CHAPTER 4

Reaction Mechanism of Transition Metal Complexes – II:

❖ Mechanism of Ligand Displacement Reactions in Square Planar Complexes

The ligand displacement in square-planar complexes is much more favorable via the associative pathway than that of the dissociative one which can be explained in terms of low steric crowding due to the lesser coordination number. In order to understand this claim, consider the general ligand displacement in square planar complexes:

$$MA_3L + E \longrightarrow MA_3E + L \quad (1)$$

Now, if the concentration of the entering ligand E is very large, the observed pseudo first-order rate law for the above reaction can be given by:

$$\text{Rate} = k_1[MA_3L] + k_2[MA_3L][E] \quad (2)$$

On rearrangement

$$\text{Rate} = (k_1 + k_2[E])\,[MA_3L] \quad (3)$$

or

$$\text{Rate} = k_o[MA_3L] \quad (4)$$

Where k_o is the observed rate constant and is equal to

$$k_o = k_1 + k_2[E] \quad (5)$$

The value of k_1 and k_2 can be calculated from the intercept and slope of the plot of the observed rate constant vs concentration of the entering group E. It has been observed that, for all type of entering ligands, the values of both k_1 and k_2 are nonzero which suggests a possibility of dissociative pathway too.

➢ *Solvent Assisted SN_2 Pathway*

The non-zero value of k_1 can also be interpreted in some other form of the associative pathway in which the solvent molecules also act as the nucleophile and compete with E to form MA_3S. The following process is responsible for the first term in equation (2).

$$MA_3L + S \underset{-L}{\overset{k_1}{\longrightarrow}} MA_3S \underset{-S}{\overset{+E}{\longrightarrow}} MA_3E \quad (6)$$

Now, as the concentration of the solvent is practically constant, the rate of the reaction depends upon the concentration of MA_3L only and becomes of first-order kinetics.

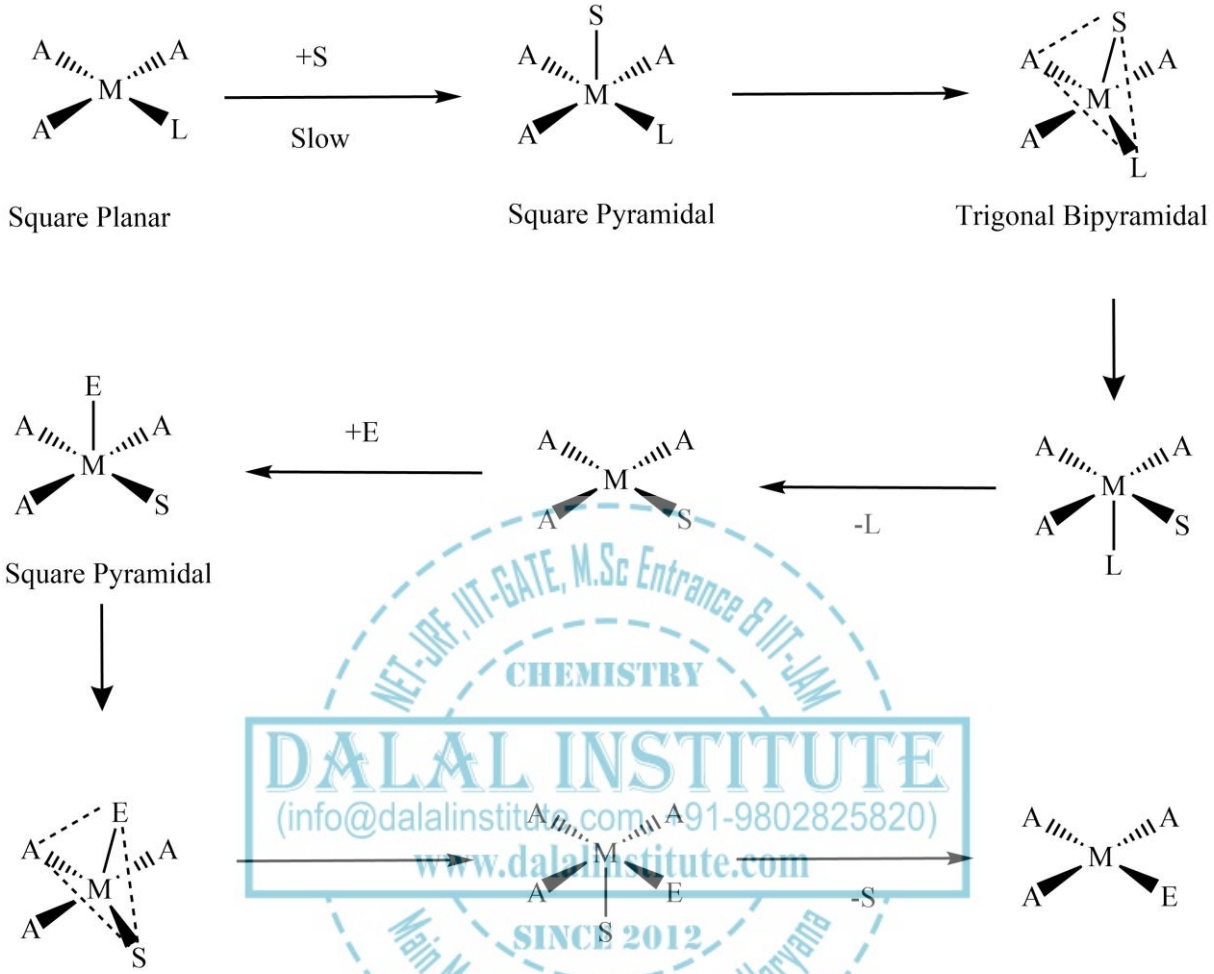

Figure 1. The systematic mechanism of solvent-assisted ligand displacement reactions in square planar complexes.

- ***Normal SN_2 Pathway***

The non-zero value of k_2 can be explained in terms of the normal associative route in which the entering ligand replaces the leaving group via a five-membered transition state. The reaction scheme can be shown as:

$$MA_3L + E \underset{-L}{\overset{k_2}{\longrightarrow}} MA_3E \qquad (7)$$

It has also been observed that the rate of the direct associative route is generally higher than the rate via solvent assistance. Moreover, the rate has also been found dependent on the nucleophilicity of the solvent suggesting a key role of the solvent attack in ligand displacement.

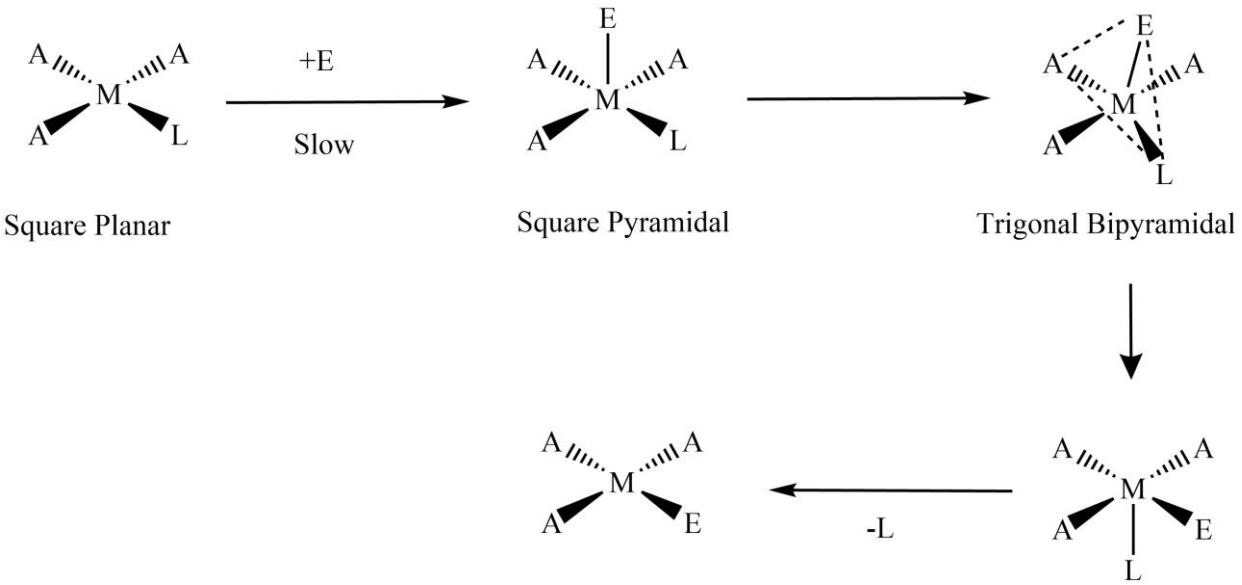

Figure 2. Mechanism of ligand displacement in square planar complexes via normal associative pathway.

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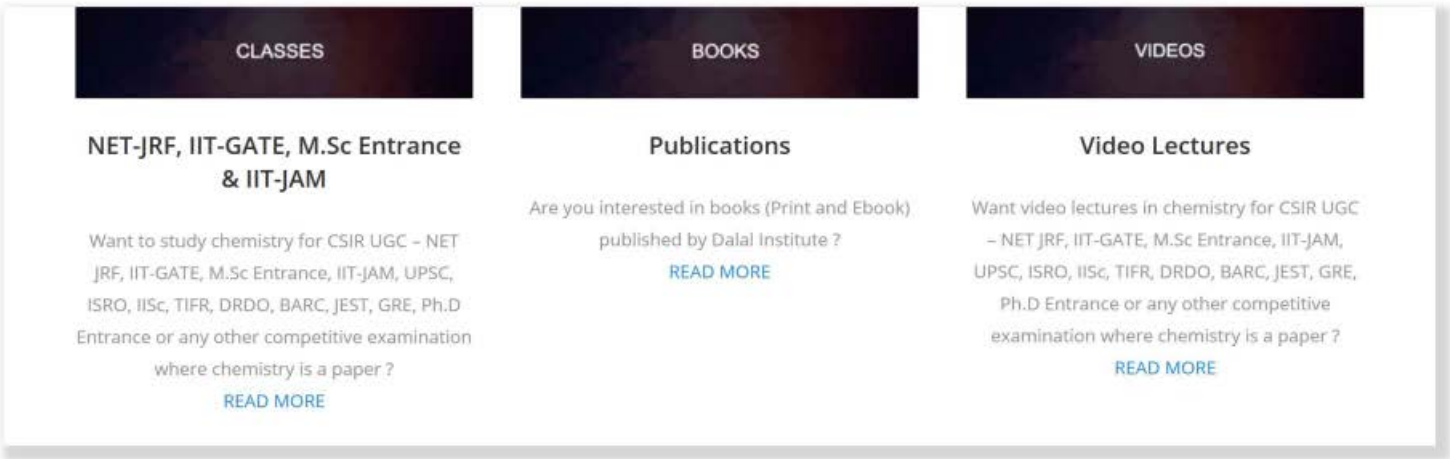

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