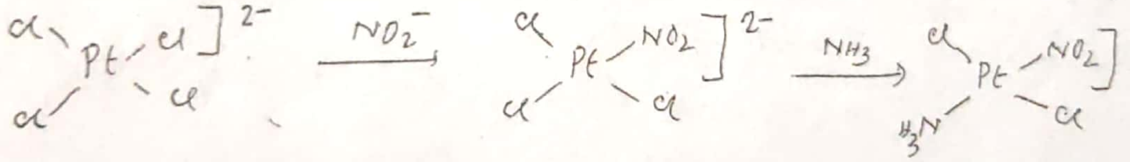
Trans-isomer.

b) Synthesis of cis- trans isomers of $[Pt(NH_3)(NO_2)Cl_2]^-$ starting from $PtCl_4^{2-}$.

Since trans effect $NH_3 < Cl^- < NO_2^-$, addition of NH_3 followed by NO_2^- gives cis-isomer and addition of NO_2^- followed by NH_3 gives the trans isomer.



Cis-isomer.

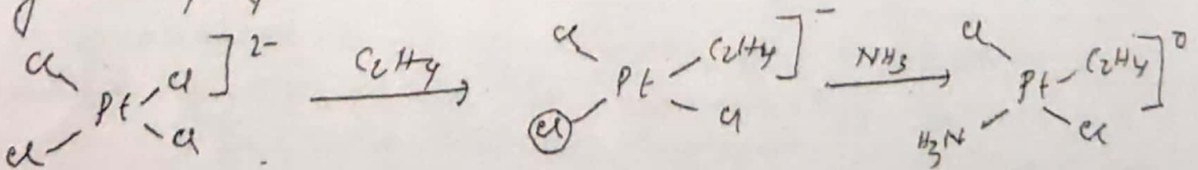


Trans isomer.

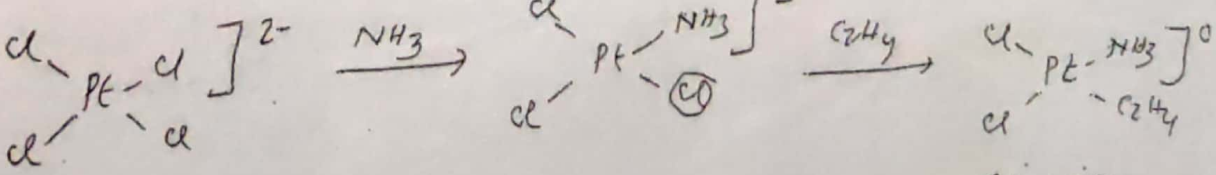
c) Synthesis of cis- and trans isomers of $[PtCl_2(NH_3)(C_2H_4)]$ from $K_2[PtCl_4]$

Trans effect $NH_3 < Cl^- < C_2H_4$

Addition of C_2H_4 followed by NH_3 gives the trans isomer while addition of NH_3 followed by C_2H_4 gives cis-isomer.



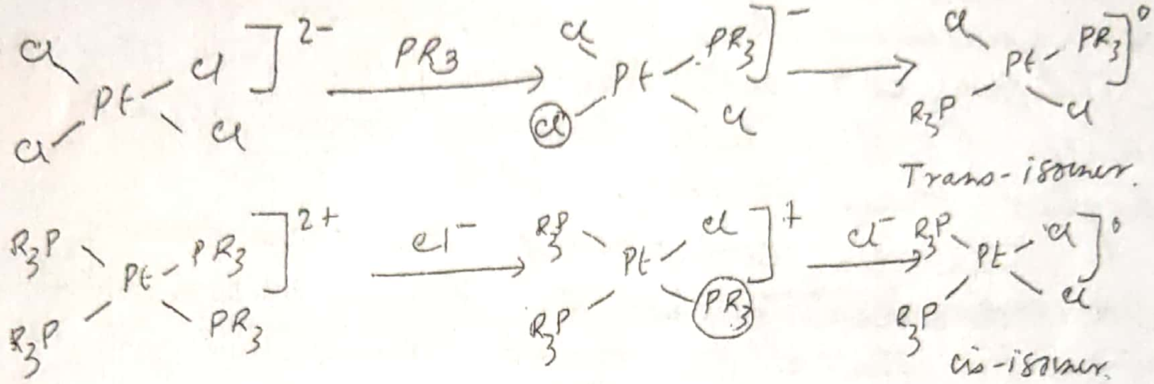
Trans-isomer



Cis isomer.

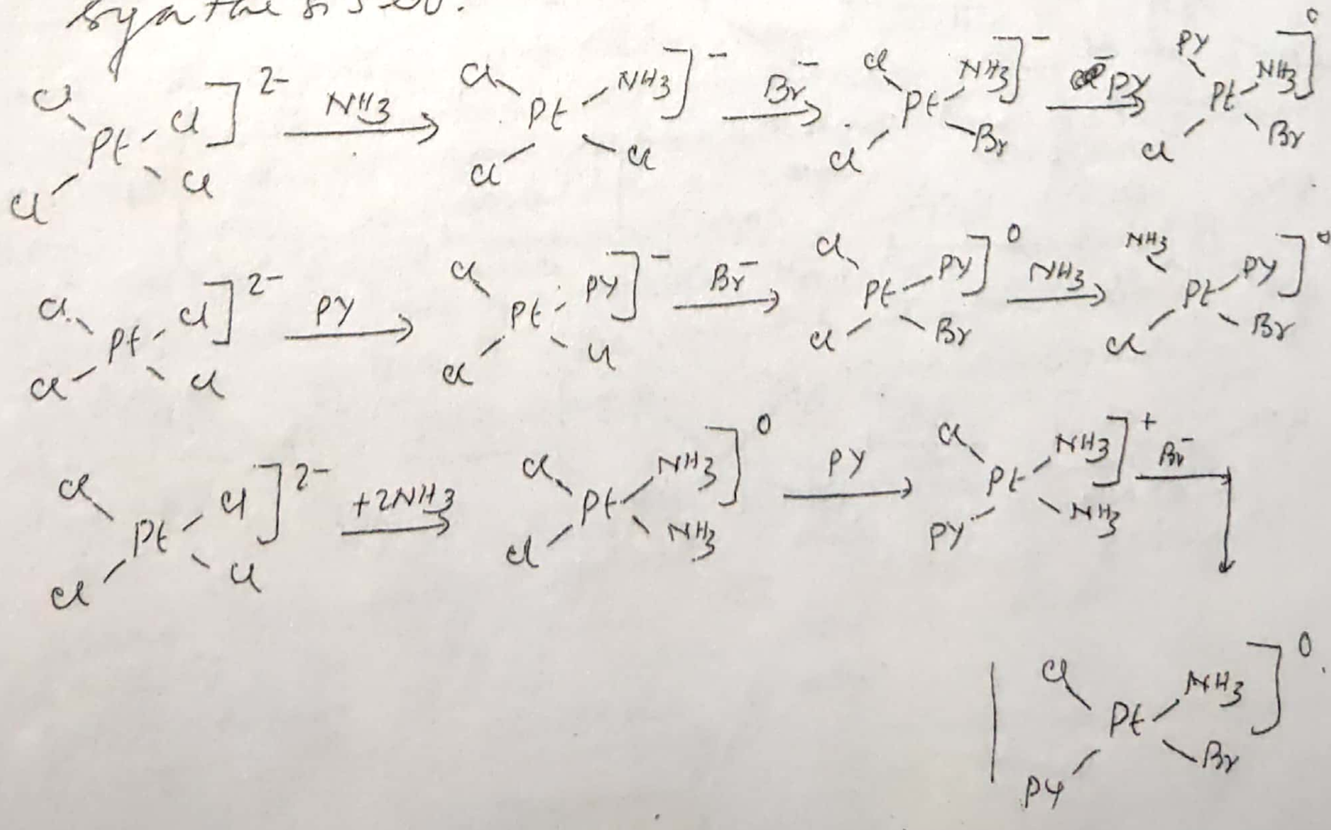
d) Synthesis of cis- and trans isomers of $[Pt(PR_3)_2Cl_2]$

Trans effect order $Cl^- < NO_2 < PR_3$
If we start with $PtCl_4^{2-}$ and add PR_3, we get the trans-product. If we start with $[Pt(PR_3)_4]^{2+}$ and add Cl^-, we get the cis-product.



e) Synthesis of the three geometrical isomers of $[Pt(NH_3)(py)BrCl]$.

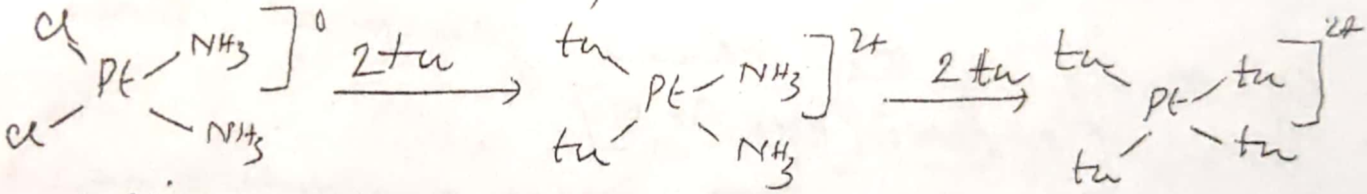
By changing the order of introducing different ligands the isomers may be synthesised.



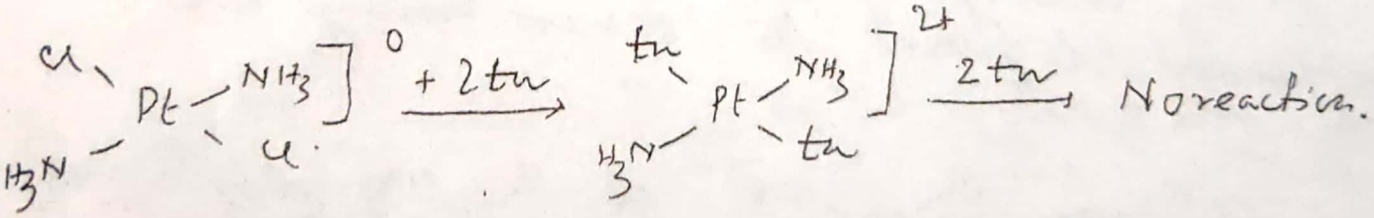
e) To distinguish cis- trans isomers of $[Pt(NH_3)_2Cl_2]$.

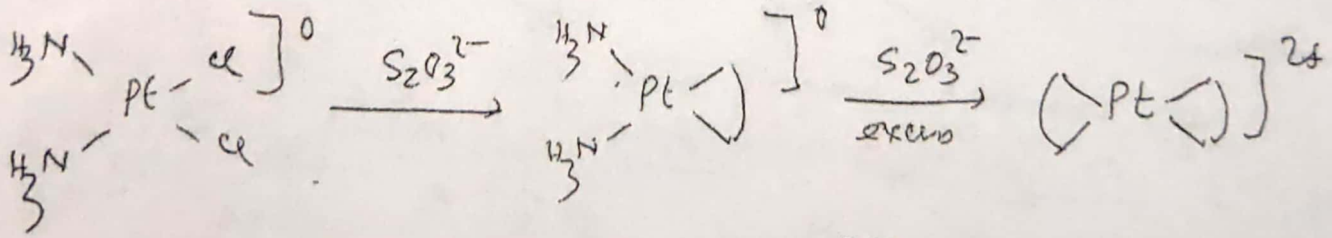
The well known Kurnakov tests for distinguishing the cis- and trans isomers of $[Pt(NH_3)_2Cl_2]$ with thiourea (tu) and thiosulphates ($S_2O_3^{2-}$) both having trans effect higher than that of Cl^-.

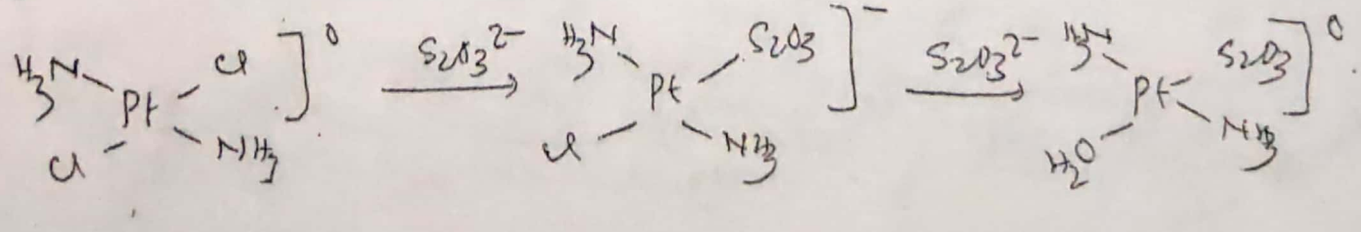
The cis compound on treatment with thiourea gives the tetrasubstituted product while the trans compound gives the disubstituted product.



cis -

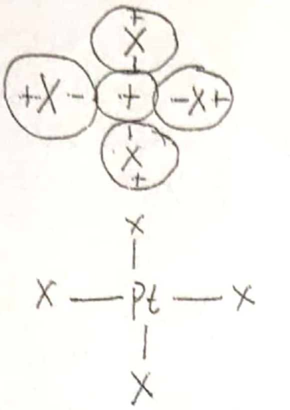


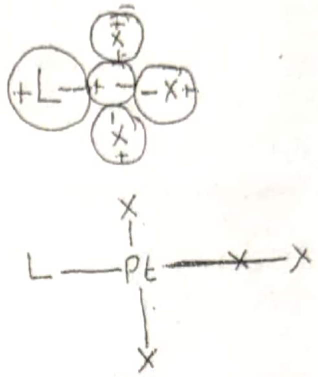




Theories of Trans-effect :

① Static Polarisation Theory: In a symmetrical complex PtX_4, there will be no net polarisation of the Pt-atom. Replacement of one X by a ligand L more polarisable than X will induce a net polarisation in Pt such that its negative end is close to the group X trans to L, causing a weakening of the M—X bond trans to L.



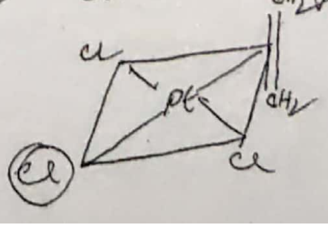


Trans orienting order of ligands:

$H_2O < OH^- \sim gly < NH_3 \sim RNH_2 < Py < Cl^- < Br^- < I^-$
$\sim SCN^- \sim N_3^- < NO_2^- < tu < PR_3 \sim AsR_3 < CN^- < CO, C_2H_4$

② π-bonding Theory: π-acceptor ligands with empty acceptor orbitals can form π bond with filled metal dπ orbitals. The M→L electron drift ~~sen~~ strengthens the M—L bond and simultaneously weakens the M–L bond trans to it. Thus the ligand lying trans to a high π-acid ligand becomes labile and is readily replaced by an incoming ligand.

In Zeiss's salt the high trans-orienting effect (due to high π-acidity) of C_2H_4 make the chloride group lying trans to it more labile than the other chloride group



Q. Square planar complexes of Pt(II) show considerable trans-effect but analogous complexes of Ni(II) and Pd(II) donot. Why?

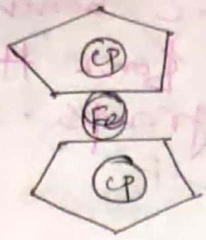
The trans-effect will be significant only when the metal ion itself undergoes easy polarisations. It is not significant when the metal ion is less polarisable.

The order of polarisability —

Ni(II) < Pd(II) < Pt(II).

Pd(II), Ni(II) [and even Pt(IV)] are much less polarisable ~~than~~ for their comparative smaller sizes and hence their square-planar complexes donot show trans-effect.

Ferrocene



Metal is sandwiched betw two parrallel Cp rings.

$$FeCl_3 + C_5H_5MgBr \longrightarrow FeCl_2 \xrightarrow{2\,C_5H_5MgBr} (C_5H_5)_2Fe$$

Crystalline Solid

orange-red

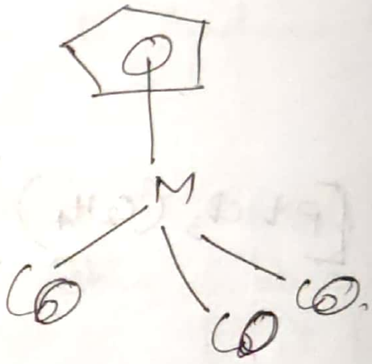
Ferrocene

$$Cp_2M \longrightarrow \text{(metallocene)}$$

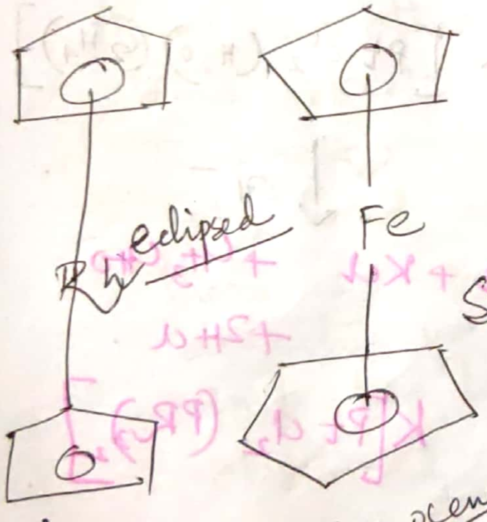
Cp_2Co

Cp_2Ni

Cp_2V



Half-sandwiched compound.



Staggered str.

Solid phase

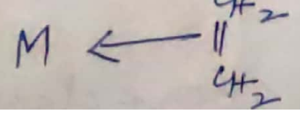
This is may be due to Crystal packing force.

Reactions:- undergoes electrophilic substitution.

Similarity with benzene.

Ferrocene

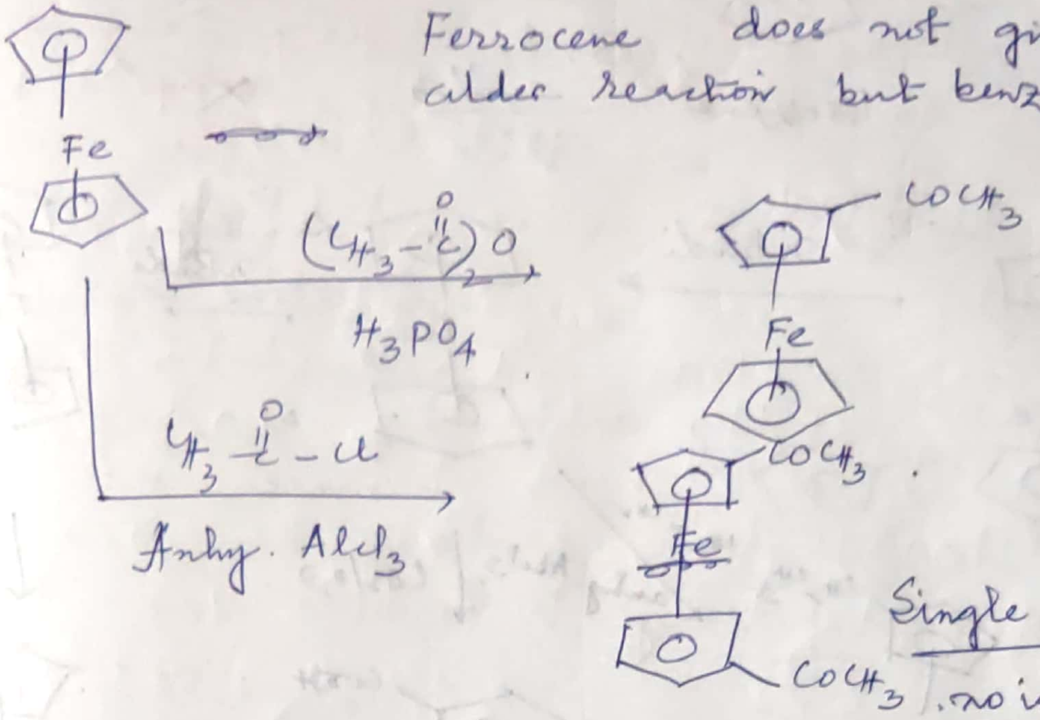
i) Ferrocene undergoes electrophilic substitution reaction at much faster rate than benzene.



Free alkenes are readily attacked by electrophiles but Co-ordinated alkene suffer attack / mostly by nucleophiles not electrophiles – explain.

Zeises's salt is intert towards oxidation.

Ferrocene does not give Diels-alder reaction but benzene does.

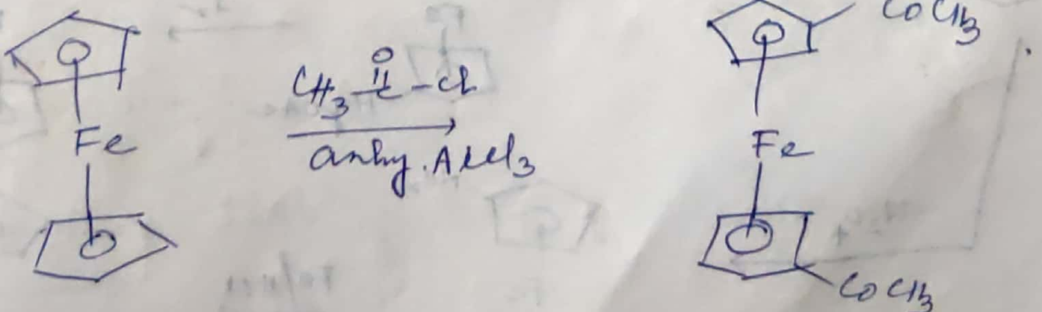


Single form
. no isomeric form

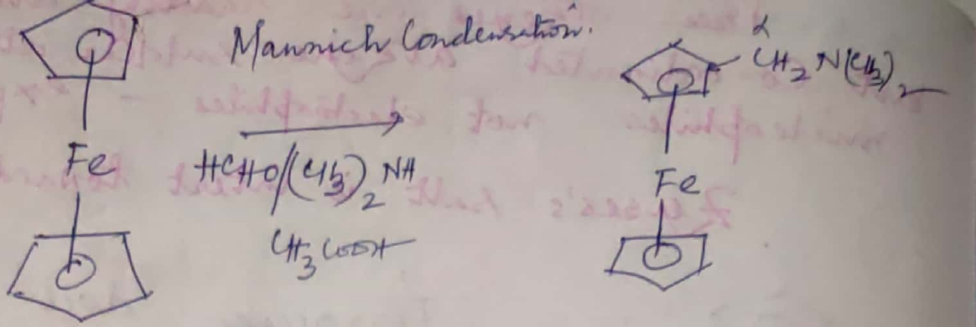
Give a Chemical evidence to show that there is free rotation of the Cp-rings around the Cp-Fe axis.

Fridel Craft acylation

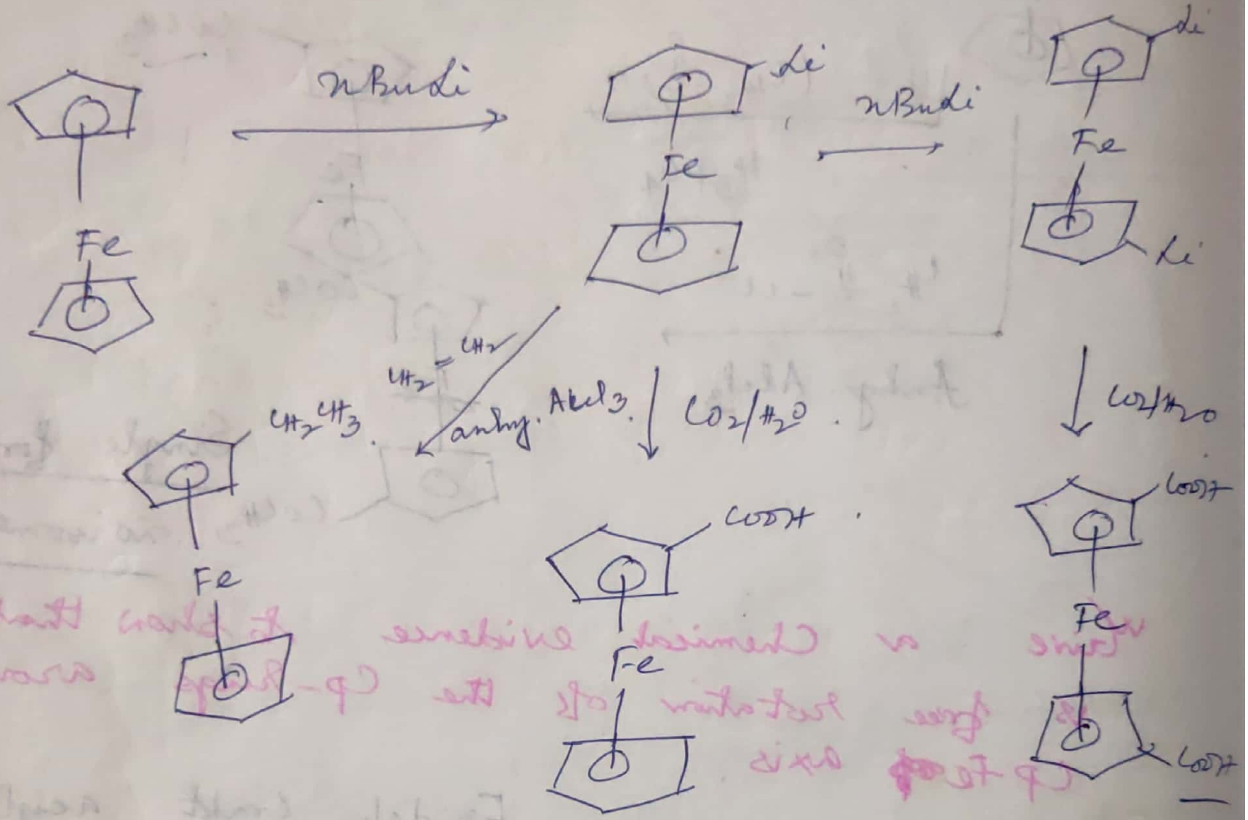
With anhy. $AlCl_3$ and $CH_3-\overset{O}{\overset{\|}{C}}-Cl$ give diacyl derivative in a single form, no isomeric product is obtained. This indicates free rotation of the ring around the internuclear axis. Had there been no free rotation, several isomeric pdts could have been obtained.

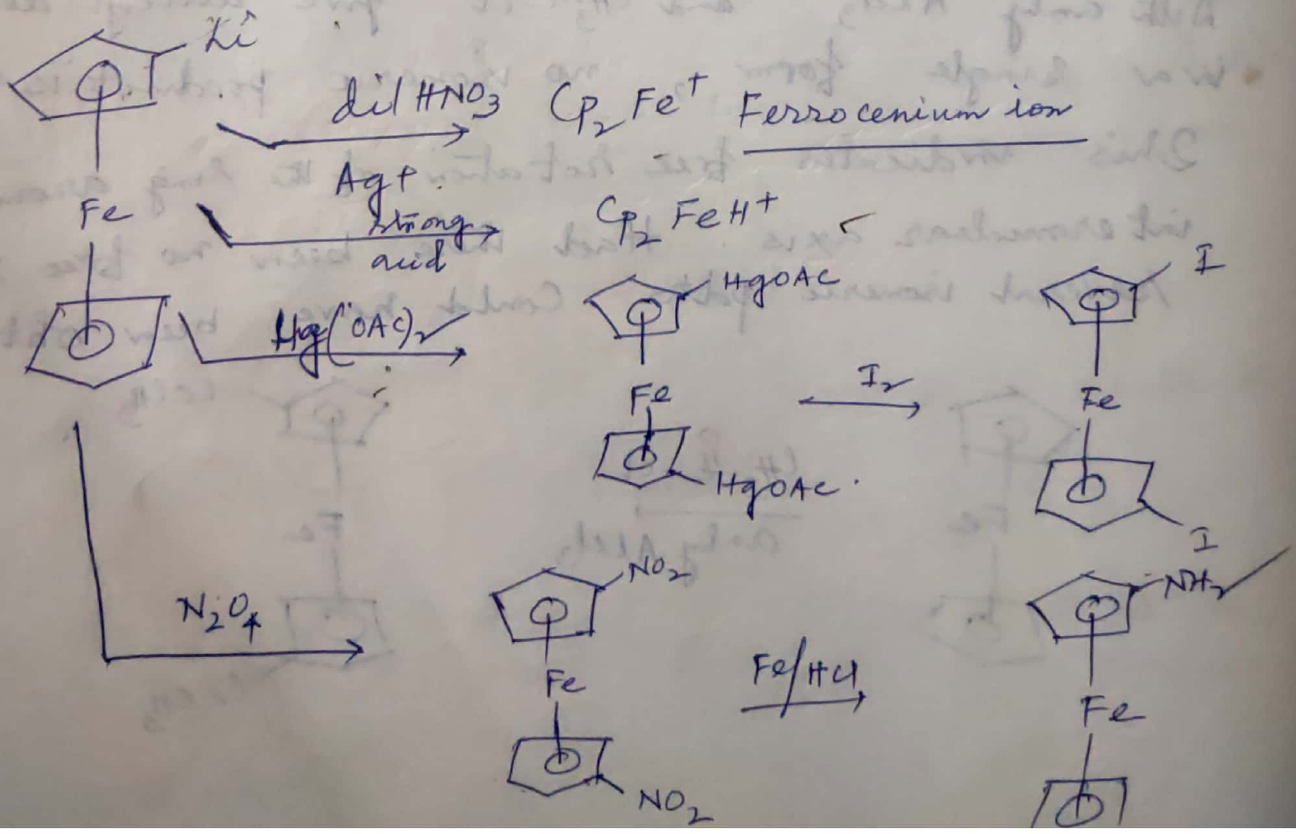


Mannich Condensation.

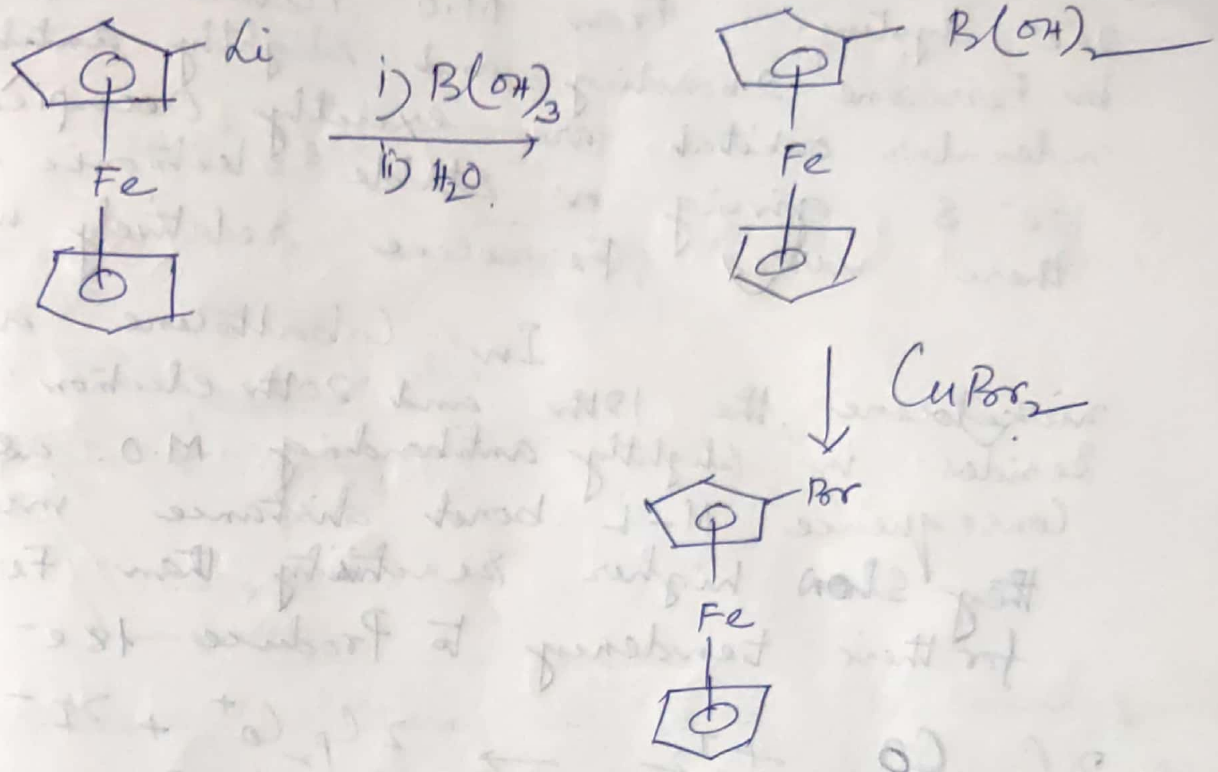


Benzene $\xrightarrow{''}$ ×





takes place in presence of conc HNO_3 and H_2SO_4 but in presence of strong acid, Ferrocene suffers oxidation and nitration takes place indirectly in this way.



***

(The Co-ordinated Cp group resist the nucleophili but assist electrophilic attack) at a faster rate tha benzene. These indicates that the electrons are more readily available at the Cp-rings of Ferrocene than in the benzene. This is a consequence of M–L π back donation increasing electron density in the rings)

$Cp_2Fe \rightarrow$ stable. $18e^-$

$Cp_2Co \rightarrow$ unstable $19e^-$

$$Cp_2Co \longrightarrow \overline{Cp_2Co^+} + e^-$$

$\downarrow$

$18e^-$

Ferrocene is stable but Cobaltocene is highly reducing.

$Cp_2Fe^+ \rightarrow$ unstable

$Cp_2Co^+ \rightarrow$ Stable

Cobaltocene and Nickelocene are more reactive than Ferrocene.

Ferrocene is an $18e^-$ system while Cobaltocene is an $19\,e^-$ system and Nickelocene is $20e^-$ system. From M.O. Picture we see that in Ferrocene 9 bonding and slightly ~~antibonding~~ non-bonding molecular orbital are exactly occupied by $18e^-$'s giving a stable electronic system these makes Ferrocene relatively unreactive.

In Cobaltocene and nickelocene, the 19th and 20th electron respectively resides in slightly antibonding M.O. as a consequence M–L bond distance increases and they show higher reactivity than Ferrocene for their tendency to produce $18e^-$ product.

$$2\,Cp_2Co + I_2 \longrightarrow 2\,\underset{18e^-}{Cp_2Co^+} + 2I^-$$

$$Cp_2Ni + PF_3 \longrightarrow \underset{18e^-}{Ni(PF_3)_4} + 2\,Cp$$

Ferrocene does not react in these way.