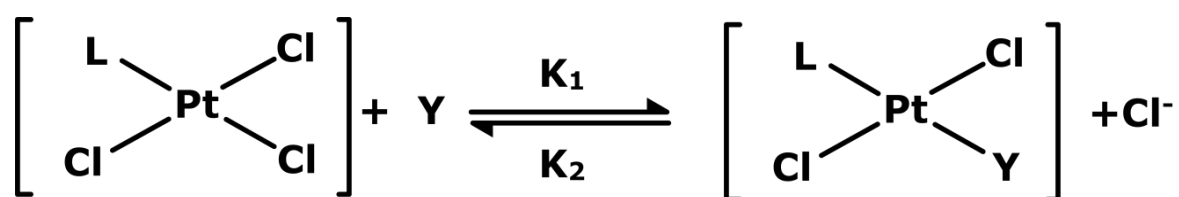


Substitution in square planar complex

The complexes of d^8 configurations are in general occupy a four-coordinate square planar geometry. In general, the kinetic studies in square planar complexes has been carried out on the Pt(II), Ni(II), Pd(II) and Au(III) complexes. However, the most extensive work has been done on Pt(II) d^8 Complexes.

The mechanism of substitution reactions of square planar complexes appears to be associative S_N^2 rather than dissociative S_N^1 . For substitution reactions of the general type:



For the reaction under pseudo-first order conditions, the concentration of Y is much larger than the Pt-complex. The usual form of the rate law is

$$-d/dt [\text{PtLCl}_3] = k_1[\text{PtLCl}_3][\text{Y}] - k_2[\text{PtLCl}_2\text{Y}][\text{Cl}^-]$$

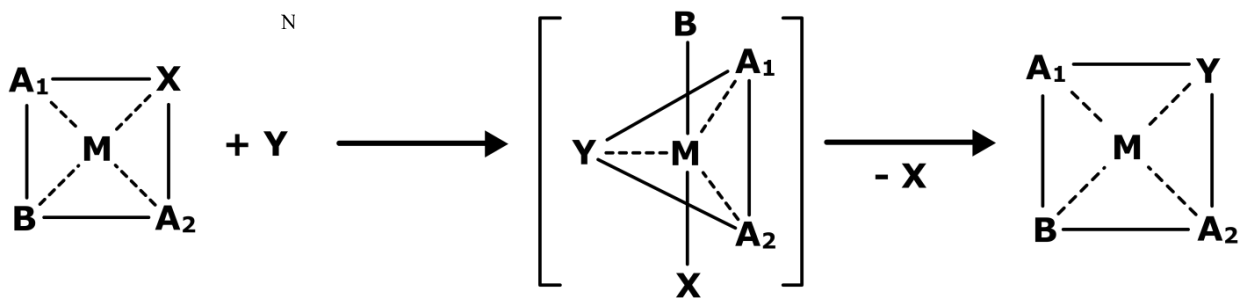
The above rate law suggests that substitution of Cl^- by Y, follows two independent pathways. Since, reaction mostly dominates in the forward direction, the reaction rate for the first reaction path is given by

$$r = k[\text{Pt L}_n \text{Cl}_{4-n}][\text{Y}]$$

This indicate that the rate determine step is bimolecular and the mechanism involved is associative S_N^2 mechanism.

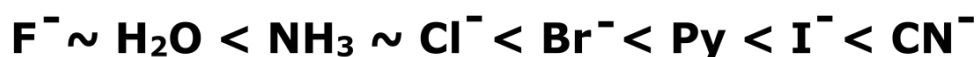
Stereochemistry

The S_N^2 Mechanism for the substitution reaction of square planar complexes follows retention of geometrical isomerism this may be illustrated as follows



In the substitution of Square Planar complex, the entering ligand Y attacks the complex from one side of the plane with the formation of trigonalbipyramidal (TBP) transition state as shown in the above scheme. The three ligands (A_1 , A_2 and Y) in its equatorial position while the two group (X and B) in its axial position. After removal of X, the TBP intermediate converted into new substituted square planer complex.

Again for many reaction of substitution at Pt (II), k_2 in the rate expression written earlier is found to increase in the sequence

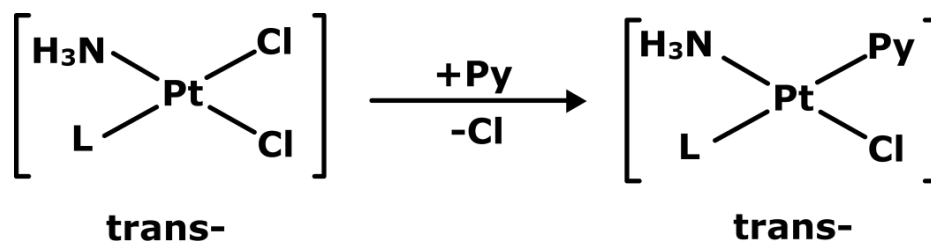


Factors affecting substitution of SPL complex

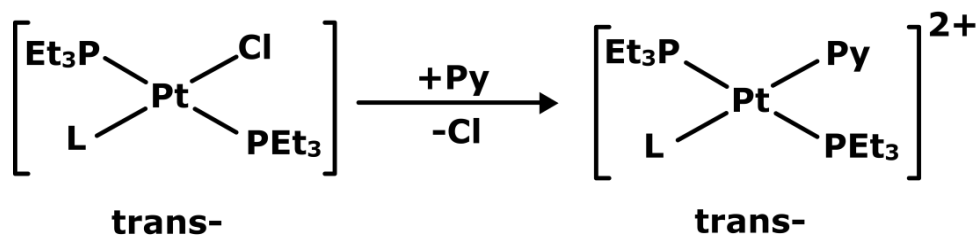
There are four kinds of factors affecting the substitution in Square planer complex. The rate of exchange of ligands is governed by either the weakening of Pt-X bond in ground state or it can stabilize transition state. Combination of both the possibility somewhat influence the rate of reaction.

1.1 Trans effect

Trans effect is the ability of a group to direct substitution into its opposite trans position. The decrease of rate of substitution in trans Pt(II) complex is the decrease of trans effect. For example,



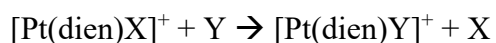
The relative rates of various L like $C_2H_4 > NO_2^- > Br^- > Cl^-$ increases as the trans effect increases, however activation energy decreases in the same way. The usual effect of trans-effect on the rate has been observed in the following reactions.



In this reaction L like $H^- > CH_3^- > C_6H_5^-$ increases as the trans- effect of these ligands increases.

1.2 Effect of labile group

The labile group present in complex can directly affects the rate of substitution reactions.



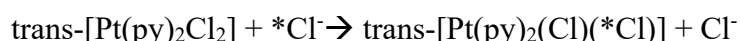
The ease of substitution of X follows the order:



It has been observed that the replacement of halides is easier than other common ligands because of the weak strength of Metal-halide bond strength.

1.3 Effect of solvent

It has been observed that the coordination ability of the solvent can easily compete with the of substitution reactions.



Some of the solvents have good coordinating ability hence these solvents doesn't affect the substitution of Cl^- ions. Like DMSO, H_2O and ROH etc.

While some of solvent having weaker coordinating ability like CCl_4 , Benzene, acetone, DMF etc. In these solvents substitution reaction is dependent on the concentration of Cl^- ions.

1.4 Effect of charge on complex

An increase in the positive charge on the complex specie decreases rate of substitution reactions. The decrease in reaction rate is observed as the charge of the complex increases, a dissociative nucleophilic substitution S_N^1 process seems to be operative.