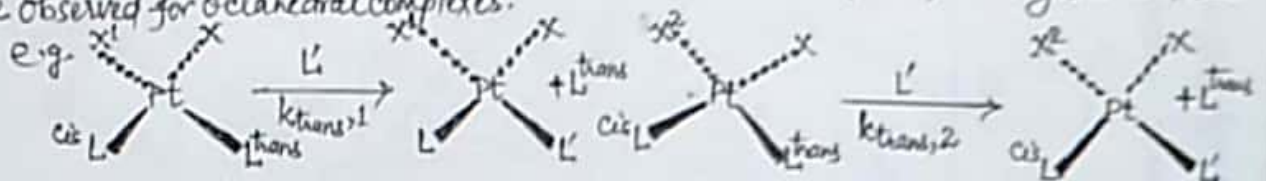


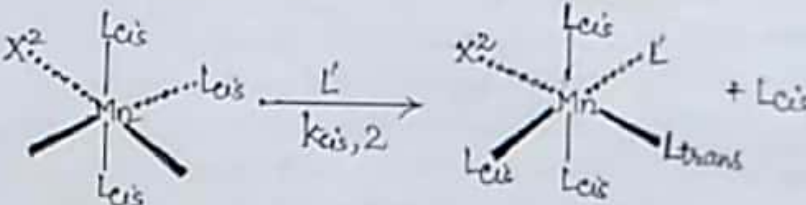
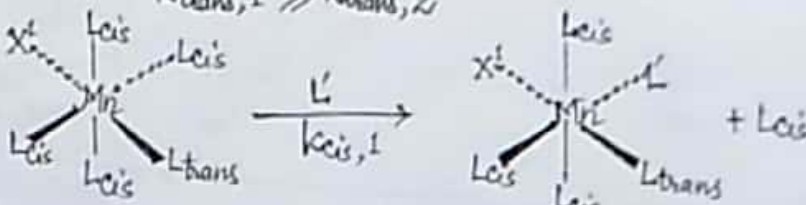
⇒ Trans effect?

[By Dr. Birendra Kumar, Maharaja College]

Chatt et al studied substitution reactions in square planar complexes of Pt(II) and showed that certain coordinated ligands in these complexes induce the incoming groups to occupy the position trans to them. They have proposed that the trans effect of a group (ligand) coordinated to a metal ion is the tendency of that group (ligand) to direct an incoming group (ligand) to occupy the position trans to that group (ligand). The trans effect which is often called the kinetic trans effect, refers to the observation that certain ligands increase the rate of ligand substitution when positioned trans to the departing ligand in the metal complexes. It is attributed to electronic effects and it is most notable in square planar complexes, although it can also be observed for octahedral complexes.



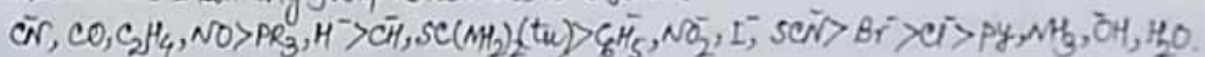
$k_{trans,1} \gg k_{trans,2}$



$k_{cis,1} \gg k_{cis,2}$ (approx)

⇒ Trans effect series?

A series of ligands in the order of decreasing trans effect is called trans effect series. The order would not necessarily be invariant but might depend on the metal complex and also on the incoming group. The series is as follows:



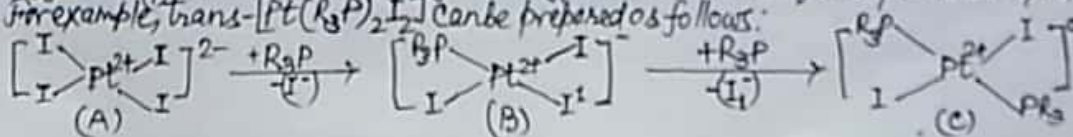
trans effect decreases →

The ligands lying at the LHS (i.e. high trans effect) of the series have vacant π or π^* orbitals which can accept electrons from metal orbital to form $M \overset{\pi}{\leftarrow} L$ ($d\pi-d\pi$ or $d\pi-p\pi$) bond. So, these ligands are called π -bonding ligands. The trans directing ability of these π -bonding ligands increases with the increase of their ability to form $M \overset{\pi}{\leftarrow} L$ bonds.

The trans effect of the ligands which are not able to form $M \overset{\pi}{\leftarrow} L$ bonds increases with the increase of their polarisability, e.g. $Cl^- < Br^- < I^-$ (increasing order of trans effect).

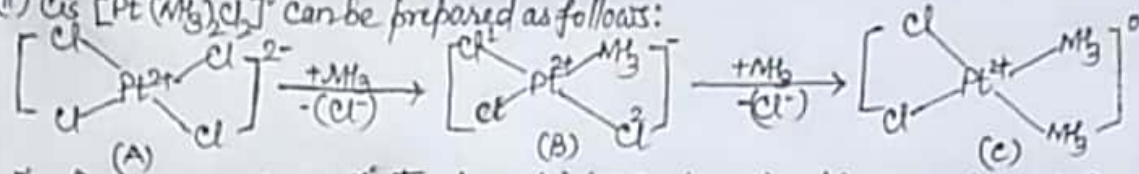
⇒ Applications of trans effect: The main applications of trans effect are:

1. Synthetic applications: Using trans effect desired square planar complexes of Pt can be prepared. For example, trans- $[Pt(PR_3)_2I_2]$ can be prepared as follows:



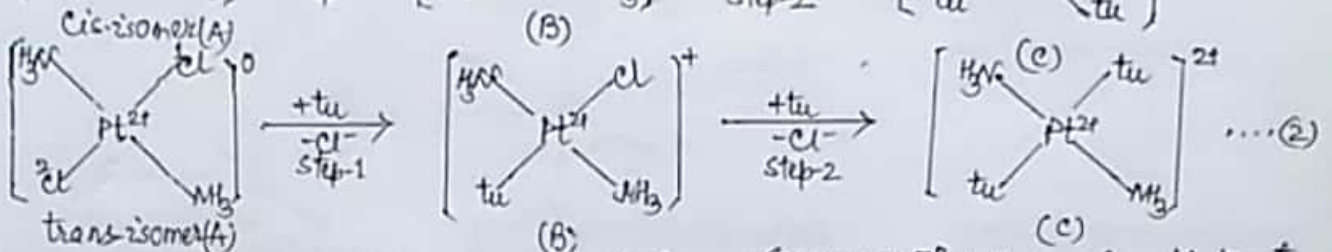
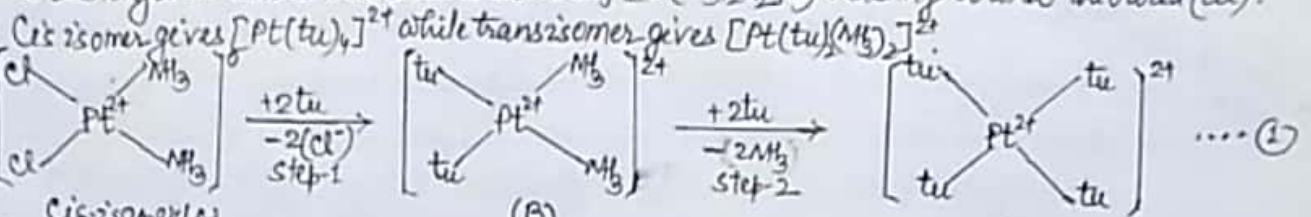
(2)
 In step-1, any one of four I⁻ ions present in (A) can be replaced by ligand R₃P. Now, in step-2 I⁻ ion present in trans position to R₃P in (B) is replaced by R₃P to form trans [Pt(R₃P)₂I₂]⁰ (C). This is because R₃P has greater trans effect than I⁻ ion.

(ii) Cis [Pt(MH₃)₂Cl₂]⁰ can be prepared as follows:



In first step, any one of Cl atom present in (A) can be replaced by MH₃ molecule to form (B). In second step, since Cl⁻ ion present in (B) has greater trans effect than MH₃, Cl⁻ atom which is trans to Cl⁻ atom in (B) is replaced by MH₃ molecule to form Cis [Pt(MH₃)₂Cl₂]⁰ (C).

2. Distinguish between cis & trans isomers: Kurnakov, a Russian Chemist, used trans effect to distinguish between cis & trans isomers of [Pt(MH₃)₂Cl₂] by reacting it with thiourea (tu).



In reaction (1), both Cl atoms present in cis-isomer of [Pt(MH₃)₂Cl₂]⁰ (A) first replaced by two tu (thiourea) molecules to form (B). Since trans effect of tu is greater than that of MH₃. So, both the MH₃ molecules which are trans to tu in (B) are replaced by two tu molecules to form [Pt(tu)₄]²⁺ (C).

In reaction (2), since Cl⁻ atom in (A) has greater trans effect than MH₃, Cl⁻ which is trans to Cl⁻ is first replaced by tu to form (B). Then, Cl atom trans to tu in (B) is replaced by tu molecule to form [Pt(MH₃)₂(tu)₂]²⁺ (C) because tu has greater trans effect than Cl⁻ atom.

⇒ Theories of Trans effect: The trans effect is the ability of a ligand to influence the substitution of another ligand which is positioned trans to it in any square planar complex. There are several theories proposed to explain the trans effect. The main theories are:

1. Polarization theory (2) π-bonding theory.

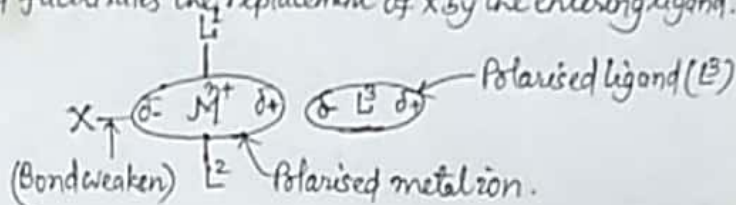
1. Polarization theory: This theory was given by A.A. Ciniberg (1935). It is electrostatic in origin. According to this theory, the ligand by electrostatic effect, weakens the bond trans to it and facilitates substitution in that position. Although subject to some criticism, the polarization theory appears to account nicely for the behaviour of ligands like hydride, methide, phenyl & chloride. In these ligands π-bonding is expected to be of minor importance. Let us consider, a square planar complex (ML₃X), three ligands designated as L¹, L² & L³ for convenience. Since M-L¹ & M-L² bonds are trans to each other and the ligands L¹ & L² are the same ligands, these bonds balance each other. On the other hand, M-X & M-L³ bonds are not able to balance each other since ligands X & L³ are different. Suppose the ligand L³ is more polarisable than X. The primary charge on the metal ion (Mⁿ⁺) polarises the charge cloud on L³ and induces a dipole in L³. Induced dipole on L³, then induces a dipole in metal ion (Mⁿ⁺). δ⁺ charge on the

(3)

metal ion faces the ligand L^{\ominus} and δ^- charge on the metal ion faces the ligand X, which is trans to L^{\ominus} . Thus, the attraction of X for metal ion is decreased, and so M-X bond becomes weaker. The weakening of M-X bond facilitates the replacement of X by the entering ligand.



Square planar complex $[ML_3X]$.

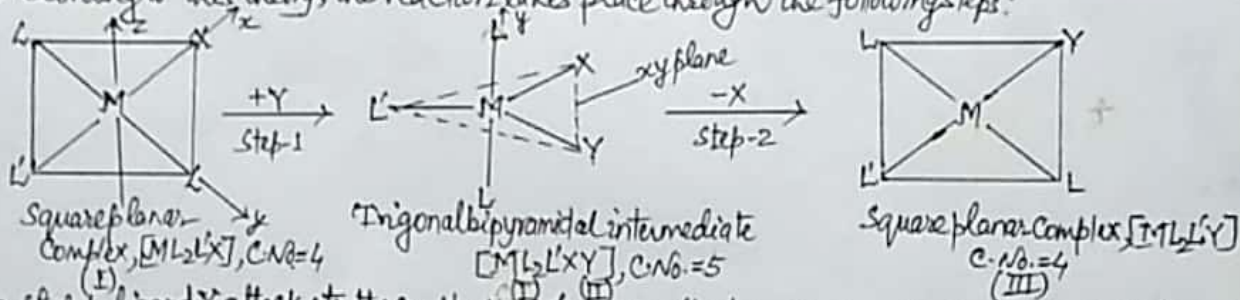


2. π -bonding theory: This theory was given by Chitt & Orgel (1955-56) to explain satisfactorily trans effect in square planar complexes containing π -acid/acceptors ligands, e.g. CN , CO , R_3P , C_2H_4 etc. Let us consider an exchange reaction in a square planar complex, $[ML_2L'X]$ as given below:

$$[ML_2L'X] + Y \longrightarrow [ML_2LY] + X$$

(Entering group) (Leaving group)

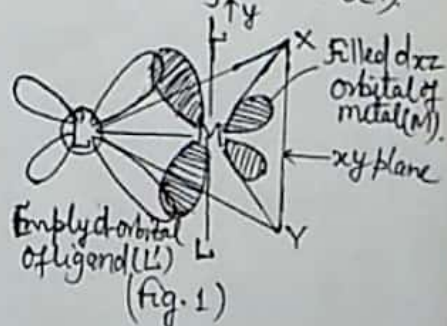
In $[ML_2L'X]$, L' is a π -acid ligand/ π -bonding ligand/trans labilising ligand whose trans effect is to be known. In the complex, L' & X are trans to each other, i.e. $M-L'$ & $M-X$ bonds are transposition. According to this theory, the reaction takes place through the following steps:



In step-1, ligand Y attacks to the complex (I) & forms coordinate complex $[ML_2L'XY]$, an activated intermediate (transition state). Here the leaving gr. (X), entering gr. (Y) and π -bonding ligand (L') form the trigonal plane (XZ) of trigonal bipyramidal geometry. In step-2, the transition state (II) loses X and square planar complex (III) formed. Here bond angle $L'MY$ which is 120° in (II) is expanded to 180° in (III), and the entering gr. (Y) is placed trans to the π -acid ligand (L').

According to this theory, transition state (II) is stabilised by the formation of $M-L'$ bond between the π -bonding ligand (L') and metal (M), and π -bond is formed in XZ plane of (II) by the overlap between the empty d orbital of π -bonding ligand (L') and filled dxz orbital of the metal (M).

Due to the formation of $dx-dx$ $M-L'$ bond, the electrons are back donated from the metal d-orbital to the ligand (L'). Consequently, the electron density between M & X in $[ML_2L'X]$ which is trans to L' is decreased, i.e. the electron density in M-X bond is decreased. The decrease in electron density in M-X bond, weakens the bond, so it (X) is easily replaced by incoming group (Y) occupying trans position to L' and form square planar complex $[ML_2LY]$. The formation of $dx-dx$ $M-L'$ bond in trigonal bipyramidal structure (II) is shown in Figure-1.



Exercise: Draw the product of the following reaction include charges if necessary:

$$[PtCl_2(CH_3)(NO_2)] + Cl^- \longrightarrow ?$$