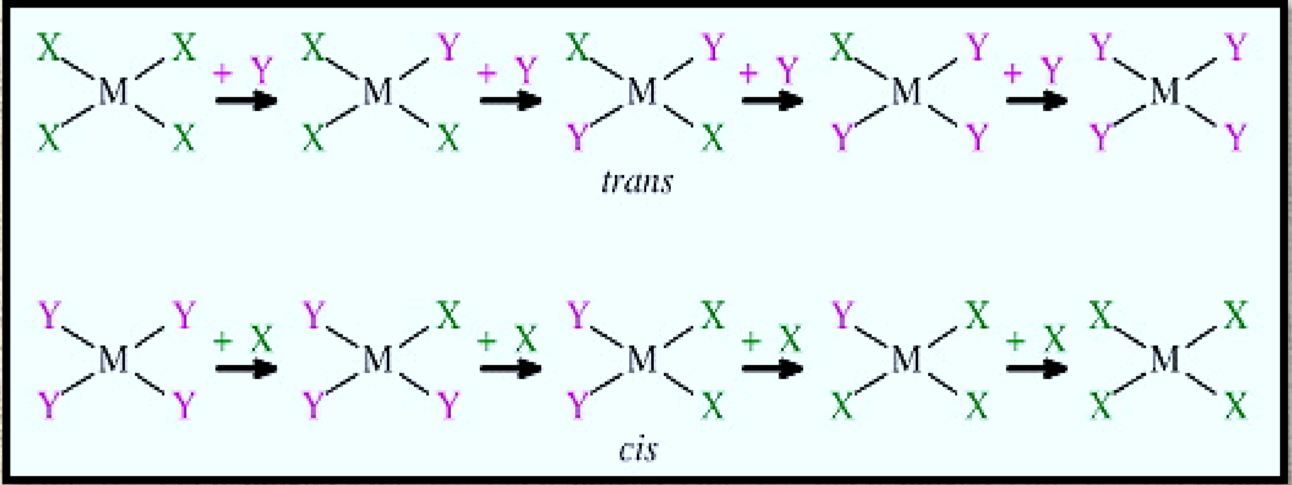
Thermodynamic and Kinetic Aspects of Metal Complexes

(Lecture-4)

B.Sc. 5th Semester (Pass Course)

INORGANIC CHEMISTRY

(As per MDU, Rohtak Syllabus)



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CONTENT

- TRANS EFFECT
- APPLICATIONS OF TRANS EFFECT
- THEORIES OF TRANS EFFECT

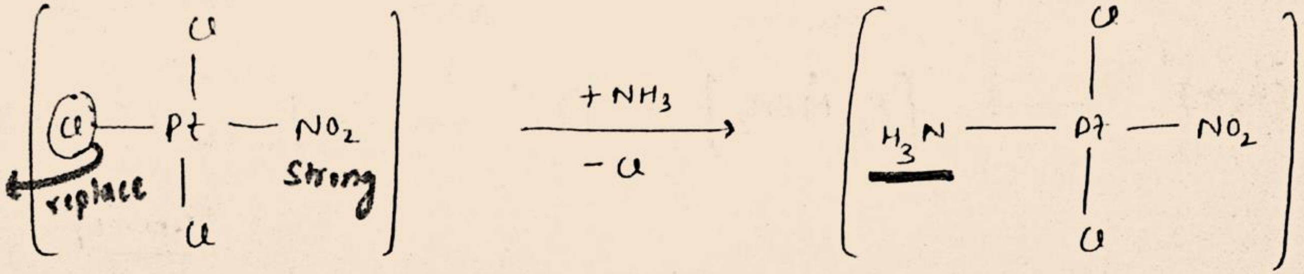
Trans Effect

The trans-effect is defined:

"The ability of a ligand to promote rapid substitution of a ligand trans to itself."

→ It is a very imp feature of sq. planar complexes in their substitution rx^n

→ The tendency of a strong trans directing (L) to send the incoming (L) to its trans position is called $\boxed{\text{trans effect}}$



trans effect of $-NO_2 > -Cl$

Hence the incoming (L) occupies trans position to the strong trans direc
(L) in substitution rx^n. This effect also influences the rx^n rate...

The general order of ligand trans-effect is

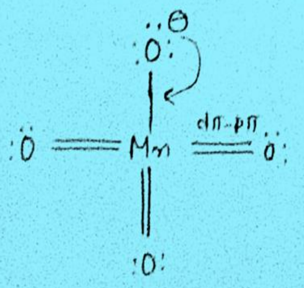
$H_2O, OH^- < NH_3, py < Cl^- < Br^- < I^- < SCN^-, NO_2^- < C_6H_5 < CH_3^-, SR_2 < H^-, PR_3 < H_2C{=}CH_2, CN^-, CO$

- The (L) of higher trans directing nature have empty π & π^* orb
  & can accept the lone pair of e^- from the central metal atom/i
  through back bonding.

eg (i) $MnO_4^- \rightarrow Mn_{25} = [Ar]\ 3d^5\ 4s^2$

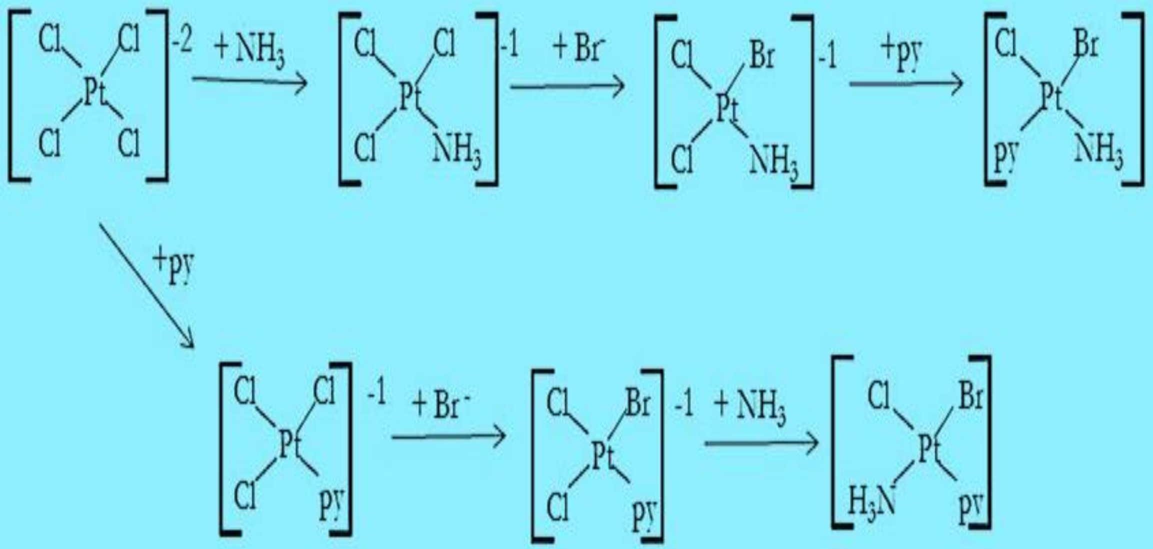
$ \rightarrow Mn^{7+} = [Ar]\ 3d^0\ 4s^0$

MnO$_4^-$ is purple color due to charge transfe



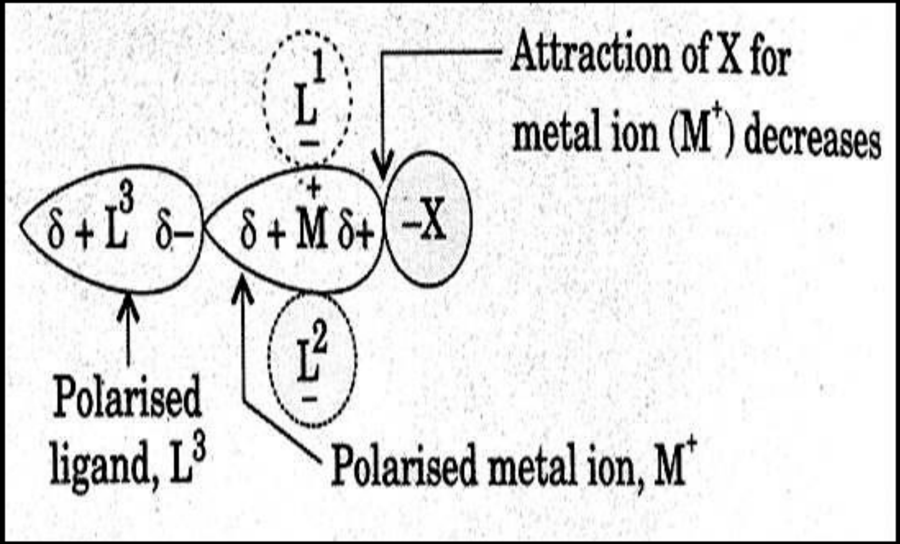
oxo-ions are always stabilized by dπ-pπ back bonding

- By ordering the sequence of addition of substituents, can use the trans effect to produce a desired isomer.

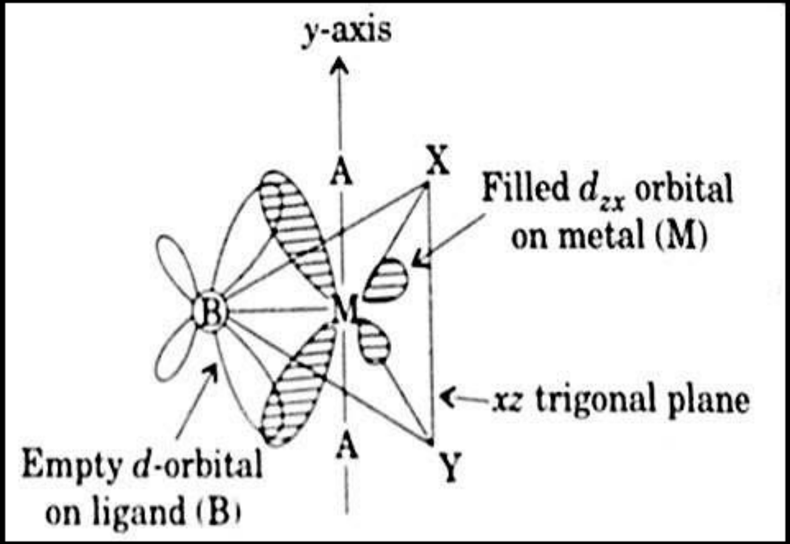


THEORIES OF TRANS EFFECT

POLARIZATION THEORY



PI BONDING THEORY



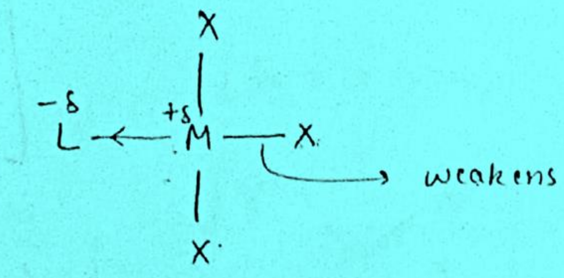
Polarization Theory

Electrostatic polarisation theory :- (Thermodynamical approach)

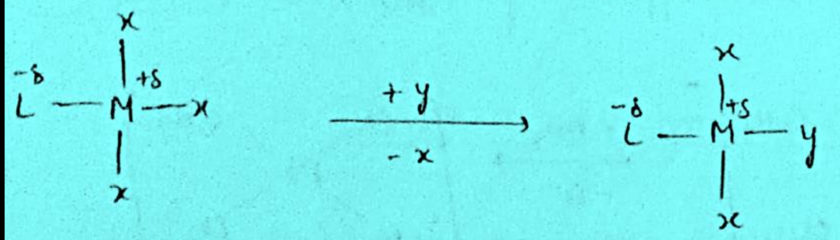
proposed by grinberg

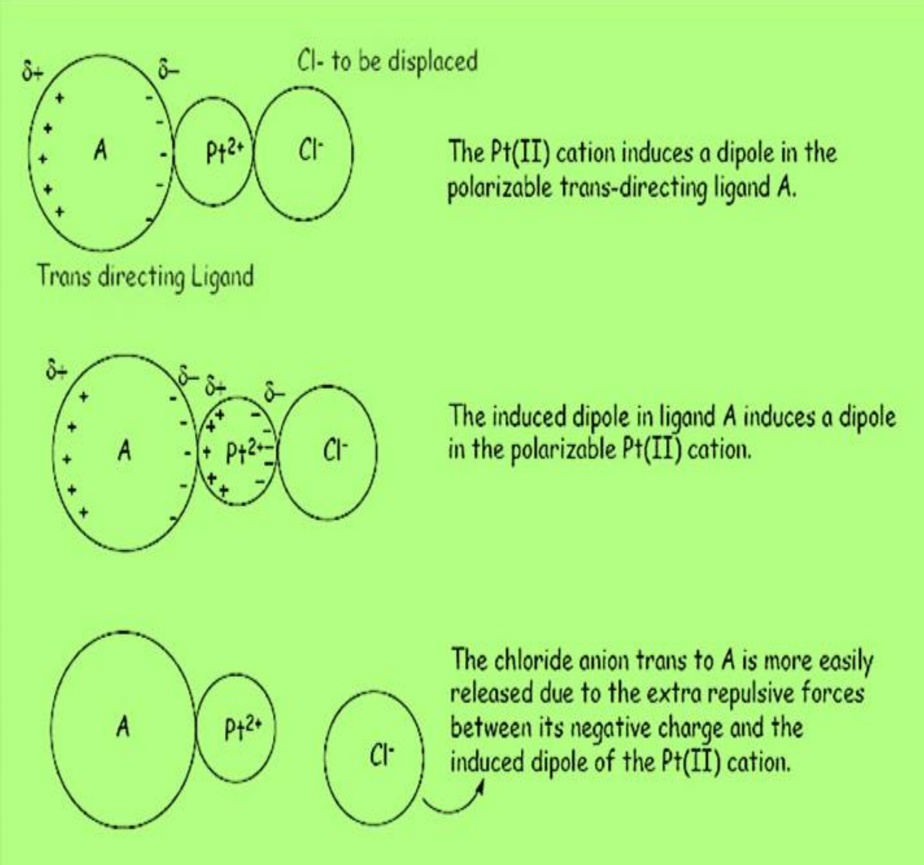
Acc. to this theory, the polarization of metal-ligand bond ($\overset{+\delta}{M} \rightarrow \overset{-\delta}{L}$) weakens the M—X bond prnt at trans position.

ie



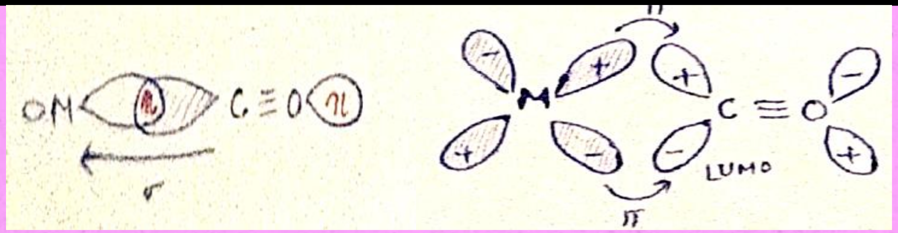
Thus it facilitates the incoming (L) to occupy the trans position.





Pi-bonding Theory

π- bonding theory :-



proposed by chatt- orgel.

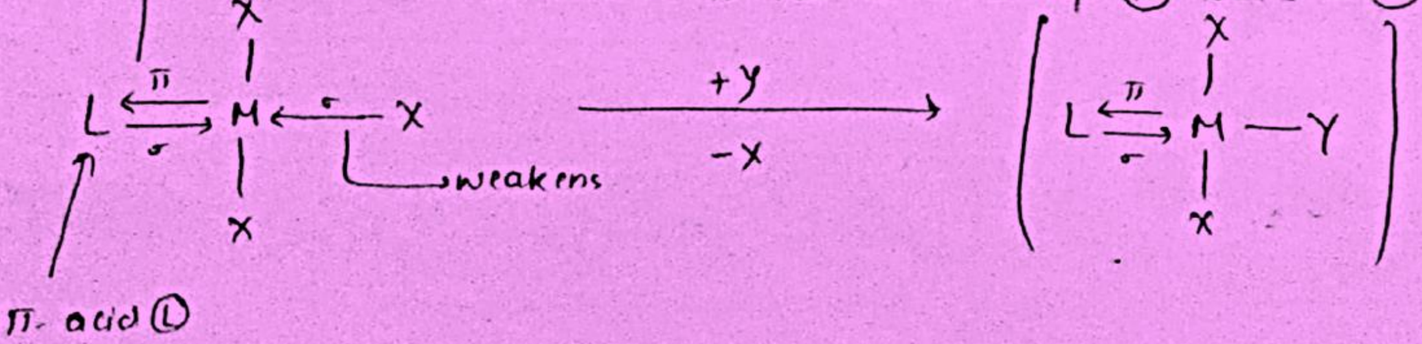
The π-acid (L) or π-acceptor (L) can form π bond (back bonding)

$$M \underset{\sigma}{\overset{\pi}{\rightleftarrows}} C\equiv O$$

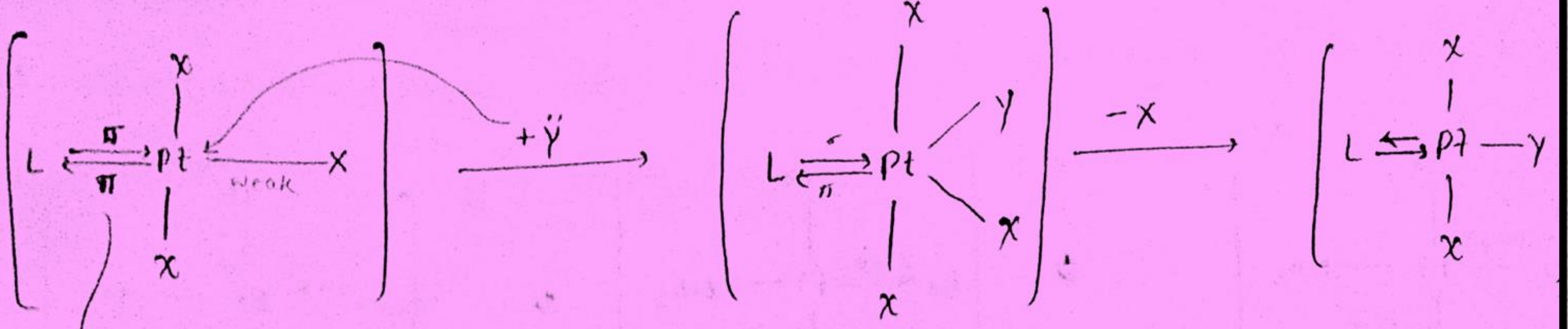
π bond also along with σ-bond with central metal ion in the complex

∴ Hence such Ligands can act as strong trans directing effect (L)

[due to π bonding, e^-s in the direction of (L) ↑ses - & diminishes it in the direction of (X) trans to (L)]



Thus M-X bond at trans position weakens with increase in bond length. So, it facilitates the entry of new (L) to form penta co-ordinated transition state.

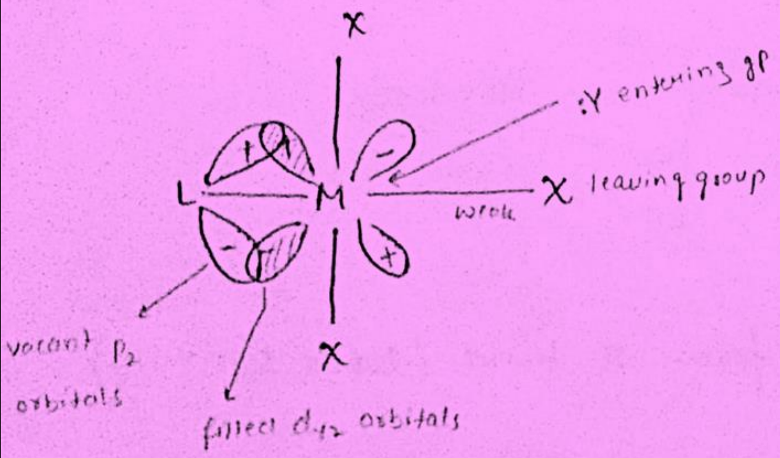


5-co-ordinated T.S

[PtLX$_2$Y]

(distorted tbp)

Back bonding



Applications

Synthesis of Pt(II) complexes

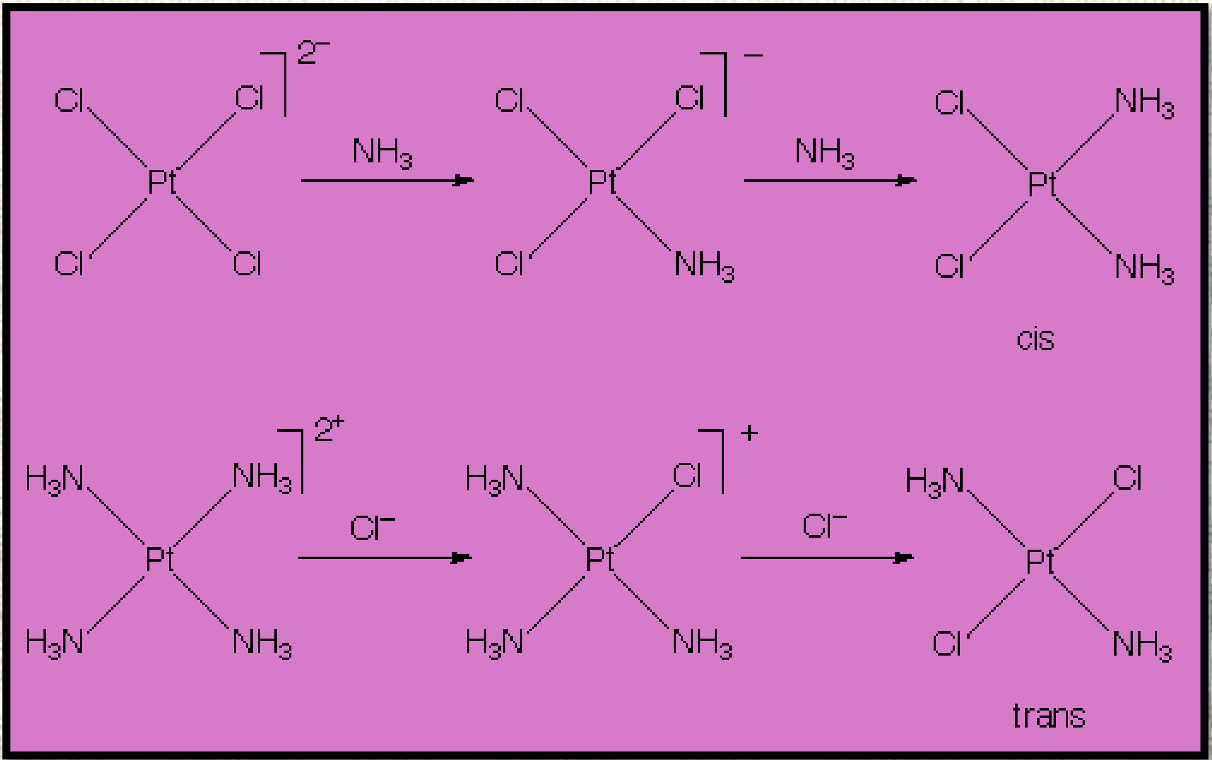
Kurnakov's test

Synthesis of other complexes

Synthesis of Pt(II) complexes

i) From $[PtCl_4]^{2-}$

ii) From $[Pt(NH_3)_4]^{2+}$



We get Cis-isomer

We get Trans-isomer

Kurnakov's test

Trans effect can be used to distinguish cis & trans isomer also

Kurnakov's test

used to distinguish cis & trans isomer

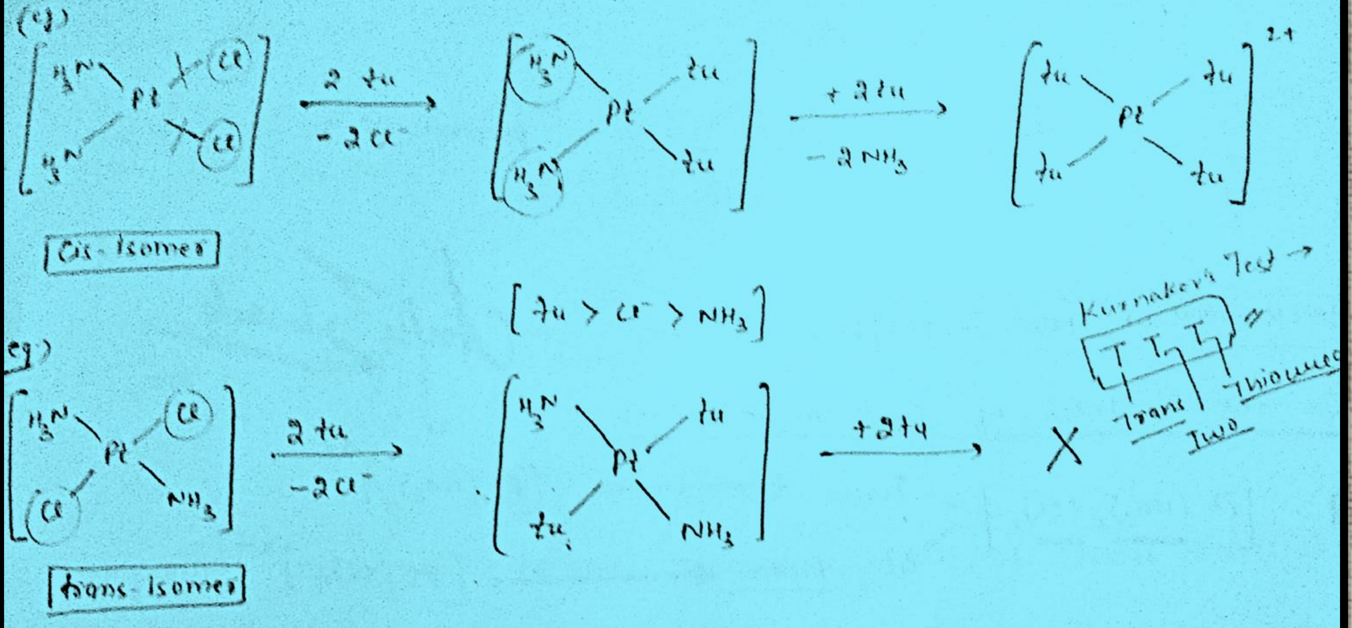
in this test, we use thiourea as (L) (attacking (L))

ie in cis-isomer → (4) thiourea used

in trans- " → (2) " "

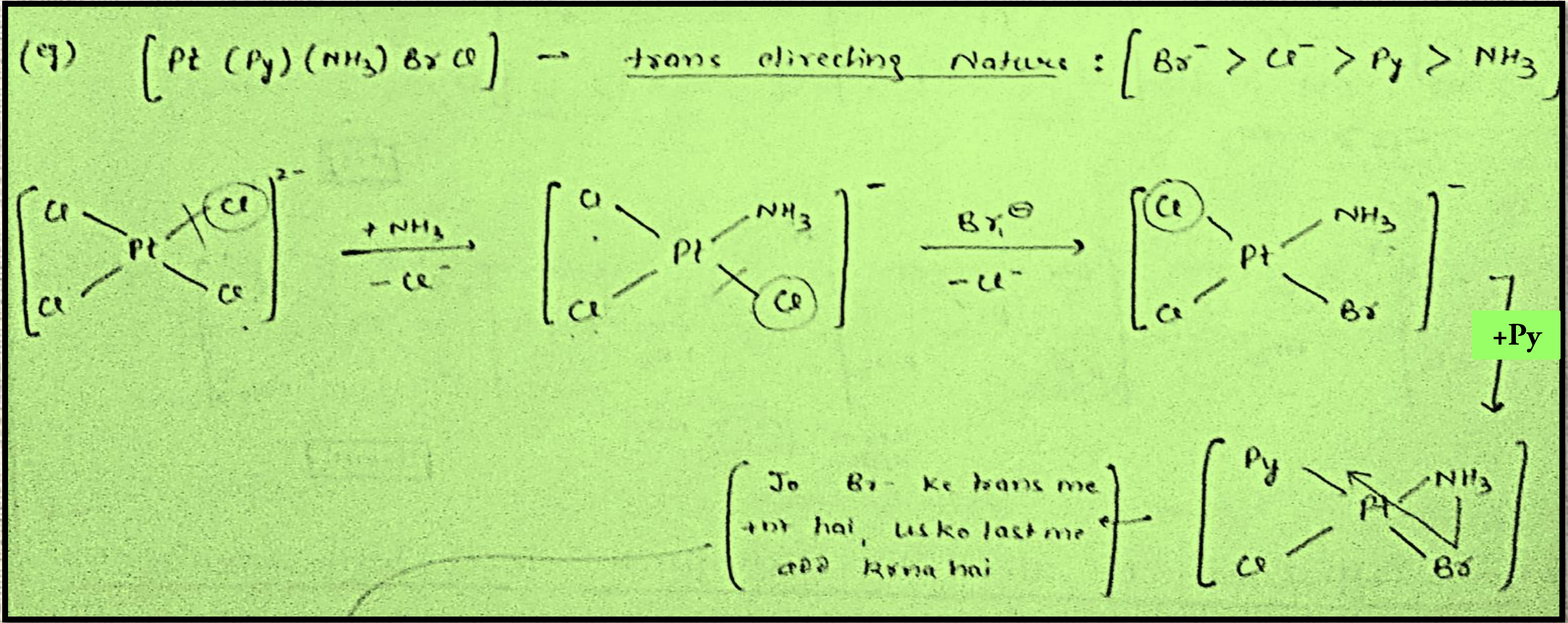
Two

trans effect tu > $-NH_3$ ∴ thiourea can replace NH_3 but $-NH_3$ cannot direct tu ...



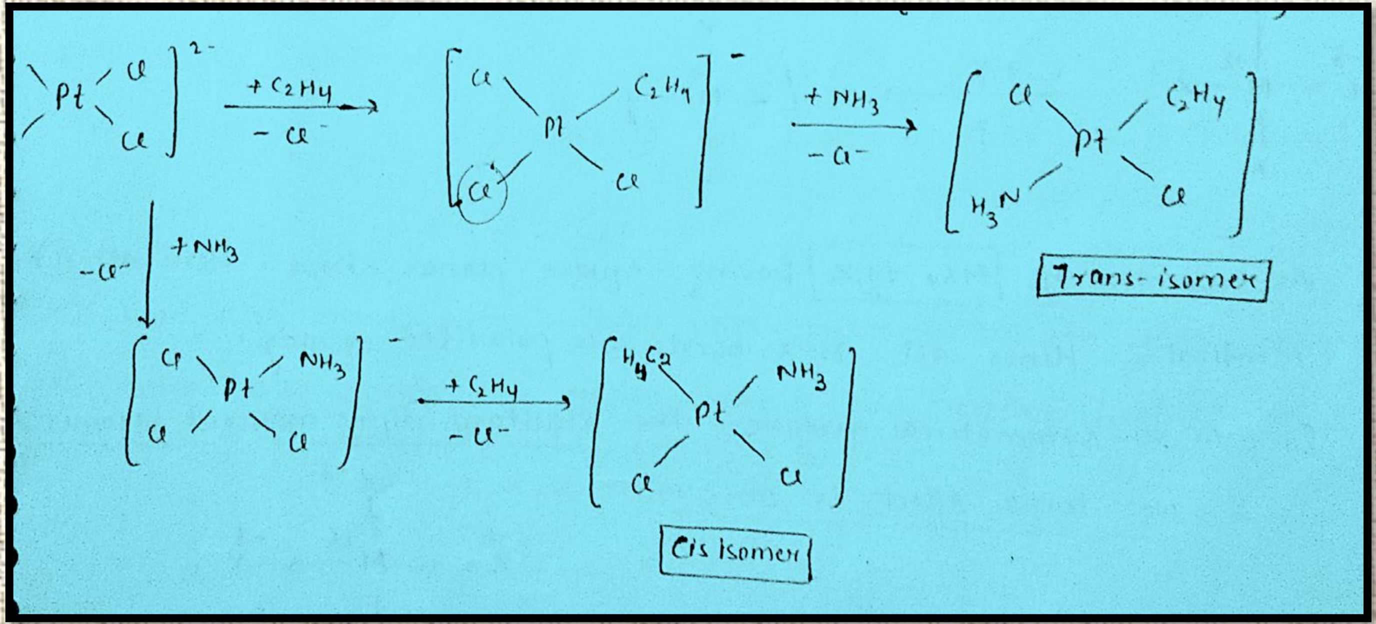
Synthesis of other complexes

For eg. We have to synthesize $[Pt(Py)(NH_3)(Br)(Cl)]$ from $[PtCl_4]^{2-}$



Try to solve this question……!!!!!!

Synthesise cis & trans isomer of $[Pt(C_2H_4)NH_3Cl_2]$ from $[Pt(Cl)_4]^{2-}$
from $[PtCl_4]^{2-}$ … order of trans effect = $[-C_2H_4 > Cl^- > NH_3]$



when to form trans-Isomer ⇒ add strong trans directing (L) first
& " " " cis- " ⇒ " weak " " " "

THANK YOU