❖ The Trans Effect

The tendency of an already attached group to direct the incoming ligand to its trans position in ligand displacement reactions in square-planar complexes is called as the trans effect and such groups are labeled as the trans-directing ligands.

It is worthy to mention that various ligands have different trans directing effects and when these ligands are arranged in increasing order of their trans effect, the order is termed as the trans-effect series which is given below.

$CN^- > C_2H_4 > CO > NO > SCN^- > I^- > Br^- > Cl^- > Py > NH_3 > OH^- > H_2O$

In other words, the trans-effect may also be defined as the labilization (the easier displacement) of the ligands trans to other trans-directing ligands. Moreover, the trans-directing ligands are also called as the spectator ligands as they are neither the entering nor the leaving group yet affect the rate of the ligand substitution considerably. Most of the people are actually quite confused about the nature of the trans-effect, weather is it kinetic or thermodynamic. The trans-effect may be classified into two types.

➢ *Kinetic Trans Effect or Trans Effect*

The kinetic trans-effect or trans-effect proper in square-planar complexes is the phenomenon in which certain ligands increase the rate of displacement of the ligands positioned trans to them. Now as this effect deals with the rate only, it must not be confused with trans-influence which involves a weakening of the trans bond and hence is thermodynamic in nature. If E is the entering ligand, T_1 and T_2 as the trans-directing groups, k_1 and k_2 as the rate constants and L is the leaving group; the process can be depicted as:

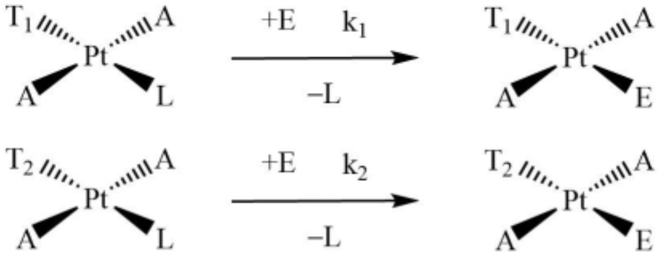


Figure 3. Kinetic trans-effect in action with $k_2 >> k_1$ showing that T_2 ligand is having greater trans-effect strength than T_1.

➢ ***Thermodynamic Trans Effect or Trans Influence***

The thermodynamic trans-effect or trans influence may be defined as the impact of a ligand on the length of the bond trans to it in the ground state of a square-planar complex. Like trans-effect, trans-influence is also independent of metal ion but depends primarily upon the geometry of the metal center.

Figure 4. Thermodynamic trans-effect in action showing that T_2 ligand is having greater trans-influence strength than T_1.

It can be seen very clearly that elongation of trans-bond-length is done more profoundly by T_2 than T_1; which infer that the thermodynamic trans-effect of T_2 ligand is higher than T_1.

➢ ***Applications of the trans effect***

1. Synthesis of the cis and trans platin: $[PtCl_2(NH_3)_2]$ exists in two isomeric forms as given below.

(a) (b)

Figure 5. (a) cis-$[PtCl_2(NH_3)_2]$ (b) trans-$[PtCl_2(NH_3)_2]$

These two isomers can be synthesized via a number of number chemical routes by exploiting the trans effect. However, the most common are given below.

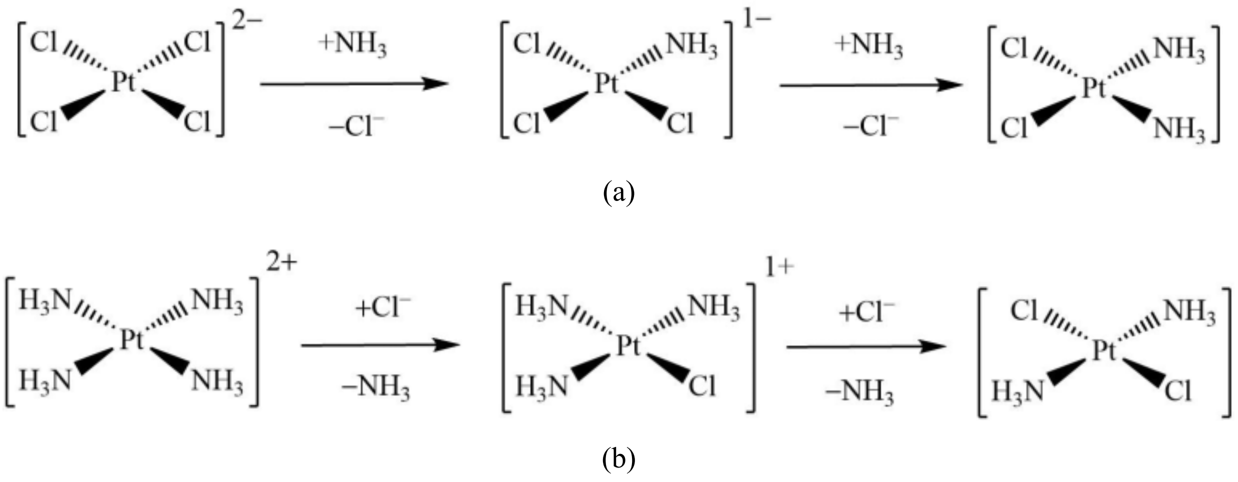


Figure 6. The general synthesis route for the preparation of cis-$[PtCl_2(NH_3)_2]$ or cis-platin and Trans-$[PtCl_2(NH_3)_2]$ or trans-platin complexes.

The initial raw materials for the synthesis of isomeric forms are different as the Cl^- has a higher trans effect than NH_3. Hence, the trans effect plays a major role in product formation. It is worth noting that the cis-platin is having very important therapeutic uses in the treatment of cancer.

2. Synthesis of the isomers of [Pt(Cl)(NH₃)(Br)(Py)]: The $[Pt(Cl)(NH_3)(Br)(Py)]$ complex can exist in three different isomeric forms which can successfully be synthesized by using the trans-effect order of the participating ligands.

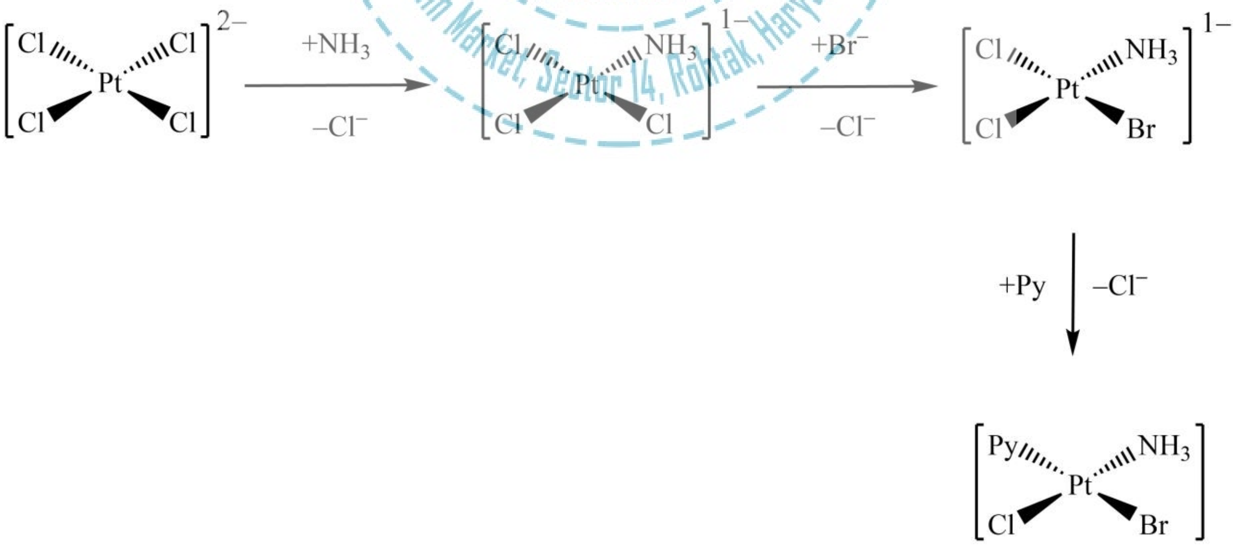


Figure 7. Continued on the next page…

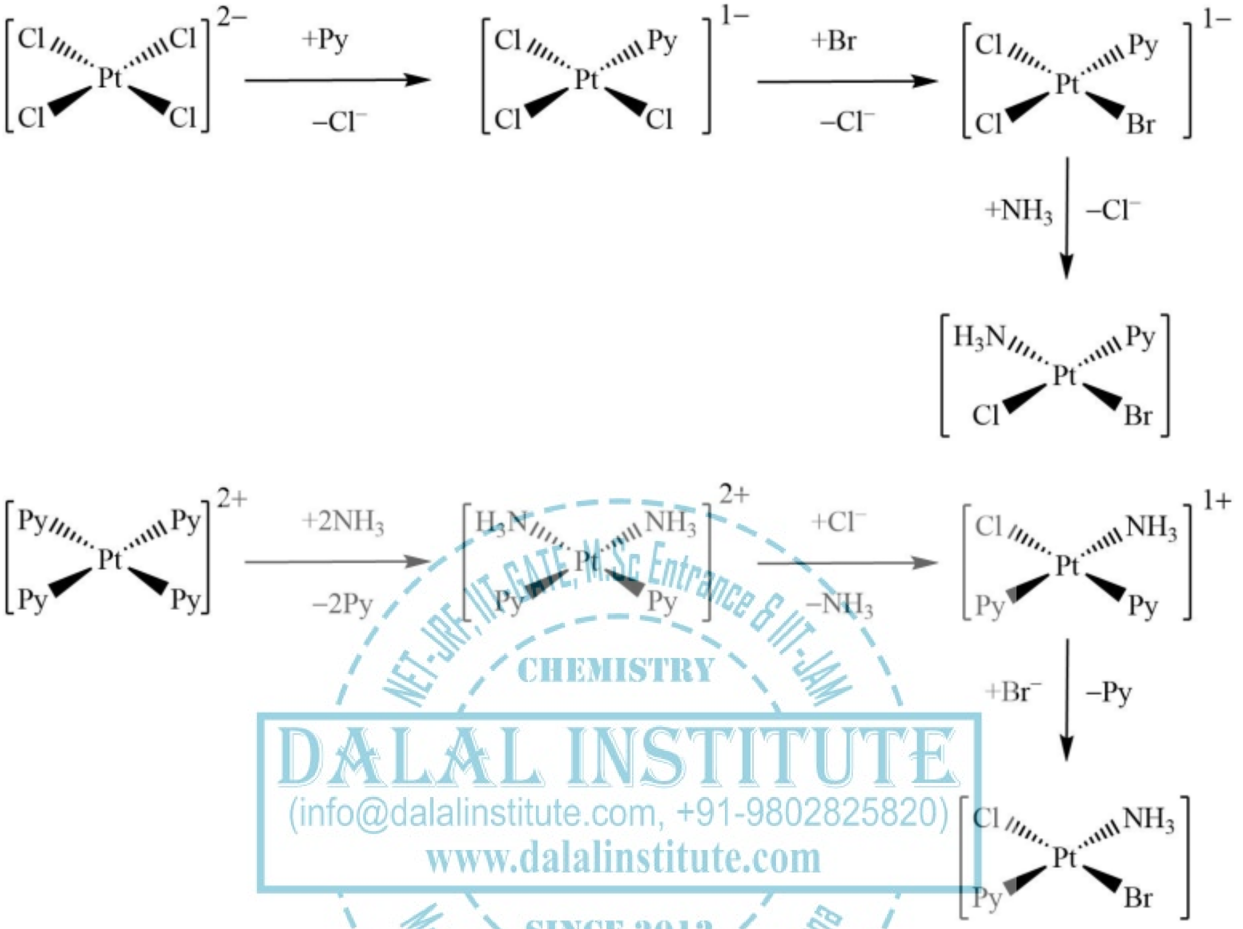


Figure 7. Synthesis route for $[Pt(Cl)(NH_3)(Br)(Py)]$ complexes.

3. Differentiating between cis and trans isomers of $[PtCl_2(NH_3)_2]$: A Russian scientist Kurnakov has used the trans effect to distinguish between the cis and trans platin. The experimental route he invented is named after him as the Kurnakov test in which thiourea is used as a primary component. The trans effect of thiourea is greater than chloride and amine ligands. The addition of thiourea to the trans platin results in the replacement of trans chloride ions and the reaction stops. However, when the thiourea is added to the cis isomer, all the four ligands are displaced and $[Pt(tu)_4]^{2+}$ is formed.

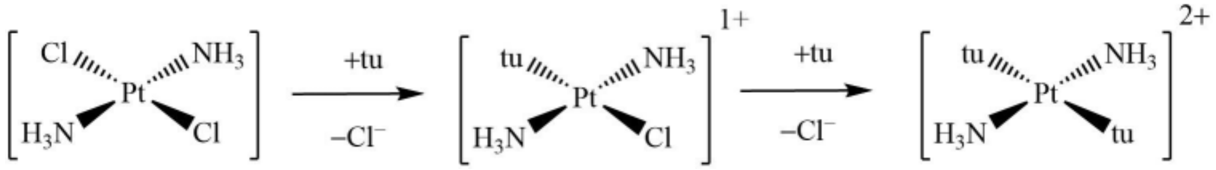


Figure 8. Continued on the next page…

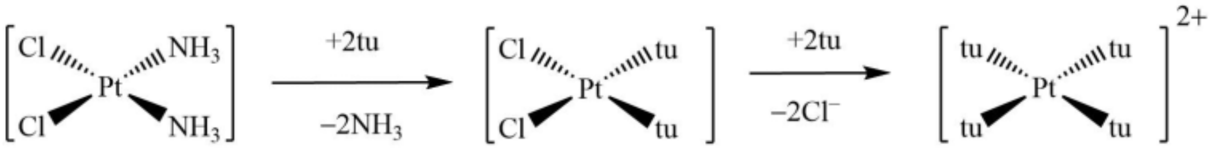
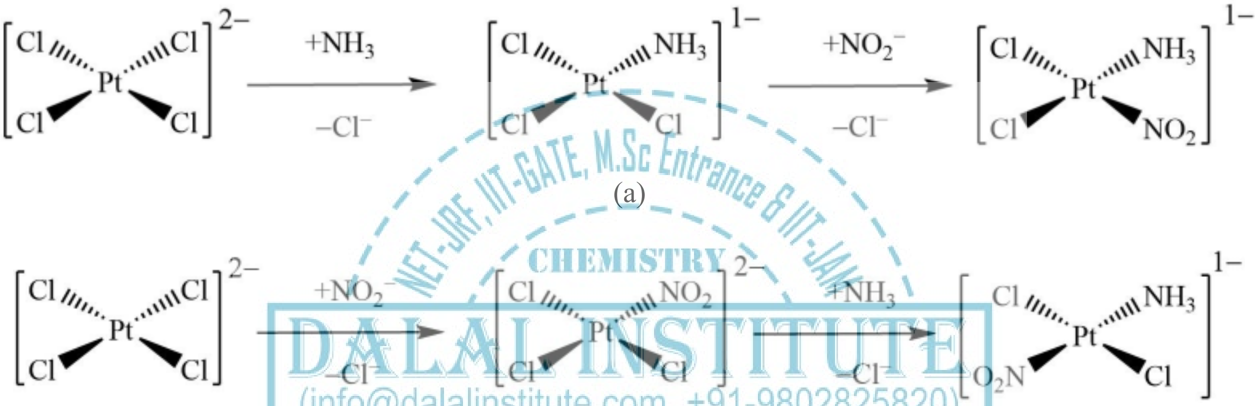


Figure 8. Differentiating route for cis and trans-platin complexes.

4. Synthesis of the isomers of $[Pt(NH_3)(NO_2)Cl_2]^{1-}$: The trans-effect order of the three groups in $[Pt(NH_3)(NO_2)Cl_2]^{1-}$ complex is $NO_2^- > Cl^- > NH_3$.



(a)

(b)

Figure 9. Synthesis route for (a) cis-$[Pt(NH_3)(NO_2)Cl_2]^{1-}$ and trans-$[Pt(NH_3)(NO_2)Cl_2]^{1-}$ complexes.

5. Synthesis of the isomers of $[Pt(C_2H_4)(NH_3)Cl_2]$: The trans-effect order of the three groups in $[Pt(C_2H_4)(NH_3)Cl_2]^{1-}$ complex is $C_2H_4 > Cl^- > NH_3$.

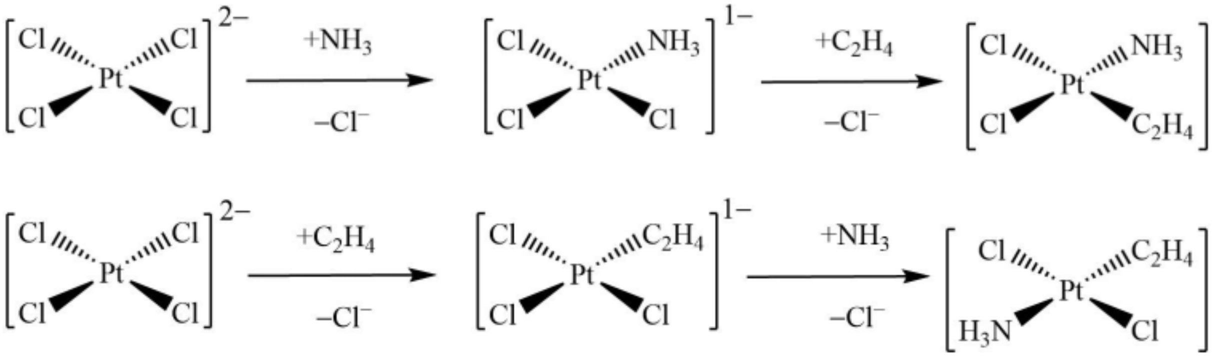
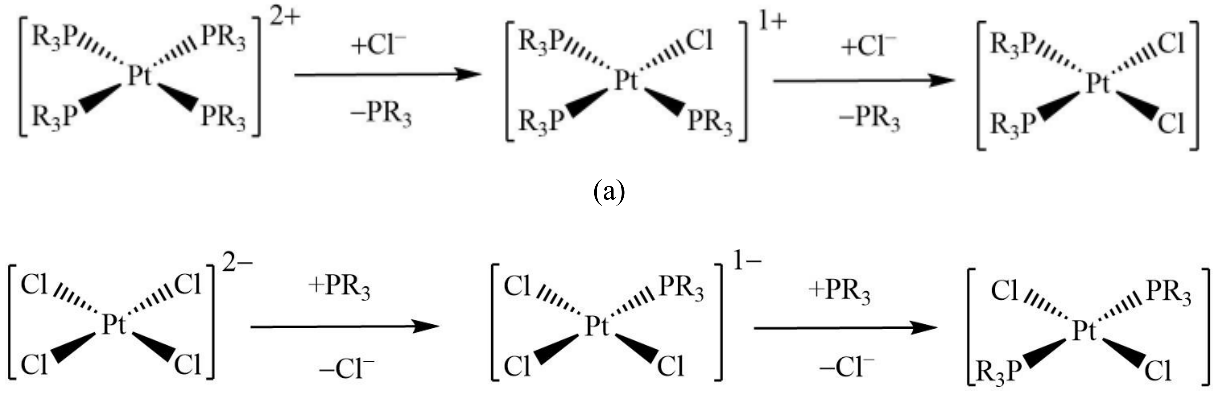


Figure 10. Synthesis route for (a) cis-$[Pt(C_2H_4)(NH_3)Cl_2]^{1-}$ and trans-$[Pt(C_2H_4)(NH_3)Cl_2]^{1-}$ complexes.

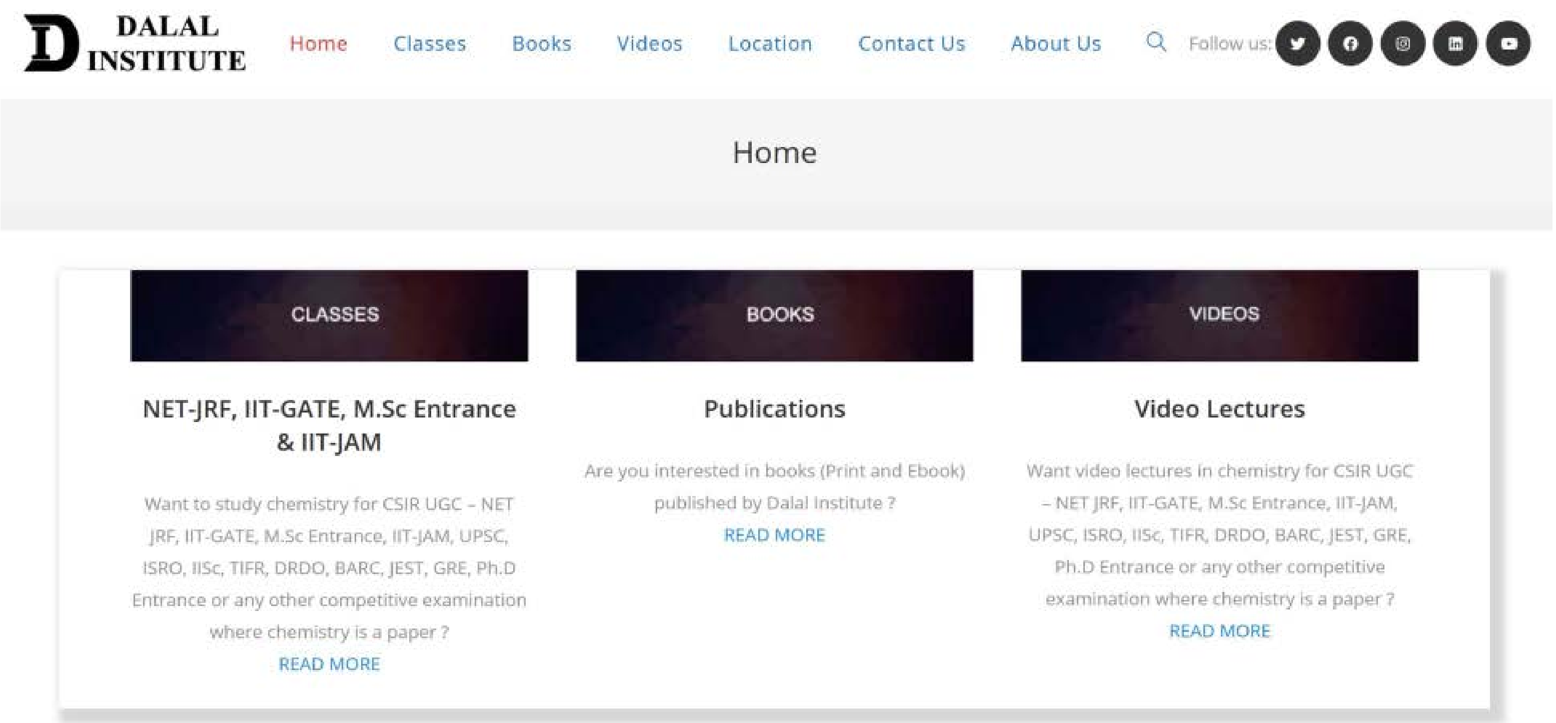
6. Synthesis of the isomers of [Pt(PR$_3$)$_2$Cl$_2$]: The trans-effect order of the two groups in [Pt(PR$_3$)$_2$Cl$_2$] complex is PR$_3$ > Cl$^-$.



(a)

(b)

Figure 11. Synthesis route for (a) cis-[Pt(PR$_3$)$_2$Cl$_2$] and trans-[Pt(PR$_3$)$_2$Cl$_2$] complexes.



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