Substitution Reaction in square planar complexes.

The most stable complexes in square planar complexes are formed by d^8 metal ions such as Ni(II), Pt(II), Pd(II), Au(III), Ir(I), Rh(I) etc which are generally low spin and diamagnetic in nature.

The square planar complexes have been studied and analyzed because.

1. Square planar complexes of Pt(II) are most stable
2. Easy to synthesize
3. Pt(II) complexes of co-ordination no 4 are always square planar complexes unlike Ni(II) complexes
4. Substitution Reaction in Pt(II) complexes undergo at slow rate and are therefore, convenient in study

The substitution Reaction involves the replacement of a ligand by other ligand.

Eg:- $PtL_3X + Y \longrightarrow PtL_3Y + X$ when X is a labile ligand.

Square planar complexes undergo 3 type of Substitution Reaction:-

1. Oxidative addition:- This involves the oxidation addition followed by reductive elimination leading to substitution re

$$PtMeCl(PPhMe_2)_2 \xrightarrow[\text{addition}]{Cl_2\ \text{Oxidative}} PtMeCl_3(PPhMe_2)_2 \xrightarrow[\text{elimination}]{\text{Reductive}} PtCl_2(PPhMe_2)_2 + CH_3Cl$$

Intermediate.

In this reaction state of Pt(II) changes to Pt(IV) and the co-ordination no changes from IV to V in intermediate. This intermediate then undergo reductive elimination of Methyl chloride to form four co-ordinated Pt(IV) complexes

2. Electrophilic substitution Reaction:- This reaction involves the replacement of ligand by

an electrophilic ligand

$Pt\,Me\,Cl\,(PPh_2Me)_2 \xrightarrow{HgCl} PtCl_2(PPh_2Me)_2 + MeHgCl$

This reaction involves the electrophilic attack of Hg(II) on Pt-C bond

3. Nucleophilic Substitution Reaction:- These are the substitution reaction in which there occur the replacement of weaker nucleophilic ligand by a strong Nucleophilic ligand in square planar complexes

$Pt\,Me\,Cl\,(PPh_2Me)_2 + N_3^- \longrightarrow Pt\,Me(N_3)(PPh_2Me)_2 + Cl^-$

(azide)

In this reaction, the strong nucleophile N_3^- replace the weaker nucleophile Cl^-

The first two type of substitution are less common in inorganic complexes (square planar complexes) but are very important in organic chemistry. However, the most common substitution Reaction in square planar complexes are Nucleophilic Substitution Reaction. The substitution of ligands in square planar complexes generally takes place through bimolecular nucleophilic displacement i.e. they follow nucleophilic substitution bimolecular mechanism (S_N2)

For eg $PtL_3X + Y \longrightarrow PtL_3Y + X$

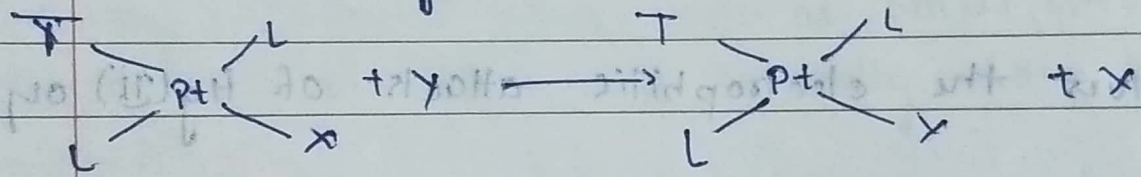
where L are Non-labile ligands, X is leaving ligand & Y is entering ligand.

$[Pt\,Cl(R)(PR_3)_2] + NH_3 \longrightarrow [Pt(R)(PR_3)_2NH_3] + Cl^-$

In a complex trans $[Pt(T)L_2X]$ where X is a leaving group T is a ligand trans to X and L are the ligands cis to leaving group i.e X. The substitution takes place as

trans $[Pt(T)l_2X] + Y \longrightarrow [Pt(T)l_2Y] + X$

The stereochemistry of Rxn is as shown below:-



Mechanism of substitution reactions of coordination compounds:

The substitution reaction of coordination compounds are of two types:

(a) Substitution nucleophilic (S_N) reaction
(b) Substitution electrophilic (S_E) reaction

As S_E reactions are less common than S_N reactions, here the mechanism of S_N mechanism is shown. The reaction can occur via following three mechanisms

(i) Dissociative or D- mechanism (SN^1 mechanism)
(ii) Associative or A- mechanism (SN^2 mech.)
(iii) Interchange or I- mechanism

I) Dissociative mechanism | SN^1 Mechanism:

The mechanism completes in following steps:

Step I $\quad ML_n \longrightarrow ML_{n-1} + L$ (slow) [dissociation of ligand]

Step II $\quad ML_{n-1} + Y \longrightarrow ML_{n-1}Y$ (fast)

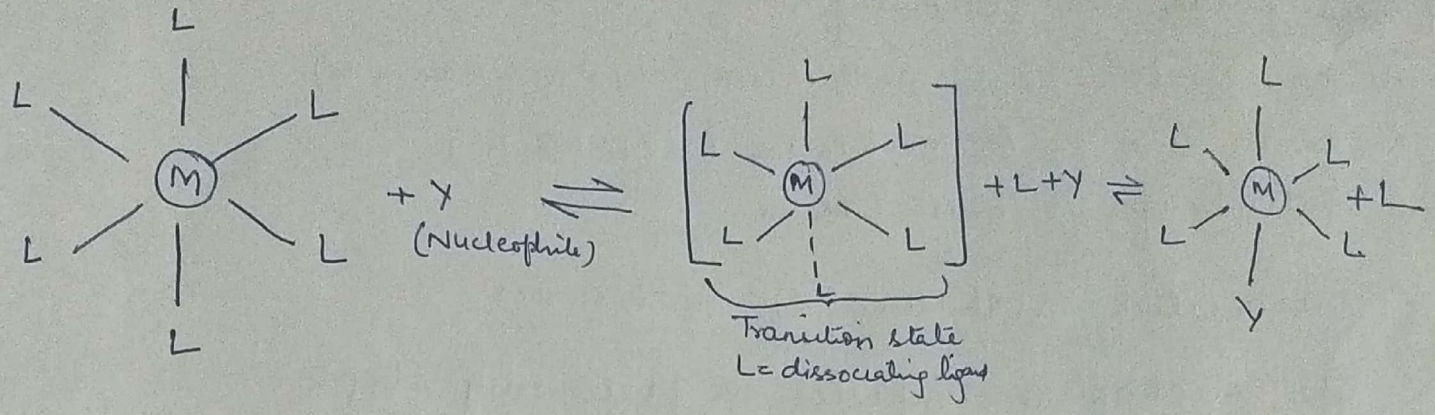
Where M is metal, Ln = 'n' no. of ligands Y = nucleophile.

Thus SN^1 indicates substitution nucleophilic unimolecular rxn.

Since (MLn) is the only one species involved in the formation of transitional state complex $(MLn-1)$, with which further rxn occurs. Hence, it is termed as unimolecular rxn. Since the activation energy for the first step which is endothermic will be high and for the second step which is exothermic will be low. The rate of overall reaction will depend on $[MLn]$ and not on $[Y]$. Thus the rxn will be of first order w.r.t Y. This can be represented as

$$(MLn) + Y \rightleftharpoons ML_{n-1} + L + Y \rightleftharpoons ML_{n-1}Y + L$$

Thus it can be seen during the formation of an activated complex in an S_N1 reaction, the coordination no. of metal is reduced. The rate determining step of S_N1 rxn is bond breaking step (first step) that forms an electron deficient intermediate. Thus S_N1 mech. is characterised by bond breaking.

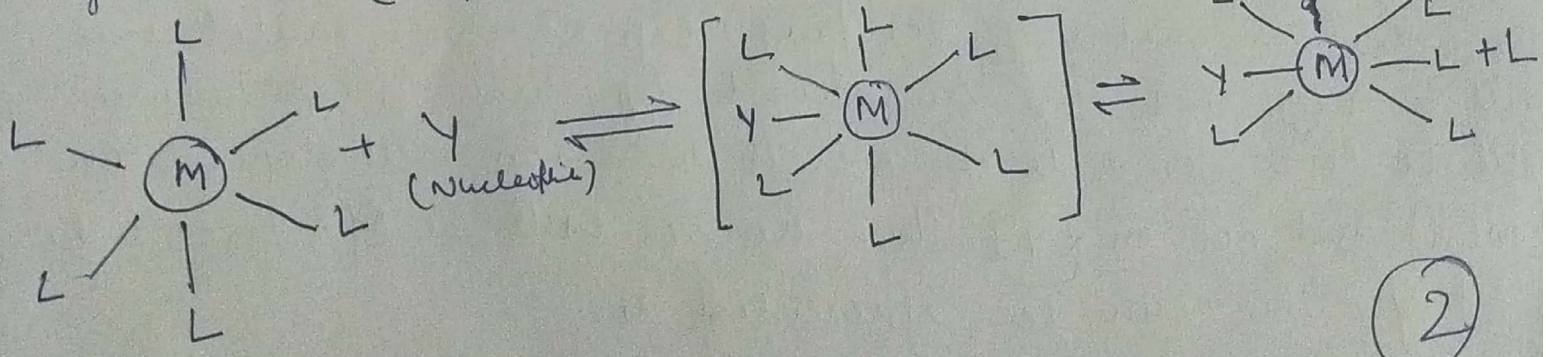


II) Associative Mechanism (S_N2): The second path of S_N reaction is S_N2 or associating mechanism and is formulated as:

$$ML_n + Y \longrightarrow ML_nY \text{ (slow)}$$

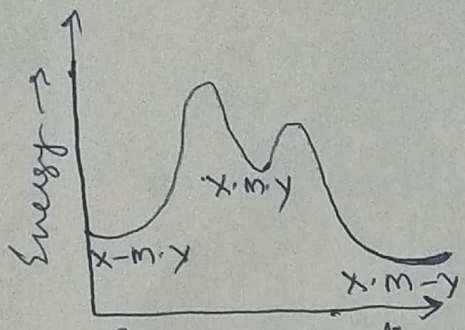
$$ML_nY \longrightarrow ML_{n-1} + L \text{ (Fast)}$$

S_N2 indicates substitution nucleophilic bimolecular rxn. In this case, the rate of rxn depends on both $[ML_n]$ and $[Y]$; in fact it is first order w.r.t ML_n & first order w.r.t Y, thus second order is the overall rxn. An illustration of S_N2 rxn is given as $(ML_n + Y \rightleftharpoons ML_nY \rightleftharpoons ML_{n-1}Y + L)$

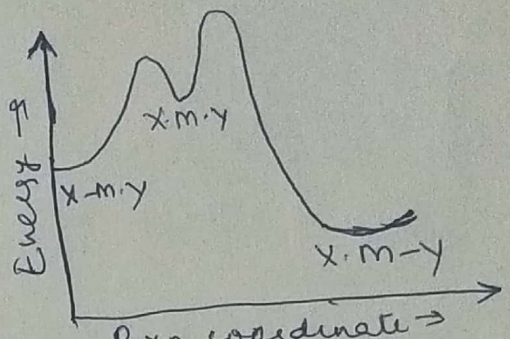


III) Interchange or I-mechanism :-

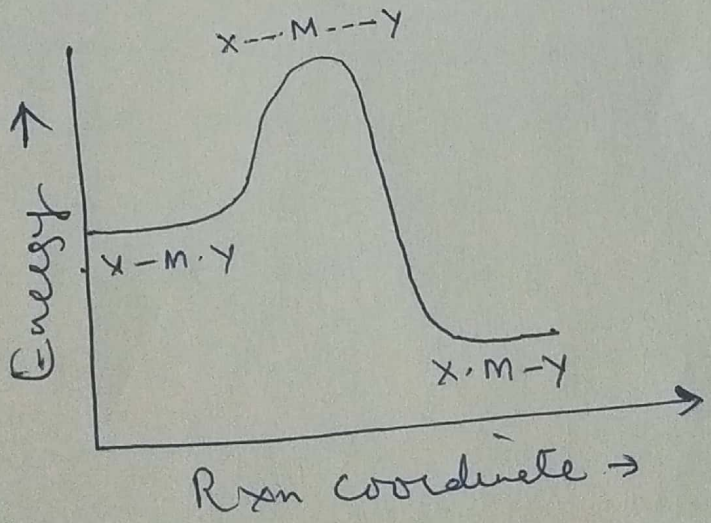
In this mechanism, the entering groups or ligands exchange in a single step by forming an activated complex but not a true intermediate. As the entering group approaches the metal center, the outgoing group leaves in a concerted manner. The reaction profile has single transition state.



Energy profile of D-Mech.



Energy profile of A-Mech.



Energy profile of I-mechanism

Mechanism of Nucleophilic substitution in square planar complexes:

The square planar substitution reaction involves a bi-molecular displacement reaction. Therefore, the substitution reaction proceeds most readily by an expansion of coordin-ation number to include the entering ligand. The metal is exposed for attack above and below the plane forming coordination no. 5. Moreover, these low spin d^8 systems have vacant p_z orbital of relatively low energy which can easily accomodate the pair of es donated by the entering ligand.

The ligand Y attacks the metal 'M' from Z-direction (probably by utilizing the empty p_z orbital of the metal) to form a 5-coordinated square pyramidal intermediate. This square planar intermediate rearranges itself into a stable trigonal bipyramidal intermediate. This trigonal bipyramidal arrangement has three ligands (Y, T & X) in equatorial plane & two ligands L, in the axial positions (Fig. c). As X-depaths from trigonal plane, the T-M-Y angle will open up and geometry will pass through a square pyramidal intermediate into square planar product ML_2TY (Fig e) with release of X. The trigonal bipyramidal species that forms during the reaction and then rearranges to give the products may exist either as an activated complex or as a true intermediate.

[Fig (B)]