

❖ Theories of Trans Effect

Owing to the kinetic nature of the trans-effect, it is quite sensible to think of activation energy in terms of the ground state (the complex before substitution) as well as activated complex. Hence, all the factors which can affect the energy of the ground state or activated complex are expected to have a profound effect on the activation energy of the ligand displacement reaction and thus expected to govern the trans effect of the attached groups. The two theories which are sought for the explanation of trans-effect are given below.

➤ *The Polarization Theory*

This theory mainly deals with the ground state of the complex and proposes that the metal center has a tendency to induce a dipole moment in the surrounding ligands by polarizing them according to Fajans' rule. In the case of MA_4 type complexes, metal ion induces an equal dipole moment in all the four surrounding ligands which are, in turn, cancel out each other due to square-planar geometry. However, in the case of MA_3B type complexes, the situation is quite different as the polarizability of all the four ligands is not anymore, the same. If the polarizability of B type ligand is higher than that of A-type then the primary charge of the metal ion will polarize the electronic cloud of A more effectively and thus will induce a strong dipole moment in A-type ligand. Furthermore, this dipole moment is also bound to induce an alternate dipole in the metal center also. The orientation of this dipole is such that it repels the negative charge on the ligand, A-type, situated trans to B. This results in the weakening and consequently lengthening of the metal-ligand bond trans to the B-type group. Therefore, according to this concept, the trans effect is directly proportional to the polarizability of the ligand. It is also worth noting that the trans-effect is more prominent with a large and more polarizable metal center. The general order can be given as $Pt(II) > Pd(II) > Ni(II)$.

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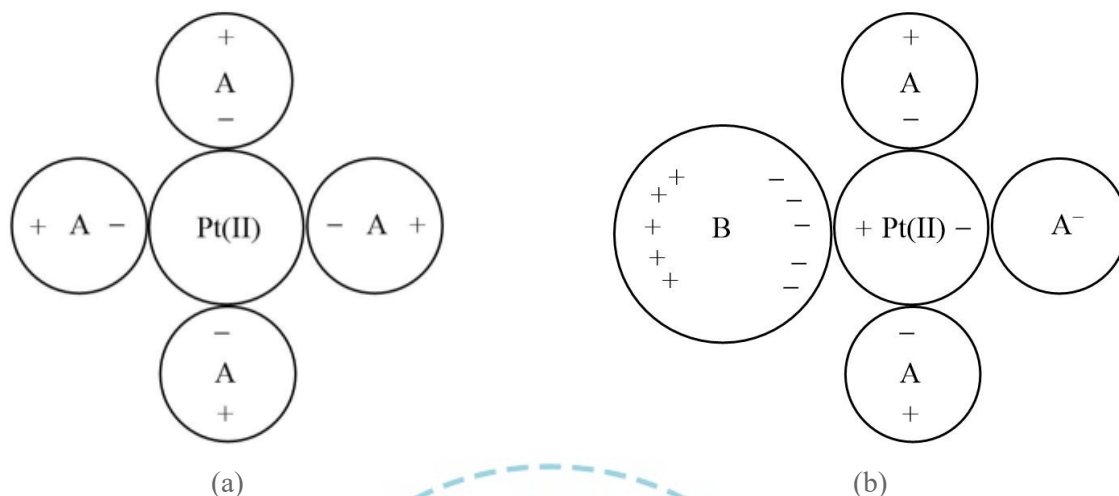


Figure 12. The effect of polarization in (a) MA_4 and (b) MA_3B complexes.

➤ The π -Bonding Theory

The nature of the trans-effect is electronic instead of steric which clearly means that the electronic profile of the ligand is primarily governing trans-effect strength of various groups. Considering the trans-effect order of halide ions, $I^- > Br^- > Cl^- > F^-$, it seems that the increasing electronegativity makes them poor σ -donor or σ -base which in turn also decreases their trans-effect strength. However, the exceptionally high trans-effect of the ligands like CO, C_2H_4 or PR_3 cannot be explained by σ -donation ability as they are not very good σ -donor but π -acceptor in nature. Therefore, we can conclude that a stronger trans-effect is the combination of both, either it should be a strong σ -base or it should show a good π -acid character.

Now, in order to understand the whole process by which the trans-directing groups speed-up the ligand displacement in square-planar complexes, we will have to recall the mechanism of ligand substitution. Let T be the trans-directing group, L as the leaving group and E as the entering group. The entering ligand binds to 16-electron Pt(II) complex to form 18-electron complex which in turn again converted into a new 16-electron complex as:

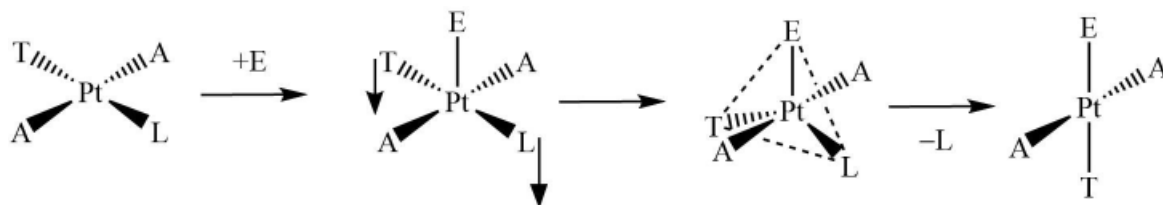


Figure 13. The mechanism of associative ligand substitution of Pt(II) complexes.

The characteristic features of this mechanism are:

- i) The entering ligand always sits at the equatorial position of the activated complex which is trigonal-bipyramidal in nature.
- ii) The trans-directing group and the leaving group are pushed down to create the equatorial plane of the activated complex.
- iii) As the entering group E attacks at the equatorial site, the leaving must also be from the equatorial plane; which is followed directly from the principle of microscopic reversibility.

The rate-determining step is when the entering ligand “E” pushes down the trans-director T and the leaving group L. Now as the equatorial sites of the trigonal-bipyramidal intermediate are richer in electron density than the axial ones, ligands with greater π -acidity like to be pushed down to get this privilege of stronger back-bonding. This forces the leaving group “L” to no other choice but to detach from the activated complex.

The transition state is stabilized by the overlap of empty π^* orbital of “T” and the filled d_{xz} orbital of the metal center. This results in a decrease in the electron density in metal-leaving group bond which makes the displacement of L by E much easier.



Figure 14. The transition state of Pt(II) complexes is stabilized by the overlap between empty π^* orbital of the trans-directing group and filled d_{xz} orbital of Pt(II) metal center.

Thus, the stronger trans-effect of π -acid ligands is explained in terms of the stabilization of the activated complex (which in turn decreases the activation energy). However, it has also been observed that the bond length between metal ion the leaving group is generally larger than the expected values when ligands with strong trans-effects are there. This suggests that these π -acid ligands affect the ground state as well and a combination on both contributes to the over trans-effect strength.

In addition to the polarization theory, the trans-effect strength of σ -donor ligands can also be explained in the activated complex framework. It can be assumed that trans-directing group T and leaving

group L are in direct competition for the σ -donation to the same metallic d-orbital. Thus, the greater σ -donation ability of the trans-director weakens the opposite bond. Though the effect is thermodynamic in nature (trans-influence), the destabilization of the ground state decreases the value of activation required for the ligand substitution making it a kinetic phenomenon too. In other words, the strong σ -donors will decrease the height of the activation barrier and consequently increase the rate of ligand displacement reactions in transition metal complexes with square-planar geometry.

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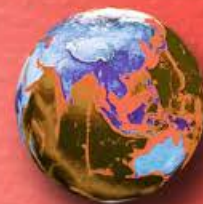
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