

<b>Faculty:</b>	Science
<b>Department:</b>	Chemistry
<b>Course:</b>	M.Sc.
<b>Semester:</b>	II
<b>Paper:</b>	I, Inorganic Chemistry
<b>Unit:</b>	5
<b>Topic:</b>	Trans Effect and Oxidation Reduction Reaction

# **Trans Effect and Oxidation Reduction Reaction**

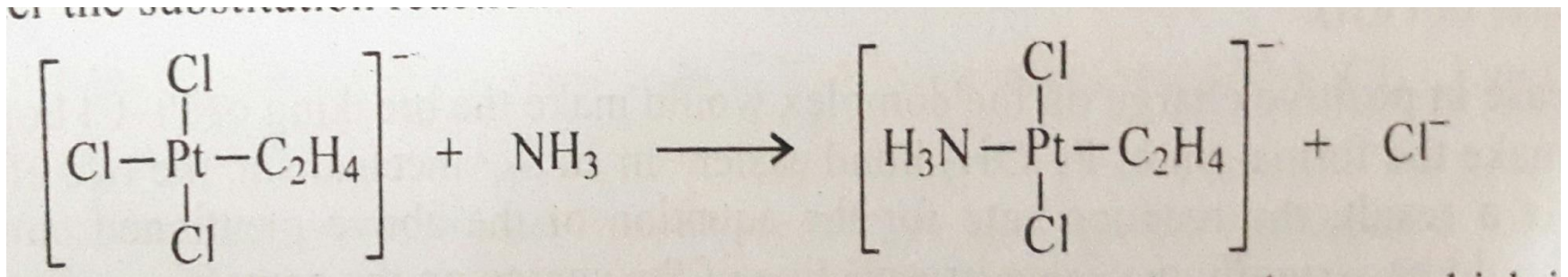
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# Trans Effect

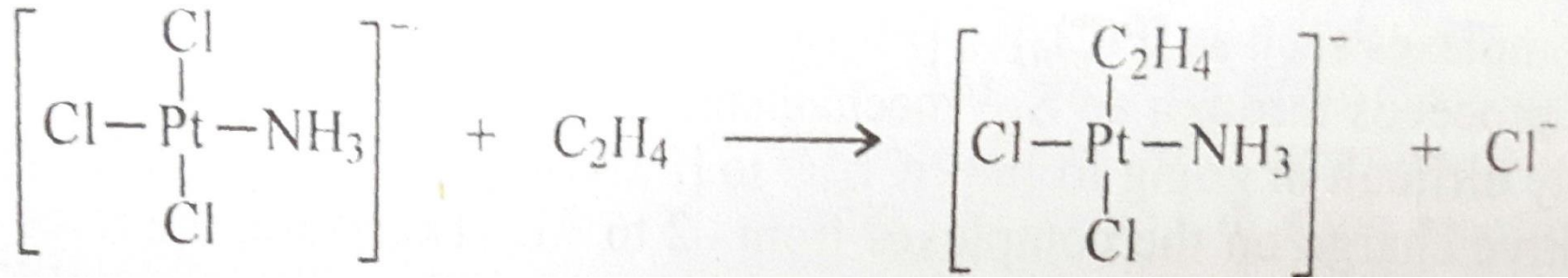
- The ability of an attached group to cause direct substitution of an incoming group in a position, trans to itself is called "***Trans Effect***"
- Consider the substitution reaction:



- C<sub>2</sub>H<sub>4</sub> has greater trans effect than Cl<sup>-</sup> ion therefore the Cl<sup>-</sup> trans to C<sub>2</sub>H<sub>4</sub> is replaced by NH<sub>3</sub>.

# Trans Effect

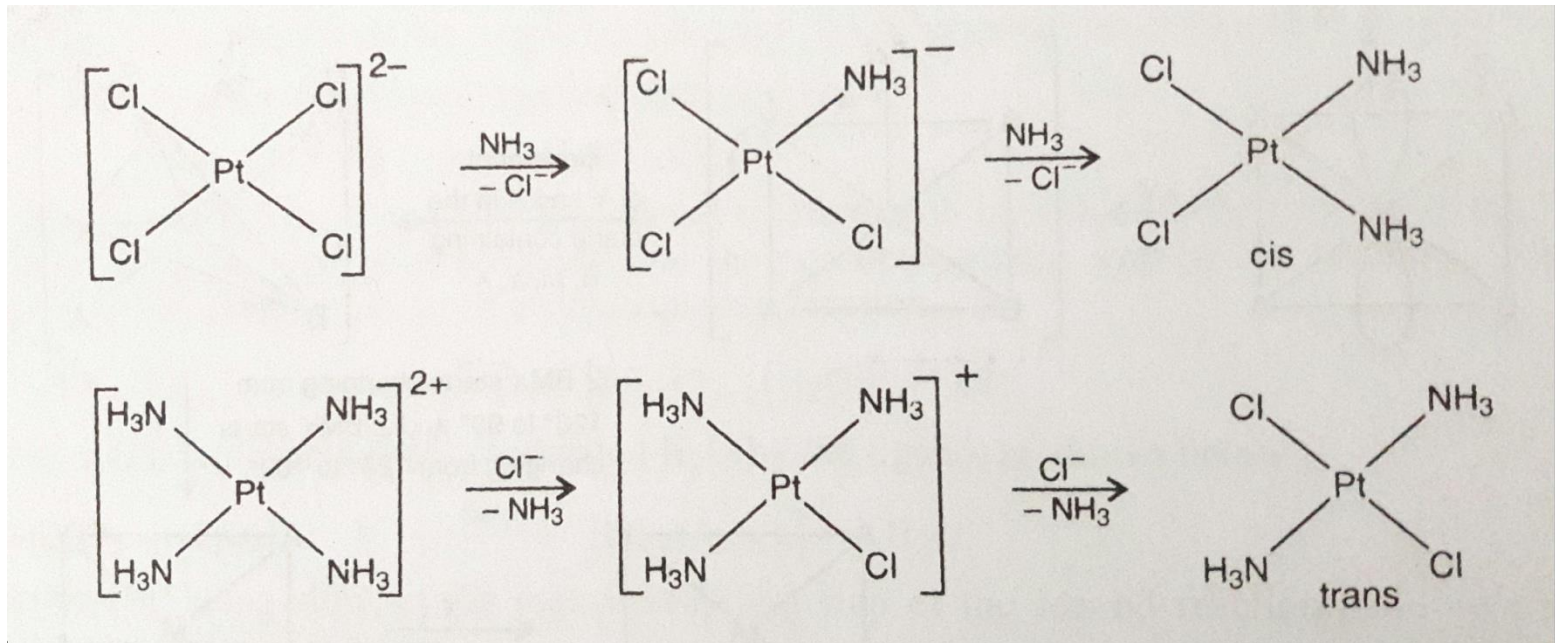
Consider another reaction:



$\text{Cl}^-$  has greater trans effect than  $\text{NH}_3$  therefore the  $\text{Cl}^-$  trans to  $\text{Cl}^-$  is replaced by  $\text{C}_2\text{H}_4$ .

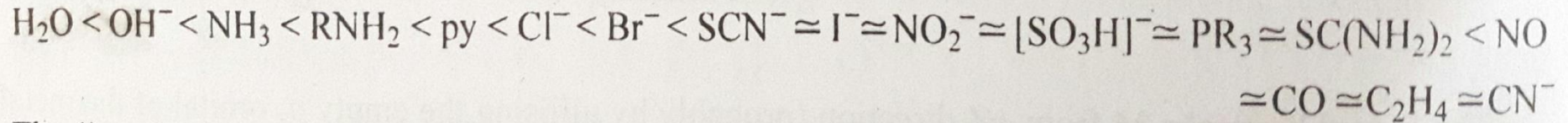
# Trans Effect

- The most important use of trans effect is the preparation of cis or trans isomers of certain given complex compounds.
- Eg. cis and trans diamminedichloroplatinum (II) ion



# Trans Effect

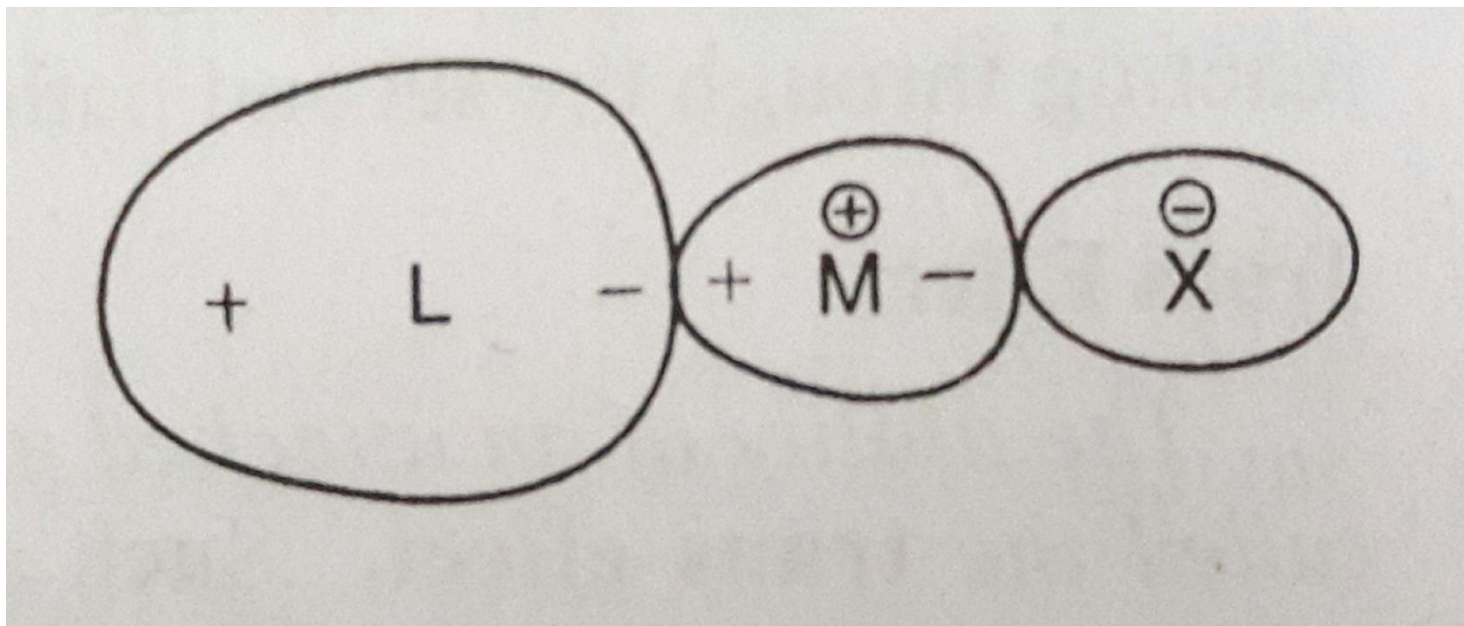
The order of ligands for the increasing trans effect is roughly as :



- The ligand showing high trans effects are those which can form pi bonds by accepting d orbital electrons from the central metal ion through a  $d\Pi$  bond.

# Theories of Trans Effect

## 1. The Polarization Theory:



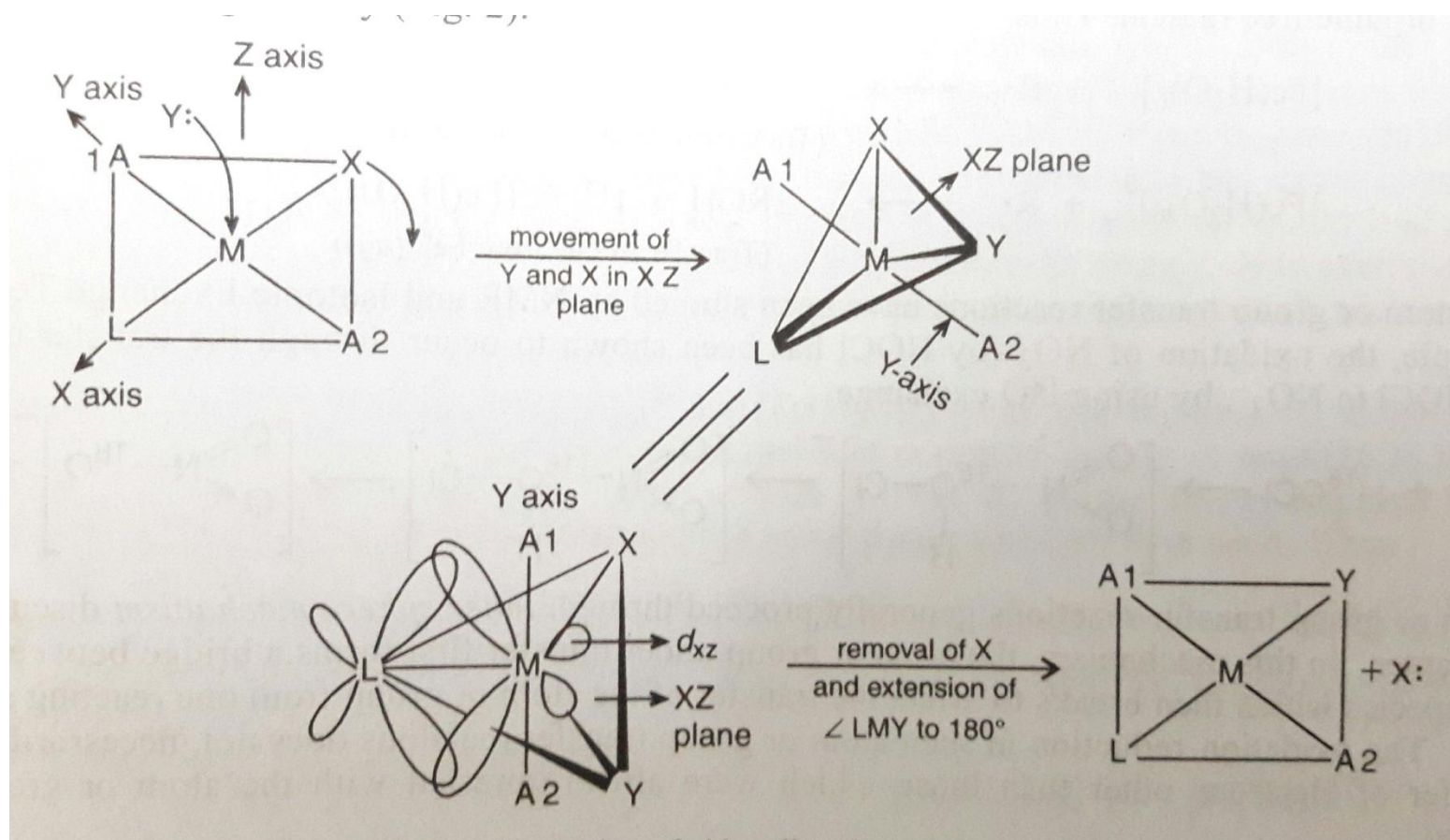
# Theories of Trans Effect

- Let us consider two bonds  $L - M$  and  $M - X$  in which  $L$  and  $X$  are trans to each other.
- Suppose  $L$  is more polarizable than  $X$ , the primary charge on  $M$  will polarize the electrons on  $L$  and thus a dipole will be induced.
- The orientation of the dipole on  $M$  is such that the negative charge on  $X$  experiences repulsion from  $M$ .
- Hence  $X$  would be less attracted to  $M$  because of the dipole developed because of  $L$ .
- This polarization theory is true for ligands that do not form pi bonds with the metal ion.



# Theories of Trans Effect

## 2. The pi Bonding Theory:



# The pi Bonding Theory

- This theory explains trans effect of those ligands which are pi acceptors like Phosphine, CO, olefins, etc.
- Consider a square planar complex in which ligand L is a pi acceptor whose trans effect we want to study (by removal of X which is trans to L).
- According to this theory, there is a correlation between the tendency of a ligand to remove the d orbital electrons from the central metal ion by pi bonding and its trans effect. i.e. trans effect of the ligand.
- The transition state in this reaction is proposed to have TBP geometry.

# The pi Bonding Theory

- The TBP state can be stabilized if the empty pi orbital of ligand L overlaps with a non-bonding filled  $d_{\Pi} (d_{xy})$  orbital of the central metal ion to form a pi bond.
- The electron from the  $d_{xy}$  orbital are withdrawn away from the incoming nucleophile Y due to the formation of M – L pi bond thus stabilizing the TBP state.