Quadrant II – Transcript and Related Materials

Programme: Bachelors degree in science

Subject: Chemistry

Paper Code: CHC- 109

Paper Title: INORGANIC CHEMISTRY (SECTION B)

Unit: Reaction Kinetics and Mechanism

Module Name: Trans- effect with respect to square planar Platinum complexes.

Module No: 13

Name of the Presenter: Ms. Varsha K. Sail

Notes:

TRANS EFFECT IN SQUARE PLANNER COMPLEX

- The important feature of substitution reaction in square planner complexes is the nonlabile ligands, that are trans to the leaving ligands
- The ligand trans to the leaving group in square planar complex may influence the rate of substitution.
- They also plays an important role in the type of isomer obtained

The ability of an attached group to direct substitution into a position trans to itself is called the trans effect.

Consider a general square planer substitution reaction.

[Pt TX_3] + Y [Pt TX_2Y] + X

- Any one of the three **X** can be replace by the **entering ligand Y.**
- The ligand X that is replaced **can be** either **cis or trans** to T ,
- Leading to **cis or trans** orientation of **Y** with respect to **T** in the product.
- The **proportion** of cis and trans product varies appreciably with the **nature of the ligand T.**
- Ligand T that **strongly favors trans substitution** to give products in the reaction are said to be **strong trans director ligand.**

A strong trans director ligand T promotes more rapid substitution of the ligand trans to itself than it does of the ligand cis to itself.

Trans effect series

The series of ligands T arranged in the order with respect to their tendency to be strong trans directors is known as ***trans effect series***

- If **T** is a strong **σ – donor** ligands or **π- acceptor** ligands ,

then it greatly accelerate **substitution** of ligand that lies **trans** to it.

- ***The order of ligand with increasing trans effect is as below***

H_2O , OH^- , NH_3, py(NC_5H_5) < Cl^- , Br^- , < SCN^- , I^- , NO^{-2}, $C_6H_5^-$ < $SC(NH_2)_2$, CH_3^-

< H^- , PR_3 < C_2H_4, CN^- , CO

- The above orders are also roughly the **order of increasing overlap** of the ligand orbital with either **σ or a π 6p orbitals**of Pt

i.e. greater the overlap , the stronger the trans effect.

Theories of trans effect: e **activated complex** both affect the activation energy required for the substitution reaction

The stability of the **ground state** and th

- As a result any factor affecting the **stability of the ground state** and the **activation complex** will influence the trans effect
- Accordingly there are **two theories.**

  1. Polarization theory

  2. The pi Bonding Theory

Former related to the ground state and later to the activated complex.

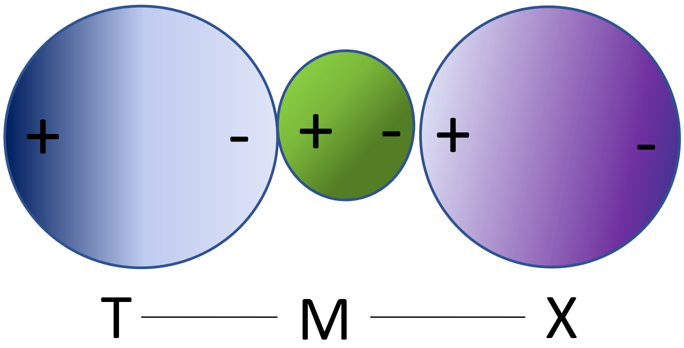
1. **Polarization theory :**

Given by **Grinberg** , who first attempted to explain trans effect

- This theory is related to the stability of the ground state

It is postulated that

- The **primary charge** on the metal ion **polarizes** the electron cloud on the **ligand T** and induce dipole moment in it.
- The dipole moment on **T** in turn **induce dipole** moment in **M**
- The orientation of the **dipole** in the metal ion is such that it **repels** the negative charge in the **ligand X** trans to T.



- As a result ligand **X is less attracted** to metal due to the presence of ligand T
- **Magnitude of trans effect** of T and its **polarizability** are monotonically **related**
- **Now,** This is largely **correct for ligands** which **do not form pi bond** with the metal such as H^-, I^- ,Cl^-

Thus,

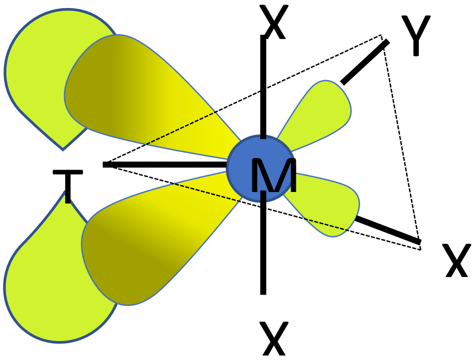
Trans effect is directly related to the polarization of the.

2. The pi bonding theory: ***ligand***

- This theory explain the trans effect of **ligands** which are **strong pi acceptor or pi acid** eg phosphines, CO, alkenes
- It relates the tendency of the ligand T to **remove d electron density** on **metal** by pi bonding to the magnitude of **their trans effect**.

For substitution reaction in the square planar,

- it suggest a **transition state** with **trigonal bipyramidal** geometry
- This transition state geometry is **stabilized**
- if **empty pi orbitals** (p,d, π*) of the ligand **T** overlap with the **non bonding filled d π orbital** of the **metal** to form pi bond.
- **Activated complex** (trigonal bipyramidal) with trans – MX_3YL is shown in the figure below

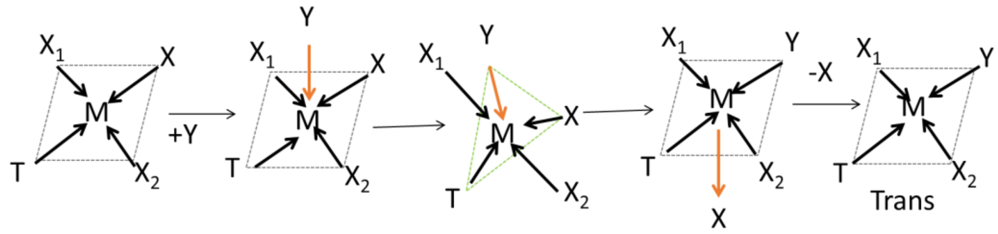


Because of this **M-T pi** interaction the **electron density** from the d_{xz} orbital of the metal ion is **drawn away** from the incoming **nucleophile Y**

Thus the trigonal bipyramidal transition state is stabilized

Hence strong π- acceptor ligands greatly accelerate substitution of ligand that lies trans to it**.** **The Steric course of ligand substitution in square planar complex.**

- The incoming ligand Y results in formation of **a trigonal bipyramidal** five coordinated **intermidiate.**
- The ligand **X_1 and X_2 occupy axial position** in the intermediate and are **cis** to the **leaving group X**
- The **ligand T** in the reaction is the **strong trans director** as T is **trans** to the **leaving group X**
- The entering ligand **Y,** the leaving **X** ligand and the trans ligand **T**, share the **equatorial position** of the triagonal bipyramidal intermediate



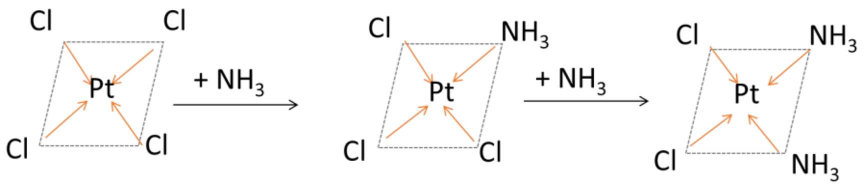
- The new ligand **Y** in the final product **occupies position** vacated by the **leaving ligand**

The reaction sequence can be summarized as follow

Application of trans effect in synthesis of isomers of square planar complex

1. Consider synthesis of cis and trans isomer of $[Pt(NH_3)_2Cl_2]^{2-}$

- The **cis isomer** is obtained by treatment of $[Pt\ Cl_4]^{2-}$ ion with ammonia.
- Because **Cl^-** has greater **trans directing effect** than NH_3 , the **incoming NH_3** will **not substitute** in the **trans** positions to the **existing NH_3**
- It will **occupy** a position **cis** to **existing NH_3**
- The reaction can be **summerizes** as follow

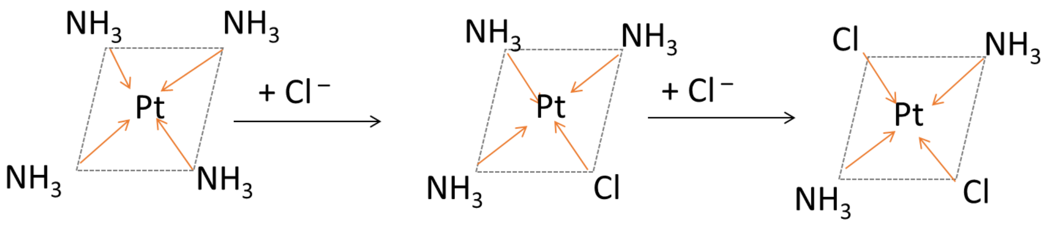


Cis $[Pt(NH_3)_2Cl_2]^{2-}$

Thus *Cis* isomer will be favored

2. The trans isomer of $[Pt(NH_3)_2Cl_2]^{2-}$ is prepared by treating $[Pt(NH_3)_4]^{4+}$ with Cl^-

- Cl^- ion has greater trans effect then NH_3,
- So the **first Cl^-** directs the second **incoming Cl^-** to its **trans** position.



trans $[Pt(NH_3)_2Cl_2]^{2-}$

Thus the product obtained is a *trans* isomer