# Advanced Transition Metal Chemistry – Inorganic Reaction Mechanisms
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## Lecture – 47
## Trans-Effect

Hello everyone. I once again welcome you all to MSB lecture series on transition metal chemistry. I am sure you are having good time reading chemistry and also enjoying life despite we have this COVID problem. Today, I shall discuss about another important topic in coordination chemistry, especially when it comes to the substitution reactions of square planar complexes, that is trans effect.

We all know that in case of square planar complexes, if you want to do substitution reaction, the preferred intermediate would be having a coordination number of 5, preferably having trigonal bipyramidal geometry. So, now let us see how this trans effect influences the entering ligand as well as leaving ligand, while we perform substitution reaction.

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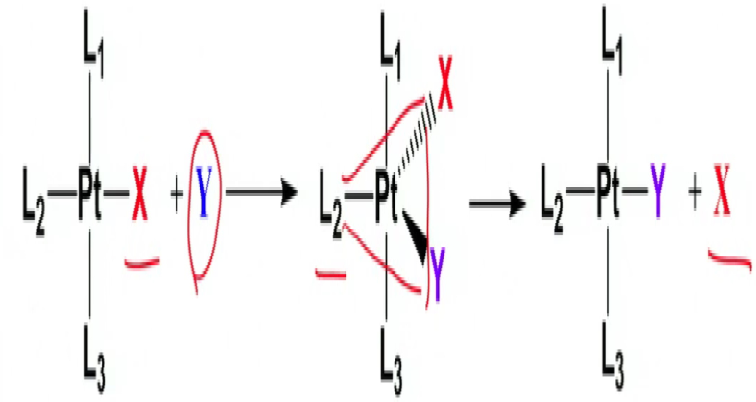

You know that as I already mentioned, when we perform substitution reaction on a square planar complex, the preferred one is an expanded intermediate that means coordination number having 5 and again the preferred geometry for that one is trigonal bipyramidal. So, in this one, I have shown here, X is the leaving group, and Y is the entering group here, and in the intermediate what happens one of the ligands, i.e. the leaving group and also the entering group will form this trigonal plane, and the other two become axial or apical.

And then once the elimination process is over, the X leaves and it will revert back to a square planar complex. And now depending upon the type of complexes we have, we can see geometric isomers, let us discuss now with this introduction. With this background, let us start looking into the trans effects.

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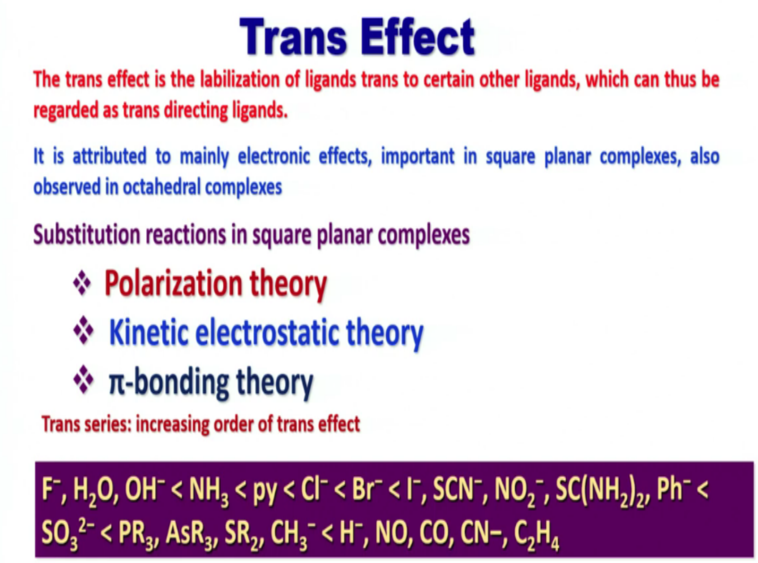

## Trans Effect

The trans effect is the labilization of ligands trans to certain other ligands, which can thus be regarded as trans directing ligands.

It is attributed to mainly electronic effects, important in square planar complexes, also observed in octahedral complexes

Substitution reactions in square planar complexes

- Polarization theory
- Kinetic electrostatic theory
- π-bonding theory

Trans series: increasing order of trans effect

$F^-, H_2O, OH^- < NH_3 < py < Cl^- < Br^- < I^-, SCN^-, NO_2^-, SC(NH_2)_2, Ph^- < SO_3^{2-} < PR_3, AsR_3, SR_2, CH_3^- < H^-, NO, CO, CN^-, C_2H_4$

So, what is trans effect? I already defined in several ways that trans effect is the labilization of ligands trans to certain other ligands, which can thus be regarded as trans directing ligands. That means, the labilizing effect of a ligand trans to itself or labilizing effect of a group trans to itself during substitution reaction to allow incoming ligand to a position trans to it, is called trans-effect.

That means, it is attributed to mainly electronic effects, important in square planar complexes and also observed to an extent in octahedral complexes. So, now as I mentioned earlier, we come across three classes of ligands. You recall my discussion about classification of ligands by donor atoms. So all ligands whatever we have at our disposal as coordination chemists or organometallic chemists, we have 3 types of ligands.

One is pure sigma donor ligands, that means they have low energy field sigma orbitals, they interact with metal orbitals to form sigma complexes. The other one is sigma donor and pi donor complexes. So, in this case, we have low energy filled sigma orbitals and low energy filled pi orbitals on entering ligands and these ligands would establish bonding with metals usually in high valent state, which are necessarily oxophilic or halophilic in nature, so that is called sigma donor and pi donor ligands.

The third one is sigma donor and pi acceptor ligands. In those cases, what we have is we have low energy filled sigma orbitals and high energy empty pi orbitals. So, they interact with appropriate metals to form this type of nonclassical complexes. So, now all these three classes of ligands would need three different type of trans theories to explain the substitution reactions.

So, those three here are: i) polarization theory, ii) kinetic electrostatic theory, and iii) pi bonding theory. And of course, you should remember, I did mention about the trans-effect order. So, this is the trans-effect series, you can see here. For example, if $OH^-$ is there, that can be readily replaced by $NH_3$ and it goes like this. Now, let us try to understand one theory at a time and which theory is applicable for what class of ligands.

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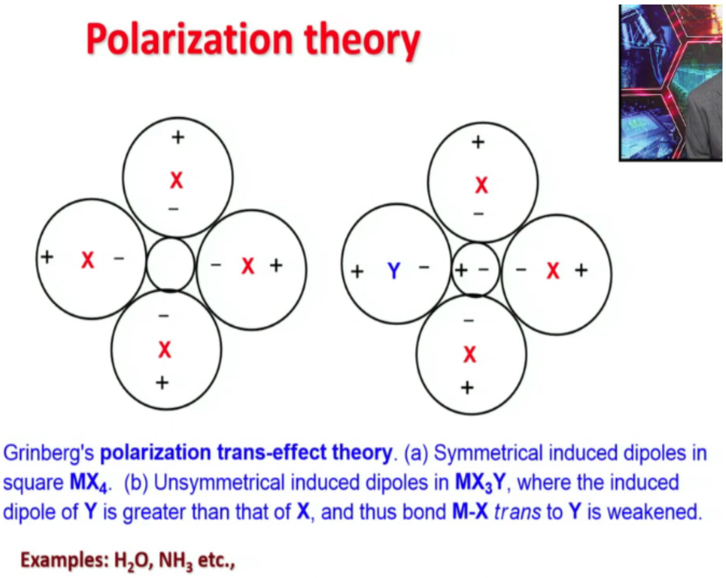

Polarization theory

Grinberg's **polarization trans-effect theory**. (a) Symmetrical induced dipoles in square **$MX_4$**. (b) Unsymmetrical induced dipoles in **$MX_3Y$**, where the induced dipole of **Y** is greater than that of **X**, and thus bond **M-X** *trans* to **Y** is weakened.

Examples: $H_2O$, $NH_3$ etc.,

Now, first is polarization theory. So, this was proposed by Grinberg, hence it is called Grinberg's polarization trans-effect theory. Here you can see I have written two diagrams. This is (a) diagram, and this is (b) diagram. The (a) diagram represent symmetrical induced dipoles in square planar complex of the type $MX_4$. That means, here all ligands are symmetrical and also we can see symmetrical induced dipole.

You should remember if there are neutral ligands and we have a cationic metal, according to crystal field theory the type of interaction we come across is ion dipolar interaction. Since it is based on electrostatic, so this is ion-dipolar. So, according to that one, if you see, if we consider four ligands which are symmetric, then the induced dipoles will be symmetric in all four directions.

So, in that case what happens we do not have any preferred elimination of one of the ligands, any ligand can go during substitution reaction. On the other hand, if you have unsymmetrical induced dipoles at metal centre, because of difference in the electronegativity of the ligands, then probably what we come across is unsymmetrical induced dipole that results in weakening of one of the bonds.

So, you can see here in case of this diagram, we see a 3 X ligands are there and 1 Y ligand is there here, and if we assume Y is stronger ligand in that case what happens it induces polarity or it polarizes the metal centre also and as a result metal will be having dipoles like this plus and minus, if the stronger ligand would have positive so that this bond is stabilized due to electrostatic interaction minus and plus, whereas here this one will be having negative dipole pointing towards the ligand.

So, here both are negative, so what happens, the repulsion starts, as a result what happens this group starts leaving. So, this is called polarization theory and if you just look into $MX_3Y$, where the inducer dipole of Y is greater than that of X, as a result what happens this is how the arrangement happens and then this bond is stabilized, whereas this bond is weakened, so this is ready for departure.

So, this is the departing ligand, and once this is departed, so entering ligand would come and substitution reaction is complete. So, that means this polarization theory holds good for ligands such as ammonia, water, which are neutral ligands; neutral sigma donor ligands. I hope it is clear. Example I have shown here, so water and ammonia, etc. So, fine, now let us look into another theory, that is called kinetic electrostatic theory.

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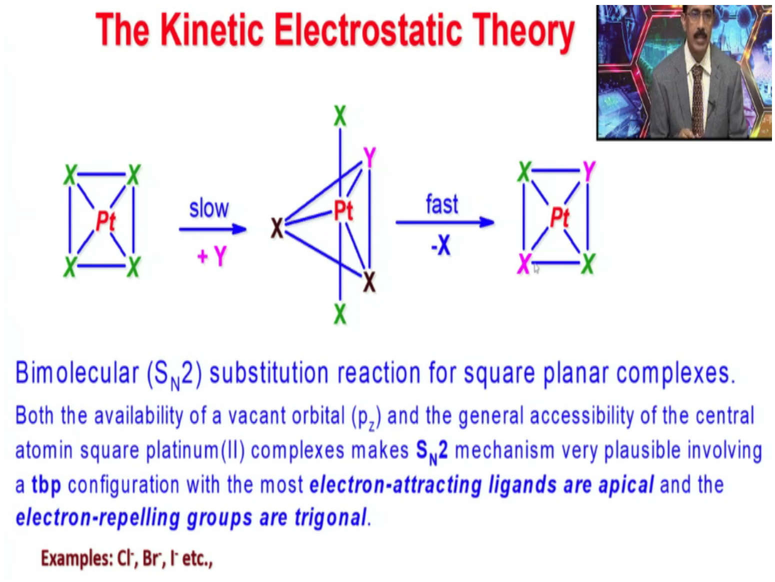

The Kinetic Electrostatic Theory

Bimolecular ($S_N2$) substitution reaction for square planar complexes.

Both the availability of a vacant orbital ($p_z$) and the general accessibility of the central atomin square platinum(II) complexes makes **$S_N2$** mechanism very plausible involving a **tbp** configuration with the most ***electron-attracting ligands are apical*** and the ***electron-repelling groups are trigonal***.

**Examples: $Cl^-$, $Br^-$, $I^-$ etc.,**

What is this one? For example, I have taken a complex like this, homoleptic platinum(II) complex and in the slow-step, entering ligand comes and it establishes a trigonal bipyramidal intermediate. As I mentioned here, during the substitution reaction, one group, along with leaving group and entering group will form trigonal plane, and the other two will be axial. In the first step, the X is eliminated.

Once X is eliminated, what will happen is this trigonal bipyramidal geometry will revert back to square planar complex. So that means, of course it is $S_N^2$ mechanism, bimolecular substitution nucleophilic, and both the availability of a vacant orbital that is $p_z$ and the general accessibility of the central atom in square platinum(II) complexes, makes $S_N^2$ mechanism very plausible, involving a trigonal bipyramidal configuration.

With the most electron attracting ligands are apical and the electron repelling groups are trigonal, this is very important. When you want to explain trans effect using the kinetic electrostatic theory, what we should remember is, we have to gauge and analyse the nature of the ligands present on the metal before, we form a trigonal bipyramidal geometry, that is, electron attracting ligand pairs are apical, and the electrons repelling groups are trigonal.

So, that means, if we have two negatively charged ligands, trans to each other, they are electron repelling groups, they will be trigonal planar. So, in the first step this happens. Now, let us look into couple of examples here.

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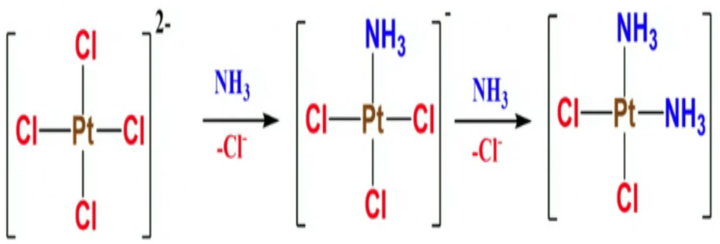

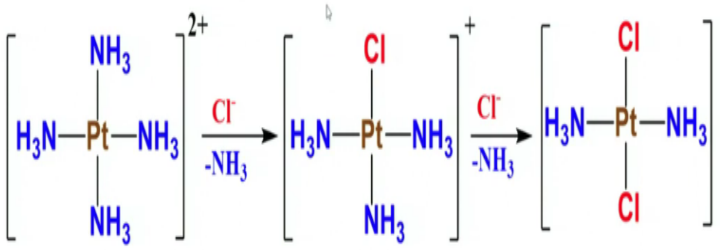

Recall how we made cis and trans-platin complexes, we took first tetrachloroplatinate, added ammonia. When ammonia is added, so here there is no preferred leaving of any of the chlorine, so it is in symmetrical, any one of these ligands can leave and then $NH_3$ comes and again when you add another ammonia, so now ammonia is going to cis position here. So, this we observed, whereas on the other end, if you take tetraammine platinum(II) complex, add chloride, again first one can go anywhere.

And next, when we add another chloride, it goes to a position trans to the chloride that is already present that result in trans complex. So, now let us see whether we can explain this one in a more satisfactory way using kinetic electrostatic theory. Kinetic electrostatic theory holds good for anionic ligands such as halides.

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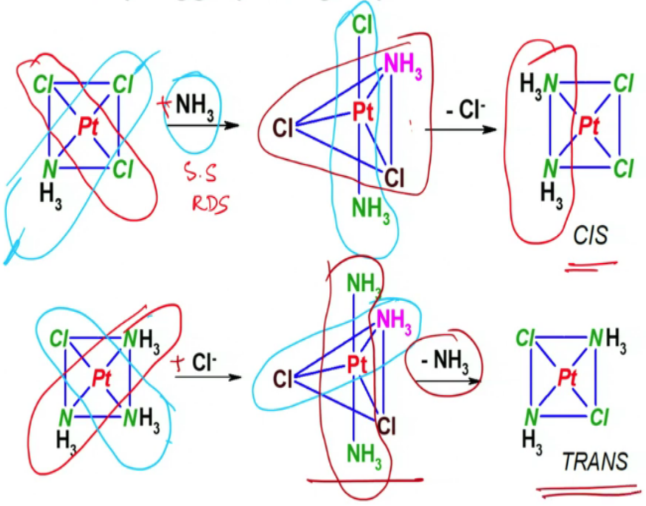
Electron attracting ligands are apical;
Electron repelling groups are trigonal planar



So, now let us try to consider this trichloro amine platinum anion. So, now we want to add one ammonia, before that, we should convert this into along with ammonia into a trigonal bipyramidal geometry. For that what we should do is we should remember this one, electron attracting ligands are apical and electron repelling groups are trigonal planar. So, now let us try to see which are electron repelling groups, and electron attracting groups.

Electron repelling groups are these two, both are negatively charged and because ammonia is there you can consider relatively electron attracting group is this one. This is electron attracting group. Now, we have entering group there. So, with this one, what happens now, this electron attracting ligands are apical, so this should be apical. So, the moment you put apical, you know the fate of the isomer, what kind of molecule, we are going to get, what kind of isomer we are going to get.

So, now this will be here, this is coming here, apical or axial. Now, the electron repelling groups are trigonal planar. So, these two chlorides along with ammonia will be forming this trigonal plane here. So, this is trigonal plane, of course in the fast step, you should remember this is the slow step and this is the rate determining step, addition of ammonia. Now, once chloride goes what would happen is already the fate of this molecule is decided, so these two are there.

So, basically when it comes back, this is going to be, see anything in the plane is going to be cis to these groups here, as a result what happens we are getting a cis isomer here. So, now let us consider the opposite of that one, mono cationic triamine chloroplatinum. So, now it is very different, electron attracting ligands are apical here and then electron repelling group because one chloride is there. So, this has to be the plane we can see here.

So, this has to be in the plane, and this is in the apical position now. So, now $NH_3$ comes and of course here plus is added, chloride is added. So, now once this ammonia is eliminated, now what would happens, it will revert back. Since we have two ammonia here itself in the intermediate, we have in mutually trans disposition, we can always anticipate that we are going to get the trans compound that is what exactly happens.

And if you go back, same thing happened here, but obviously we had no explanation here. With better explanation came into picture because we have understood what is the trans effect and how trans effect is playing when we are using anionic ligand such as halides using kinetic electrostatic theory. So, what is important is, this one should remember, when we are generating an intermediate having coordination number 5 with geometry trigonal bipyramidal.

We should remember the electron attracting ligands are apical, electron repelling groups are trigonal planar. We should not take literally, the meaning of this one, among these pair of ligands which are electron attracting and which are electron repelling ,we should see. If we have anionic ligand pair in the trans disposition, they are essentially electron repelling groups and if we have neutral ligands or catatonic ligands, probably they will be electron attracting ligands.

So based on this assumption, if we generate trigonal bipyramidal intermediate, obviously we can explain very nicely which isomer is going to form and that is what exactly happens. So, this is kinetic electrostatic theory: holds good for anionic ligands such as halides.

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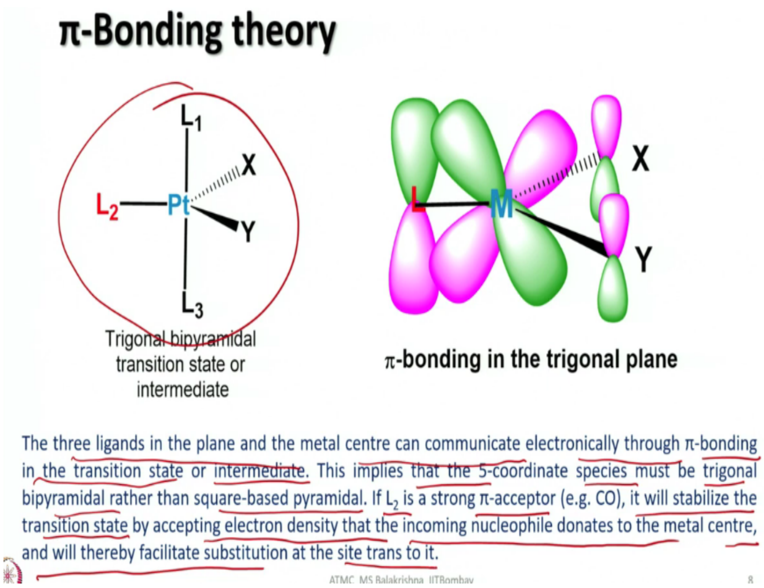

π-Bonding theory

Trigonal bipyramidal transition state or intermediate

π-bonding in the trigonal plane

The three ligands in the plane and the metal centre can communicate electronically through π-bonding in the transition state or intermediate. This implies that the 5-coordinate species must be trigonal bipyramidal rather than square-based pyramidal. If $L_2$ is a strong π-acceptor (e.g. CO), it will stabilize the transition state by accepting electron density that the incoming nucleophile donates to the metal centre, and will thereby facilitate substitution at the site trans to it.

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Now, let us move on to the third theory. This is called pi bonding theory. As the name suggests, this holds good for substitution reactions having pi-back bonding ligands. For example, if have triphenylphosphine, if you have carbon monoxide, if you have ethylene or even N-heterocyclic carbenes, you can anticipate the role of pi bonding theory in the substitution reactions of square planar complexes.

So, here I have mentioned again, you can see here; I have written this trigonal bipyramidal transition state or intermediate, and now if you just look into this complex and let us say we have a ligand here, this is capable of having back donation from the metal and if we consider one of the orbitals say $d_{xy}$ is the electron filled metal orbital that is ready for interaction with appropriate pi bonding orbitals present on the metal.

So it may be sigma star with teritiary phosphines or pi star with N-heterocyclic carbene, carbon monoxide, cyanide, etc. So, the three ligands in the plane and the metal centre can communicate electronically through pi bonding in the transition state or intermediate, this intermediate I am talking about. This implies that five coordinate species must be trigonal bipyramidal rather than square-based pyramid.

One should remember, if L is a strong pi acceptor like carbon monoxide, it will stabilize the transition state by accepting electron density that the incoming nucleophile donates to the metal centre and will thereby facilitate substitution trans to it. So, that means when the ligands are coming, you should remember ligands are always coming with a pair of electrons and they are looking for nucleophilic site.

So, here in the pi bonding theory how efficiently a trans directing pi acceptor ligand generates a vacant site having less electron density at a position trans to itself. How do you explain this one? Let us consider interaction of say sigma star or pi star of CO with one of the metal pi bonding orbitals, preferably $d_{xy}$, $d_{yz}$ or $d_{xz}$. Since we have placed this molecule in $d_{xy}$ plane let us consider $d_{xy}$.

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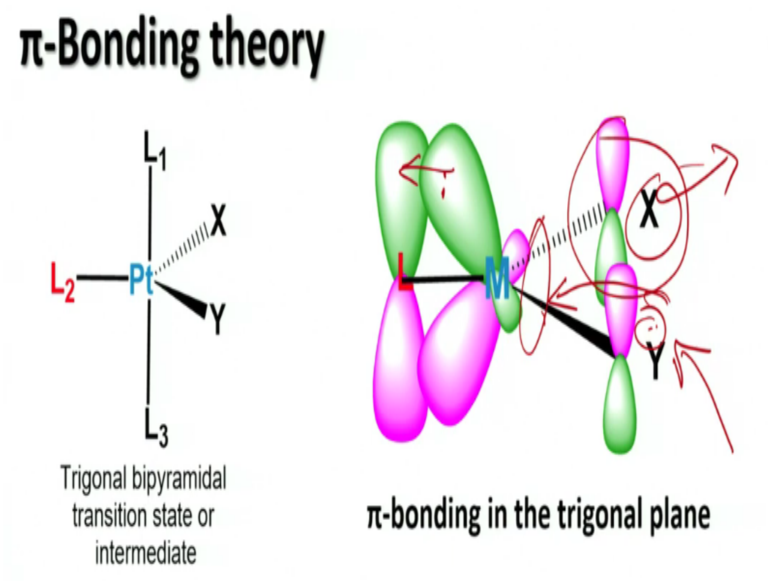

π-Bonding theory

Trigonal bipyramidal transition state or intermediate

π-bonding in the trigonal plane

You can see here, so here since it is a better pie acceptor ligand, so this electron density is moving, as a result what happens since entire electron density is pulled towards strong pi acceptor ligand, here less electron density is left, as a result let us say this is leaving group and this is the entering group, what happens? This can leave, whereas this one is coming with a pair of electrons.

And this is an extent nucleophilic site, so substitution is completed. So, this is how pi bonding ligands facilitate substitution at a position trans to itself. That means first of all by taking electron density what happens, it leaves, so that it can go and then next one is coming with a pair of electrons, this is looking for a nucleophilic centre, it generates nucleophilic centre trans to itself.

And once the substitution is over and this is eliminated, it would revert back to square planar complex having appropriate geometry or confirmation, cis or trans in case if there is a provision for isomerization or formation of two isomeric species.

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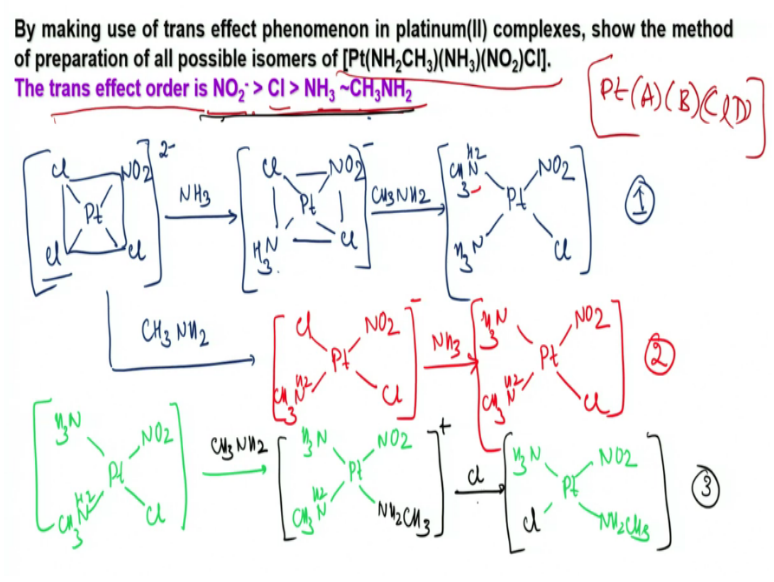

By making use of trans effect phenomenon in platinum(II) complexes, show the method of preparation of all possible isomers of [Pt($NH_2CH_3$)($NH_3$)($NO_2$)Cl].

The trans effect order is $NO_2^- > Cl > NH_3 \sim CH_3NH_2$

So let us see by using this trans effect how we can make some isomers, for example if you consider this complex here, if you consider this complex, it is, this one is something like this AB C and D. So, all ligands are different and it is neutral complex and if all ligands are different and also whatever the ligands that are present have also provided trans order for these things and starting with simple metal complex of our choice.

First of all we should know when we have four different type of ligands in a square planar complex, how many isomers are possible or we should make out that one? With this one, we can have a maximum of 3 geometric isomers. Let us see how we can make or how we can prepare these 3 isomers using the trans effect order that is provided here $NO_2^- > Cl^- > NH_3 >$ $MeNH_2$.

Let me start with a complex of this type, the simplest one having 3 chlorides and 1 $NO_2$ and this is 2–. Now we shall add first ammonia. When we add ammonia, we should know where it goes, since $NO_2$ is the strongest trans directing group among all, obviously $NO_2$ labilizes a group trans to itself means, this should say goodbye, this chloride should go. It has no option other than leaving that place. So, now we have one negative charge.

Now let us add methylamine. Now we should see where methylamine goes. Now we have two chlorides there, among chlorides what happens, one of the chlorides should go. So, we made one, this is one isomer, of course it is convenient, if we write down first all possible isomers and then look for the preparative method starting from an appropriate substrate molecule or metal complex.

Now, what I would do is I would start with again this, now instead of adding $NH_3$ what I would do is I would add first $CH_3NH_2$. When it goes to, the position does not change, in place of ammonia here methylamine would go, so no change. The rest of the ligands would remain same at their respective positions. So, now I shall add ammonia. Now ammonia can go here, so we end up getting a neutral molecule, this is the second isomer.

So, we are left with one more isomer. For this one, I can start with one of these compounds that we have already made. For this one, what I would do is I would take this itself. This compound itself I shall take, for that one, $NO_2$ position remains same, chloride remains same, I am taking $NH_3$ here and then here $CH_3NH_2$. So, now I am adding one more methylamine to this one so that it becomes very clear where it is going.

This should not change and of course this is already there, this would not change. So, this comes here. So now we have positive charge. So now we will add Cl. If we add we should tell where it goes now, the next question is if I am adding here where it goes? Now, just go back to this one, among all this is the strong $NO_2^-$, see the strong trans directing group obviously this chloride should go to a position trans to $NO_2$.

This is the third isomer. So, now you know how effectively we have used this trans directing series and we have prepared all the three isomers possible for this combination of four ligands of general formula MABCD. So similarly, it is very interesting whatever the complexes you come across having A B C D or A A B C or A B C D, of course in case of A B C D you can have 3, when you have $A_2B_2$ you can have 2 isomers.

In these cases, just look into a combination of different type of ligands having different trans directing abilities and try to familiarize with this trans effects series of performing substitution reaction. So let me take another interesting example before I conclude trans effect with square planar complexes and move on to the substitution reactions in octahedral complexes. Until then have an excellent time reading and understanding inorganic reaction mechanism. Thank you for your kind attention.