



PERIYAR ARTS COLLEGE, CUDDALORE.
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by

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UNIT-IV

Substitution

**Reactions of Square
Planar Complexes**

INTRODUCTION

❖ Complexes of d^8 configuration such as Pt(II), Pd(II), Ni(II), Ir(I), Rh(I) and Au(III) usually 4- coordinate with **square planar geometry**.

VIII			I B	II B
Fe	Co	Ni	Cu	Zn
Ru	Rh	Pd	Ag	Cd
Os	Ir	Pt	Au	Hg

❖ Complexes of Pt(II) are suitable for rate studies because they are stable, relatively easy to synthesize and undergo ligand exchange reactions at rates that are slow enough to allow easy monitoring.

Reaction rates for Pt(II) : Pd(II) : Ni(II) are approximately 1 : 10^5 : 10^7

❖ Substitution reactions which involve the **replacement of one ligand by another** are called nucleophilic substitution (SN) since ligands are nucleophiles.

CLASSIFICATION OF MECHANISMS OF NUCLEOPHILIC SUBSTITUTION REACTIONS

1. Dissociative Mechanism (D) or S_N^1 -Substitution Nucleophilic Unimolecular mechanism
2. Associative Mechanism (A) or S_N^2 - Substitution Nucleophilic Bimolecular mechanism
3. Interchange dissociative (I_d) Mechanism
4. Interchange Associative (I_a) Mechanism
5. Substitution Nucleophilic Unimolecular Conjugate Base Mechanism (SN_1CB)

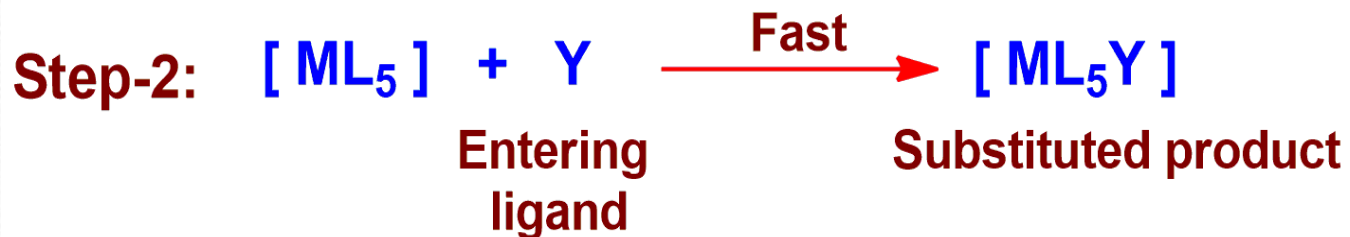
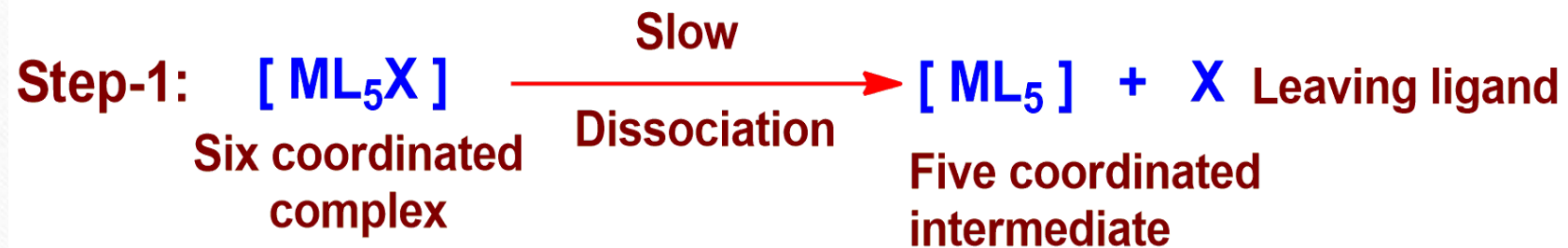
Dissociative Mechanism (D) or S_N¹-Substitution Nucleophilic
Unimolecular mechanism

The substitution reaction is

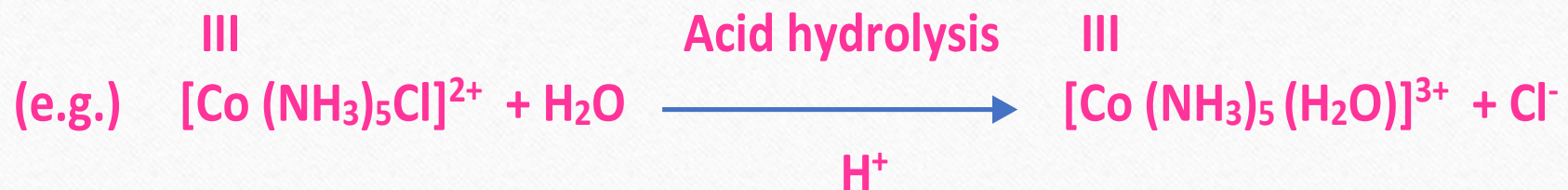


- ❖ Here, M-X bond is fully broken before the M-Y bond begins to form.
- ❖ In this mechanism, first the reactant complex undergoes dissociation losing the leaving ligand(X) and changes into an intermediate with coordination number lesser by one unit than the reactant complex. Then the vacancy created in the coordination sphere is filled by the new ligand(Y) fastly to give the substituted product.

Dissociative Mechanism



Rate = $k_1 [ML_5X]$ So, the reaction is first order



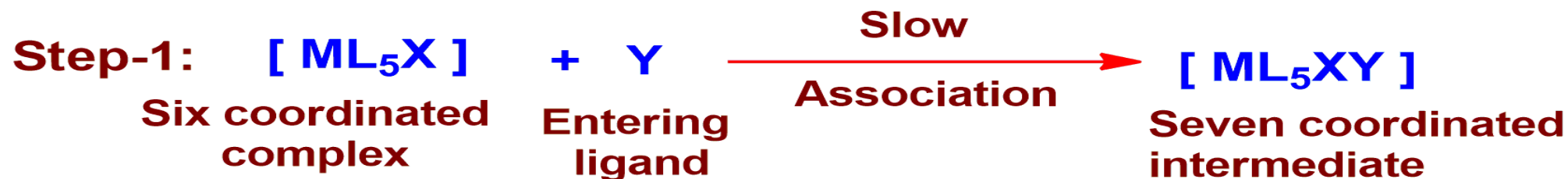
Associative Mechanism (A) or S_N² - Substitution Nucleophilic Bimolecular mechanism

The substitution reaction is

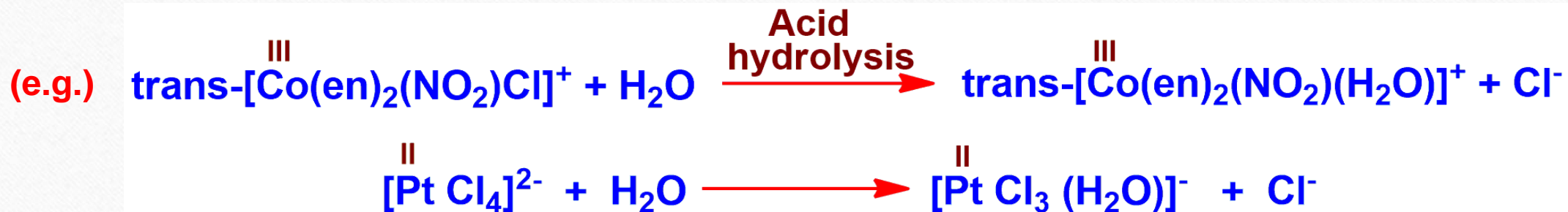


- ❖ Here, M-Y bond is fully formed before the M-X bond begins to break.
- ❖ In this mechanism, first the new ligand, 'Y' adds on to the reactant complex to form an intermediate with one coordination number higher than that of the reactant complex. Then the intermediate complex undergoes dissociation fastly to yield the substituted product.

Associative Mechanism



Rate = $k_2 [ML_5X] [Y]$ So, the reaction is second order



Interchange Mechanism

- ❖ An Interchange mechanism takes place in one step. i.e. The leaving and entering groups exchange in a single step by forming transition state, but not a true intermediate.



- ❖ In dissociative interchange mechanism (I_d), the M-Y bond begins to form before the M-X bond is fully broken. Here bond breaking is more important than bond making.
- ❖ In associative interchange mechanism (I_a), the M-X bond begins to break before the M-Y bond is fully formed. Here bond making is more important than bond breaking.

Note:

- ❖ Values of ΔS^\ddagger (entropy of activation) are particularly useful in distinguishing between associative and dissociative mechanisms. A large negative value of ΔS^\ddagger is indicative of an associative mechanism, i.e. there is a decrease in entropy as the entering group associates with the starting complex.
- ❖ The pressure dependence of rate constants leads to a measure of the volume of activation, ΔV^\ddagger . A reaction in which the transition state has a greater volume than the initial state shows a positive ΔV^\ddagger whereas a negative ΔV^\ddagger corresponds to the transition state being compressed relative to the reactants.
- ❖ A large negative value of ΔV^\ddagger indicates an associative mechanism; a positive value of ΔV^\ddagger suggests that the mechanism is dissociative.

Mechanism of ligand substitution reactions in Square planar complexes

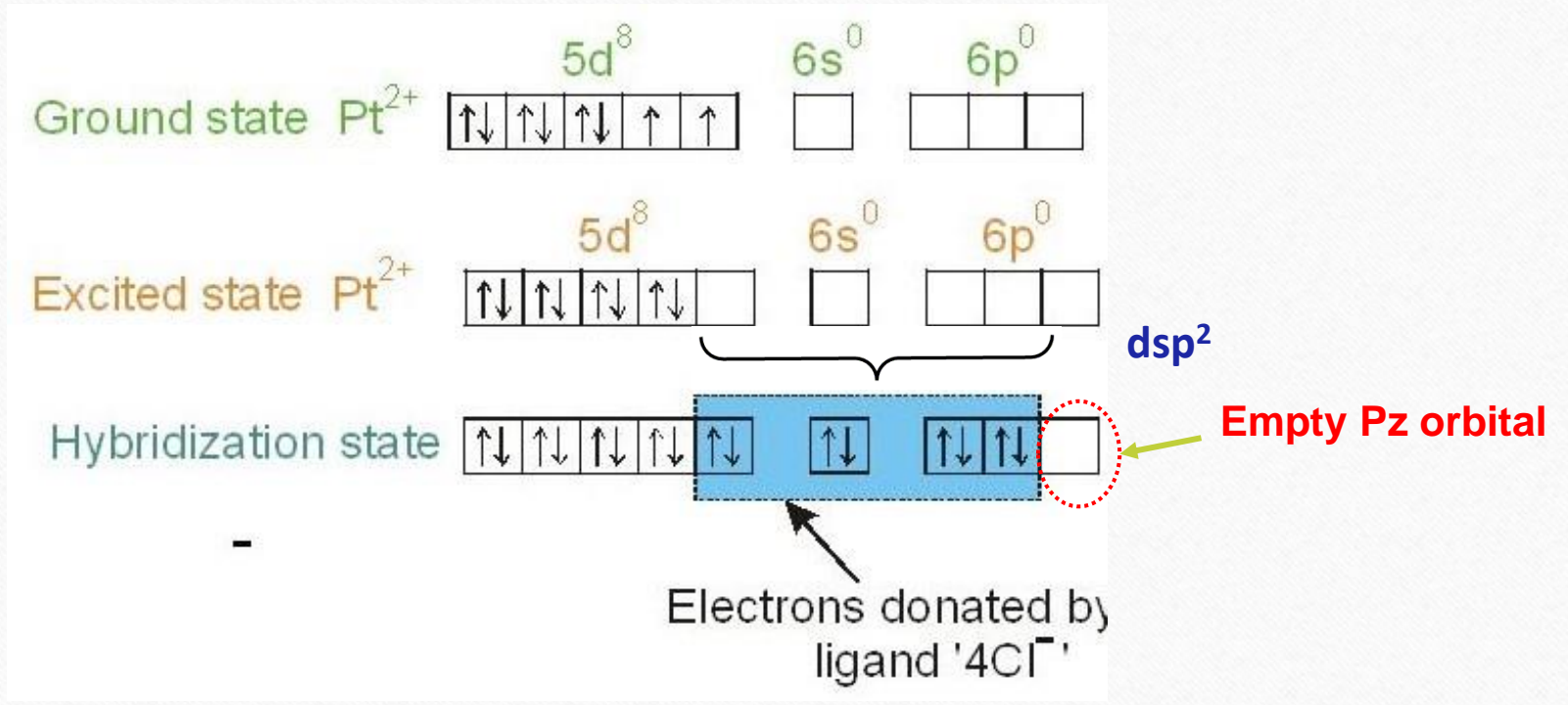
- ❖ The mechanism of substitution reactions of Square planar complexes appears to be associative (A) or S_N^2
- ❖ i.e. Ligand substitution reactions in Pt(II) square planar complexes proceed by bimolecular displacement (S_N^2) mechanism involving either the solvent or the entering ligand as the nucleophilic agent.

Evidences in favour of Associative type S_N^2 Mechanism

1. Availability of empty P_z orbital to form five-coordinated intermediates

- ❖ In case of Pt(II), which is a d^8 system, five empty metal orbitals (one 'd', one 's' and three 'p') of comparable energies are available for sigma bonding. But, during the formation of SPL complex, only four metal orbitals are used up. The fifth orbital (P_z) of metal ion is empty & low energy and it can easily accept an electron pair donated by the attacking ligand to form a five coordinated intermediate through an association mechanism.

Formation and electronic structure of $[\text{PtCl}_4]^{2-}$



dsp^2 – hybridisation \longrightarrow Square planar geometry

2. The relation between the reactivity of SPL complexes and the nature of the central metal ion



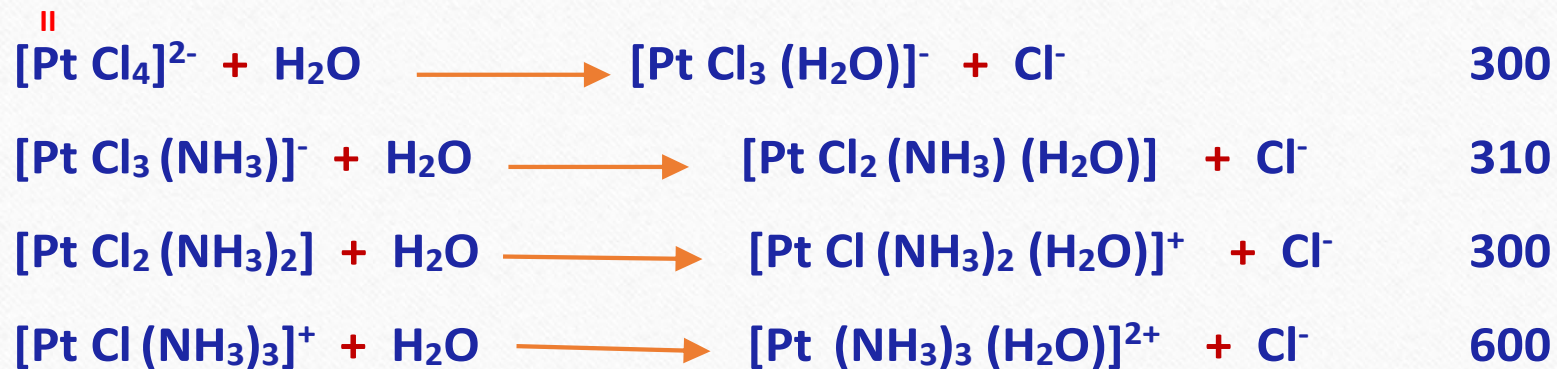
The reaction rates of reaction (i) : (ii) : (iii) = 50,00,000 : 1,00,000 : 1

- ❖ It is known that the square planar Ni(II) ($3d^8$) expands its coordination number ($4 \rightarrow 5$) with greater ease than the square planar Pd(II) expands its coordination number with much greater ease than the square planar Pt(II) ($5d^8$).
- ❖ Such a relationship clearly indicates the formation of an intermediate with a higher coordination number during the substitution reactions of SPL complexes of Ni(II), Pd(II) and Pt(II) through S_N^2 associative mechanism.

3. The relation between the rates of the substitution reaction and the charge of the complex.

- ❖ The rates of hydrolysis reaction of SPL Pt(II) complexes having different charges are given here.

k/min at 25°C



- ❖ In the above series of complexes, the charge of the reactant complex changes from -2 to +1. The rupture of the Pt-Cl bond should become more difficult as the charge of the complex becomes more positive. But the formation of a new bond should become easier in the same order.
- ❖ The rates of hydrolysis increases as the positive charge of the complex increases which indicates, this substitution occurs through S_N^2 associative mechanism.

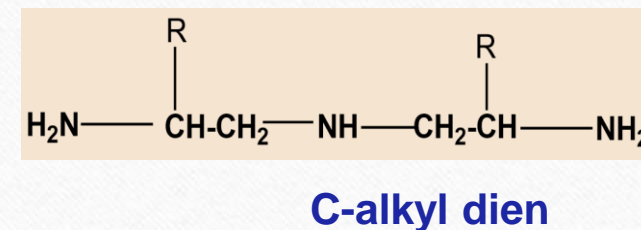
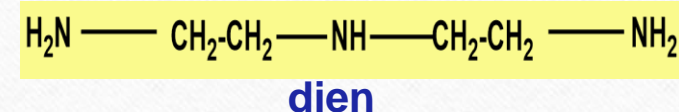
4. Effect of bulkiness (steric effect) of other ligands on the rate of substitution reaction



$$k_a > k_b$$



- ❖ As the bulkiness of the inert ligand increases, the rate of substitution decreases. Because, the bulkier ligand prevents the entry of the incoming ligand, NH_3 . Thus, it indicates this substitution reaction occurs through S_N^2 associative mechanism.

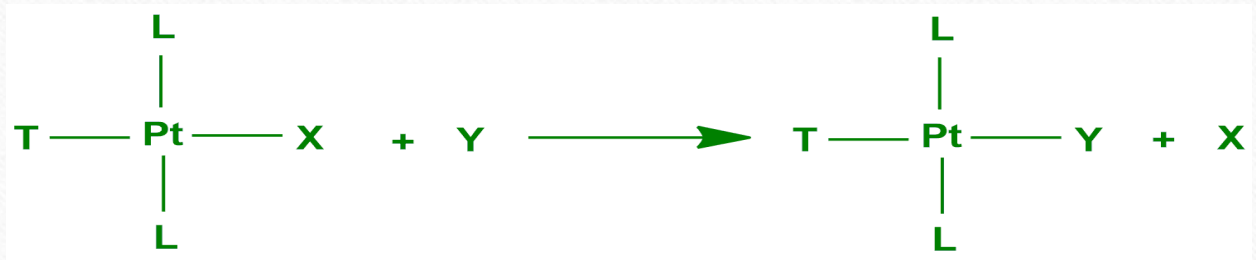


5. Effect of entering group

- ❖ The rates of substitutions in SPL complexes are found to be greatly affected by the change in the nature of entering ligand (Y)
- ❖ This clearly indicates that the entering ligand takes part in the rate determining step.

6. Rate law and mechanism of substitution reaction in SPL complexes

Consider the ligand substitution reaction of Pt(II) SPL complex in aqueous medium (e.g.) $[\text{Pt L}_2\text{T X}]$



X- leaving ligand
Y- entering nucleophilic ligand
T- the ligand trans to X

The rate law is

$$\text{Rate} = k_1[\text{Pt L}_2\text{T X}] + k_2[\text{Pt L}_2\text{T X}] [\text{Y}]$$

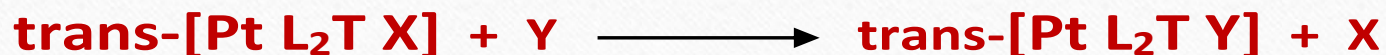
- ❖ The rate equation indicates that the complex $[\text{Pt L}_2\text{T X}]$ is reacting in **two different path ways**.
- ❖ **Both path ways** are considered to be **associative**, in spite of the difference in order.

- ❖ The ' k_2 ' term easily fits an **associative mechanism** in which the incoming ligand nucleophilic ligand, Y attacks the reactant complex to form a 5-coordinate intermediate, which then dissociates (Pt-X bond) to give the substituted product.
- ❖ The ' k_1 ' term, which is first order with respect to reactant complex and independent of [Y], would suggest a dissociative pathway. However, strong evidence supports the view that this pathway also is associative.
- ❖ Thus, ' k_1 ' term is a **solvent-assisted reaction**, in which solvent molecules (S) will be the nucleophiles and will therefore compete with Y for the reactant complex to form the solvento complex $[\text{Pt L}_2\text{T S}]$ and then itself being replaced by Y to give the substituted product $[\text{Pt L}_2\text{T Y}]$.
- ❖ The solvent (S) attacking step is the slow step.
- ❖ So the rate of that reaction pathway = $k' [\text{Pt L}_2\text{T X}] [\text{S}]$. Since the solvent is present in large excess, its concentration remains practically a constant. Therefore, rate = $k_1 [\text{Pt L}_2\text{T X}]$ where k_1 is the pseudo first order rate constant.

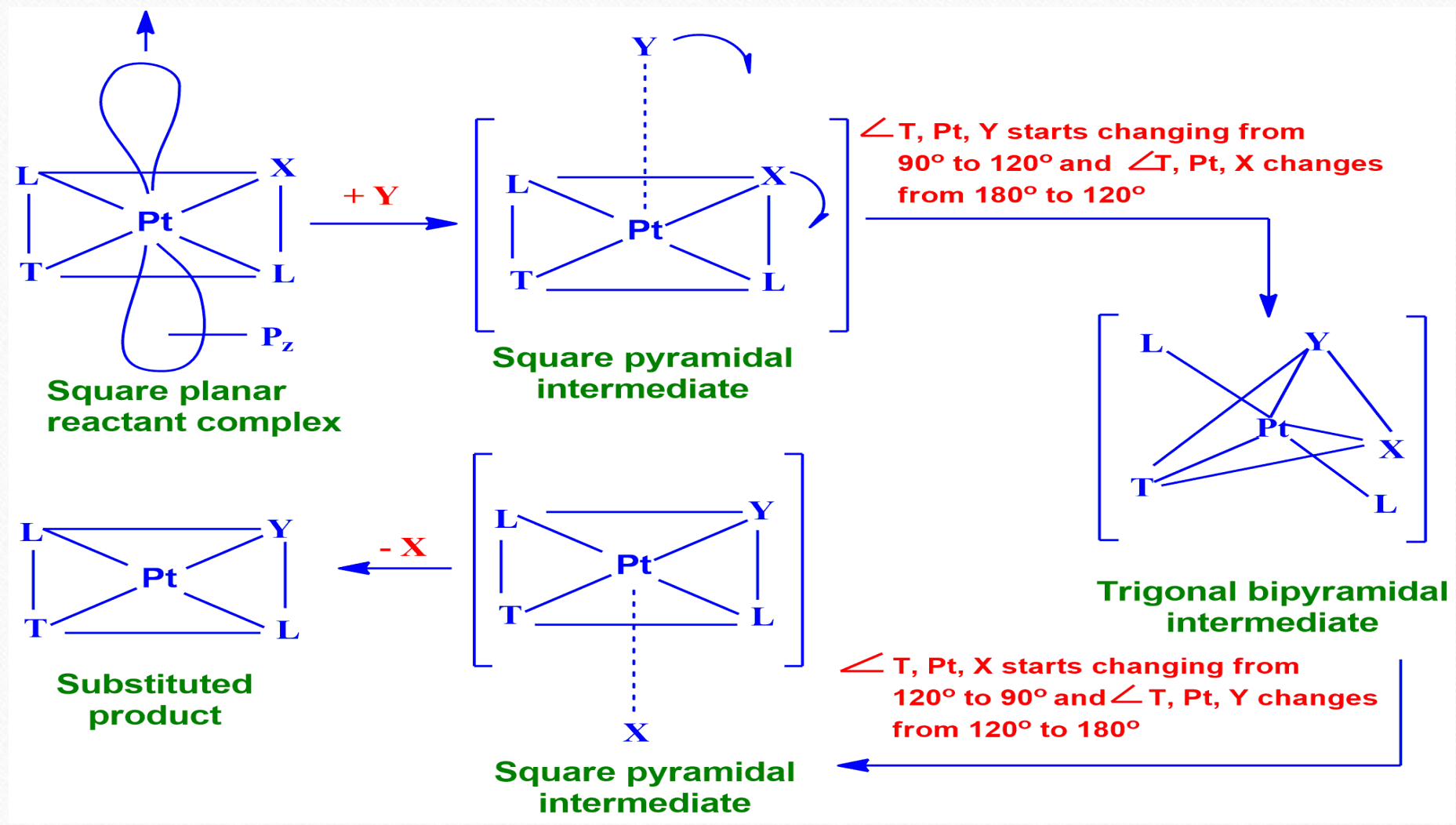
7. Stereospecificity and mechanism of substitution reactions in SPL complexes

- ❖ Ligand Substitution in SPL complexes occurs with **retention of configuration**. i.e. cis complex yields cis-product and trans complex yields trans-product. Thus, the substitution reaction is entirely **stereospecific**.
- ❖ Stereospecificity is possible with a trigonal bipyramidal intermediate containing the entering ligand, leaving ligand and trans ligand in the trigonal plane. This is a strong evidence for associative type (S_N^2) mechanism.
- ❖ If the reaction proceeds by a dissociative type mechanism, then a 3-coordinate intermediate would have been obtained. In this intermediate, which is a planar one, the entering(Y) group may attack from all sides and may lead to both cis- and trans-isomers. Actually this doesn't occur.

Consider the SPL substitution reaction,



Mechanism proposed for the substitution reactions of SPL complexes



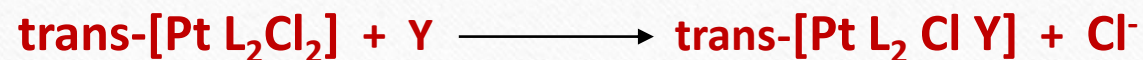
Retention of configuration

Factors affecting the rates of substitution reactions in SPL complexes

1. Effect of entering group (Y)
2. Effect of leaving group (X)
3. Steric effect of other groups
4. Solvent effect
5. Trans effect

1. Effect of entering group (Y)

- ❖ A strong Lewis base(Y) is likely to react rapidly, but the hard-soft nature of the entering ligand has even larger effect on the rate.
- ❖ Pt(II) is a soft acid, so soft ligands(Y) react more readily with it.



- ❖ The order of entering ligand reactivity for the above reaction, with different Y was found to be as follows:



Soft ligands

Hard ligands

2. Effect of leaving group (X⁻)

- ❖ The leaving group also have a significant influence on the rate.
- ❖ The effect of leaving ligands on the rate is nearly reverse of the effect of entering ligands effect.
- ❖ Hard ligands such as NH₃ , Cl⁻ and H₂O leaving quickly whereas soft ligands with considerable π-bonding ability such as CN⁻ and NO₂⁻ leave with difficulty in the reaction,

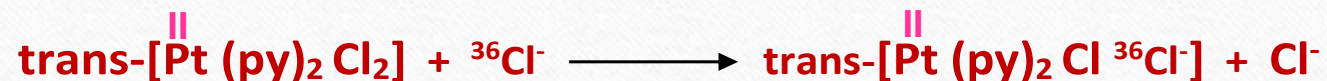


X ⁻	k
CN ⁻	1
H ₂ O	10 ⁵

3. Solvent effect

- ❖ It has been found that with the increase in the coordinating ability of the solvent, the overall rate of the reaction also increases.

Consider the rate of exchange of $^{36}\text{Cl}^-$ with the SPL complex,



- ❖ Under the experimental condition, the solvents are divided into two categories:
 - Those solvents, where the rate of exchange of $^{36}\text{Cl}^-$ with the cpx does not depend on $[\text{Cl}^-]$. These solvents are **good coordinating solvents** and provide almost entirely a **solvent path** for the exchange reaction. E.g. $(\text{CH}_3)_2\text{SO}$, H_2O , ROH . Here, $k_1 \gg k_2$
 - Those solvents, where the rate of exchange of $^{36}\text{Cl}^-$ with the complex depends on $[\text{Cl}^-]$. These solvents are **poor coordinating solvents** and contribute little to the overall rate of the exchange reaction. E.g. CCl_4 , C_6H_6 , m-cresol, acetone, DMF
Here, $k_2 \gg k_1$

4. Steric effects of other groups

- ❖ Steric crowding at the reaction Centre by bulky groups can block the approach of attacking nucleophile and will decrease the rate of associative S_N^2 reactions.

Consider the rate constant of replacement of Cl^- by H_2O in the SPL complex,



L	pyridine	2-methyl pyridine	2,6-dimethyl pyridine
k(rate constant)	8×10^{-2}	2.0×10^{-4}	1.0×10^{-6}

- ❖ The methyl groups adjacent to the N-donor atom greatly decrease the rate. In 2-methyl pyridine cpx, it block the position either above or below the plane of metal centre for nucleophilic attack. In the case of 2,6-dimethyl pyridine cpx, the methyl groups block the positions both above and below the plane.

5. TRANS EFFECT

- ❖ The effect of the ligand trans to the leaving ligand on the rate of substitution reaction in square planar complexes is called trans effect.
- ❖ Chat et al have proposed that the trans effect of a group coordinated to a metal ion is the tendency of that group to direct an incoming group to occupy the position trans to that group.
- ❖ Trans effect may also be defined as the labilisation of ligands trans to other trans directing ligands.

Trans Effect-continued

- ❖ A σ -strong donor ligand or π - acceptor ligand greatly accelerates substitution of a ligand that lies in the trans position.

❖ Trans Effect series

High end

→ Trans effect decreases → Trans effect decreases →

CN^- , CO , C_2H_4 , NO > PR_3 , H^- > CH_3^- , C_6H_5^- , tu , R_2S > NO_2^- , I^- , SCN^- > Br^- > Cl^- > Py > NH_3 , RNH_2 > OH^- > H_2O

Low end

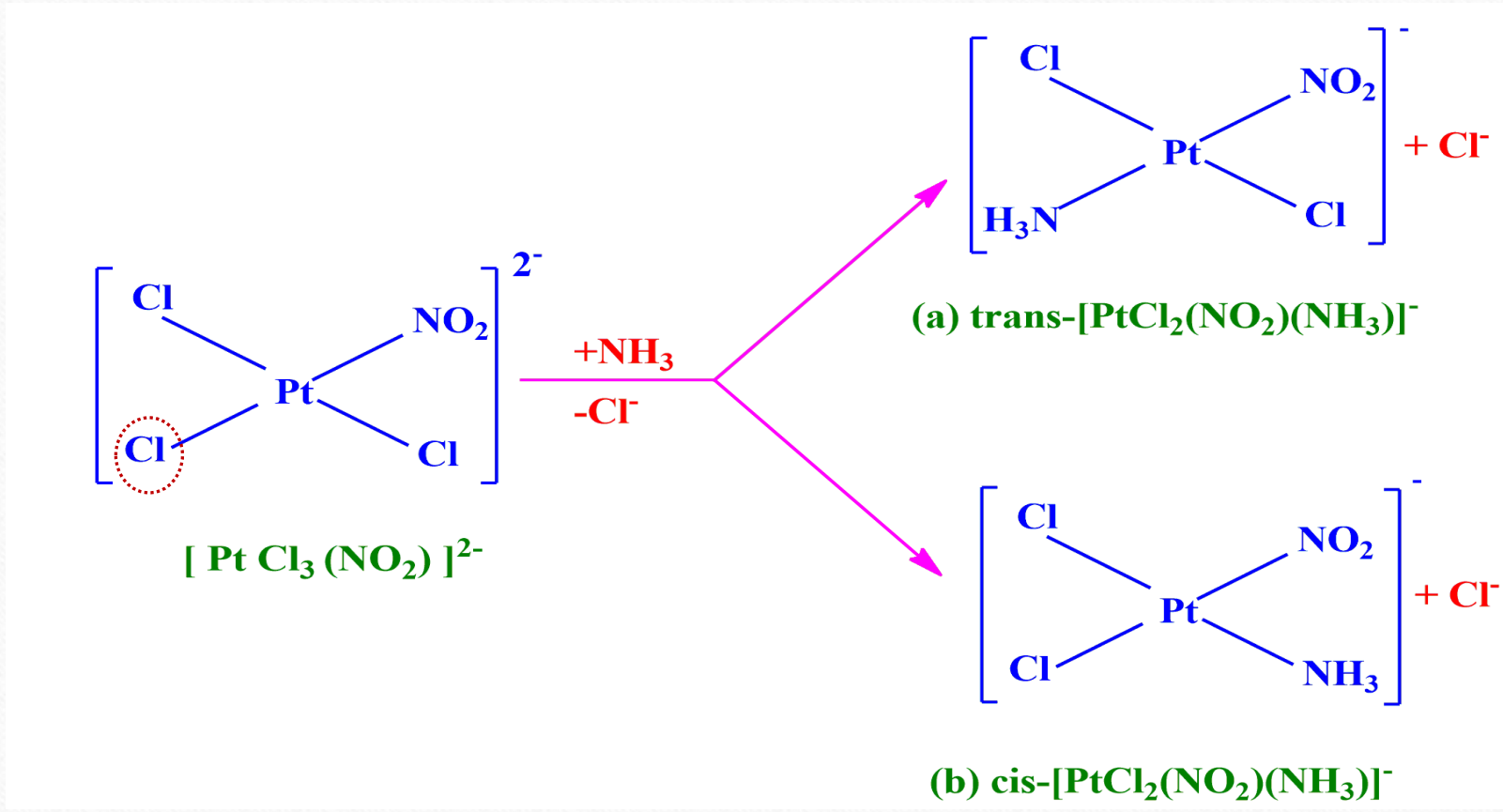
- ❖ The ligands lying at the high end of the series have vacant π or π^* orbitals which can accept electrons from metal orbital to form $\text{M} \rightarrow \text{L} \pi$ -bond. These ligands are called π -bonding ligands.
- ❖ The ligands lying at the low end of the series are easily polarisable ligands.

$\text{I}^- > \text{Br}^- > \text{Cl}^-$

→ Polarizability decreases →

→ Trans effect decreases →

ILLUSTRATION OF TRANS EFFECT



The trans effect order is NO₂⁻ > Cl⁻ > NH₃

Applications of Trans Effect

① Synthesis of geometrical isomers of Pt(II) SPL complexes

(i) Synthesis of cis- and trans- $\text{[Pt} \overset{\text{||}}{\text{Cl}}_2 (\text{NH}_3)_2\text{]}$

(ii) Synthesis of cis- and trans- $\text{[Pt} \overset{\text{||}}{\text{Cl}}_2 (\text{NH}_3) (\text{NO}_2)\text{]}^-$

(iii) Synthesis of geometrical isomers of $\text{[Pt} \overset{\text{||}}{\text{Br}} (\text{Cl}) (\text{NH}_3) (\text{py})\text{]}$

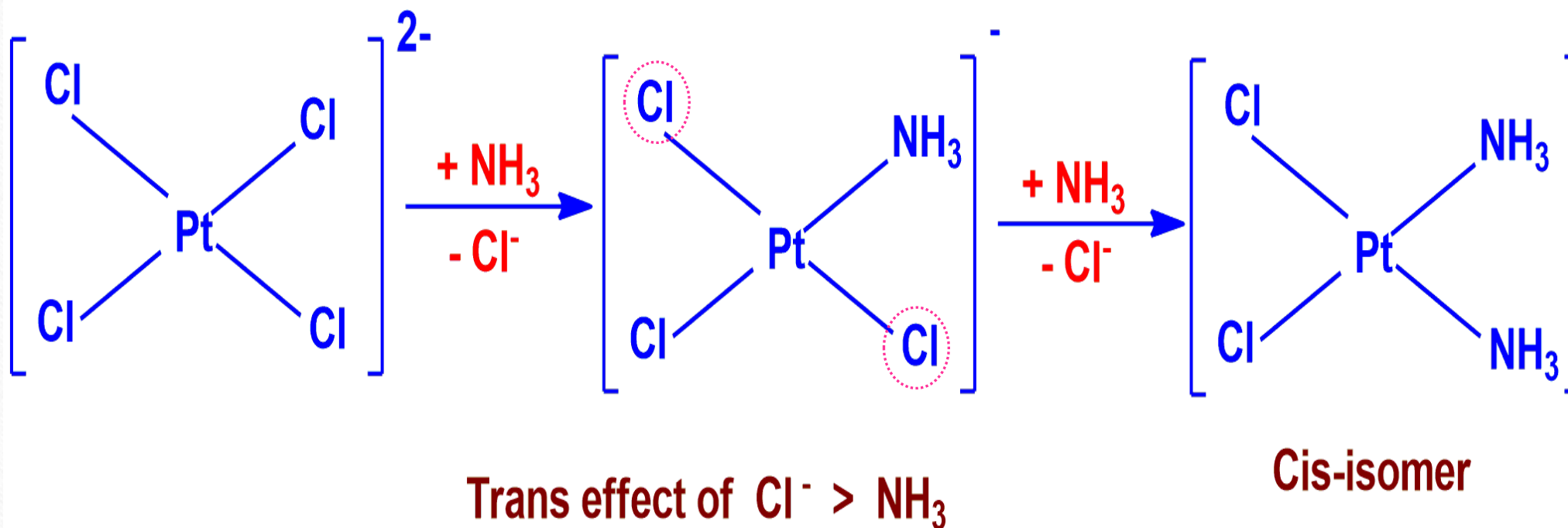
② To distinguish between cis-and trans-isomers of $\text{[Pt X}_2 \text{A}_2\text{]}$ type complexes:

[Kurnakov's test]

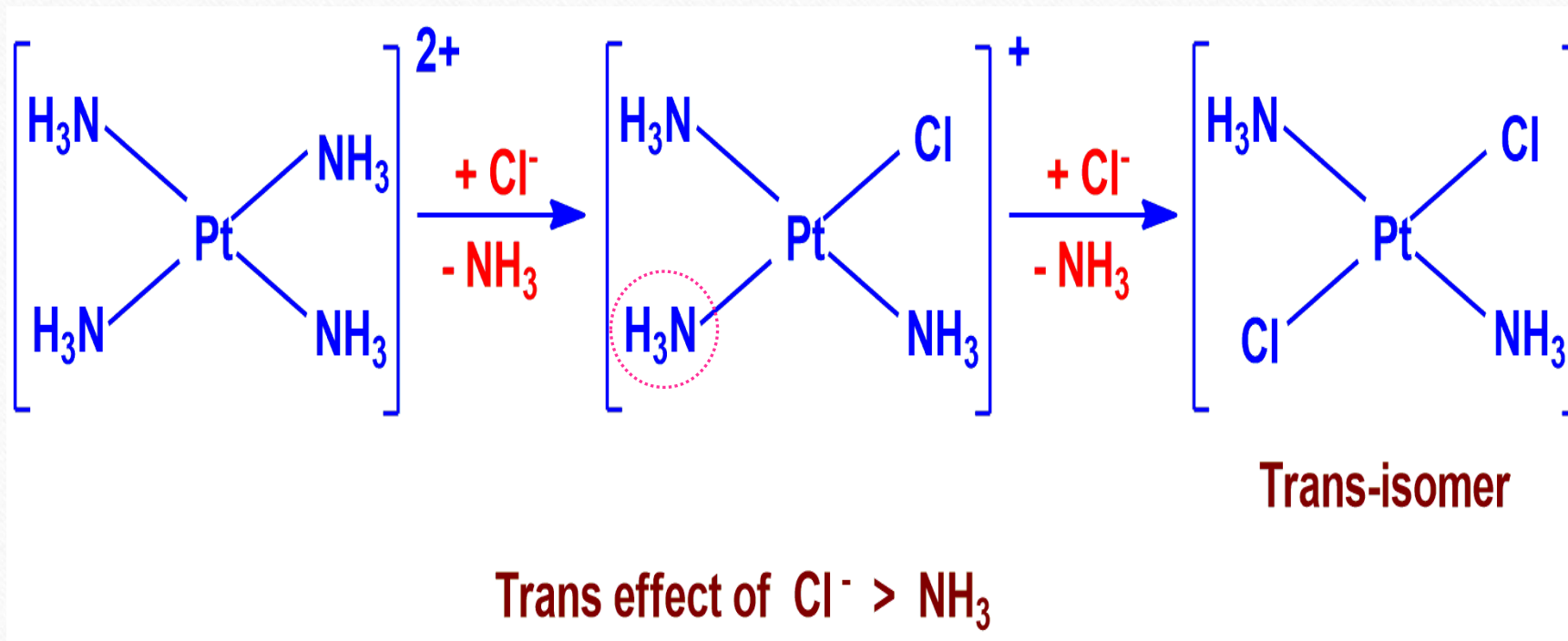
① Synthesis of geometrical isomers of Pt(II) SPL complexes

(i) Synthesis of cis- and trans- $[\text{Pt Cl}_2 (\text{NH}_3)_2]$

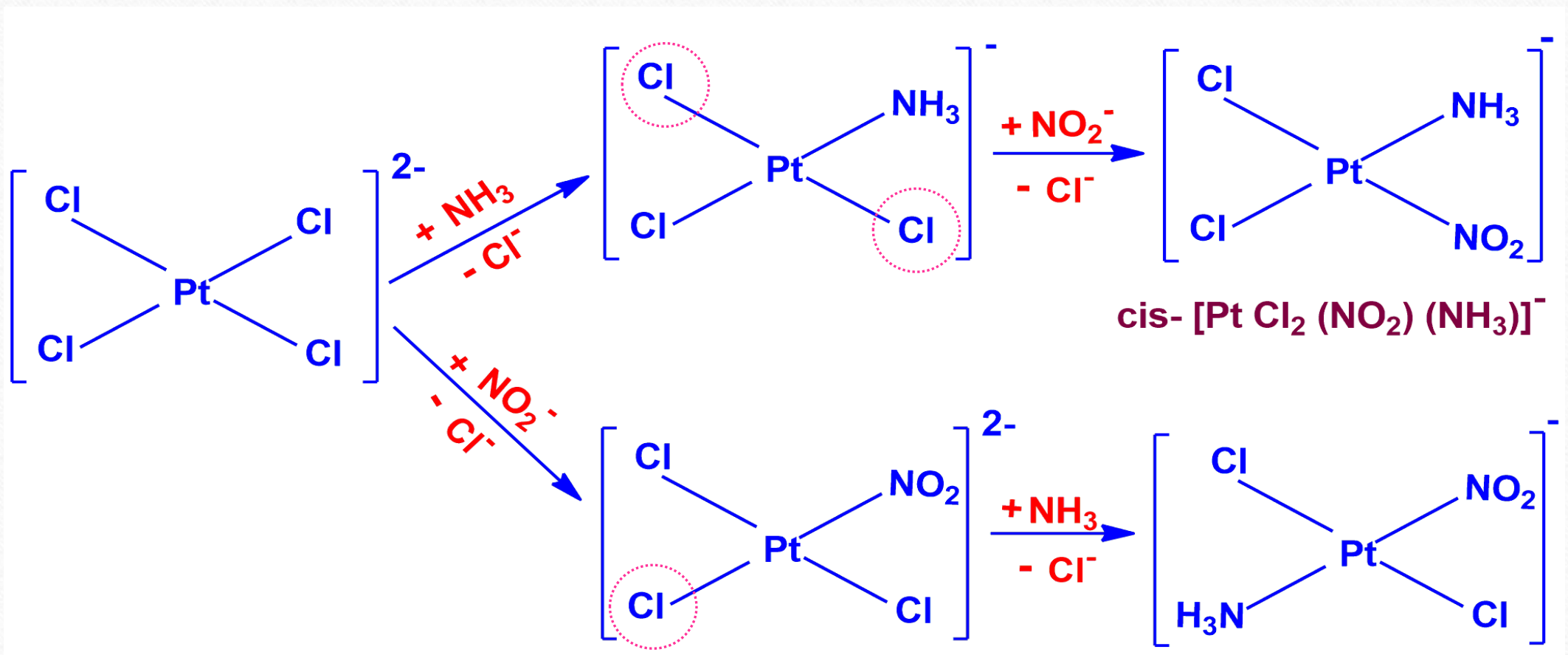
- cis- $[\text{Pt Cl}_2 (\text{NH}_3)_2]$ is obtained by treating $[\text{Pt Cl}_4]^{2-}$ ion with NH_3



- trans-[Pt Cl₂(NH₃)₂]⁰ is obtained by treating [Pt (NH₃)₄]²⁺ ion with Cl⁻



(ii) Synthesis of cis- and trans- $[\text{Pt Cl}_2 (\text{NH}_3) (\text{NO}_2)]^-$ from $[\text{Pt Cl}_4]^{2-}$

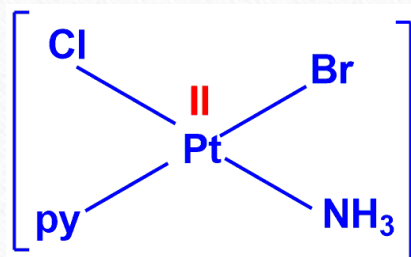


The trans effect order is $\text{NO}_2^- > \text{Cl}^- > \text{NH}_3$

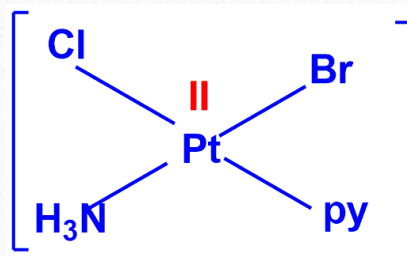
trans- $[\text{Pt Cl}_2 (\text{NO}_2) (\text{NH}_3)]^-$

(iii) Synthesis of geometrical isomers of $[\text{Pt}(\text{Br})(\text{Cl})(\text{NH}_3)(\text{py})]$ from $[\text{PtCl}_4]^{2-}$

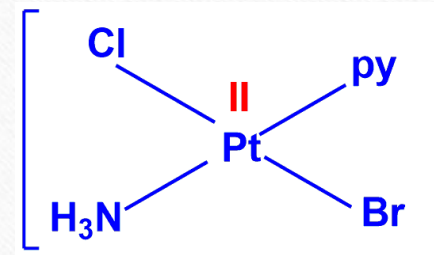
❖ This complex exists in three different geometrical isomeric forms. They are



(i) trans (Cl-NH₃)



(ii) trans (Cl-py)



(iii) trans (Cl-Br)

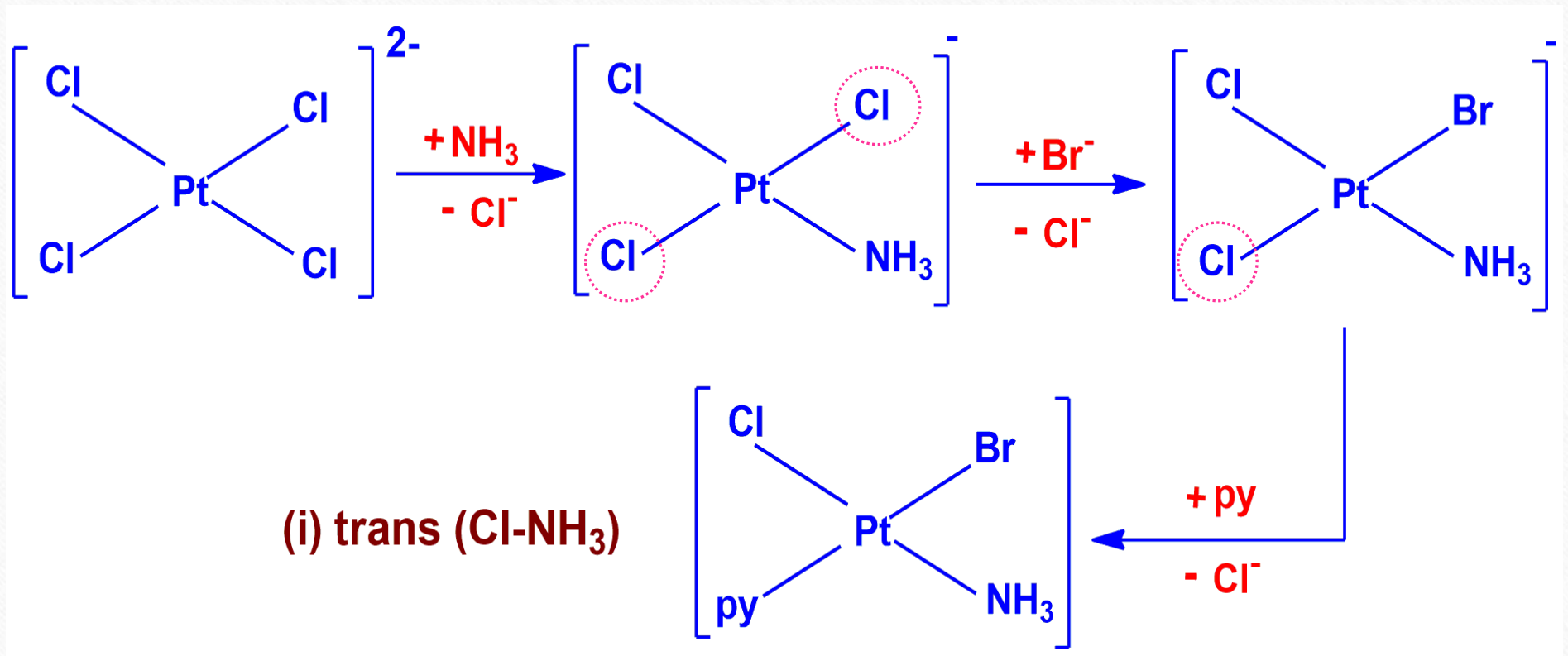
❖ They can be synthesized based on two facts:

(i) The trans effect order is $\text{Br}^- > \text{Cl}^- > \text{py} > \text{NH}_3$

(ii) When other things being equal, Pt-Cl bond is more labile than Pt-N bond

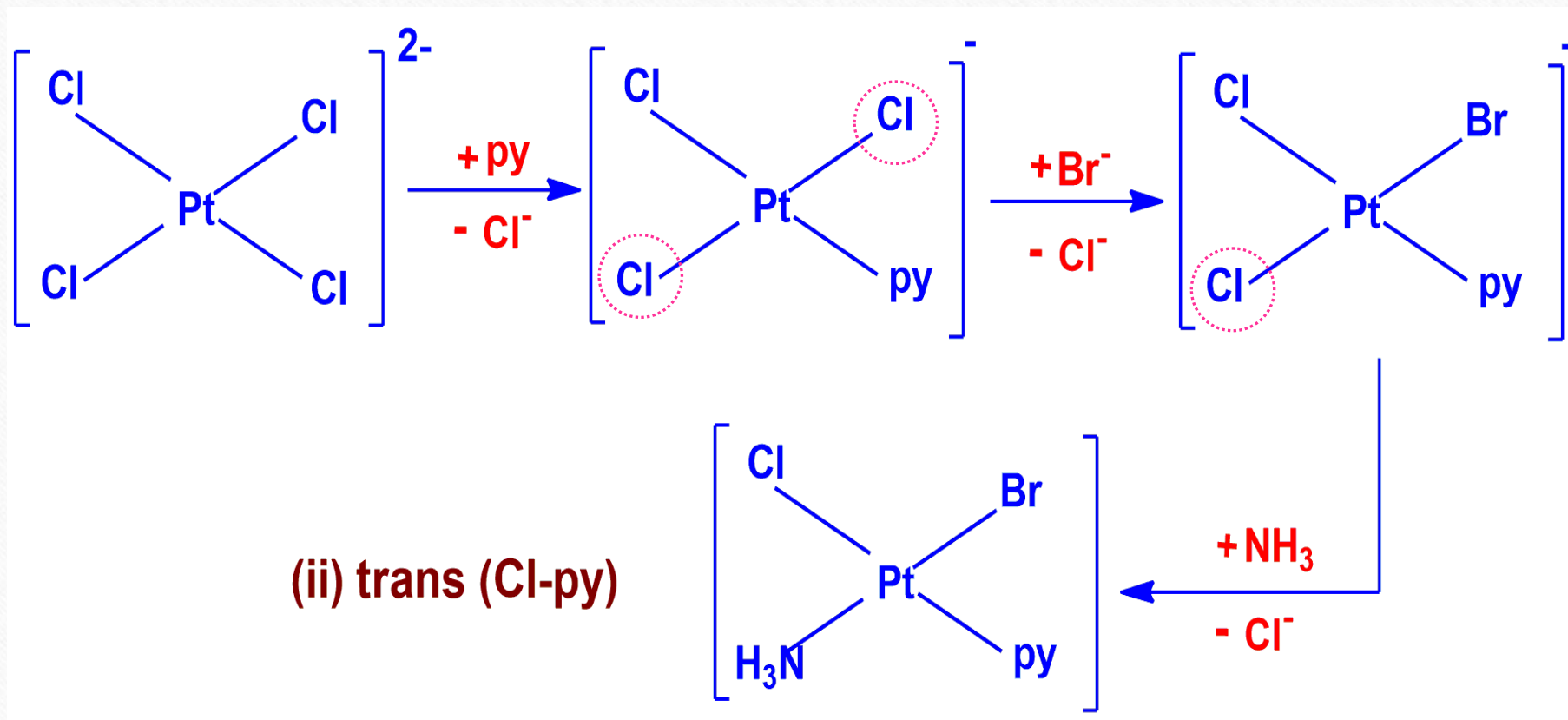
Synthesis of isomer (i) trans (Cl - NH₃)

The trans effect order is Br⁻ > Cl⁻ > py > NH₃



Synthesis of isomer (ii) trans (Cl - py)

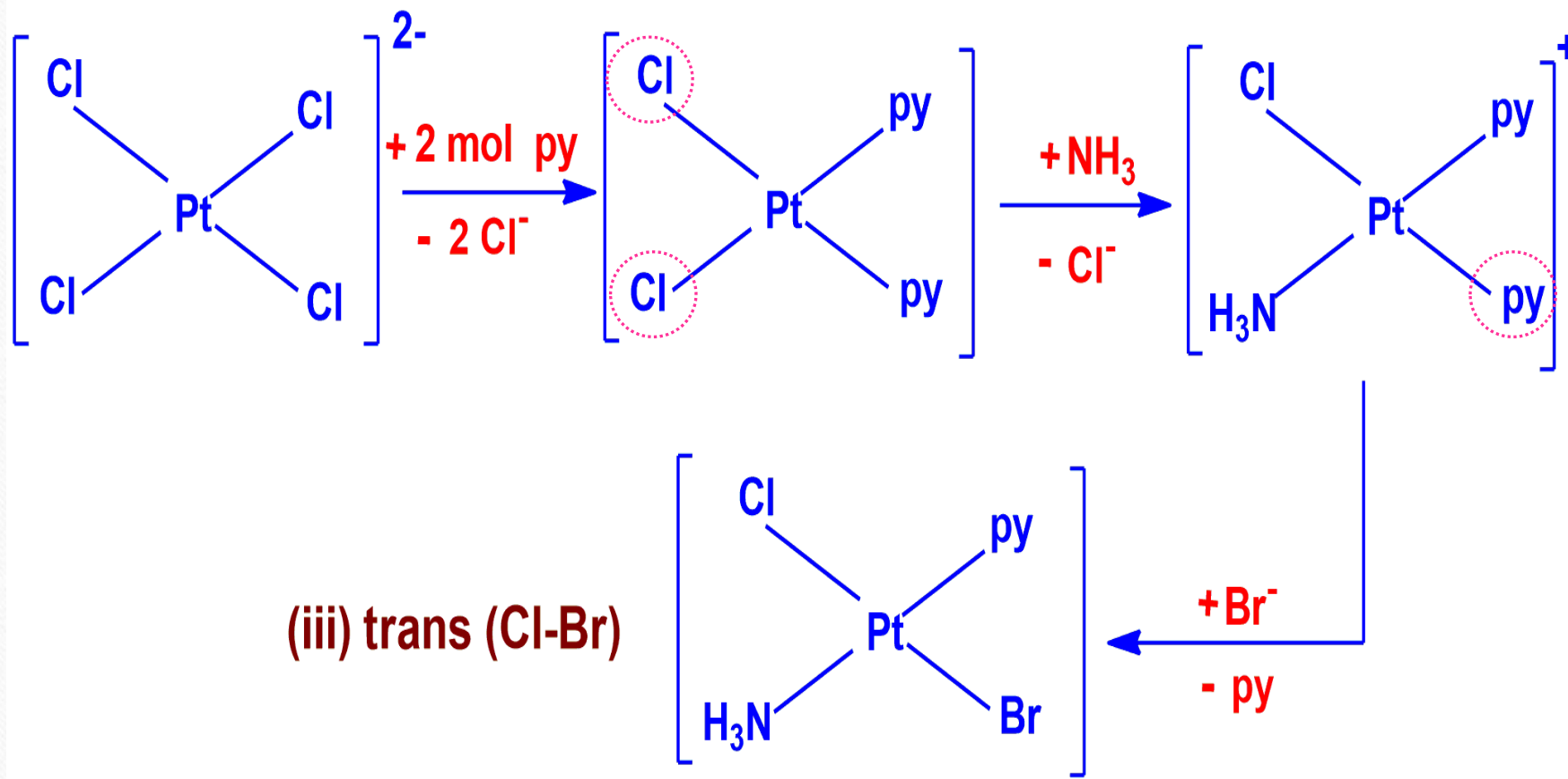
The trans effect order is $Br^- > Cl^- > py > NH_3$



(ii) trans (Cl-py)

Synthesis of isomer (iii) trans (Cl - Br)

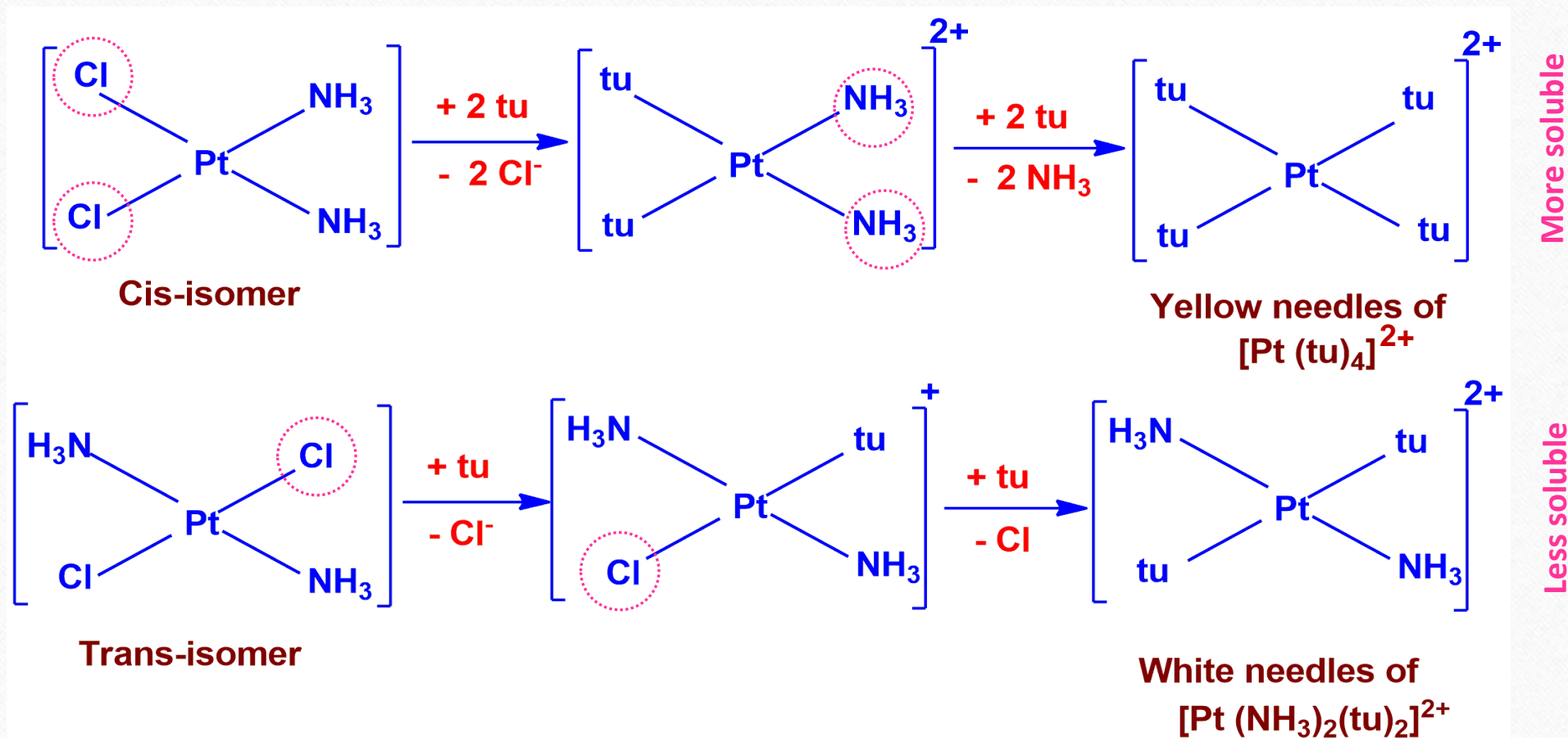
The trans effect order is $Br^- > Cl^- > py > NH_3$



② To distinguish between cis-and trans-isomers of $[Pt X_2 A_2]$ type complexes:

[Kurnakov's test]

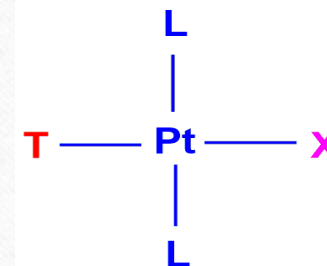
The trans effect order is $tu > Cl^- > NH_3$



Trans-effect and Trans-influence

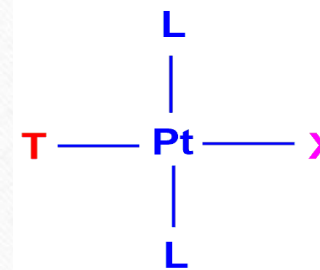
Trans-influence

- ❖ The **trans-influence** refers to the extent to which the ligand **T** weakens the bond trans to itself in the **ground state** of a complex.
- ❖ So, trans-influence is a **thermodynamic, ground state effect**.
- ❖ Trans-influence correlates with the **σ -donor ability** of the trans ligand.
- ❖ Trans-influence is assessed by measuring bond length, stretching frequencies and Metal-Ligand NMR coupling constants.



Trans-effect

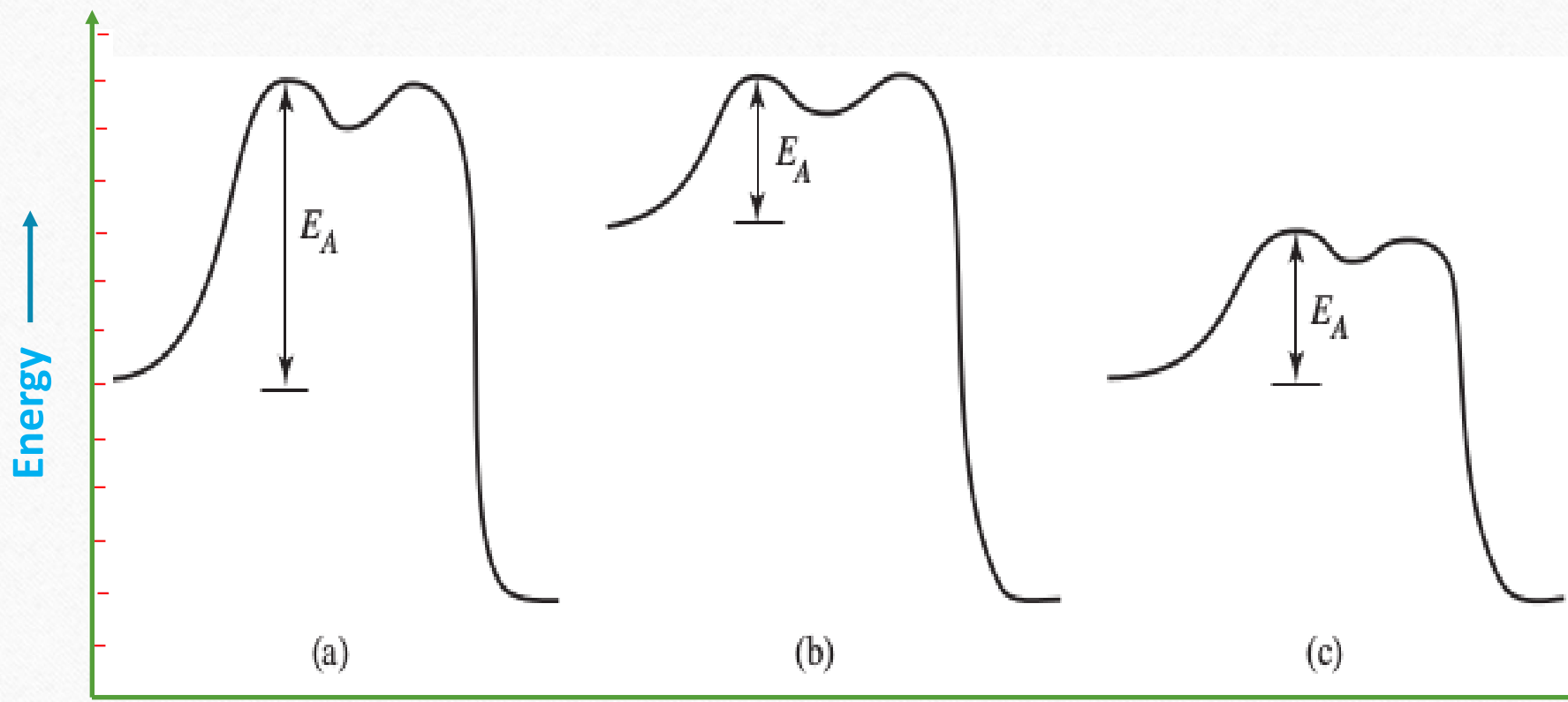
- ❖ Trans-effect refers to the effect of the ligand **T** on the rate of substitution reactions of ligands trans to it.
- ❖ Thus, trans effect is a kinetic effect depends upon the activation energy.
- ❖ So, trans effect is the transition-state effect.
- ❖ Trans-effect correlates with the π - acceptor ability of the trans ligand.



Explanation of Trans effect

- ❖ It is generally accepted that the **trans effect arises from two separate influences:** one arising in the **ground-state** and the other in the **transition-state** itself.
- ❖ **i.e.,** There are **two possible modes** by which the trans ligand, **T** can enhance the rate of the substitution reaction.
- ❖ It can either **destabilize the ground-state** by **weakening the metal-ligand (Pt-X) bond trans to T ligand** or it **can stabilize the 5-coordinate transition-state**.
- ❖ **Both the modes will increase the rate of the reaction, because, the activation energy, E_a is decreased in both cases.**

Fig. Activation Energy and the trans Effect.

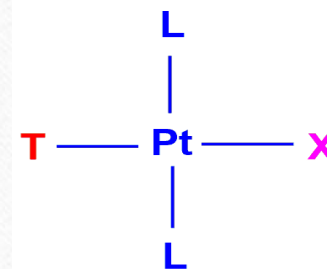


(a) Poor trans effect:
low ground state, high
transition state.

(b) σ -Bonding effect:
higher energy ground
state (trans influence).

(c) π - Bonding effect: lower
energy transition state, (trans
effect).

1. Polarisation Theory (or) Ground-state Effects (or) σ -bonding effects - Grinberg



- ❖ It is a thermodynamic effect because it deals with M-X bond weakening in the ground state.
- ❖ The effect of T on the M-X bond in a SPL complex can be viewed in terms of metal orbitals which is common for T and X ligands. E.g. P_x & $d_{x^2-y^2}$
- ❖ If the ligand T is a strong donor, the Pt-T bond is very strong, because it uses larger part of these metal orbitals and leaves lesser part for the Pt-X bond.
- ❖ As a result, Pt-X bond is weaker and so the energy of the reactant increases in the ground state thereby reducing the energy of activation, E_a . Thus, this σ -bonding effect of the trans ligand increases the rate of substitution.

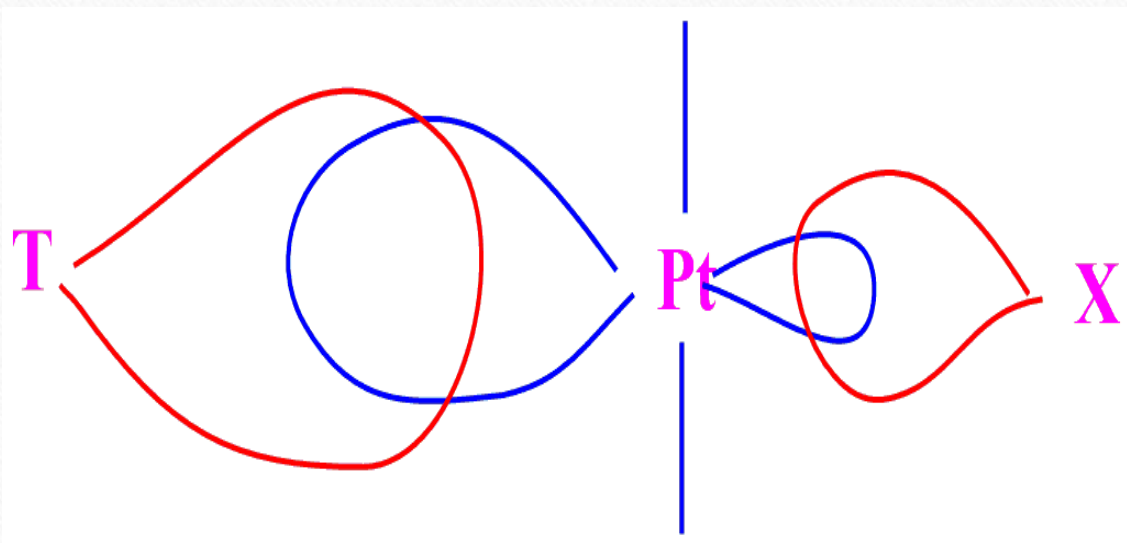


Fig: σ -bonding effect:

A strong bond between Pt and T
weakens the Pt-X bond

❖ Based on the relative σ -donor properties of the ligands, the trans effect order is



One of the earliest theory was the **Polarization theory** proposed by **Grinberg**, in which a **good trans-directing ligand** was visualized as being **more polarizable**.

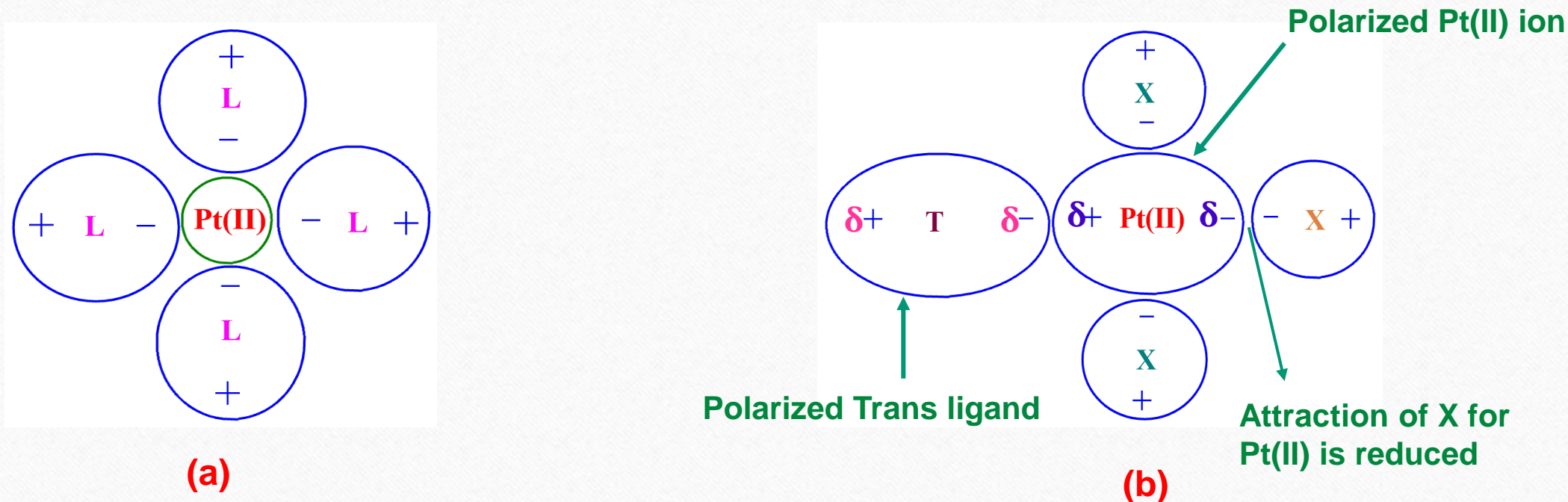


Fig. Effect of polarization in (a) $[Pt L_4]$ and (b) $[Pt X_3 T]$ complexes

- ❖ This figure represents the polarization of metal ion induced by a highly polarizable trans ligand, **T** in $[Pt X_3 T]$ complex as compared to $[Pt L_4]$ complex.

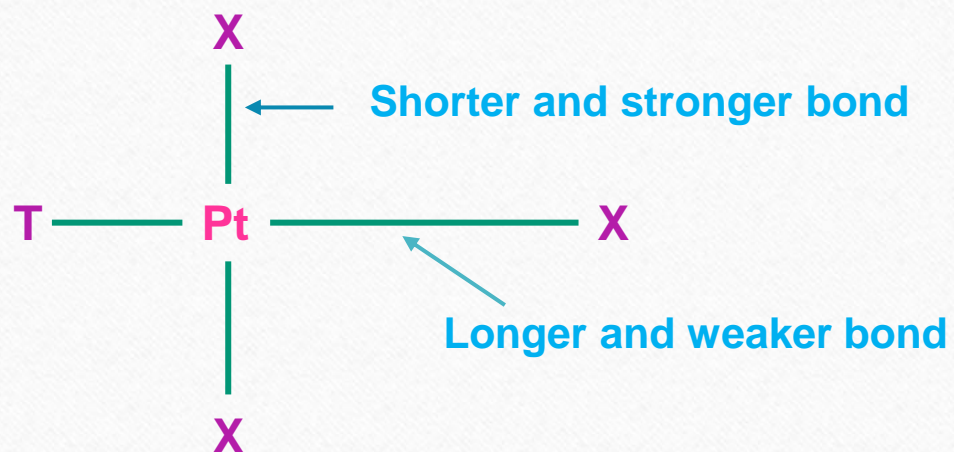


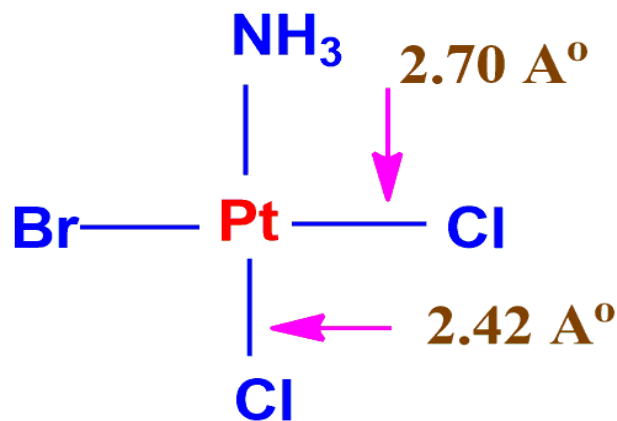
Fig. (c) Result of polarization theory

- ❖ A/c to this theory, the **primary positive charge of Pt(II)** induces a dipole in all the four ligands. If the four ligands are identical as in (a), then the dipoles induced by the metal ion cancel out each other and the **resultant dipole is zero (Fig.(a))**. Here none of the four ligands shows trans effect
- ❖ If the four ligands are not identical as in Fig.(b), then the induced dipoles do not cancel out each other.

- ❖ The two X ligands which are similar and trans to each other balance each other. But the other two trans ligands, T and X, which are not similar, the induced dipoles do not balance each other.
- ❖ If T is large and has greater polarizability than the leaving ligand X, the dipole induced by the primary positive charge of Pt(II) on the ligand T further induces a corresponding dipole in the metal ion, Pt(II) itself. i.e., the metal ion and the trans ligand, T both become polarized in such a way that the +ve charge at the point of Pt(II) directly opposite to T is reduced.
- ❖ Hence, the attraction of X for Pt(II) is reduced and the bond trans to T (Pt-X) is weakened and consequently lengthened. i.e., Pt-X bond trans to T is weaker and longer than Pt-X bonds that are cis to T (Fig.(c))
- ❖ This facilitates the replacement of X by Y(entering ligand) at a point trans to T.

Evidences in favour of the Polarization Theory

- ❖ This theory predicts that trans effect is important only when the central metal ion itself is polarizable and large in size. Actually the order of importance of trans effect is $\text{Pt(II)} > \text{Pd(II)} > \text{Ni(II)}$. Because, the size and polarizability decrease in the same order.
- ❖ If the ligand T is highly polarizable in $[\text{Pt X}_3 \text{T}]$ complex, then Pt-X bond trans to T is longer than Pt-X bond cis to T. This is evident from the following example.



The trans effect order is



Merit and defect of Polarization theory

Merit:

- ❖ This theory explain very well the trans effect of ligands that are present at the low end of trans effect series, like H_2O , OH^- , NH_3 , Cl^- , Br^- , etc.

Defect:

- ❖ This theory cannot explain the high trans-effect of the ligands like PR_3 , C_2H_4 , CN^- , CO , etc. which lie at the high end of the trans-effect series.

π - bonding theory (or) Transition-state theory

- Chatt and Orgel

- ❖ In order to explain the trans-effect of ligands such as PR_3 , NO , C_2H_4 , CN^- , CO , etc. Chatt and Orgel gave the π - bonding theory.
- ❖ According to this theory, the vacant π or π^* orbitals of π – bonding ligands accept a pair of electrons from the filled d-orbitals of the metal (d_{yz} or d_{xz} orbitals) to form $\text{M} \rightarrow \text{L}$ π - bond. (d π - p π overlapping or d π - d π - overlapping).
- ❖ A/C to Orgel, the very good π - acceptor ligands effectively withdraw electron density that will accumulate on the metal as a result of adding a fifth ligand (y), thereby stabilizing the 5-coordinate transition-state.

- ❖ So, the energy of the 5-coordinate trigonal bipyramidal transition state is lowered which results in the lowering of energy of activation (E_a) of the substitution reaction. Thus, the rate of the ligand substitution is increased due to the presence of π -bonding trans ligands.

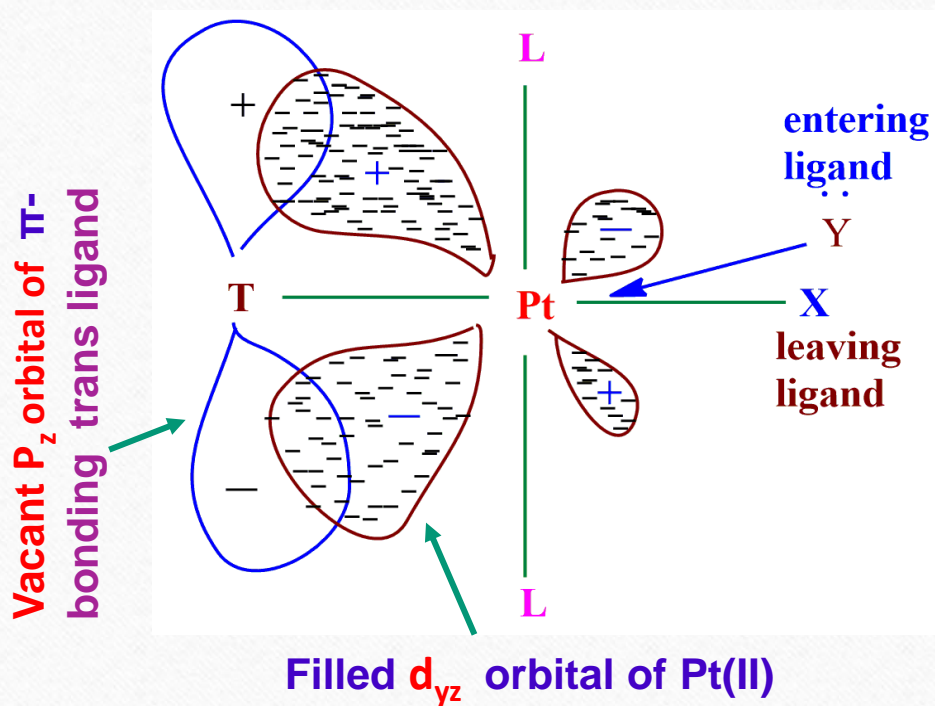


Fig.(i) Formation of $d-p \pi$ bond in TBP 5-coordinated transition-state

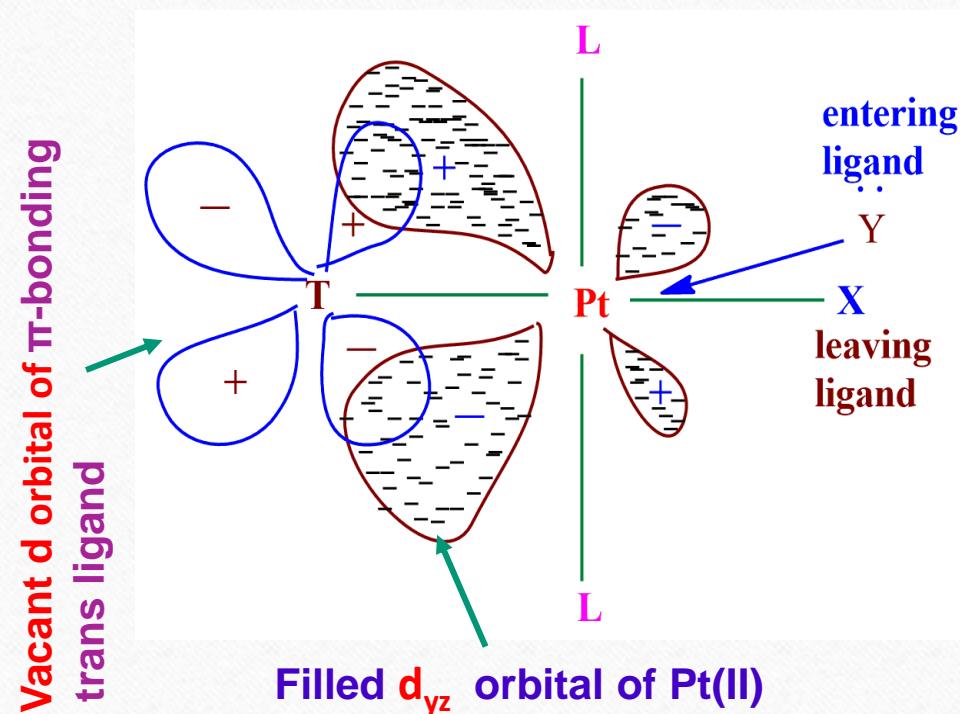


Fig.(ii) Formation of $d-d \pi$ bond in TBP 5-coordinated transition-state

❖ In the structure of TBP 5-coordinated intermediate, π - bonding trans ligand occupy the equatorial position and the two cis-inert ligands occupy the axial positions.

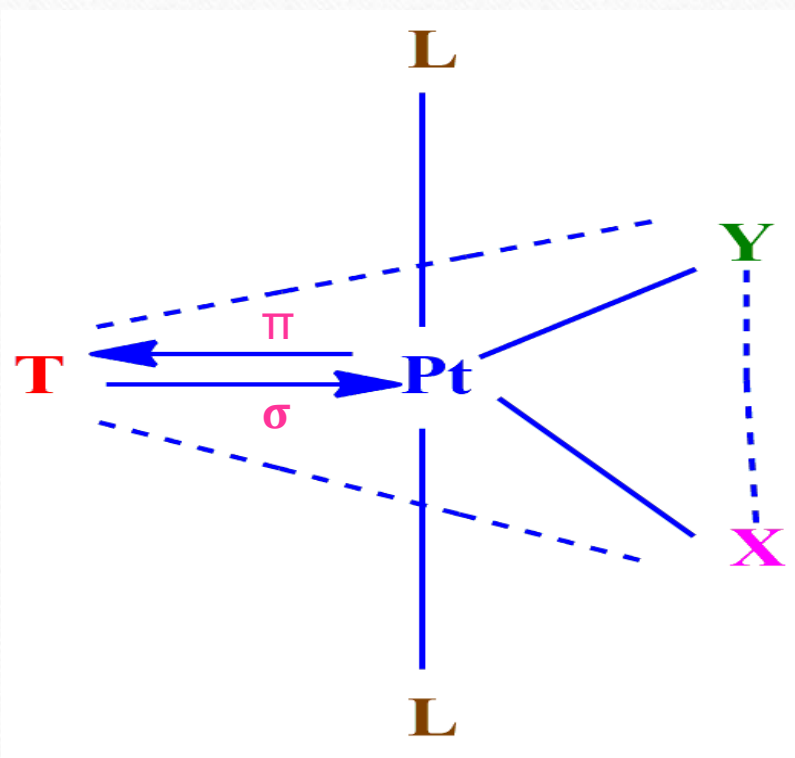
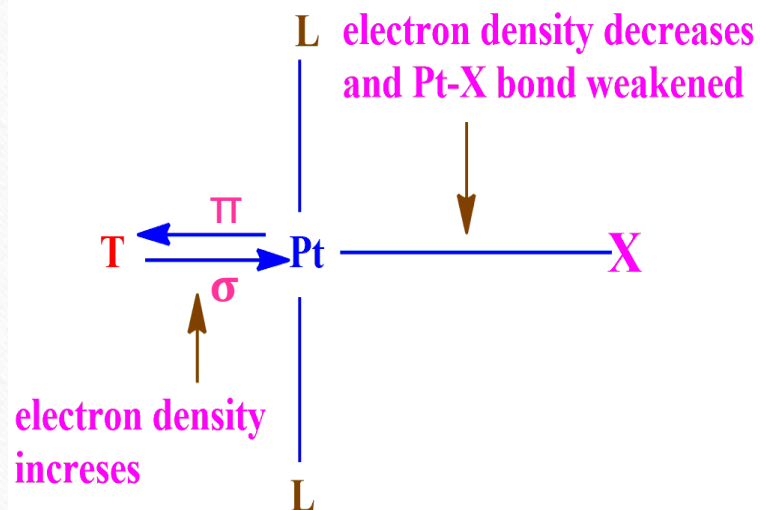


Fig.(iii): Formation of trigonal bipyramidal 5-coordinated transition-state.

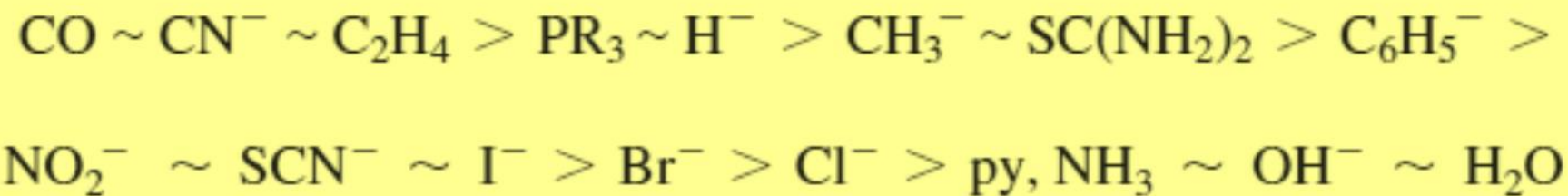
- ❖ According to Chatt, the formation of $M \rightarrow L$ π -bond in the complex increases the electron density in the direction of T ligand and diminishes the electron density in the direction of X trans to T.
- ❖ Thus, Pt-X bond trans to T is weakened. This facilitates the approach of the entering ligand Y with its lone pair in the direction of diminished electron density to form the 5-coordinated transition state complex, which on losing X, yields the substituted complex.



Based on the relative π -acceptor ability of ligands, the trans effect order is



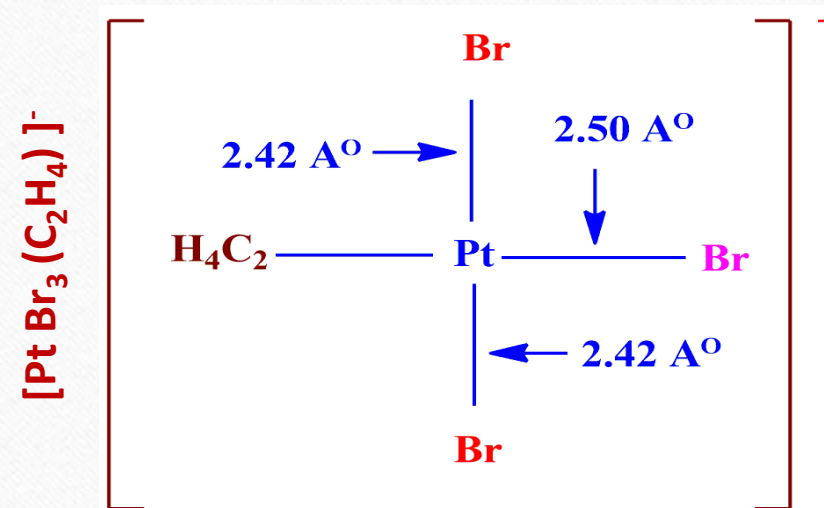
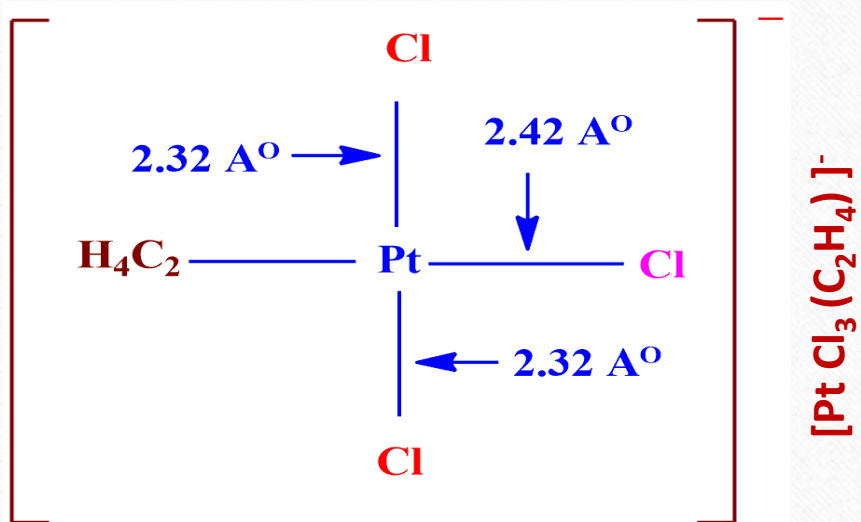
- ❖ The overall trans effect list is the result of the combination of the two effects (σ -bonding and π -bonding):



- ❖ Ligands highest in the series are strong π -acceptors, followed by strong σ -donors. Ligands at the low end of the series have neither strong σ -donor nor π -acceptor abilities.

Evidences in favour of the π -bonding Theory

- ❖ The Pt-X bond trans to the π -bonding C_2H_4 ligand in complexes of $[Pt X_3 (C_2H_4)]^-$ type has been found to be longer than that cis to it. Trans effect of $C_2H_4 > X^-$



Merit of π -bonding Theory

- ❖ It explains the trans effect of π -acceptor ligands which lie at the high end of trans effect series

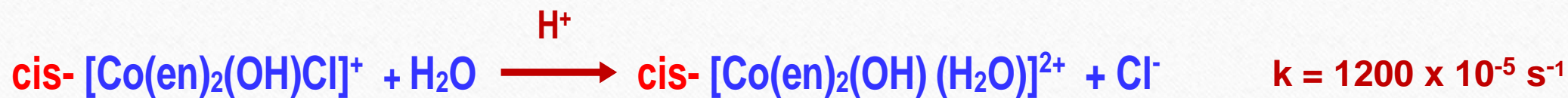
SUMMARY OF TRANS EFFECT

- The Trans effect gives the relationship between the reaction rate and the nature of the ligand trans to the leaving group
- The ability of a group to direct substitution into its opposite position (i.e. trans) in the square planar complex is called the trans effect.
- The Trans directing ability of the π -bonding ligands increases with the increase of their ability to form metal–ligand π -bond.
- The Trans effect of the ligands which are not able to form metal-ligand π -bonds, increases with the increase of their polarizability.
- Ligands highest in the series are strong π -acceptors, followed by strong σ -donors. Ligands at the low end of the series have neither strong σ -donor nor π -acceptor abilities.

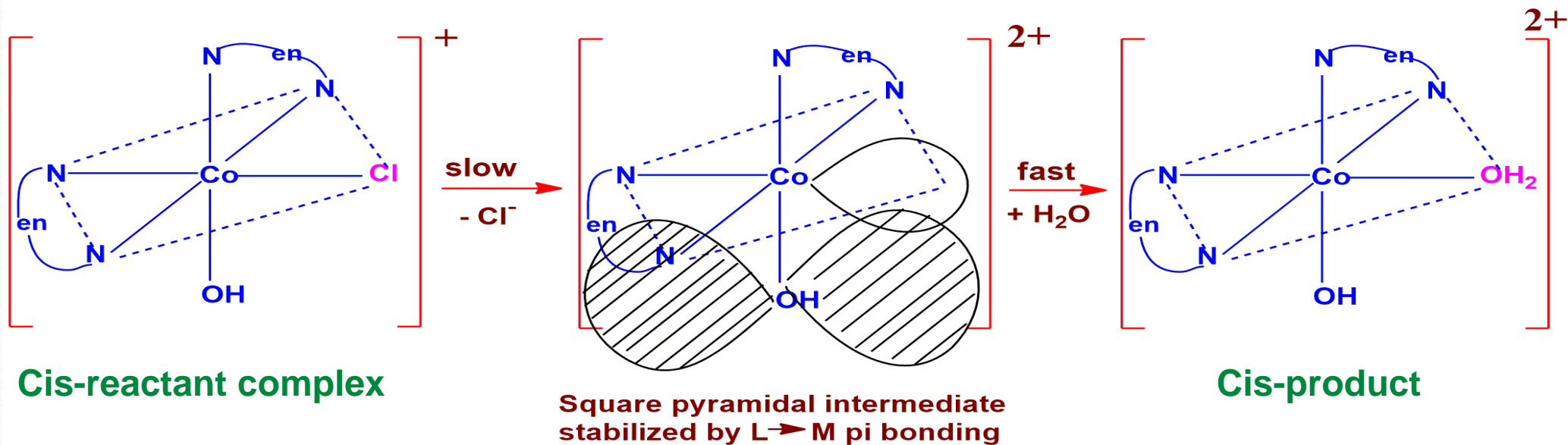
CIS-EFFECT

❖ Cis-effect is more common in substitution reactions of octahedral complexes. Certain inert ligands, such as NH_2^- , OH^- , Cl^- , Br^- , SCN^- , etc., which contains filled p-orbitals (π -donor ligands) greatly accelerate the rate of acid hydrolysis of an octahedral complex when they are present in the cis-position to the leaving group as compared to the analogous reaction in which the leaving group is trans to these π -donor ligands. This is called cis-effect.

❖ For example, consider the rates of the following acid hydrolysis reactions:



- ❖ In the above reactions, when the π -donor ligand OH^- is cis to the leaving ligand Cl^- , the reaction rate is about 8 times faster than that when it is in the trans position.
- ❖ The ligands that shows strong cis-effect are those that have unshared electron pairs in addition to the pair that is used in the formation of usual $\text{L} \rightarrow \text{M} \sigma$ -dative bond. The above acid hydrolysis reaction undergoes by dissociative $\text{S}_{\text{N}}1$ mechanism. The rate increase due to cis-ligands has been attributed to the stabilization of the SP intermediate by donating the extra unshared electron pair to the metal ion along the cis position through $\text{p}\pi\text{-d}\pi \text{L} \rightarrow \text{M} \pi$ -bonding.
- ❖ By forming this $\text{L} \rightarrow \text{M} \pi$ -bonding, the cis ligands, lowers the positive charge on the metal ion and hence stabilize the five coordinate SP intermediate. So the rate increases and the product is 100% cis-isomer.



- ❖ When these donor ligands are present in the trans position, the empty hybrid orbital (d^2sp^3) of **Co(III)** ion in **SP** intermediate is **incapable** of forming **L \rightarrow M π -bond** with the filled p-orbital (**unshared pair**) of the coordinated **OH⁻** ligand because of lack of symmetry. This rules out the possibility of formation of **SP** intermediate during the aquation of **trans- [Co(en)₂(OH)Cl]⁺**. So, it proceeds through a **TBP** intermediate which can be stabilized by **L \rightarrow M π -bonding** as shown below.

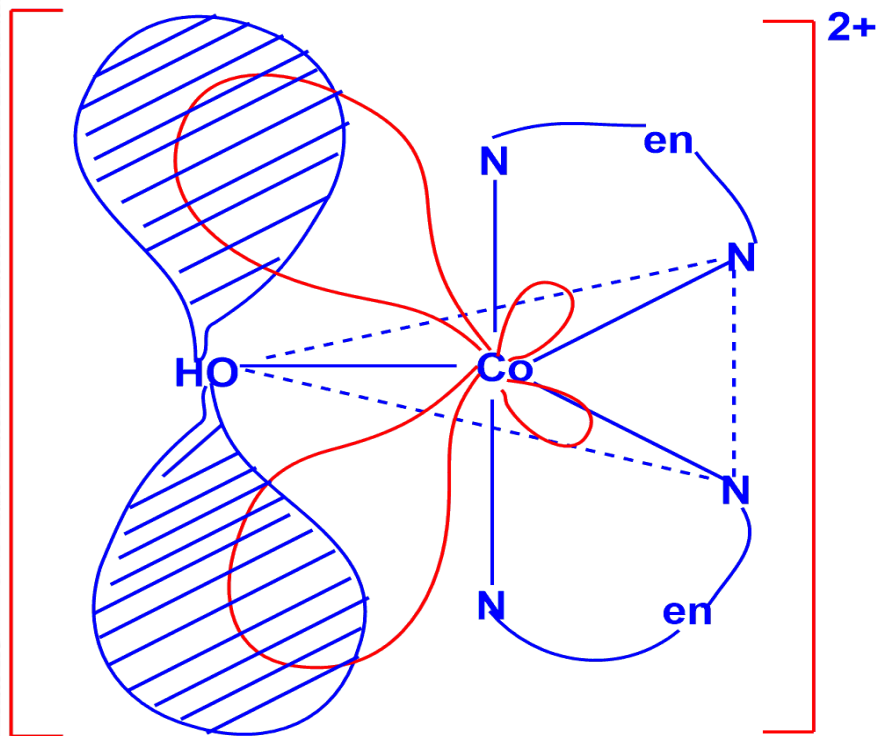


Fig: TBP intermediate is stabilized by $L \rightarrow M$ π -bonding

- ❖ The formation of TBP intermediate requires more energy than SP intermediate and thus makes the substitution difficult. TBP intermediate always produces a mixture of cis- and trans-products.

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THANK YOU

