

# Inorganic Reaction Mechanism

(Chemistry-DSE-1002F1: **Physical and Inorganic Chemistry**, Section-II)

BY

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# Inorganic Reaction mechanism

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- 3  $SN^1$  and  $SN^2$  reaction for inert and labile complexes
- 4 Mechanism of substitution in cobalt (III) octahedral complexes
- 5 Trans effect and its theories
- 6 Applications of trans effect in synthesis of Pt (II) complexes

# Introduction

## Substitution in Coordination Complexes

1. Nucleophilic Substitution (SN) Reaction
2. Electrophilic Substitution (SE) Reaction

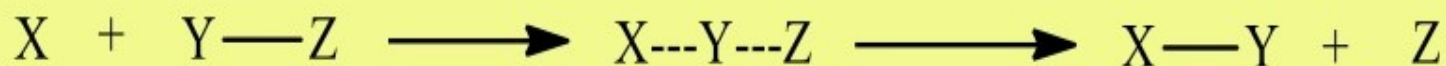
*Langford and Gray*

Mechanism	Dissociative		Associative	
Intimate	D		A	
Stoichiometric	SN <sup>1</sup> (Id)	SN <sup>1</sup> (D)	SN <sup>2</sup> (Ia)	SN <sup>2</sup> (A)

# TERMS OF SIGNIFICANCE

## ■ Transition state complex or activated complex:

- The most unstable species having the maximum energy and very short life-time.
- Cannot be isolated.



- **Activation Energy** : Energy difference between the reactants and the activated complex.
- **Attacking Reagents** : May be electrophile or nucleophile.

# **Classification of Mechanisms**

1. Dissociative (D)
2. Associative (A)
3. Interchange (I)

# MECHANISMS OF LIGAND SUBSTITUTION REACTIONS IN OCTAHEDRAL COMPLEXES

These reactions can be classified into different types depending upon the nature of intermediate formed.

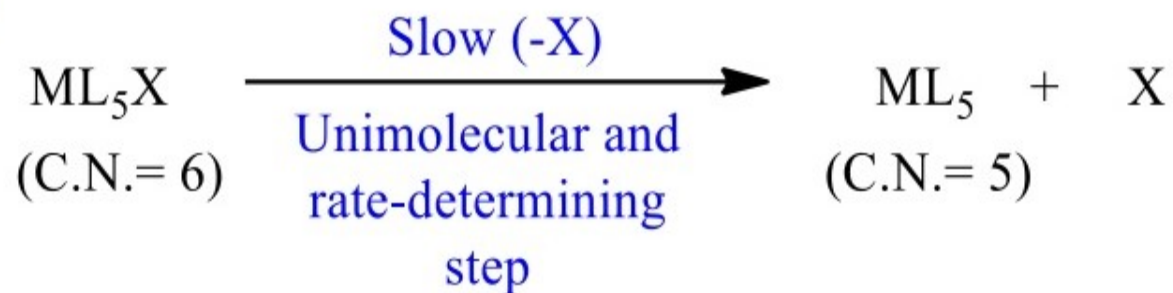
## **$S_N1$ or Dissociation mechanism :**

- It indicates Unimolecular Nucleophilic Substitution or 1<sup>st</sup> order.
- M-X bond is fully broken before the formation of M-Y bond.
- Intermediate is detected in the rate determining step in which the central metal has a lower coordination number than it has in the reactant.

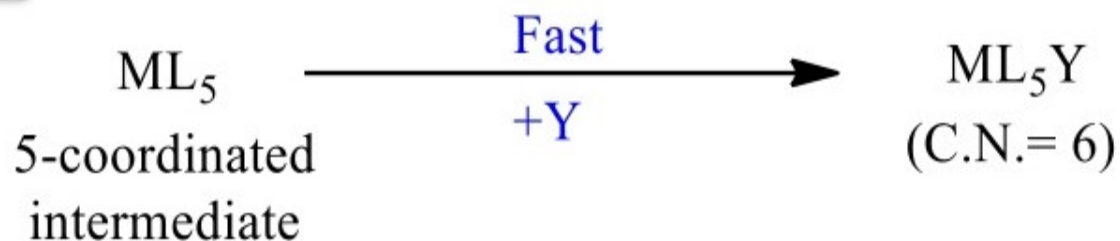


# The two step mechanism

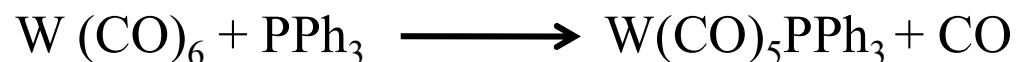
Step 1



Step 2



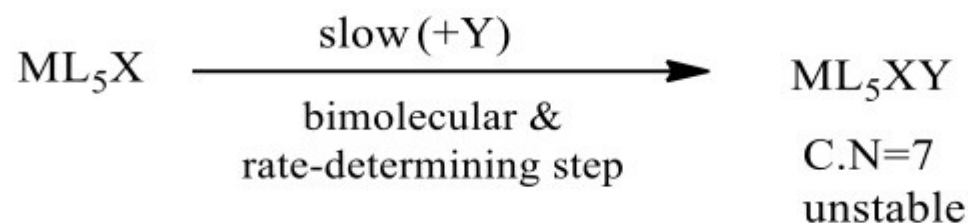
$$\text{Rate} = k [\text{ML}_5\text{X}]$$



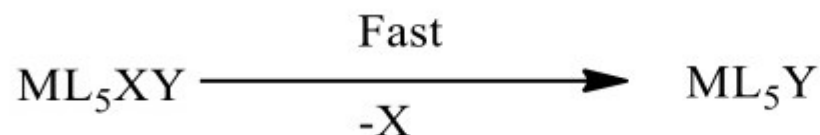
# $S_N2$ or Association mechanism

- Intermediate at the rate-determining step has a higher coordination number than that in the reactant.
- M-Y bond is fully formed before the breaking of M-X bond.
- It is of 2<sup>nd</sup> order and also involves two steps.

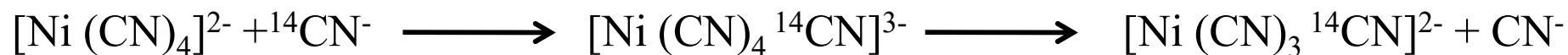
Step 1



Step 2



$$\text{Rate} = k[ML_5X][Y]$$





## Concerted path or Interchange mechanism (I)

- ➡ No evidence of formation of intermediate.
- ➡ Activated complex contain both substrate and the ligand
- ➡ Two types:
  - Interchange associative ( $I_a$ )**
  - Interchange dissociative ( $I_d$ )**

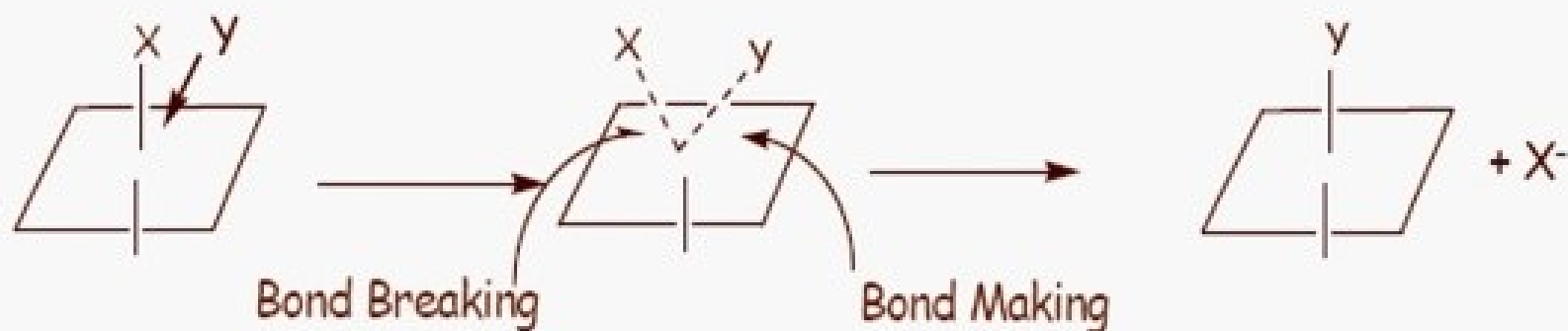
In **Interchange associative** mechanism, the rate depends on the nature of the entering group and bond-making is more important than bond-breaking.

In **Interchange dissociative**, the rate does not depends on the nature of the entering group and bond-breaking is more important than bond-making.

# INTERCHANGE MECHANISM

- ▮ It is a continuous single step process
- ▮ Two types exist
  - ▮ **Interchange associative ( $I_A$ )** -  
Bond making more important
  - ▮ **Interchange dissociative ( $I_D$ )** -  
Bond breaking more important

As Y begins to bond X begins to leave. i.e. the bond making to Y and bond breaking to X occur simultaneously (organic  $S_N2$ )



Although we speak generally about associative and disassociative reaction mechanisms, the terms A and D are reserved for situations where 7 and 5 coordinate intermediates have actually been isolated and positively identified. If no intermediates have been isolated or identified the designations  $I_d$  and  $I_a$  are more appropriate.



Id (dissociative interchange)

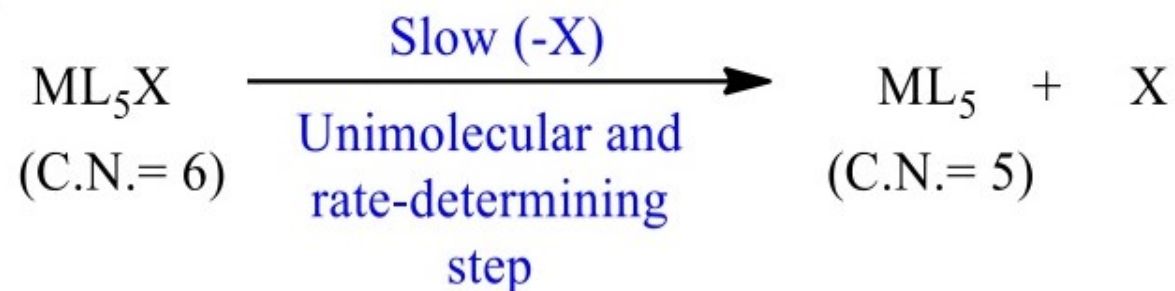


Ia (associative interchange)

## The rate determining step

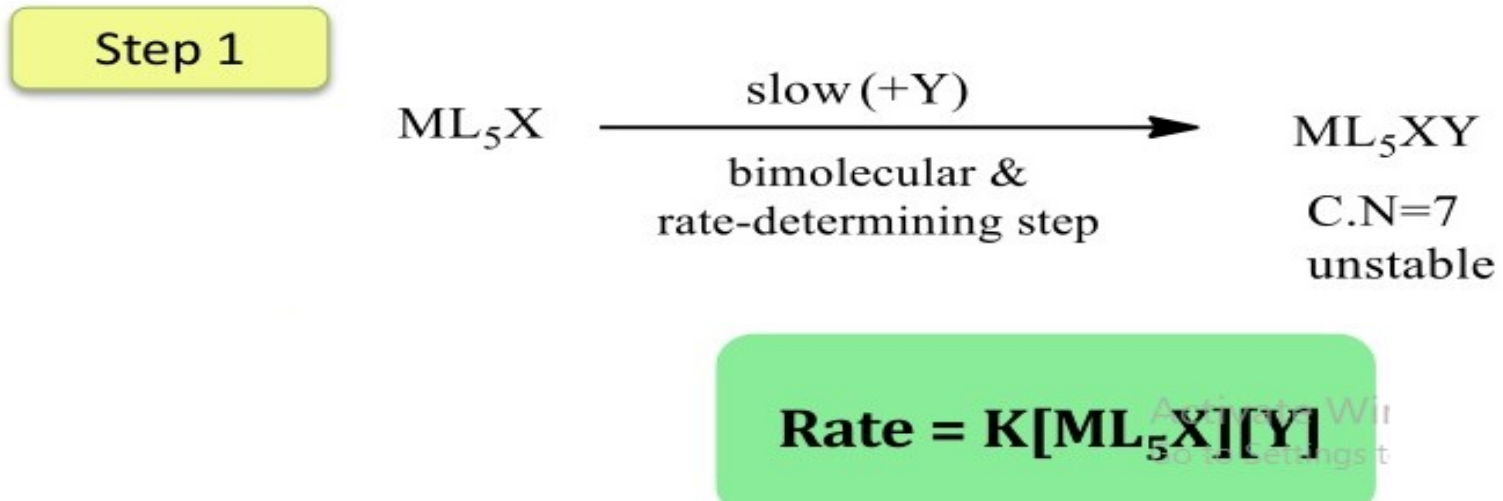
I) In Dissociative mechanism

Step 1

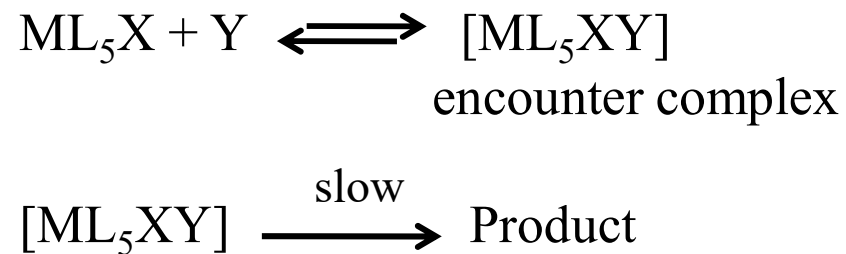


$$\text{Rate} = k [\text{ML}_5\text{X}]$$

## II) In Associative mechanism



## III) In Interchange mechanism



free energy

*transition state*

*transition state*

$\Delta G_1^\ddagger$

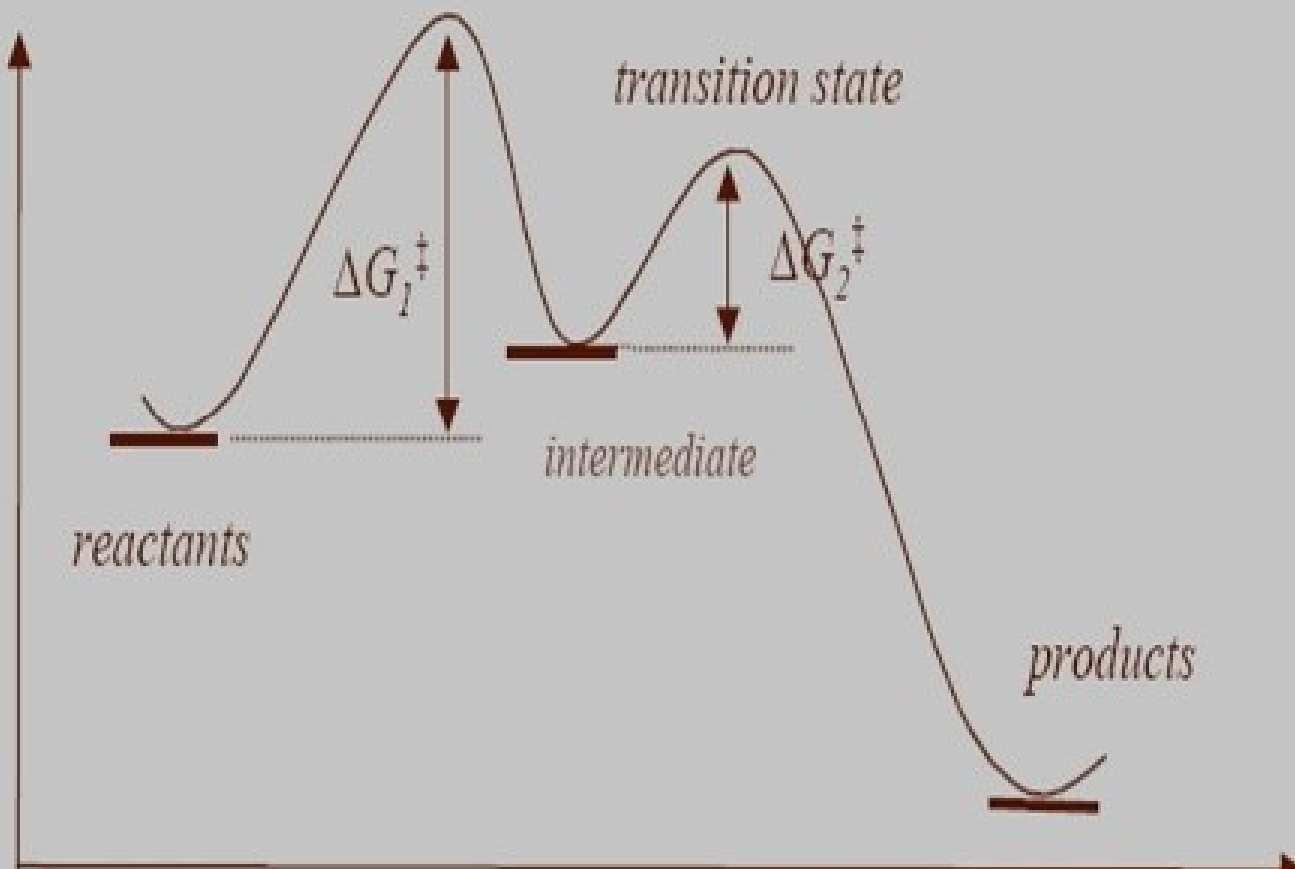
$\Delta G_2^\ddagger$

*reactants*

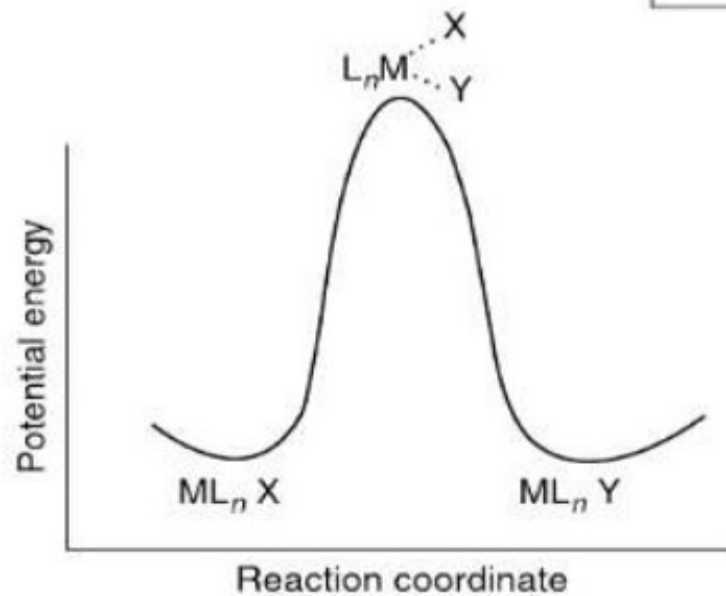
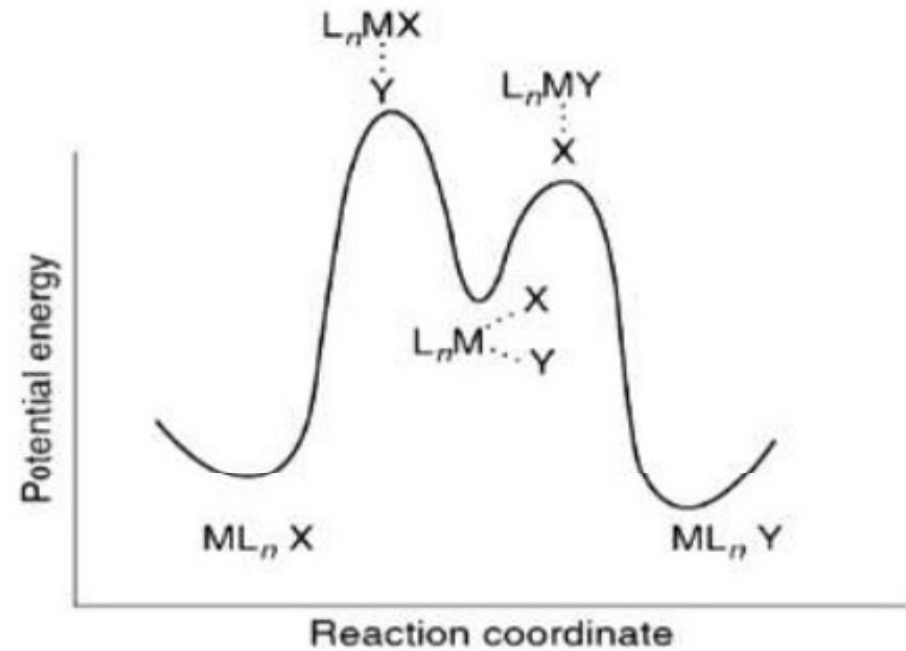
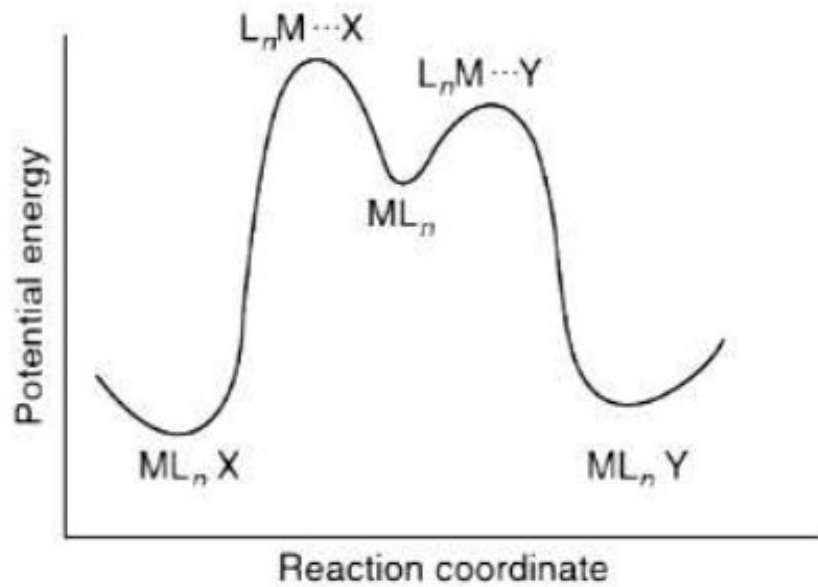
*intermediate*

*products*

reaction  
coordinate



# Reaction energy Profile Diagrams





# $SN^1$ and $SN^2$ reaction for inert and labile complexes

- Complexes in which exchange of one or more ligands are rapidly exchanged are called labile complexes.
- If the rate of ligand exchange is slow then the complex is said to be inert.
- Lability is not related to the thermodynamic stability of a complex.
- A stable complex may be labile or inert , so as the unstable complex .



## Explanation of lability and inertness according to VBT

- VBT classifies octahedral complexes into two types.
- Inner orbital complexes –  $d^2sp^3$
- Outer orbital complex –  $sp^3d^2$
- The two d-orbitals involved in the hybridization are the  $e_g$  set of orbitals.

## Outer orbital complexes

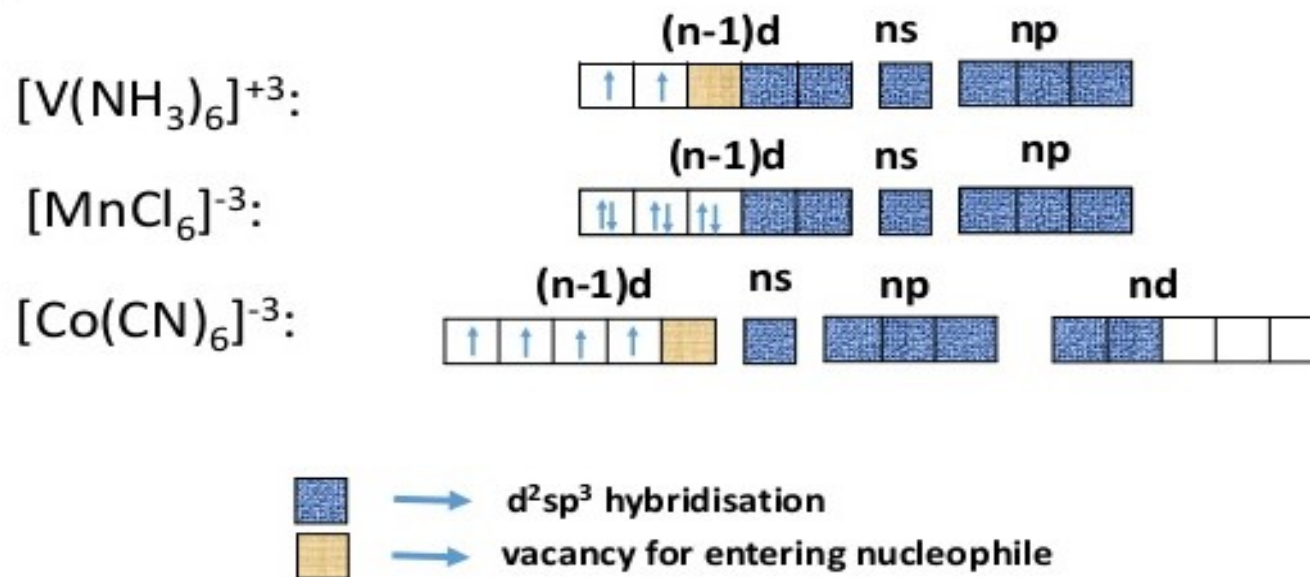
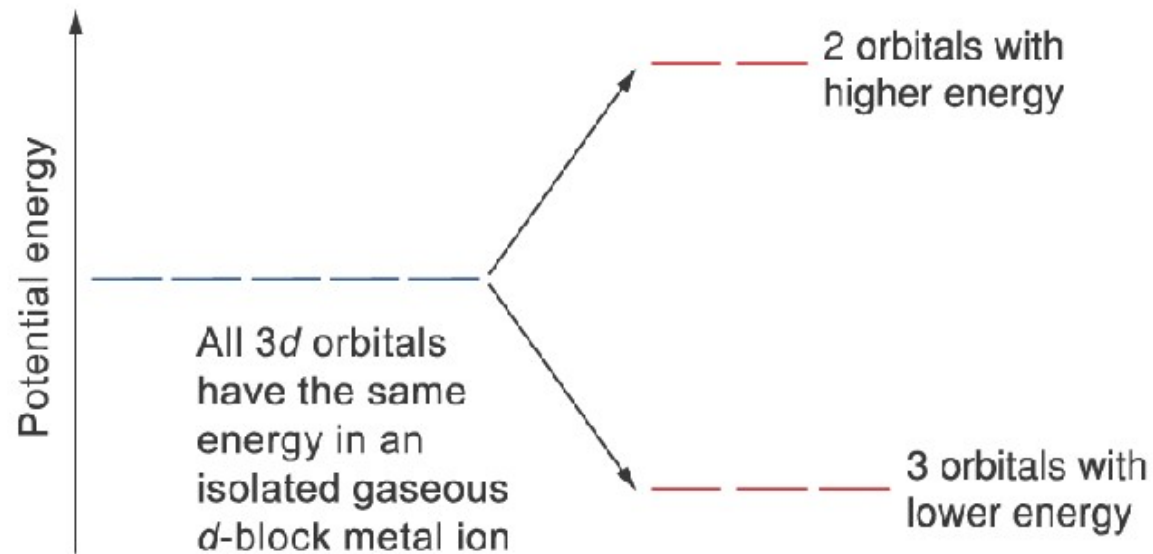
- The complexes having  $sp^3d^2$  hybridization are called outer orbital complexes.
- In terms of VBT these bonds are weaker.
- They are generally labile.
- Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II) and Cr(II) are labile.

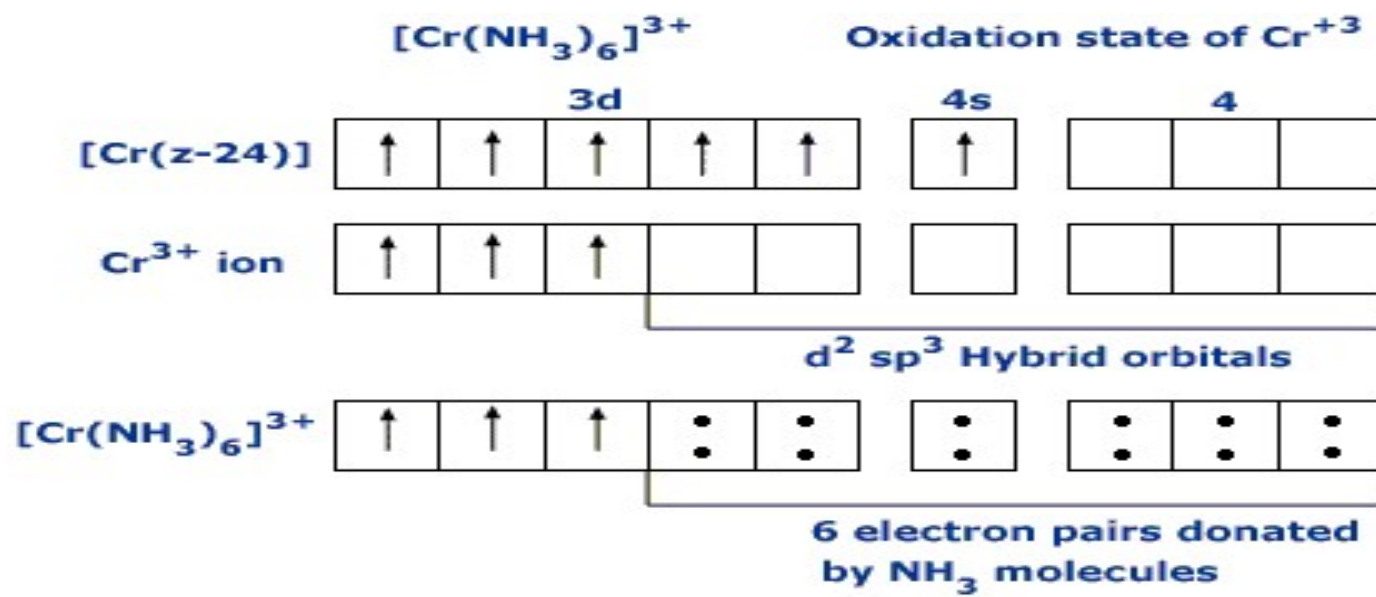
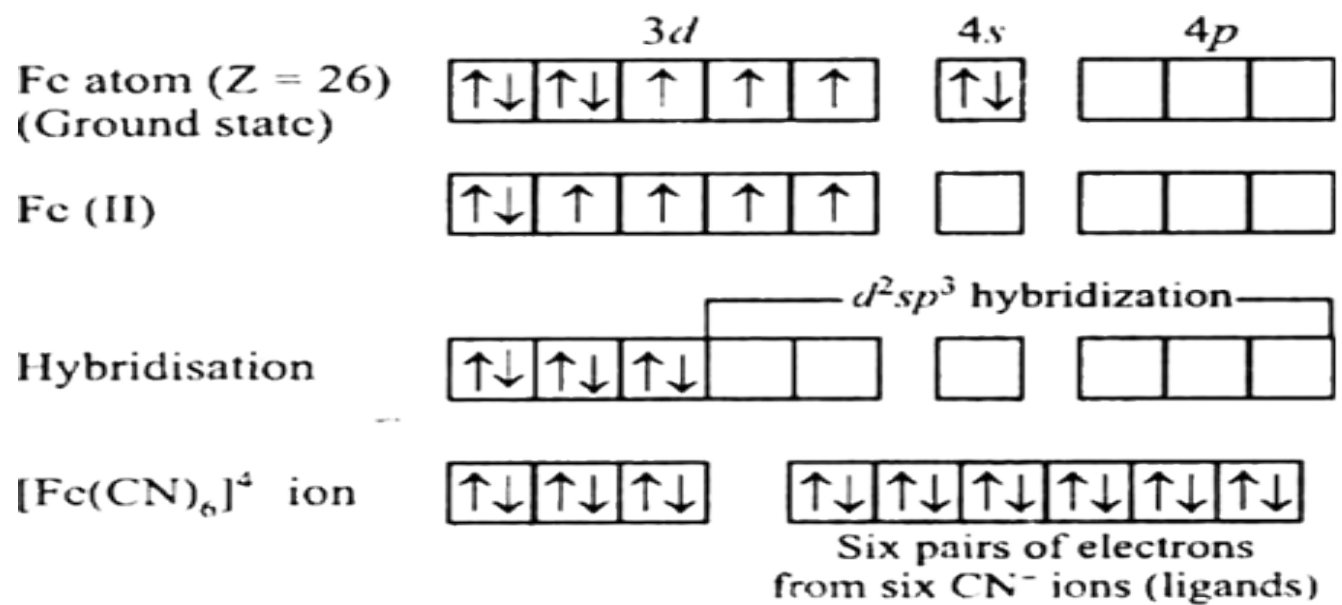
# Inner orbital complexes

- These complexes generally have  $d^2sp^3$  hybridization.
- The hybrid orbitals are filled with the ligand electrons.
- The  $t_{2g}$  orbitals of metal accommodate the d electrons of the metal.
- If the  $t_{2g}$  levels are left vacant then the complex can associate with an incoming ligand and the complex is labile
- If all the  $t_{2g}$  levels are occupied then the complex becomes inert.

**Labile-  $SN^2$**

**Inert-  $SN^1$**



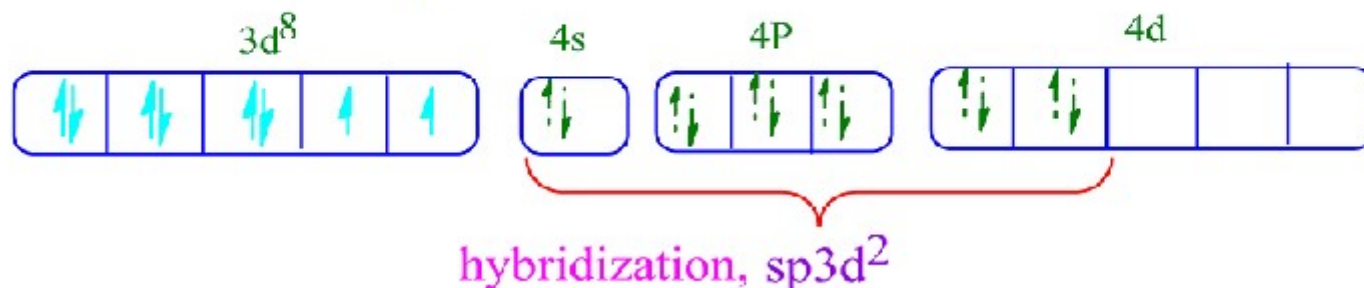


$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  ion.

Outer-orbital complex.

$\text{Ni}^{2+}$  ion :  $3d^8$  system

Electronic configuration of  $\text{Ni}^{2+}$  ion



## Labile and inert complexes on the basis of CFT

- According to CFT the ligand field splits the d-orbitals.
- This splitting leads to a decrease in energy of the system whose magnitude depends on the number of d electrons present.
- if the CFSE value increases by association or dissociation of a ligand then the complex is labile.
- On the other hand it is inert when there is a loss in CFSE value.



> **H.TAUBE** has described the complexes as labile if they have half life( $t^{1/2}$ ) of reaction under 30 sec while the reactions having half life greater than 30 sec are termed as inert.

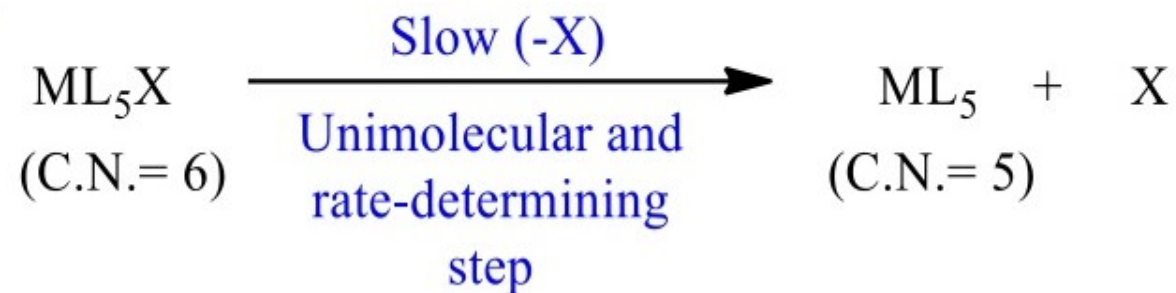
$t^{1/2} < 30$  sec  
 $t^{1/2} \geq 30$  sec

LABILE complex  
 INERT complex

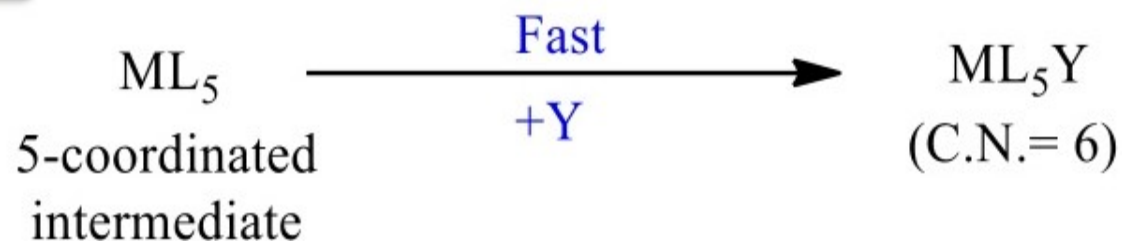
No. of d electrons & electron configuration	Nature	Example
<b>d<sup>0</sup></b>	<b>Labile</b>	<b>[CaEDTA]<sup>2-</sup></b>
<b>d<sup>1</sup>; t<sub>2g</sub><sup>1</sup>e<sub>g</sub><sup>0</sup></b>	<b>Labile</b>	<b>[Ti(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup></b>
<b>d<sup>2</sup>; t<sub>2g</sub><sup>2</sup>e<sub>g</sub><sup>0</sup></b>	<b>Labile</b>	<b>[V(phen)<sub>3</sub>]<sup>3+</sup></b>
<b>d<sup>3</sup>; t<sub>2g</sub><sup>3</sup>e<sub>g</sub><sup>0</sup></b>	<b>Inert</b>	<b>[V(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup></b>
<b>d<sup>4</sup>(high-spin); t<sub>2g</sub><sup>3</sup>e<sub>g</sub><sup>1</sup></b>	<b>Labile</b>	<b>[Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup></b>
<b>d<sup>4</sup>(low-spin); t<sub>2g</sub><sup>4</sup>e<sub>g</sub><sup>0</sup></b>	<b>Inert</b>	<b>[Cr(CN)<sub>6</sub>]<sup>4-</sup></b>
<b>d<sup>5</sup>(high-spin); t<sub>2g</sub><sup>3</sup>e<sub>g</sub><sup>2</sup></b>	<b>Labile</b>	<b>[Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup></b>
<b>d<sup>5</sup>(low-spin); t<sub>2g</sub><sup>5</sup>e<sub>g</sub><sup>0</sup></b>	<b>Inert</b>	<b>[Mn(CN)<sub>6</sub>]<sup>4-</sup></b>
<b>d<sup>6</sup>(high-spin); t<sub>2g</sub><sup>4</sup>e<sub>g</sub><sup>2</sup></b>	<b>Inert</b>	<b>[Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup></b>
<b>d<sup>6</sup>(low-spin); t<sub>2g</sub><sup>6</sup>e<sub>g</sub><sup>0</sup></b>	<b>Inert</b>	<b>[Fe(CN)<sub>6</sub>]<sup>4-</sup></b>
<b>d<sup>7</sup>, d<sup>8</sup>, d<sup>9</sup>, d<sup>10</sup></b>	<b>Labile</b>	

## i) $\text{S}_{\text{N}}1$ – Unimolecular nucleophilic substitution reaction

Step 1

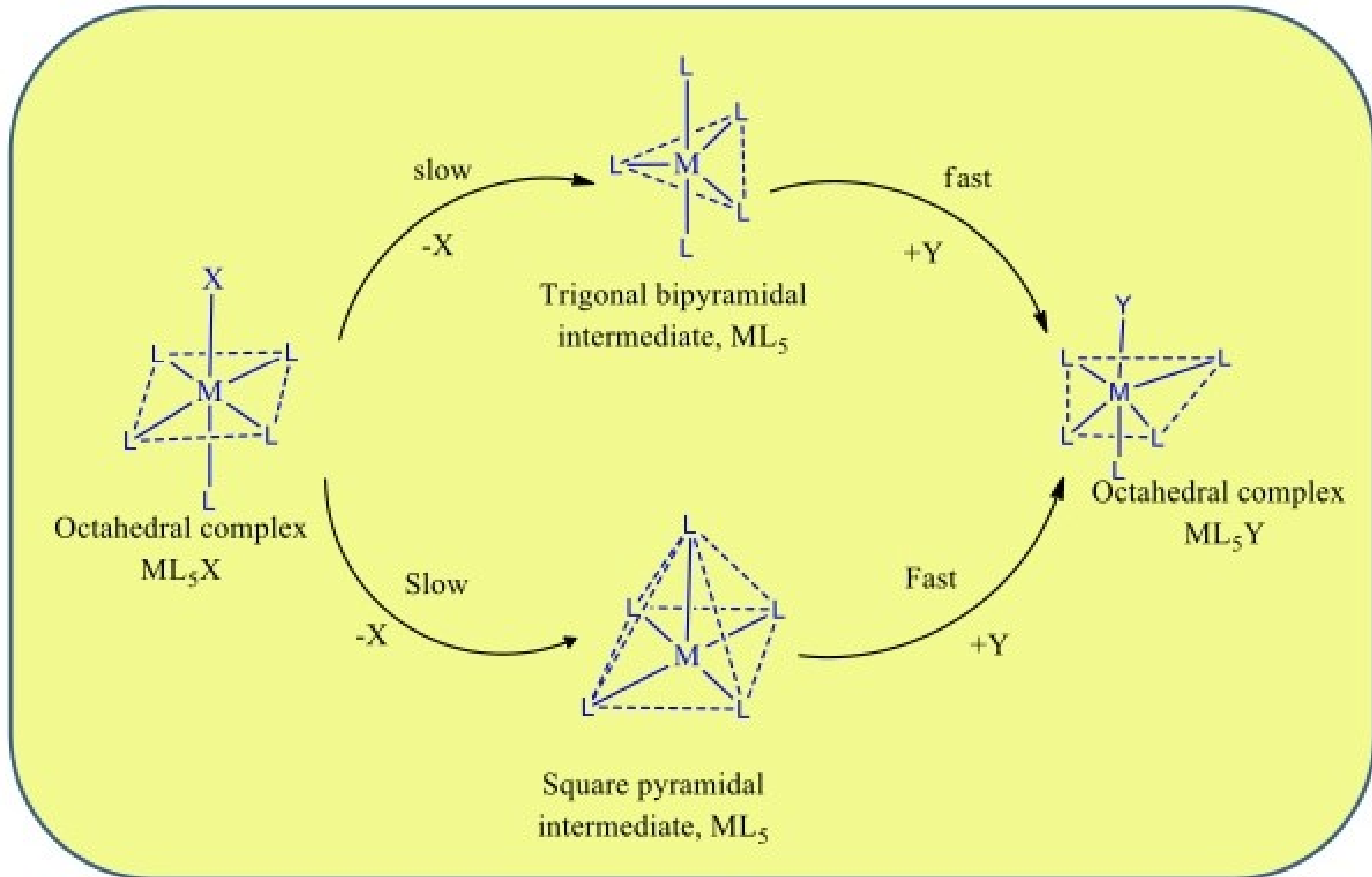


Step 2



$$\text{Rate} = k [\text{ML}_5\text{X}]$$

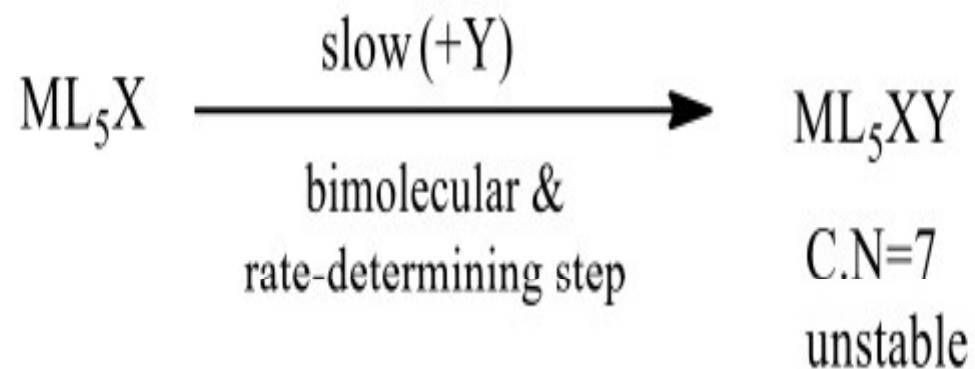
# DIAGRAMMATIC REPRESENTATION OF DISSOCIATION



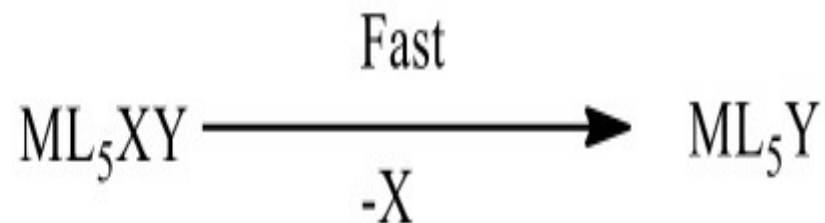


## i) $\text{S}_{\text{N}}2$ – Bimolecular nucleophilic substitution reaction

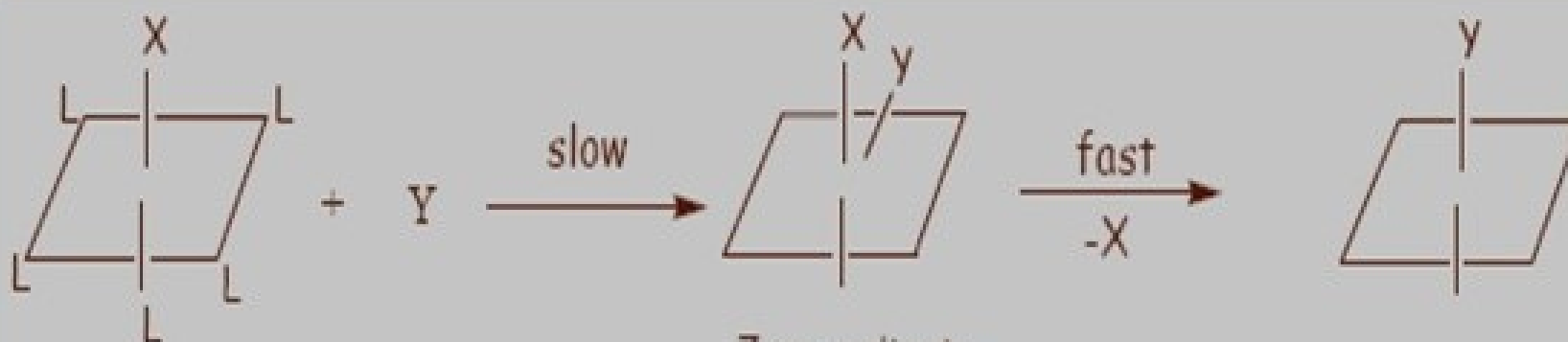
Step 1



Step 2

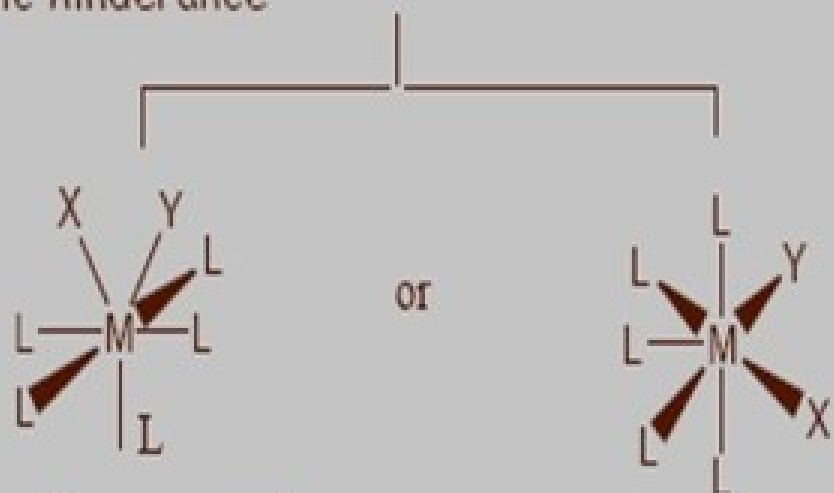


$$\text{Rate} = k[\text{ML}_5\text{X}][\text{Y}]$$



7 co-ordinate intermediate

the first step is slow since the incoming Y causes steric hinderance



"monocapped octahedron"

"pentagonal bipyramidal"

## Mechanism of substitution in Cobalt (III) Octahedral complexes

### HYDROLYSIS REACTIONS

- These are the substitution reactions in which a ligand is replaced by a water molecule or by  $\text{OH}^-$  groups.
- The reactions in which an aquo complex is formed by the replacement of a ligand by  $\text{H}_2\text{O}$  molecule are called **acid hydrolysis** or **aquation**.
- The reactions in which a hydroxo complex is formed by the replacement of a ligand by  $\text{OH}^-$  group are called **base hydrolysis**.
- The reactions in which  $\text{H}_2\text{O}$  molecule is replaced by anionic ligand then is known as **anation reaction**.

## AQUATION REACTIONS OF METAL COMPLEXES

- Ammine complexes of Co(III) are the most studied.
- Water is the medium of reaction.
- Usually replacement of  $\text{NH}_3$  derivatives is very slow, so only other ligands are considered.



- Rate =  $k \cdot [\text{Co}(\text{NH}_3)_5\text{X}]^{2+} \cdot [\text{H}_2\text{O}]$

- Rate =  $k' \cdot [\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$

# ACID HYDROLYSIS

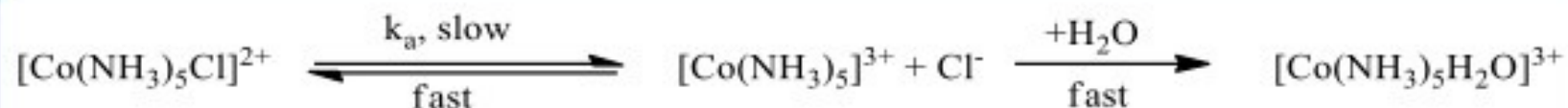
- Occurs in neutral and acid solutions ( $\text{pH} < 3$ )
- Rate is independent of water molecule



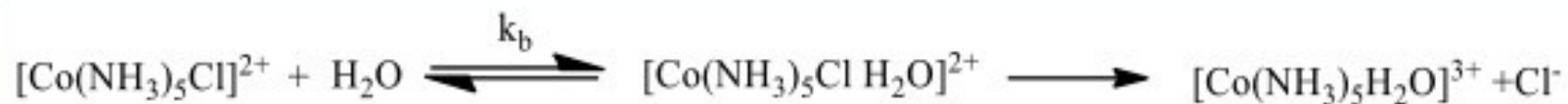
$$\text{Rate} = k[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$$

# Mechanism of Acid Hydrolysis

## ➔ Dissociative Mechanism



## ➔ Associative Mechanism



# A OR D ??? - DECIDING FACTORS

- ▮ Charge on the complex
- ▮ Steric factors
- ▮ Effect of leaving group
- ▮ Effect of solvent
- ▮ Presence of pi-donors and acceptors as spectator ligands

## CHARGE ON THE COMPLEX

- The increase in positive charge decreases the rate of reaction following a dissociative mechanism because the breaking the metal-ligand bond becomes difficult.

For aquation of the Ru complexes the trend is as shown

$[\text{RuCl}_6]^{3-}$	$1.0 \text{ s}^{-1}$
$[\text{RuCl}_3(\text{H}_2\text{O})_3]^0$	$2.1 \times 10^{-6} \text{ s}^{-1}$



## EFFECT OF LEAVING GROUP

Complex	Rate constant $s^{-1}$
$[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]^{2+}$	$\sim 10^{-5}$
$[\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$	$\sim 10^{-6}$
$[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$	$\sim 10^{-8}$

Thus it is proved that **M-X bond breaking is very much important in aquation reactions** than bond formation.

# EFFECT OF LEAVING GROUP

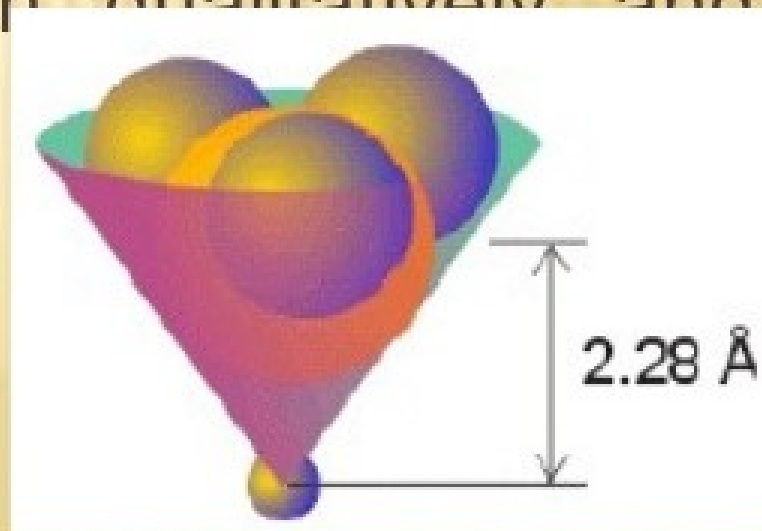
- ▮ The rate of aquation of  $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$  depends on the stability of M-X bond.
- ▮ If the M-X bond is more stable rate of reaction is low.
- ▮ The order of reactivity is  
$$\text{HCO}_3^- > \text{NO}_3^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{F}^- > \text{SCN}^- > \text{NO}_2^-$$
- ▮ This is the order of decreasing thermodynamic stability of the complexes formed with these groups

## STERIC EFFECTS OF INERT LIGANDS

- ▮ When the non-leaving ligands are bulky, they will be crowding the central metal ion.
- ▮ The incoming ligand will find it difficult to approach the central metal ion slowing down the rate of reaction taking place by associative mechanism.
- ▮ Instead, if the reaction takes place by dissociative mechanism, the rate of the reaction will increase because the crowding around the metal ion is reduced.

# $O_h$ : STERIC EFFECTS ON SUBSTITUTION

- Steric crowding around the metal centre favors dissociative activation
- Dissociative activation relieves crowding around the complex
- Steric crowding has been qualitatively and quantitatively explored
  - Tolman Cone Angle



## Factors affecting acid hydrolysis

- ▶ Crowding of a reaction centre may favor a dissociative process.
- ▶ Due to inductive effect rate increases. Increasing alkyl substitution will distort the electron density towards the metal atom and favors dissociative process.
- ▶ The rate decreases with increase in the overall charge on the metal. This indicates dissociative process.
- ▶ Ligands possessing lone pair of electron favor dissociative process and ligands which withdraws electron from the metal centers by delocalization of electron pairs favor associative process.

## Base Hydrolysis

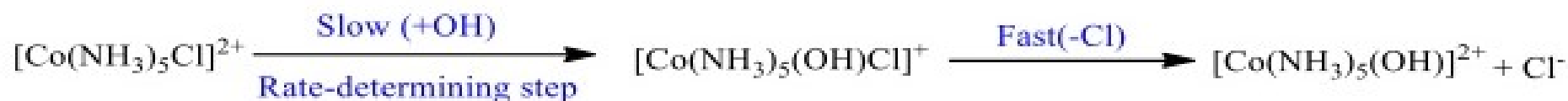
- ➔ Occurs in basic solutions ( $\text{pH} > 10$ ).
- ➔ Two types of mechanisms in octahedral complexes.
  - $S_N2$  or Associative mechanism.*
  - $S_N1CB$  or Dissociation mechanism.*

*$S_N1CB$  Mechanism is more favored than  $S_N2$  Mechanism*

Acid-Base properties of the complexes are more important than the nucleophilic properties of  $\text{OH}^-$  in  $S_N1CB$  Mechanism.

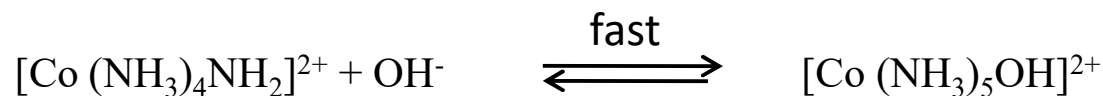
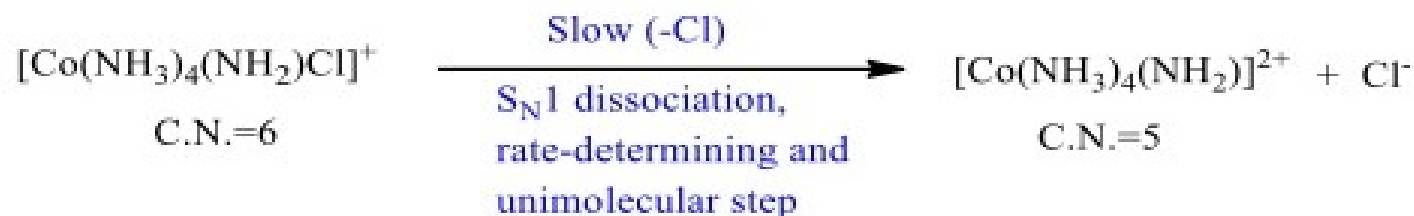
Reactions occurring in non hydroxylic solvents like Dimethyl sulphoxide, can be explained by  $S_N1CB$  mechanism but not by  $S_N2$ .

## $S_N2$ or Associative mechanism



$$\text{Rate} = k[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} [\text{OH}^-]$$

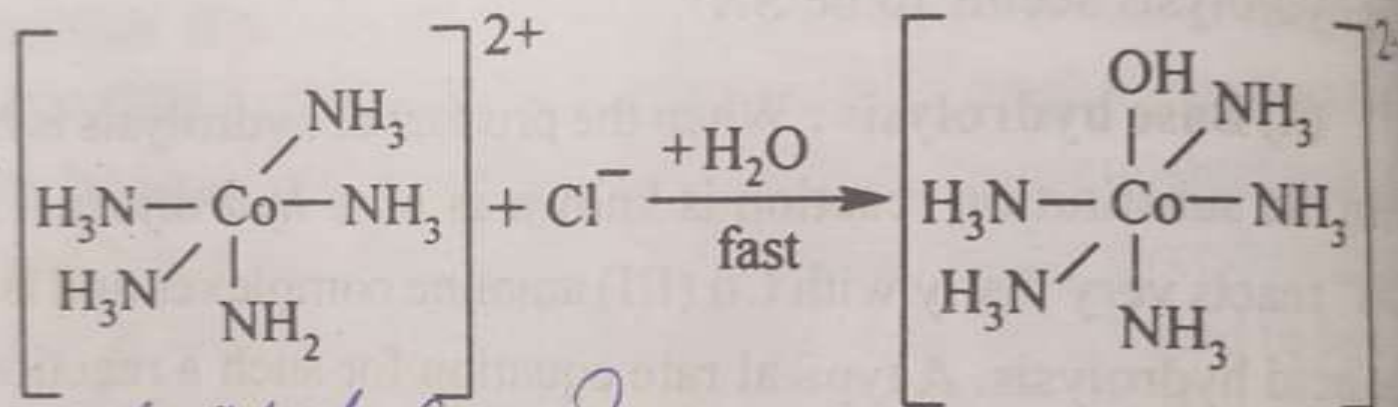
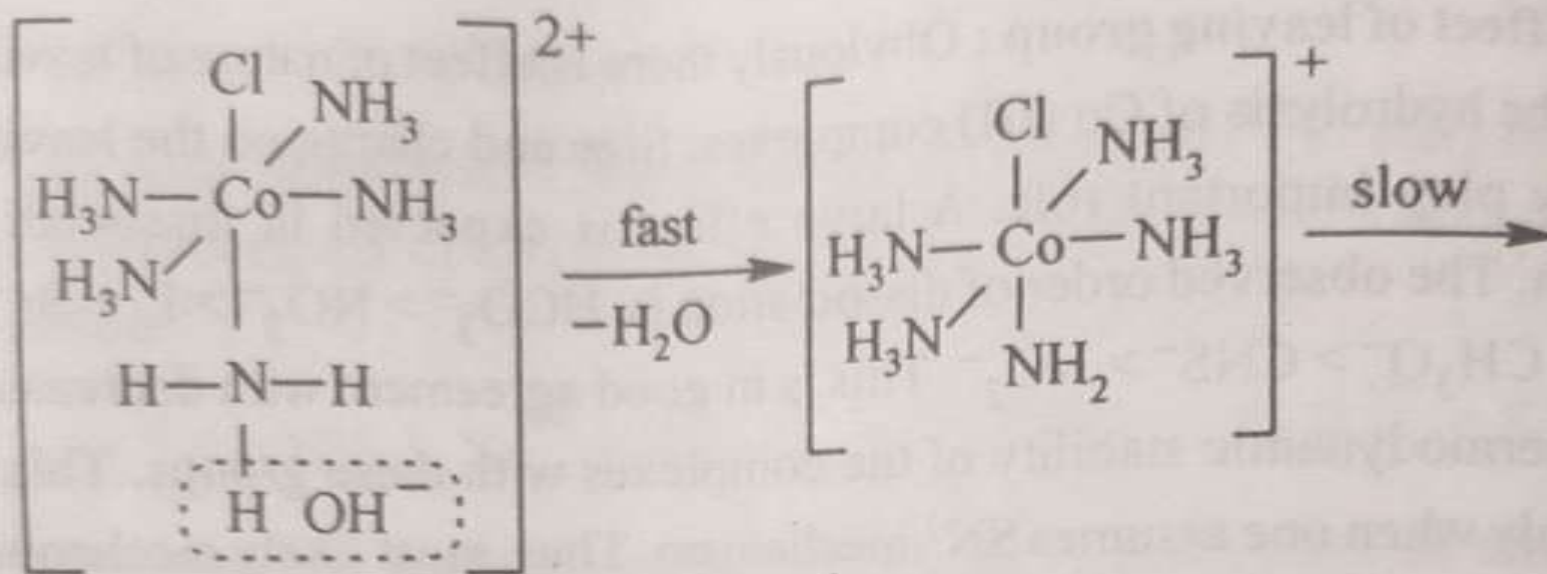
## $S_N1CB$ or Dissociation mechanism



- Rate =  $k_1[\text{CB}]$ ; where CB= Conjugate Base ,

$$[\text{CB}] = \frac{K [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} [\text{OH}^-]}{[\text{H}_2\text{O}]}$$





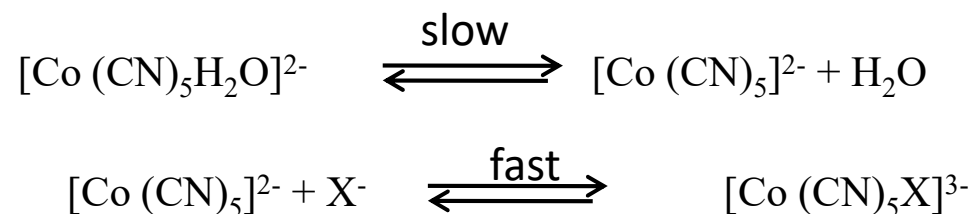
*Intermediate compound.*

# Anation Reactions


- ➡ Aquo ligand or H<sub>2</sub>O molecules from an aquo complex is replaced from the coordination shell by some anion.
- ➡ It is the reverse of acid-hydrolysis.
- ➡ These are Bimolecular and the rate depends on the concentration of the complex and the anion

**E.g.**





- The Substitution reactions of Co(III) and Cr(III) complexes were the first extensively studied due to the inertness of these two metals.
  
- Most evidences support the  $I_d$  mechanisms for substitution in Co(III) complexes and a little dependence of reaction rates on the nature of the incoming ligand. The reaction in which  $\text{H}_2\text{O}$  replaces  $\text{Cl}^-$  in  $[\text{Co}(\text{NMeH}_2)_5\text{Cl}]^{2+}$  takes place 22 times faster than the same reaction for  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ . The dissociation of  $\text{Cl}^-$  ligand is encouraged by the greater steric requirements of methylamine.
  
- If the reaction proceeded by an  $I_a$  or Association pathway, the order of rates would be the opposite because the rate of the reaction is decreased due to the steric repulsion of the incoming ligand.



## ➤ *Trans effect*

- The *trans effect* is best defined as the effect of a coordinated ligand upon the rate of substitution of ligands opposite to it.
- **Or** The ability of a ligand in a square planar complex to direct the replacement of the ligand *trans* to it.
- It was recognized by Werner (1893) and elaborated by Chernuyayev (1926).
- By comparing a large number of reaction rates Langford and Grey set up a trans directing series.
- In the trans-directing series, the ligands are arranged in the increasing order of trans effect as follows:  
$$\text{H}_2\text{O} < \text{OH}^- < \text{F}^- \approx \text{RNH}_2 \approx \text{py} \approx \text{NH}_3 < \text{Cl}^- < \text{Br}^- < \text{SCN}^- \approx \text{I}^- \\ \approx \text{NO}_2^- \approx \text{C}_6\text{H}_5^- < \text{SC}(\text{NH}_2)_2 \approx \text{CH}_3^- < \text{NO} \approx \text{H}^- \approx \text{PR}_3 < \\ \text{C}_2\text{H}_4 \approx \text{CN}^- \approx \text{CO}$$

# TRANS EFFECT

- ▣ **Definition**

The trans effect is best defined as the effect of a coordinated ligand upon the rate of substitution of ligands opposite to it.

**Or**

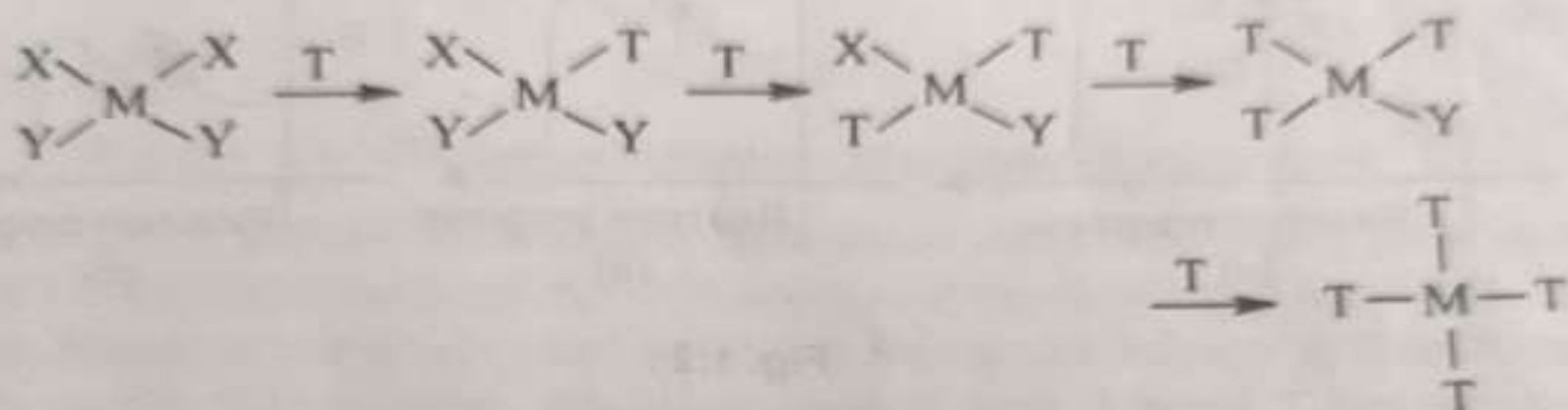
The ability of a ligand in a square planar complex to direct the replacement of the ligand trans to it.

- ▣ The trans effect is given as the following **series**:

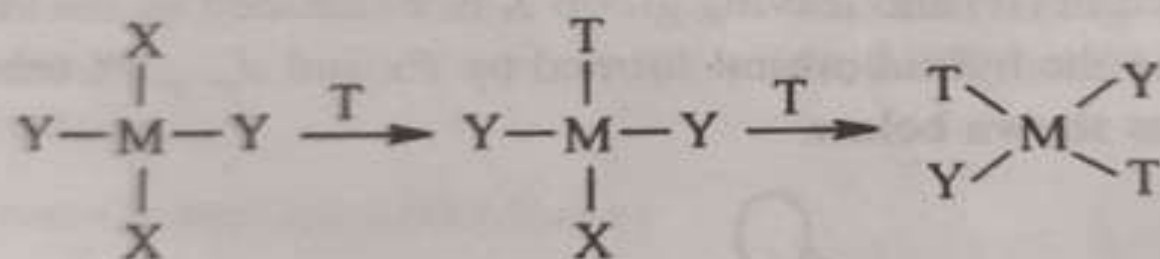


It can be illustrated by the reactions and diagrams as follows -

(i) Cis complex :



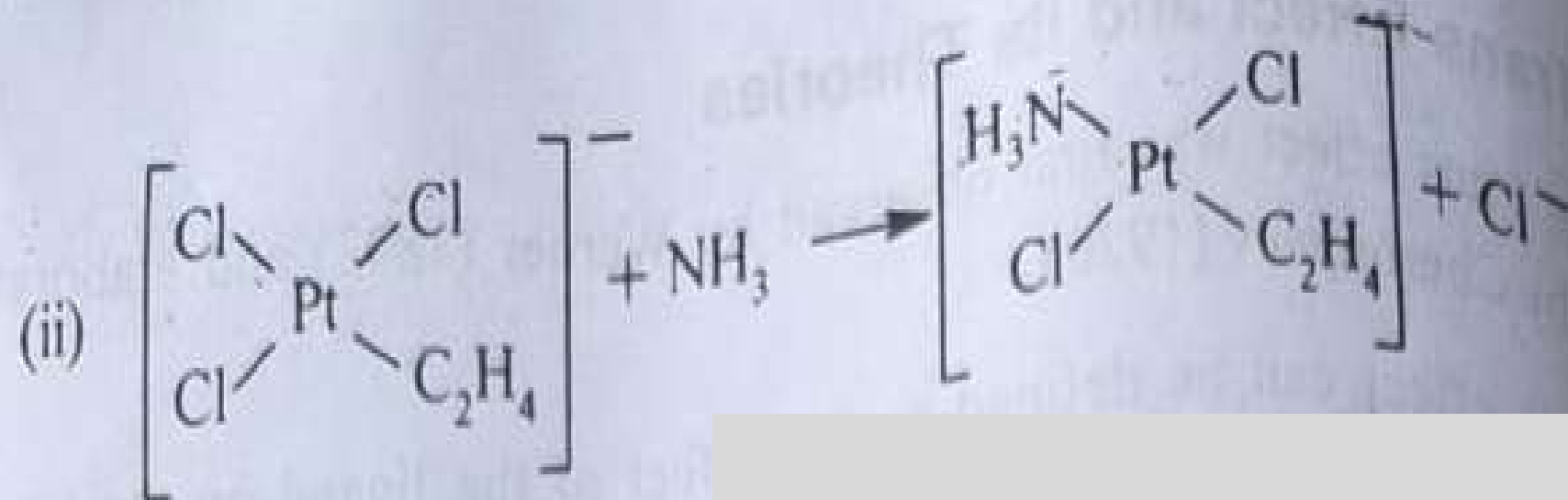
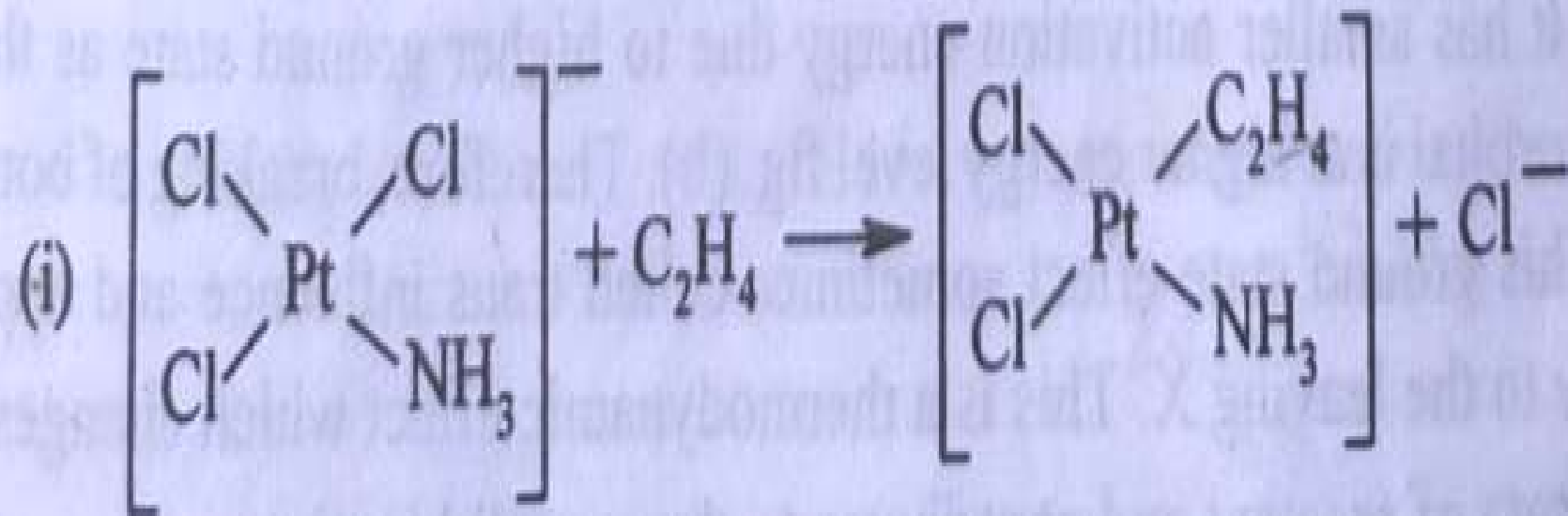
(ii) Trans complex :

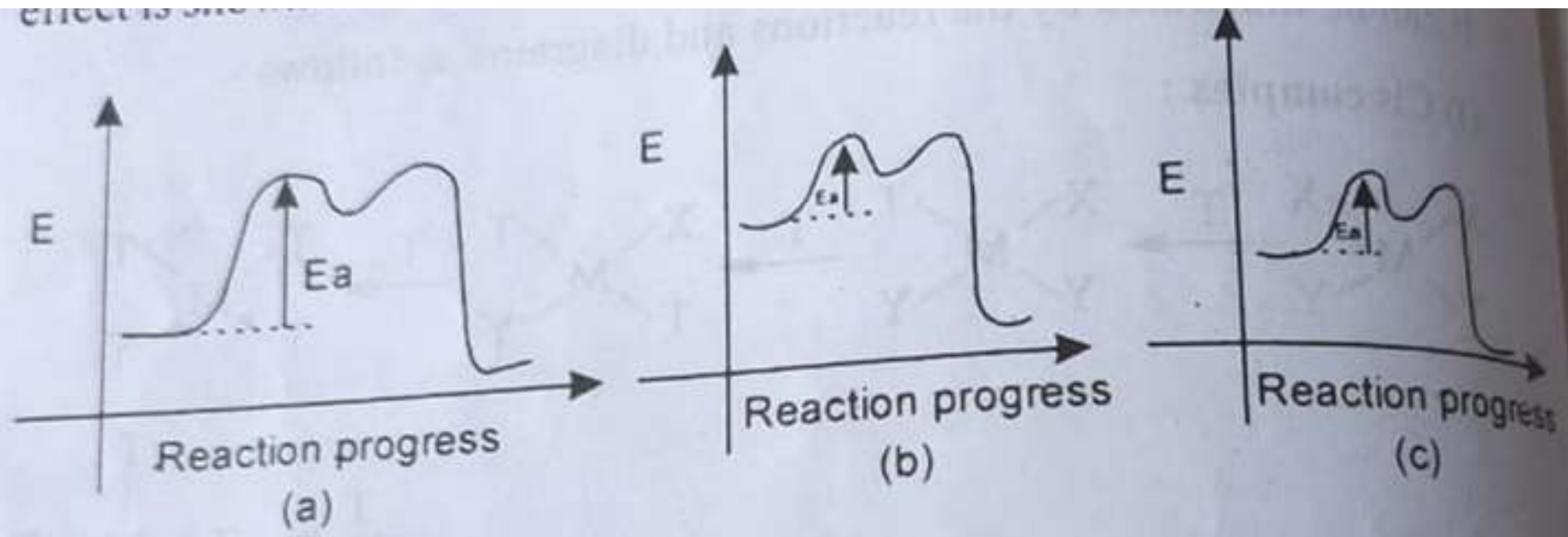


where, T = (thiourea) trans directing group

X = labile group

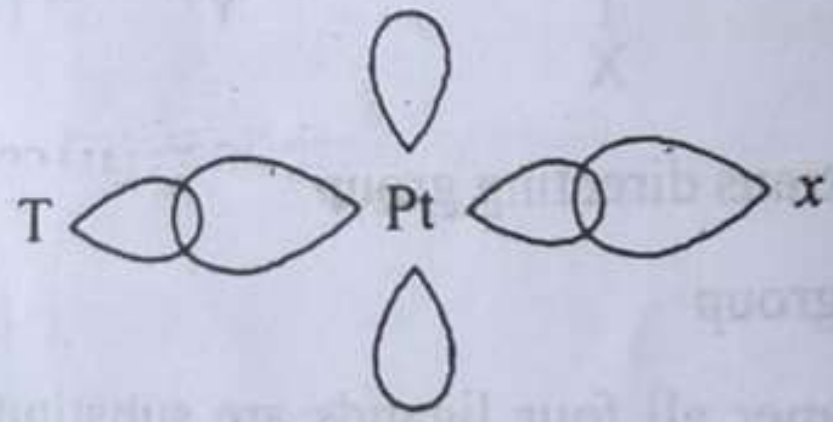
In case of cis isomer all four ligands are substituted one by one but in trans isomer only two labile groups are replaced by T. Another example can be illustrated.





**Fig. 1.2:**

Here,  $E_a$  = activation energy,  $E$  = energy.



**Fig. 1.3 : Sigma bonding effect**



# **THEORIES OF TRANS EFFECT**

**Two general theories of trans effect are:**

**The polarization theory**

**pi-Bonding theory**



# 1. *Electrostatic Polarisation Theory*

- This theory is primarily concerned with effect in the ground state.
- It was given by A.A. Grinberg.
- According to polarization theory, the ligand, by electrostatic effects, weakens the bond trans to it and facilitates substitution in that position.
- Support for this theory is demonstrated by looking at the *trans* directing series.

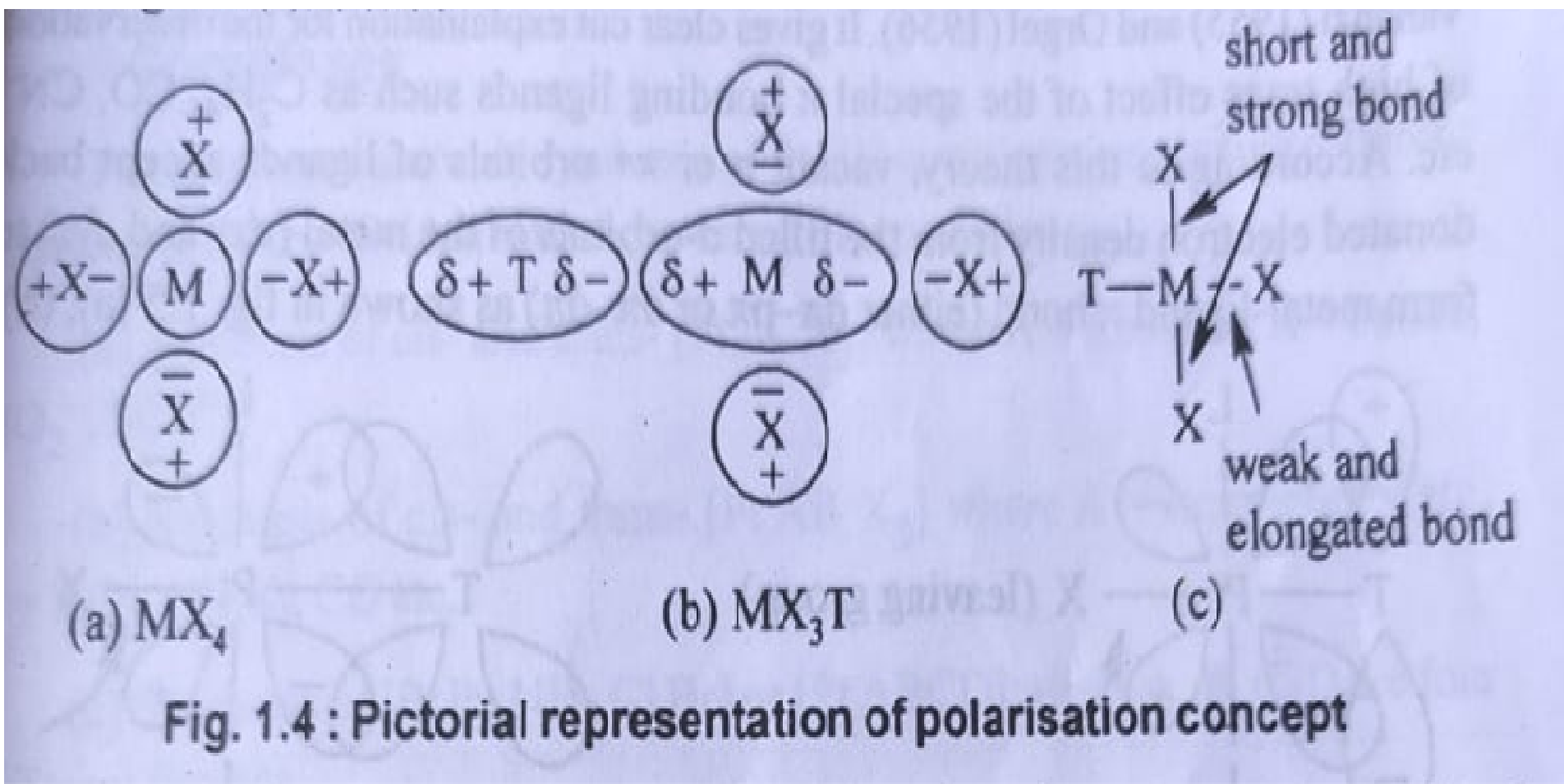


- The **more polarizable** ligands such as  $\text{SCN}^-$ , and  $\text{I}^-$  and the ligands containing  $\pi$ -clouds e.g.  $\text{CN}^-$  are **high** in the series..
- **Less polarizable** ligands such as ammonia or water are lower in the series.
- Additional support comes from the observation that  $\text{Pt(II)}$  complexes demonstrate a more pronounced *trans* effect than those of the less polarizable  $\text{Pd(II)}$  and  $\text{Ni(II)}$  cations.

# POLARIZATION THEORY

It was given by A.A GRINBERG(1935).

According to this theory, the Ligand, polarized by central metal and more polarizable ligand can induce polarization in metal ion, as a result of this the bond between metal and the ligand which causes induce dipole becomes strong and due to trans influence the M-L bond trans to it labilize and break. .



# POLARIZATION THEORY

Consider two types of square planar complexes of platinum (II)

Pt  $X_4$  type complex.

Pt L  $X_3$  type complex.

## **PtX<sub>4</sub> TYPE COMPLEX**

**When the complex contains four identical ligands as in PtX<sub>4</sub>**

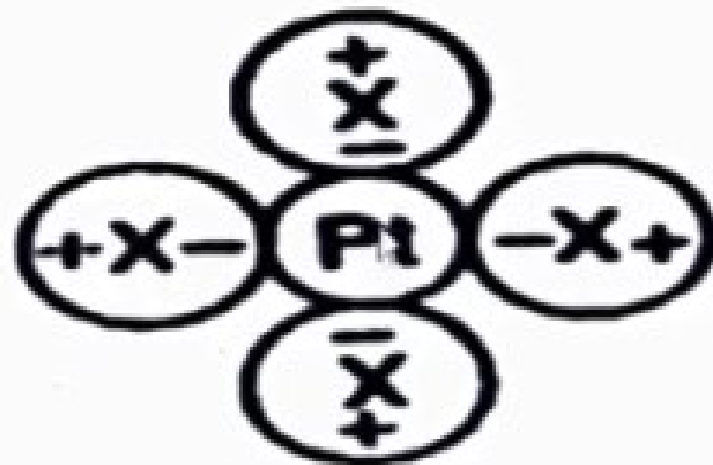
**each polarized by the metal ion to the same extent.**

**no induced dipole result in on the central metal ion.**

**Thus, none of the four ligands show trans effect.**

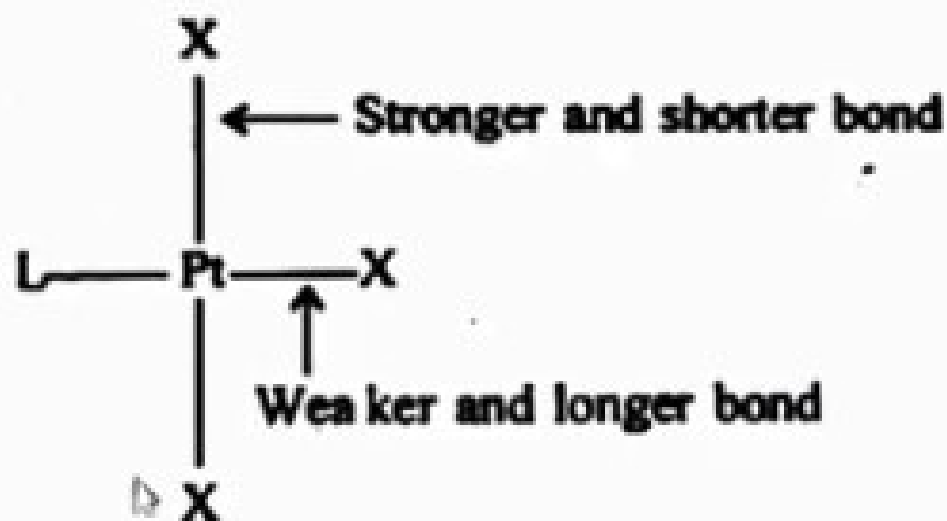
## $PtX_4$ TYPE COMPLEX

- **X**: same ligands
- Metal-ligand bond length is same due to absence of polarization.



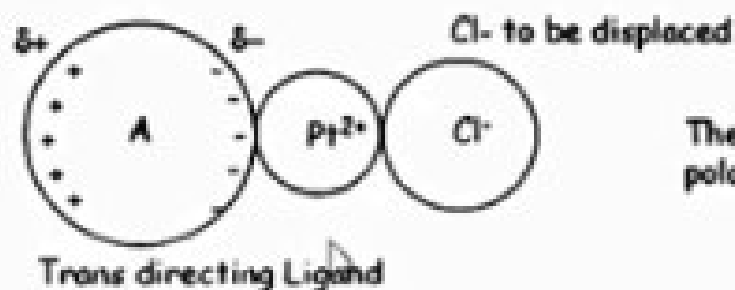
## PtLX<sub>3</sub> TYPE COMPLEXES

- L: more polarizing ligand than X
- X: identical ligands.

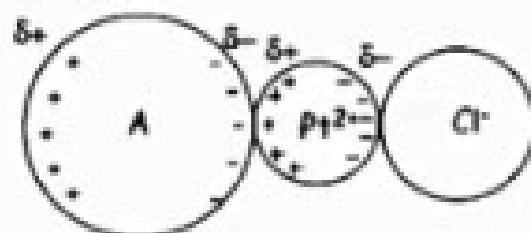




# If we take example of $\text{PtCl}_3\text{A}$ type of complex



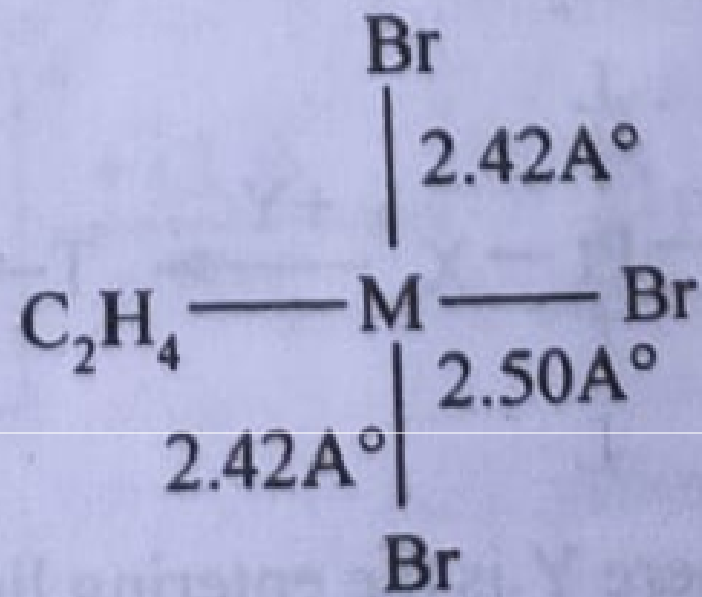
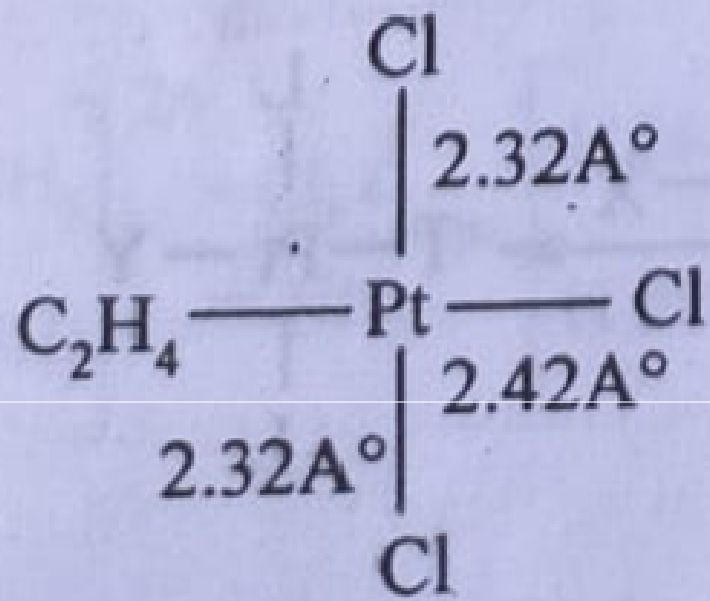
The  $\text{Pt}(\text{II})$  cation induces a dipole in the polarizable trans-directing ligand  $\text{A}$ .



The induced dipole in ligand  $\text{A}$  induces a dipole in the polarizable  $\text{Pt}(\text{II})$  cation.



The chloride anion trans to  $\text{A}$  is more easily released due to the extra repulsive forces between its negative charge and the induced dipole of the  $\text{Pt}(\text{II})$  cation.

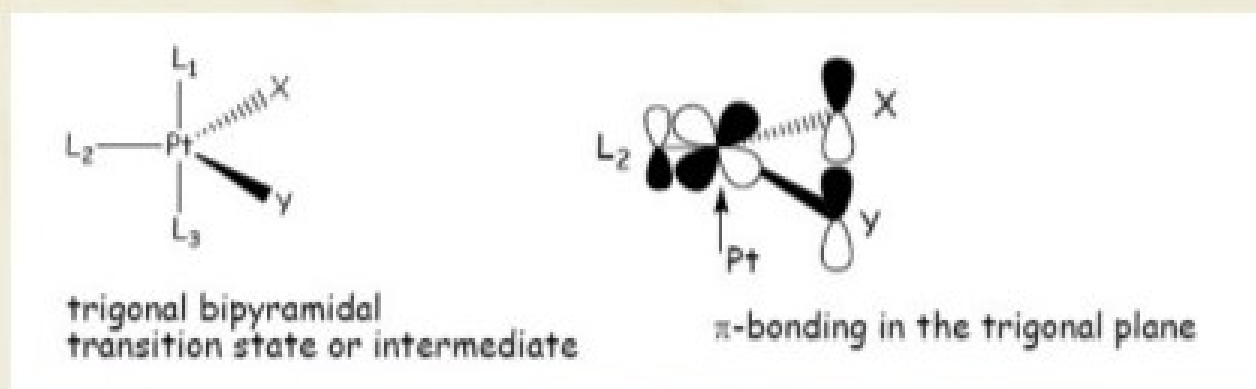


## **Weakness(limitations)**

**The emphasis on the trans bond limits the application of Polarization theory to the trans influence(it is a thermodynamic factor which facilitates substitution of ligand) only. It also fails in explaining the high trans effect of the bonding ligands like  $\text{PR}_3$ ,  $\text{NO}$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_4$  which lie at the high end of the series.**

## 2. $\Pi$ Bonding Theory

- In the trigonal plane of the 5-coordinate transition state or intermediate, a  $\pi$ -bonding interaction can occur between a metal d-orbital (e.g.  $d_{xy}$ ) and suitable orbitals (p atomic orbitals, or molecular orbitals of  $\pi$ -symmetry) of ligand  $L_2$  (the ligand trans to the leaving group) and  $Y$  (the entering group).
- These 3 ligands and the metal center can communicate electronically through  $\pi$ -bonding only if they all lie in the same plane in the transition state or intermediate.



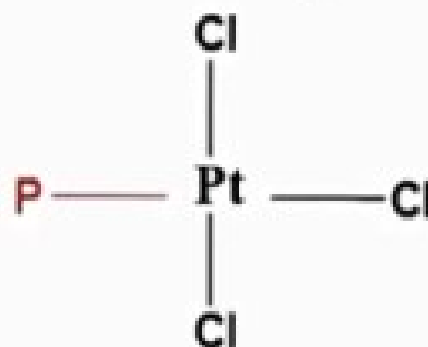
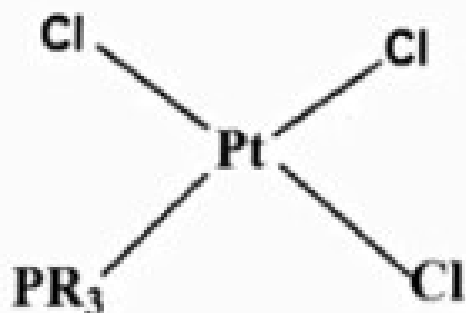
- In other words, strong trans directing ligands are those capable of forming strong back bonding ( $\pi$ -acceptors), for example, CO,  $CN^-$ , olefins etc. or strong  $\sigma$ -donors such as  $CH_3^-$ ,  $H^-$ ,  $PR_3$  etc. Strong  $\pi$ -donors such as  $H_2O$ ,  $OH^-$ ,  $NH_2^-$ , etc. are weak in their trans directing properties.

## **Pi-BONDING THEORY**

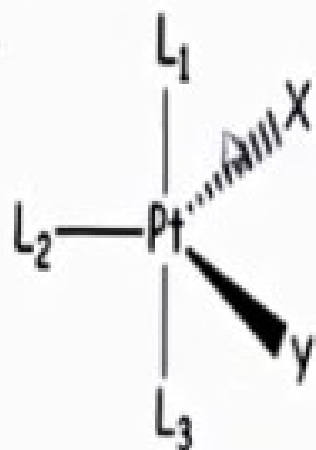
- **This theory was given by Chat in 1955 and Orgel in 1956.**
- **According to this theory vacant pi and pi\* orbitals of pi acceptor ligands accept pair of electrons from filled d-orbital of metal to form M-L pi bond.**

# PI-BONDING THEORY

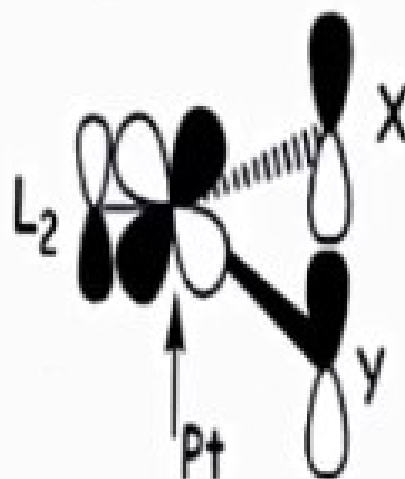
- In case of Pt(II) square-planar complex,  $[\text{Pt}(\text{R}_3\text{P})\text{Cl}_3]$  (P is the pi-bonding ligand) the  $d_{yz}$  orbital of Pt(II) with a pair of electrons overlaps with the empty  $p_z$  orbital of the pi-bonding ligand to form pi-bond.
- The formation of pi-bond in the complex increases the electron density in the direction of P and diminishes it in the direction of the ligand, R trans to L.



**Ex. Pt  $L_3X$  type of complex, Y is an entering ligand.**

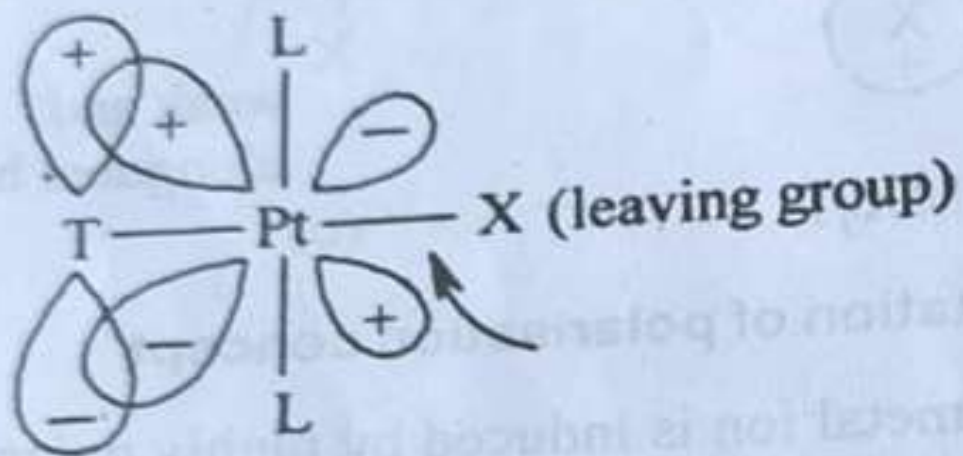


trigonal bipyramidal  
transition state or intermediate

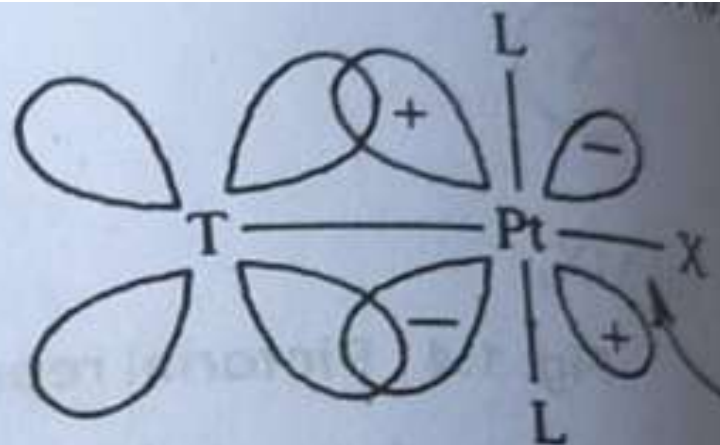


$\pi$ -bonding in the trigonal plane

form metal-ligand  $\pi$  bond (circle)

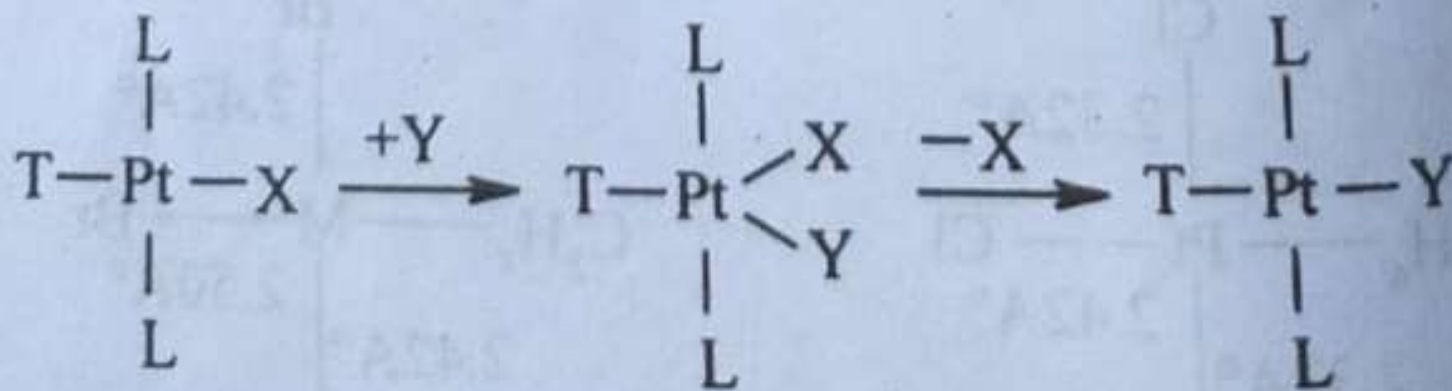


(a)



(b)

Fig. 1.5 : (a) -  $\pi^* \leftarrow d\pi$  bonding, (b) -  $d\pi \leftarrow \pi^*$  bonding.



where Y is the entering ligand.



## Pi-BONDING THEORY

- The weakening of Pt-X bond trans to L facilitates the approach of the entering ligand.
- Ligands which show pi-bonding trans effect are  $PR_3$ , NO, CO,  $C_2H_4$ .
- Ligands which follow pi-bonding theory have more difference in energy(activation energy) between ground and transition state.

## Limitations

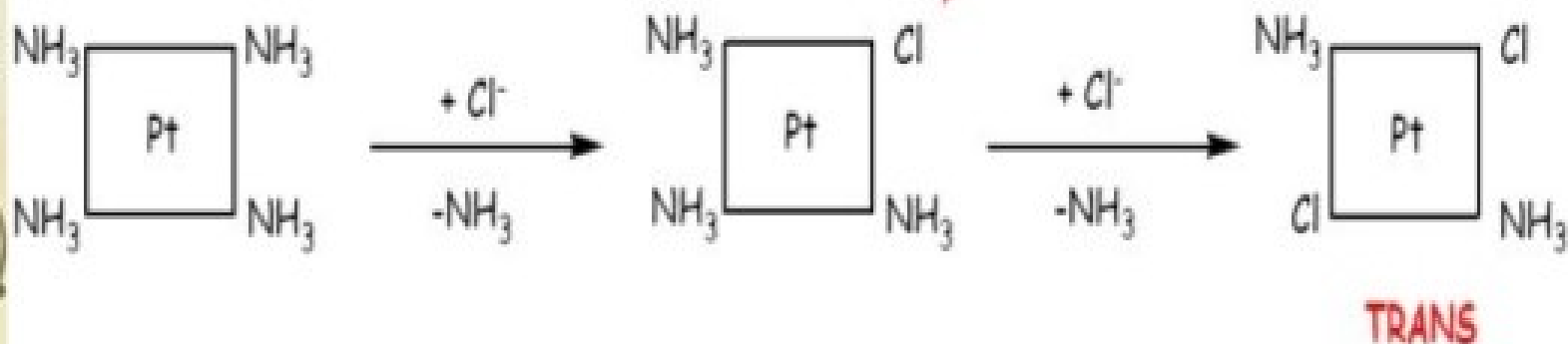
- ❑ Trans effect and trans influence are not distinguished.
- ❑ Fails to explain trans directors ligands which are unable to form pi bond. E.g.  $\text{H}^-$ ,  $\text{NH}_3$  and  $\text{CH}_3^-$
- ❑ Pi bonding alkenes not shows trans effect for nitrogen ligands.

# Applications of Trans Effect in Synthesis of Pt (II) Complexes

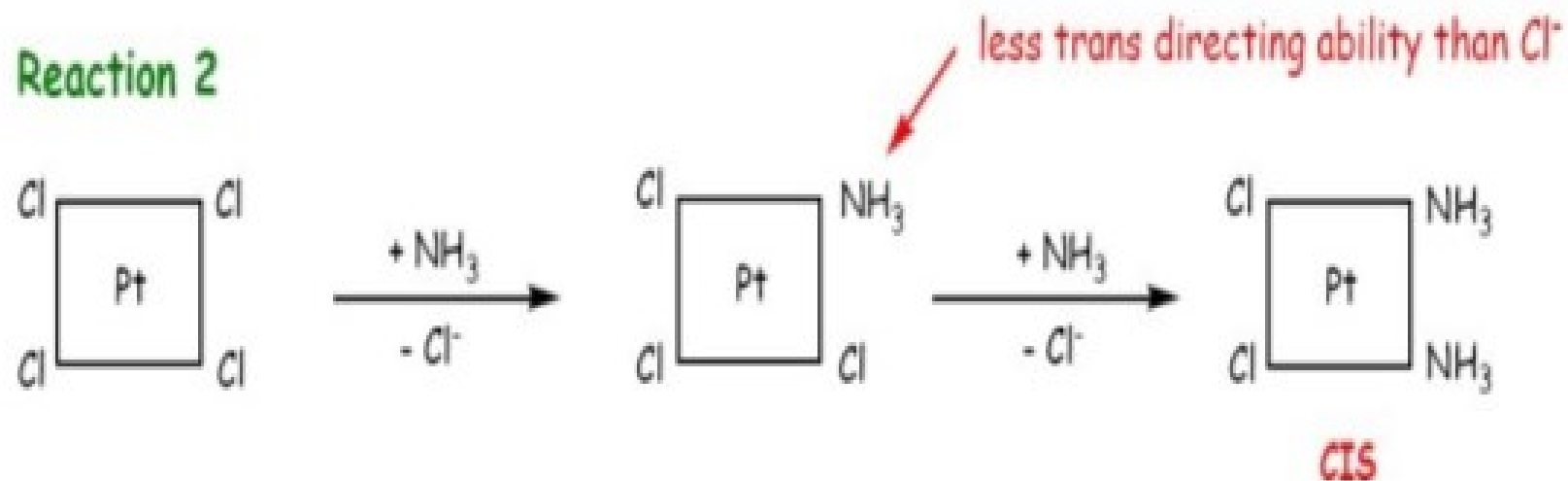
- a. Synthesis of cis- and trans –  $[\text{PtA}_2\text{X}_2]$   
where A= Ammine, X= halide,  $\text{NO}_2^-$ ,  $\text{SCN}^-$
- b. Synthesis of cis- and trans –  $[\text{PtABX}_2]$   
where A= Ammine, Py etc. B=  $\text{NO}_2^-$ , CO etc. X= halide
- c. Synthesis of  $[\text{PtABCD}]$  where A, B, C, D are four different ligands

# 1. Synthesis of isomers of $Pt(NH_3)_2Cl_2$

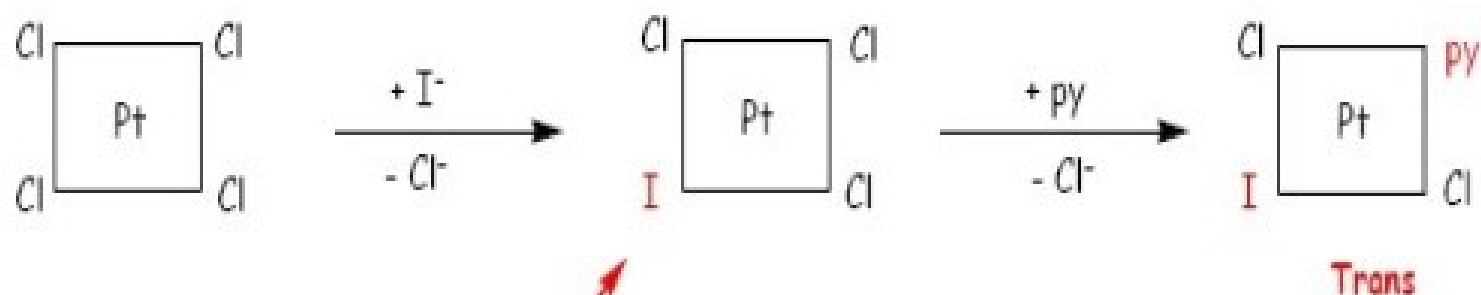
## Reaction 1



## Reaction 2

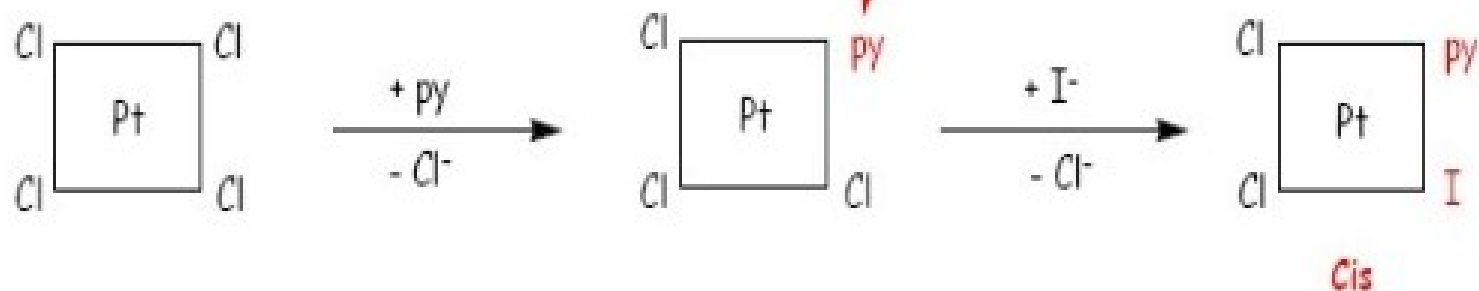


## 2. Preparation of *cis* and *trans* $PtCl_2I(py)$ from $PtCl_4^{2-}$ , $I^-$ and $py$ .



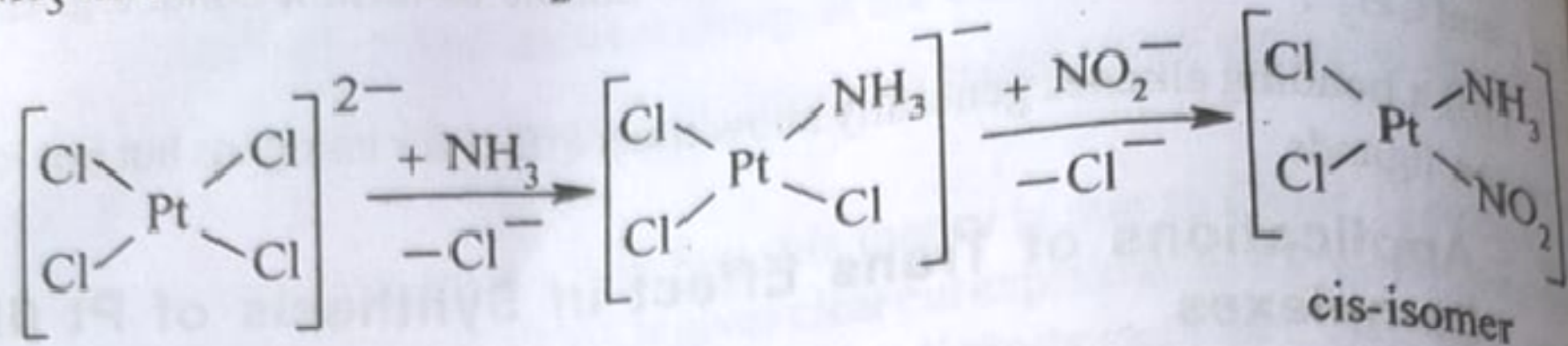
higher than  $Cl^-$  in the trans directing series, directs  $py$  trans to it

lower than  $Cl^-$  in the trans directing series,  $Cl^-$  directs  $I$  trans to  $py$

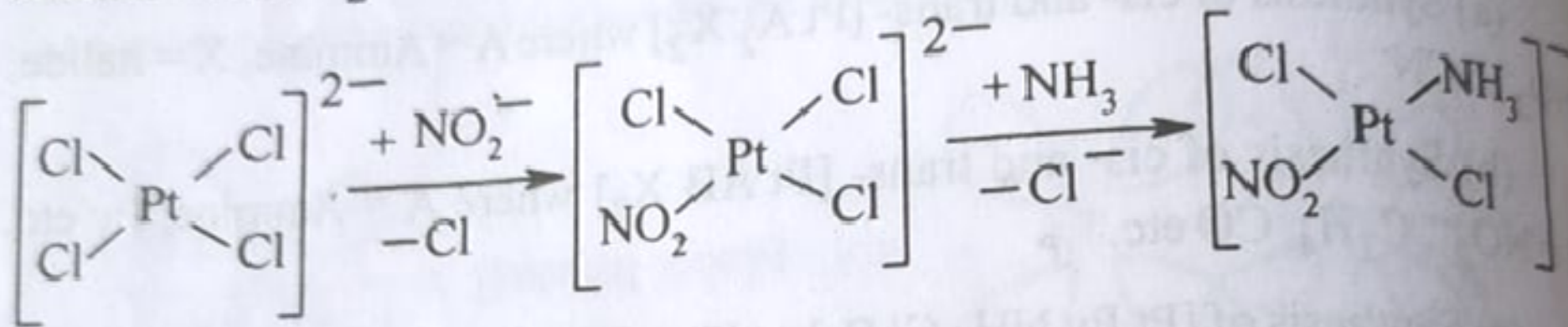


(b) Synthesis of cis- and trans- isomers of  $[Pt AB X_2]$

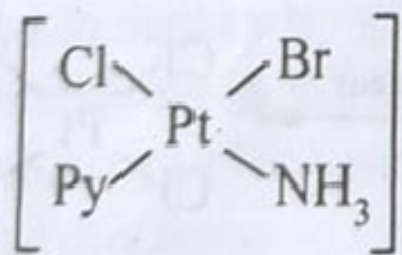
e.g. (i) In order to get cis-  $[Pt Cl_2 (NO_2) (NH_3)]^-$ ,  $[Pt Cl_4]^{2-}$  is reacted with  $NH_3$  first and then with  $NO_2^-$ .



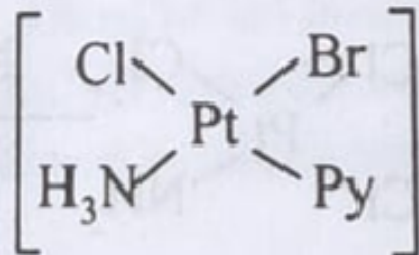
(ii) In order to get trans isomer of  $[Pt Cl_2 (NO_2) (NH_3)]^-$   $[Pt Cl_4]^{2-}$  is reacted with  $NO_2^-$  first and then with  $NH_3$ .



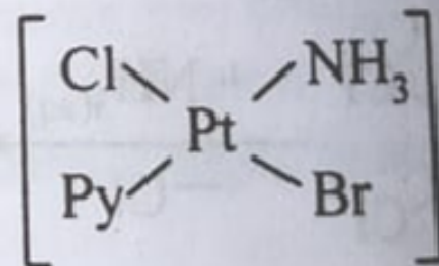
(c) Synthesis of isomers of  $[Pt ABCD]$  : e.g.  $[Pt (Py) (NH_3) BrCl]$ . This complex shows three isomers as follows.



(I)



(II)



(III)

All these isomers can be synthesised from  $[Pt Cl_4]^{2-}$  by changing the order of reaction with different ligands. e.g.,

(i) For (I) complex  $[Pt Cl_4]^{2-}$  reacts with  $NH_3$  first, then with  $Br^-$  and at last with Py.

(ii) For (II) complex order of reaction is Py first then  $Br^-$  and at last  $NH_3$  with  $[Pt Cl_4]^{2-}$ .

(iii) For (III) complex order of reaction is  $NH_3$ , Py and  $Br^-$ .

Thank You