

# Reaction mechanism CC13

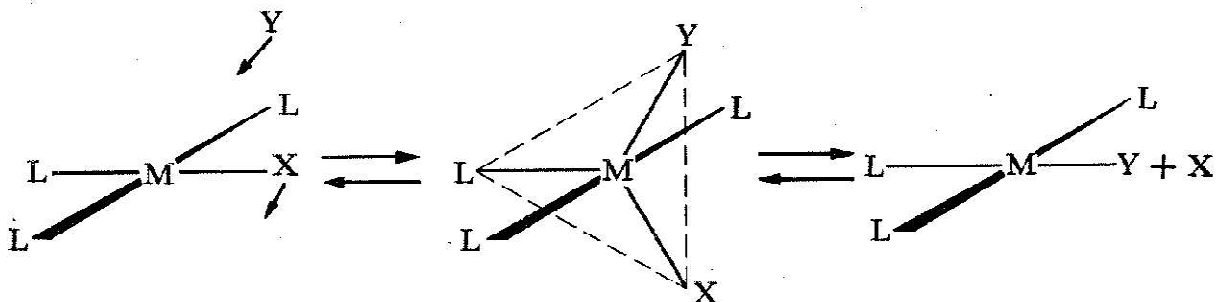
## SQUARE PLANAR COMPLEXES and TRANS EFFECT

### Model for square-planar substitutions

#### Steric Course

Of the important metal-complex geometries, the square-planar structure is best suited for substitutions by a pathways, since there are two coordination positions open for the attack of an incoming group. From purely steric considerations, the geometry of the transition state is expected to be approximately trigonal bipyramidal, since this arrangement minimizes the mutual repulsions of the five ligands. A square pyramidal structure is another reasonable possibility for the transition state. It should be noted, however, that the difference between an "approximate trigonal bipyramid" and an "approximate square pyramid" may be vanishingly small.

Since the steric factors are so favorable for associative activation, we shall develop an associative mechanism via a trigonal-bipyramidal intermediate as the most reasonable model for square-planar substitutions. This process is shown in the Figure. Although a two-step stoichiometric associative mechanism may not operate in every case, the five-coordinate intermediate should serve as a useful model of the transition state in substitutions which are better designated  $I_a$ .



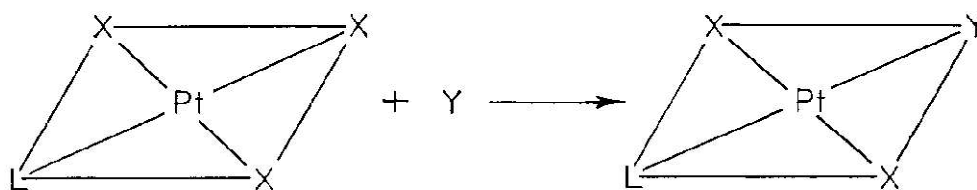
Associative mechanism for square-planar substitutions via a trigonal-bipyramidal intermediate

### Syntheses of Platinum (II) Complexes

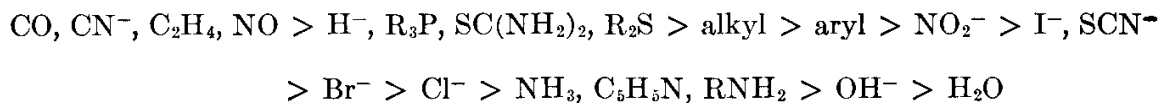
Square planar complexes are largely found among the low-spin  $d^8$  system, examples of which are provided by the triad Ni(II), Pd(II), and Pt(II). Compounds of the same type are also formed by Rh(I), Ir(I), Ag(III), and Au(III). The *trans* effect may be described as the influence which a ligand has on the ease of replacement of a group in the *trans* position. Thus, for a reaction of the

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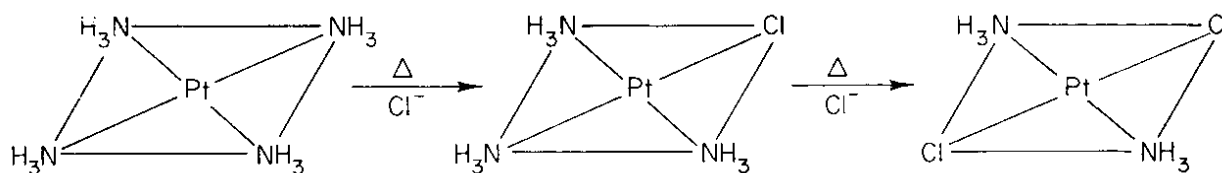
type shown L is said to have a large *trans* effect if the reaction is fast but a small *trans* effect if the reaction is slow.



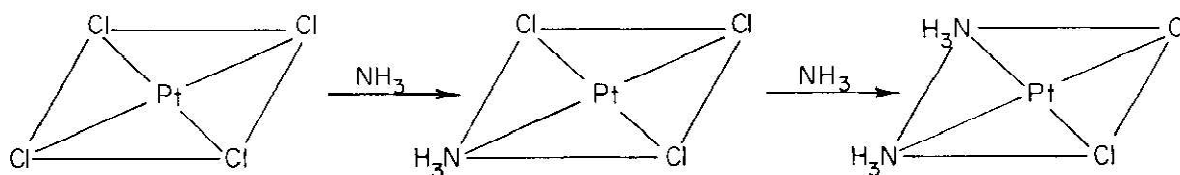
Many qualitative and some quantitative observations now show that the *trans* effect of L decreases in the order:



Since the *trans* effect order is  $\text{Cl}^- > \text{NH}_3$ , *trans* and *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  are prepared by the following procedures. Starting with the tetraammine, and in the final step the ammonia opposite chloride ion was more readily replaced yielding the *trans* isomer.



Instead starting with the tetrachloro complex, the *cis* isomer is obtained because of the greater reactivity of the chlorides opposite each other than that opposite ammonia in the final step.

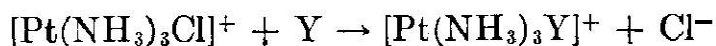


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By a judicious application of this principle it has been possible to prepare many different geometric isomers of platinum(II) complexes, including the three possible isomers of complexes containing four different ligands such as  $[\text{PtNH}_3\text{pyNO}_2\text{Cl}]$ . In addition, Kurnakov noted that *cis*- $[\text{PtA}_2\text{X}_2]$ , where A is ammonia or an amine and X is a halide ion, reacts with thiourea (tu) to yield  $[\text{Pt}(\text{tu})_4]^{2+}$ . Under similar experimental conditions the reaction product for the *trans* isomer is *trans*- $[\text{PtA}_2(\text{tu})_2]^{2+}$ . It is suggested that the large *trans* effect of thiourea results in the ready replacement of the A groups *trans* to it in the initially formed *as*- $[\text{PtA}_2(\text{tu})_2]^{2+}$ . For the *trans* isomer the A groups are *trans* to each other and therefore not activated by the coordinated thiourea. This difference has been used, particularly by Russian chemists, to distinguish between *cis* and *trans* isomers, and the method is called **Kurnakov's test**.

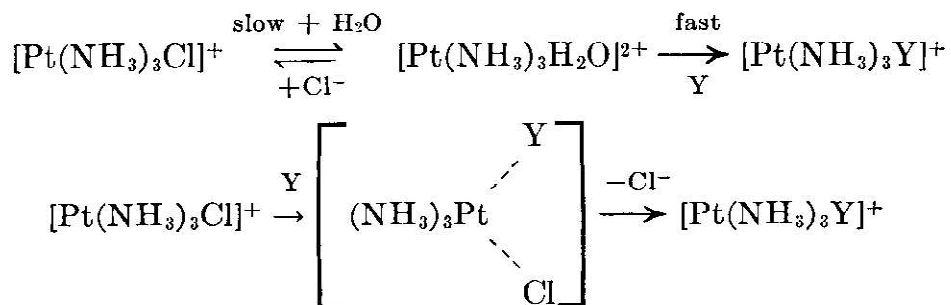
### Mechanism of Nucleophilic Displacement Reactions in square planner complexes

Detailed kinetic studies have been made on the reaction of several different platinum(II) complexes with a variety of different reagents. These results all show that the reactions are of the  $\text{SN}_2$  type. A two-term rate law is generally observed for a reaction of the type represented. The rate law has a term zero-order in Y and one first-order in Y.



$$\text{rate} = k_{\text{H}_2\text{O}}[\text{Pt}(\text{NH}_3)_3\text{Cl}^+] + k_{\text{Y}}[\text{Pt}(\text{NH}_3)_3\text{Cl}^+][\text{Y}]$$

This result is explained on the basis of a water (or other solvent) path where the rate does not depend on Y, and a direct displacement path which does depend on the entering nucleophile.



Both the reaction with the solvent and that with the nucleophile are believed to proceed by an  $\text{SN}_2$  mechanism. This is surely true for the direct displacement path which is first-order in the entering ligand. It is also in accord with the observation that the rates of hydrolysis (as well as

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chloride ion exchange) are very similar for the series of complexes  $[\text{PtCl}_4]^{2-}$  through  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ . That the charge on the complex has little effect on its rate of reaction suggests there are compensating opposing effects. Thus a charge neutralization process (bond making) is enhanced by a large positive charge on the complex and retarded by a negative charge; the reverse is true for a charge separation process (bond breaking) which is enhanced by a negative charge on the complex and retarded by its increasing positive charge. For an  $\text{SN}_2$  process where bond making and bond breaking are of comparable importance in the transition state, it is expected that the opposing effects of the charge on the complex will cancel and the rates of reaction will be mostly insensitive to the charge on the complex. This is not true for an  $\text{SN}_1$  type reaction, as would appear from the fact that  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  reacts a thousand times faster than does  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ .

There are yet other reasons for assigning an  $\text{SN}^2$  label to reactions of platinum (II) complexes. For example, its reactivity with different reagents can adequately be explained on the basis of the nature of the reagent in terms of the current theories of bonding in these systems. Likewise, both for steric and electronic reasons it is known that the coordination number of square complexes is readily expanded to five or six, supporting the plausibility of a low energy bimolecular reaction path.

### Factors Which Affect The Rate Of Substitution

- i). Role of the Entering Group
- ii). The Role of The Leaving Group
- iii). The Nature of the Other Ligands in the Complex
- iv). Effect of the Metal Centre

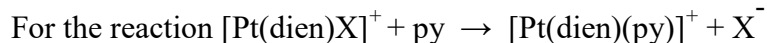
#### i). Role of the Entering Group

The rate of substitution is proportional to the nucleophilicity of entering group i.e. for most reactions of Pt(II), the rate constant increases in the order:  $\text{H}_2\text{O} < \text{NH}_3 = \text{py} < \text{Br}^- < \text{I}^- < \text{CN}^-$

The ordering is consistent with Pt(II) being a soft metal centre.

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## ii). The Role Of The Leaving Group



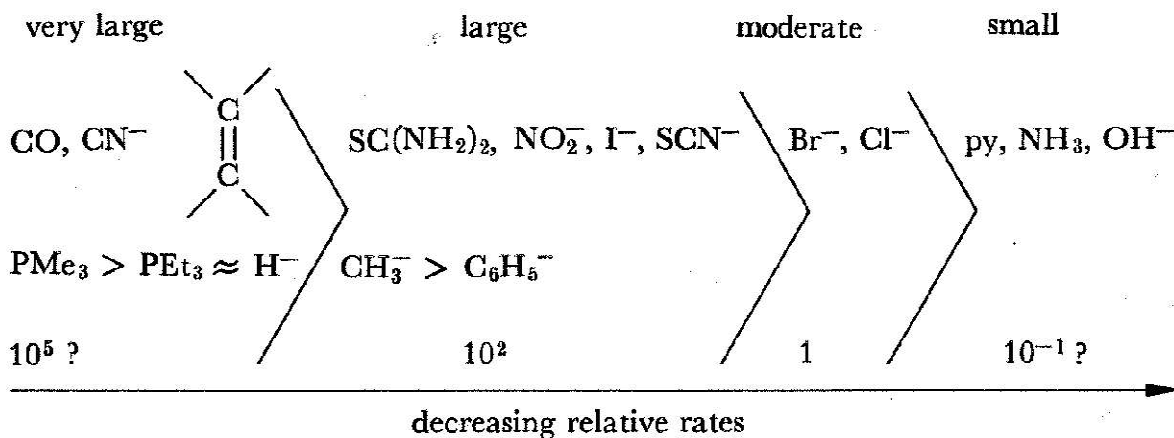
In H<sub>2</sub>O at 25 °C the sequence of lability is; **H<sub>2</sub>O** > **Cl<sup>-</sup>** > **Br<sup>-</sup>** > **I<sup>-</sup>** > **N<sub>3<sup>-</sup></sub>** > **SCN<sup>-</sup>** > **NO<sub>2<sup>-</sup></sub>** > **CN<sup>-</sup>** with a spread of over 10<sup>6</sup> in rate across series. The leaving group does not affect the nucleophilic discrimination factors only the intrinsic reactivity. The series tend to parallel the strength of the Metal-L bond.

## iii) The Nature of other Ligands in the Complex

### Trans Effect

The kinetic trans effect in square-planar substitutions, first recognized by Werner and elaborated on by Chernyaev refers to the special effects of trans substituents on the lability of a leaving group. Of all the specific ligand effects in metal complex substitution reactions, the trans effect is probably the most dramatic, spanning several orders of magnitude in rate. Although the trans-effect order of ligands is undoubtedly dependent to some extent on the substrate, the generally accepted "average" order is in the table below.

### Trans effect order



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Rate data are now available on the *trans* labilizing influence of various ligands in reactions of platinum(II) complexes. Some of this information is summarized in Table The quantitative results are generally in agreement with previous qualitative observations made on the basis of syntheses and reactions of these systems.

TRANS EFFECT ON THE RATES OF REACTION OF SOME Pt(II) COMPLEXES WITH PYRIDINE AT 25°C<sup>a</sup>

Compound	Ligand	$k$ (sec <sup>-1</sup> M <sup>-1</sup> )
$\begin{array}{ccc} \text{L} & & \text{NH}_3 \\ & \diagdown & / \\ & \text{Pt} & \\ & / & \diagdown \\ \text{Cl} & & \text{Cl} \end{array}$	Cl Br NO <sub>2</sub> C <sub>2</sub> H <sub>4</sub>	6.3 × 10 <sup>-3</sup> 18 × 10 <sup>-3</sup> 56 × 10 <sup>-3</sup> Very fast
$\begin{array}{ccc} \text{L} & & \text{PEt}_3 \\ & \diagdown & / \\ & \text{Pt} & \\ & / & \diagdown \\ \text{Et}_3\text{P} & & \text{Cl} \end{array}$	H PEt <sub>3</sub> CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> Cl	1.8 × 10 <sup>-2</sup> 1.7 × 10 <sup>-2</sup> 1.7 × 10 <sup>-4</sup> 3.3 × 10 <sup>-5</sup> 1 × 10 <sup>-6</sup>

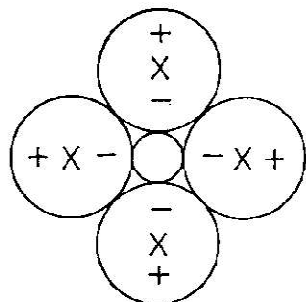
<sup>a</sup> Data taken from Zvyagintsev and Karandosheva (1955) and Basolo *et al.* (1961).

For the complex [PtNH<sub>3</sub>LCl<sub>2</sub>], where L is *trans* to the Cl<sup>-</sup> that is being replaced, the data show a *trans* effect ratio for Cl<sup>-</sup>: Br<sup>-</sup>: NO<sub>2</sub><sup>-</sup>: C<sub>2</sub>H<sub>4</sub> of approximately 1:3:9: > 100. For the compound *trans*-(Pt[P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>LCl), the relative labilizing influence of L is given by the approximate ratio 1:30:170:17,000:18,000 for Cl<sup>-</sup>: C<sub>6</sub>H<sub>5</sub><sup>-</sup>: CH<sub>3</sub><sup>-</sup>: P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>: H<sup>-</sup>, respectively. Attempts have been made to explain the *trans* effects of different ligands on the basis of one unified theory. However, in order to account for all of the known facts, currently two theories are used. The *polarization* theory is applied to non- $\pi$ -bonding ligands such as F<sup>-</sup>, H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>3</sub><sup>-</sup>, and H<sup>-</sup>, whereas the  $\pi$  bonding theory is applicable to ligands such as C<sub>2</sub>H<sub>4</sub>, CO, PR<sub>3</sub> etc. There is, as expected, no definite line of demarcation between these extreme ligand types, so that borderline cases such as the halide ions do exist.

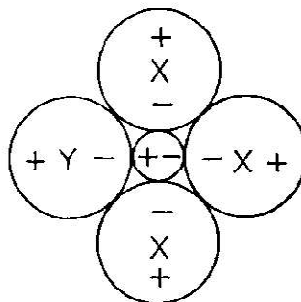
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## Polarization Theory

For explaining the kinetic *trans* effect in square planar Pt(II) complexes



(a)



(b)

Grinberg's polarization *trans* effect theory, (a) Symmetrical induced dipoles in square  $\text{MX}_4$ . (b) Unsymmetrical induced dipoles in  $\text{MX}_3\text{Y}$ , where the induced dipole of Y is greater than that of X; thus bond  $\text{M}-\text{X}$  *trans* to Y is weakened.

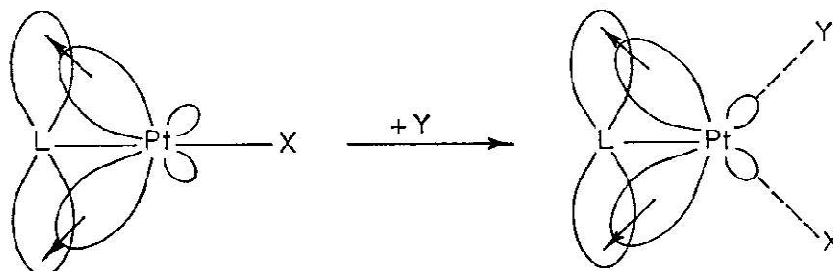
Grinberg's polarization *trans* effect theory requires that the metal ligand bond strength for the leaving group be weakened by a ligand in the *trans* position of high *trans* effect. This can best be understood by considering the figure. Since ligand L is more polarizable than X, the electron cloud of L is distorted more towards the central metal ion, causing its electron cloud to distort directly away or in the direction of the ligand in *trans* position. Thus, the greater the polarization of L, the greater it polarizes the metal, which puts a greater electron density in the *trans* position and results in a weakening of the metal-ligand bond. This then explains the *trans* effect order of  $\text{I}^- > \text{Br}^- > \text{Cl}^-$  which is also the order of decreasing polarizability of the halide ions.

## $\pi$ -bond theory

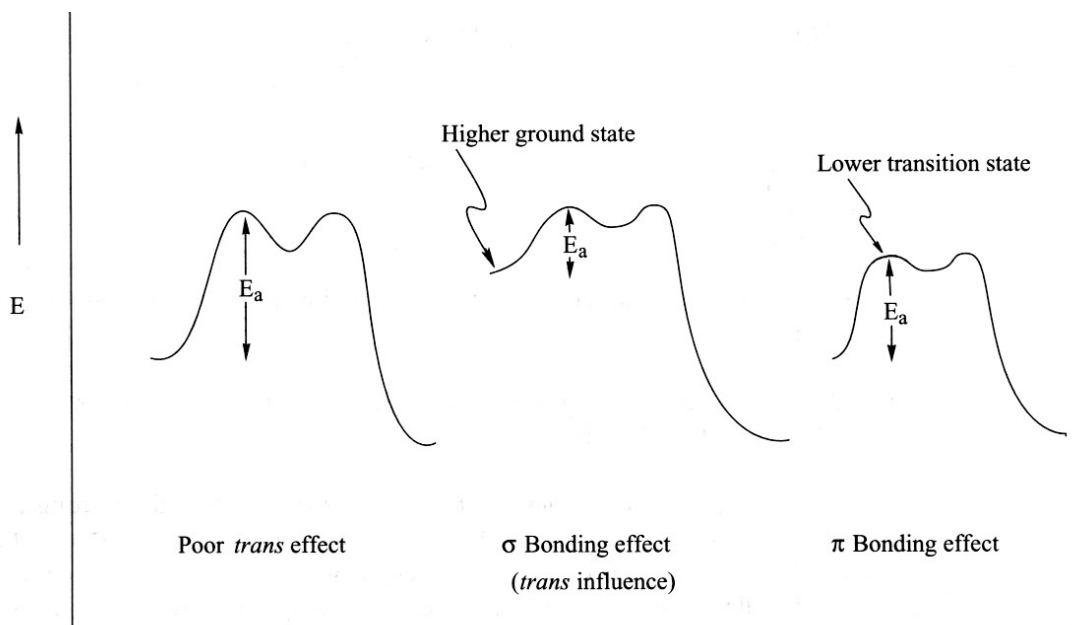
The  $\pi$ -bond theory of Chatt and Orgel explains the large *trans* directing influence of ligands such as  $\text{CH}_2=\text{CH}_2$ ,  $\text{CN}^-$ , CO,  $\text{PR}_3$ , and  $(\text{NH}_2)_2\text{CS}$ . These ligands all have the ability to  $\pi$ -bond with the metal by the backdonation of electrons from the filled nonbonding  $d$  orbitals on the metal into vacant orbitals on the ligand,  $\text{M} \rightarrow \text{L}$ . The stabilizing influence that such a delocalization of nonbonding electron density towards the ligand has on the five-coordinated state proposed for reactions in these systems is shown in Figure. If ligand L *trans* to the departing group X does not  $\pi$ -bond, then the electron density near the entering Y and departing X is high and the transition state is less stable than if this electron cloud were not present. It follows that this electron cloud can be largely removed by its delocalization towards a  $\pi$  bonding ligand L which is in the same trigonal plane as that of the attacking and leaving groups. This then stabilizes the transition state

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more than it does the ground state so that the difference in energy between the two is less than a system with no  $\pi$  bonding, and because of this smaller activation energy the reaction is faster. It is certainly well recognized that  $\pi$ -bonding ligands stand very high in the *trans* effect series.



*Trans* effect of  $\pi$ -bonding ligand L which stabilizes the five-coordinated transition state for the displacement of X by Y in *trans*-  $[\text{PtA}_2\text{LX}]$ .



Activation energy and the *trans* effect