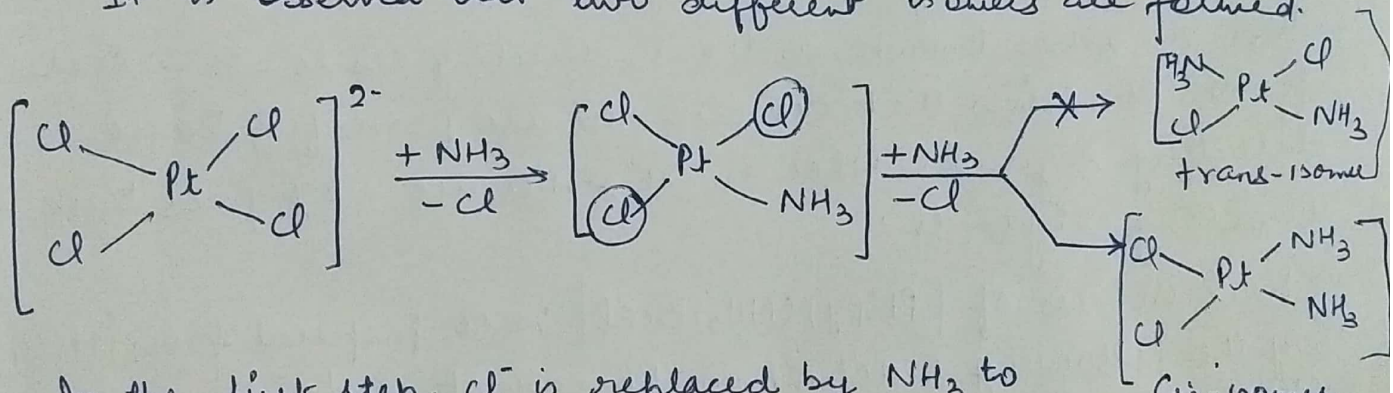
Trans Effect :- The ability of an attached group to direct substitution into a position trans (i.e. opposite) to itself is called trans-effect. Such a substitution has a marked effect on the rate of reaction. This effect of ligand trans to the leaving group is the most important aspect in the studies of square planar substitution reactions of complexes of Pt(II). By changing the nature of this ligand, it is possible to cause changes of many orders of magnitude. In 1926, Chernyaev introduced the concept of trans-effect in Pt complexes.

Let us illustrate this by considering the preparation of two geometric isomers of $[PtCl_2(NH_3)_2]$ complex. This can be prepared either by:

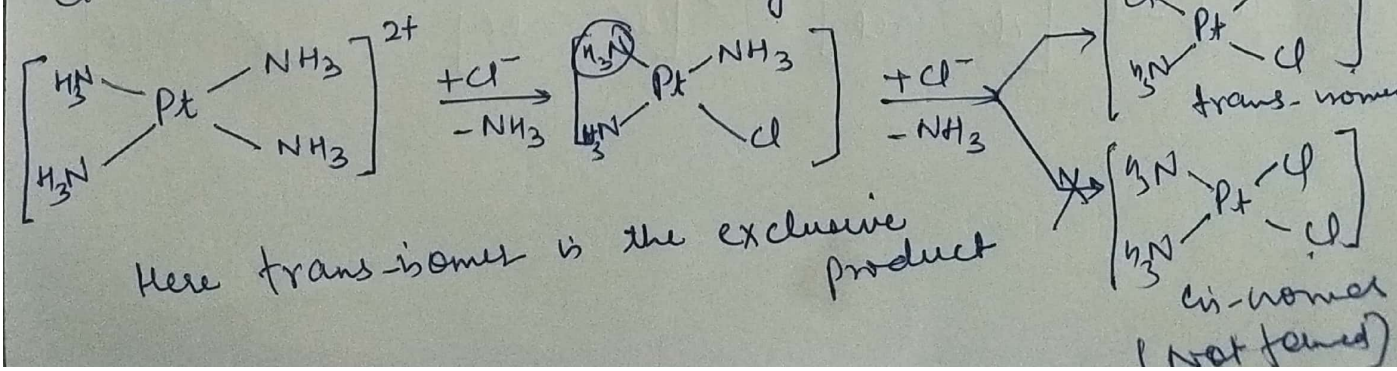
(i) replacement of Cl^- in $[PtCl_4]^{2-}$ by NH_3 or

(ii) replacement of NH_3 in $[Pt(NH_3)_4]^{2+}$ by Cl^-.

It is observed that two different isomers are formed.



In the first step, Cl^- is replaced by NH_3 to form $[PtCl_3(NH_3)]^-$. This is a simple displacement reaction & since all the four groups present are identical only one compound is formed. In the second step, two products can be formed. However, it is observed that only one product is formed, cis-$[PtCl_2(NH_3)_2]$ in which substitution of a ligand occurs trans to Cl^- ion. The ligand trans to Cl^- has been circled. Similarly,



Here trans-isomer is the exclusive product

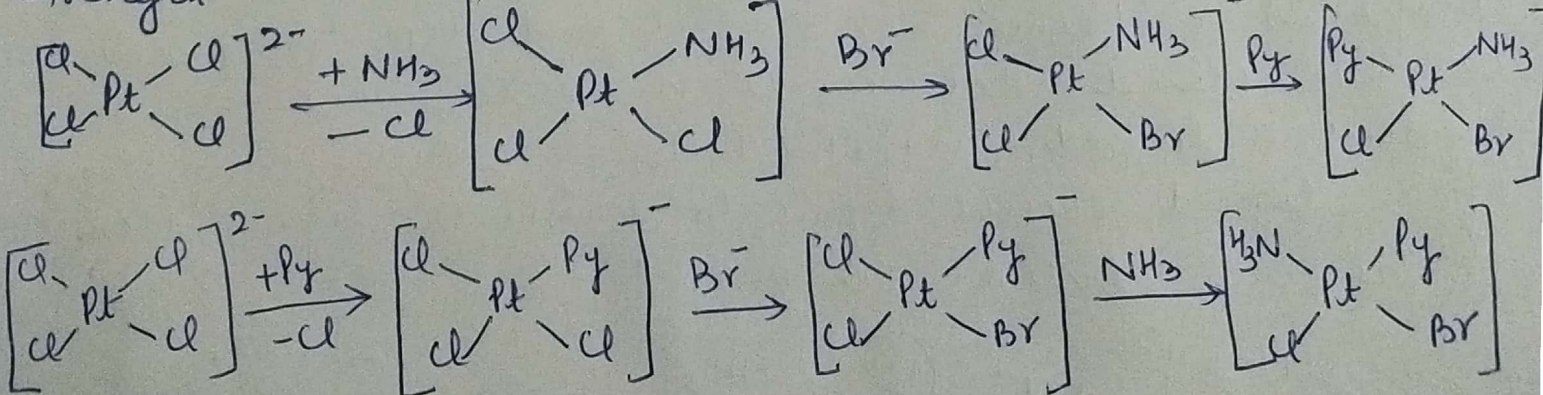
In the above case, the first step involves the replacement of any one NH_3 molecule by Cl^- because all four groups are identical. In second step, two products are possible but only one product is exclusively formed in which substitution of ligand occurs trans to a Cl^- ion. So, these two examples shows that the main isomer obtained is the one which is formed by replacement of ligand trans to Cl^- ion. This is known as trans-effect. It may also be defined as the labilization of ligands trans to certain other ligands which can then be regarded as trans-directing ligands. The different ligands can be arranged in the following decreasing order of trans-directing effect:

$CN^-, CO, NO, C_2H_4 > PR_3, H^- > CH_3^-, C_6H_5^-, SR_2 > SO_3H^- > NO_2^-, I^-,$

$SCN^- > Br^- > Cl^- > Py > RNH_2, NH_3 > OH^- > H_2O$.

This is also known as trans-directing series. It is clear from the series that CN^-, CO & NO are powerful trans directing ligands whereas OH^- & H_2O are very poor trans directing ligands.

Three isomers of $[Pt(py)(NH_3)BrCl]$ were prepared from $[PtCl_4]^{2-}$ by the following reactions on the basis of greater trans effect of the ligands Br^- & Cl^- compared to Py & NH_3 and the fact that the Pt-N bond strength is greater than the Pt-Cl bond strength.



Theories of Trans Effect :→

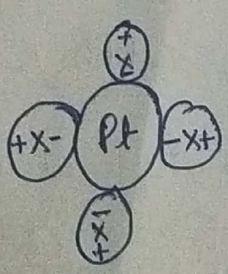
Several theories have been put forth for the explanation of trans-effect: Two important theories representing different approaches are discussed below:

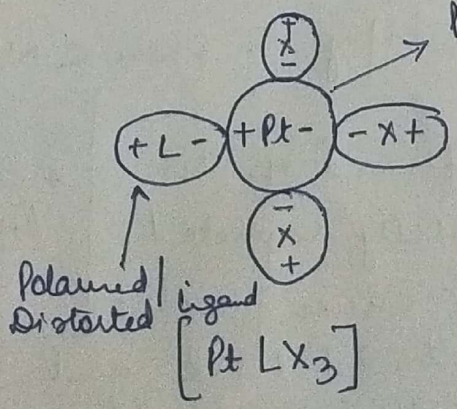
(i) Polarisation Theory (ii) π-bonding theory

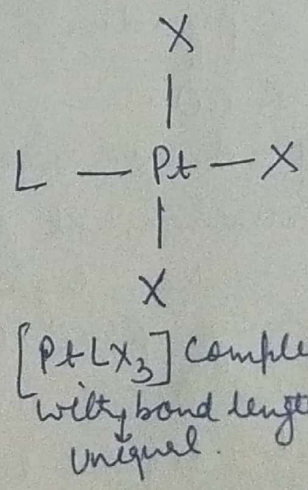
(i) Polarisation Theory:

~~This theory is primarily concerned with the effects on the ground state in terms of weakening of Pt-X bond trans to~~

This theory was given by Grinberg in a completely symmetric complex such as PtX_4^{2-}. All the ligands are identical. According to Grinberg in a completely symmetric complex such as PtX_4^{2-}, the dipole moment of all the bonds will be same. There dipoles induced by Pt(II) cancel each other & resultant dipole is zero. Thus none of the ligands show 'trans effect'. However, if a more polarisable ligand 'L' is introduced, its polarisability will induce an additional uncompensative dipole in the molecule. This will effect the distribution of charge. This induced dipole in the metal will oppose the natural dipole of the ligand trans-to polarising ligand as shown



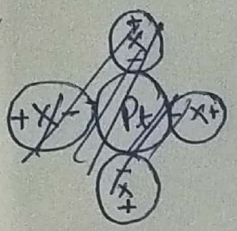




The polarisation theory is supported by following facts

(i) Trans effect is most important with the large and polarisable metal atom/ions.

(ii) Trans directing groups are more polarisable as they are large or multi-bonded system such as CN^-, CO etc. Thus the induced dipole repel the negative charge density in a bonded ligand 'X' which reduces attraction between Pt and X. This results in the weakening and lengthening of Pt–X bond which has been clearly explained on the basis of X-ray studies.



π-bonding Theory: A second approach that involves the weakening of trans bond is ~~static~~ π-bonding theory. Acc. to this theory, the trans-directing ligand is capable of accepting π-electrons from the central metal. Figure given below explains the interaction of π-electron acceptor orbitals on ligands such as CO, C_2H_4 with a transition metal that is believed to result in weakening of trans metal ligand bonds. The π-bonding results in a reduction of electron density in the interligand region. This makes nucleophilic attack much easier. In addition π-bonding interaction stabilizes the 5-coordinate intermediate as is evident in associative mechanism. The π-accepting tendency of ligands decreases in order, $C_2H_4 > CO, CN^- > NO_2 > SCN^-$

Due to this π-bond back-donation, the weakening of the bond between the metal and trans ligand is affected to large.

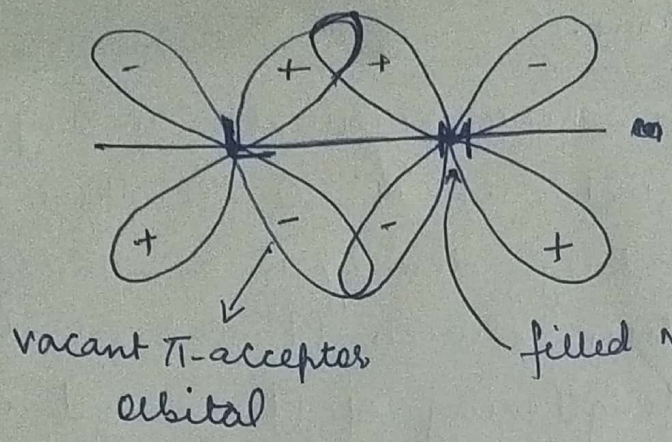


Fig: π-bonding interaction

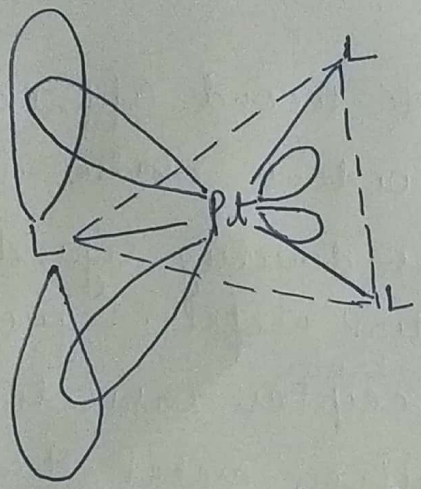


Fig: π-bonding in Trigonal bipyramidal transition state