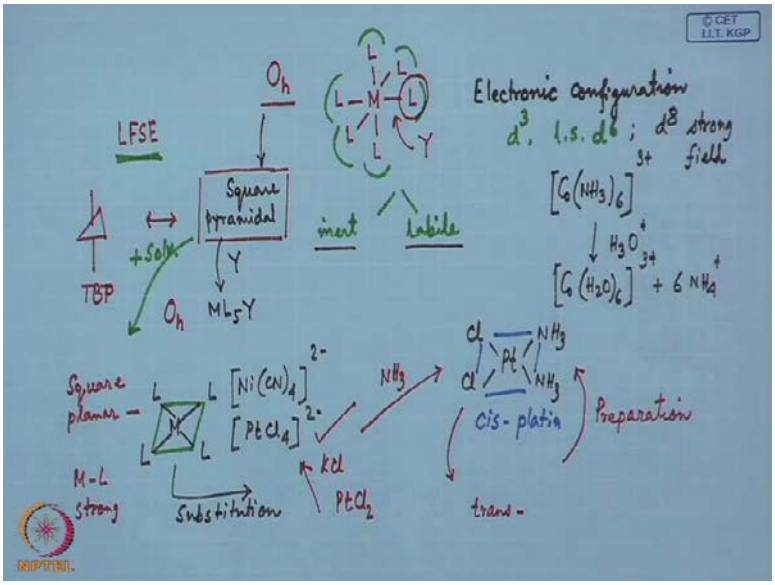
Coordination Chemistry
Prof. Debashis Ray
Department of Chemistry
Indian Institute of Technology, Khargapur

Lecture - 38
Reaction Mechanism – IV

(Refer Slide Time: 00:26)



Good evening everybody. So, we are still with the substitution reactions, and we were discussing about how the substitution is taking place on an octahedral geometry where we have the metal centre connected to six ligands, and this six ligand can be of one type or can be of different types and we were talking about the corresponding substitutions related to that of the incoming ligand or incoming group which is Y. So, when we find that in this particular case depending upon the corresponding electronic configuration. So, this electronic configuration is important, and that particular electronic configuration when we get that say for d 3 or some low spin d 6 metal ion, they behave something differently with that of the corresponding species which is coming to attack that particular metal centre and in that particular case not only the electronic configuration but also the coordination environment, this particular environment which is an octahedral environment; that is also important.

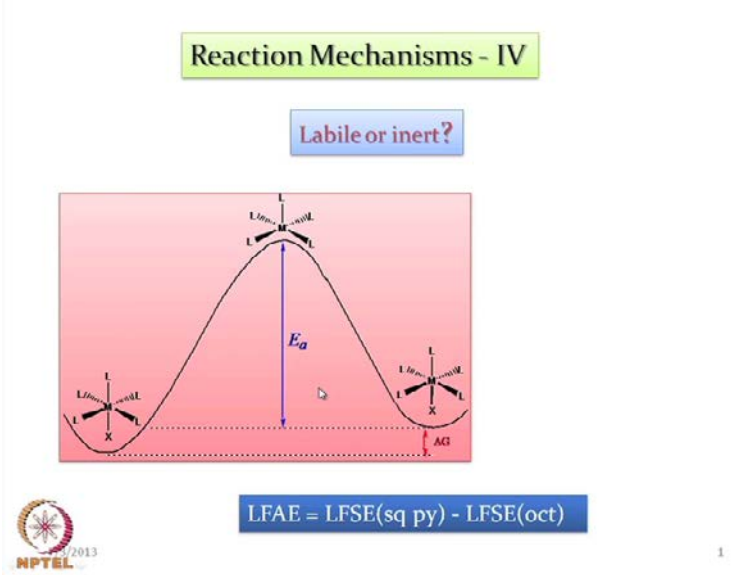
And we got two types of these molecules which are inert or labile; inert in terms of substitution and labile also in terms of the corresponding substitution. So, these molecules when they go for this type of reactions we find that if this particular L, one

particular L is dissociating from the centre; that means the metal centre, there we can have a one particular geometry which is after removal of one L is the square pyramidal one and this particular square pyramidal centre then accepts Y giving M L 5 Y. So, if we just consider that there are some electronic configurations for these metal centres where we can have some certain amount of stabilization. So, if we just consider the corresponding ligand field, stabilization energies what we have seen that the particular d electron configuration can have a particular ligand field stabilization in one geometry which is different in some other geometry.

So, if we are able to compare the corresponding thing this means when it is moving from octahedral geometry to a square pyramidal geometry to again back to the octahedral geometry, what is happening? So, to get this intermediate which is a square pyramidal one how these ligand field stabilization energy changes that we can see. So, straightway what we can do is that we just simply calculate out the corresponding ligand field stabilization energy for this electron configuration in octahedral geometry and then we get the same ligand field stabilization energy for the other geometry; that means the square pyramidal geometry when we have taken out one particular ligand from the metal environment; that means the corresponding interaction with the d electrons and it is different d orbital's would be different and we get different amount of stabilization due to a new geometry which is forming for a square pyramidal one.

And also we should concentrate our attention on whether this particular square pyramidal one is getting stabilized because it can immediately go from a square pyramidal one to a trigonal bi-pyramidal geometry or TBP geometry because it immediately can move from there to the TBP geometry which has a different LFSE value compared to that of our square pyramidal geometry or the same square pyramidal geometry can accept one solvent molecule to this particular position which is giving rise to the vacancy. So, this particular thing when it goes for the corresponding attachment of the solvent molecule or the solvolysis reaction we again immediately get back the corresponding octahedral geometry. So, if we just simply able to compare the corresponding LFSE for octahedral geometry and the corresponding LFSE for square pyramidal geometry, then the difference between these two LFSE value will tell us something about the corresponding stabilization or the energy of activation for these compounds.

(Refer Slide Time: 05:44)



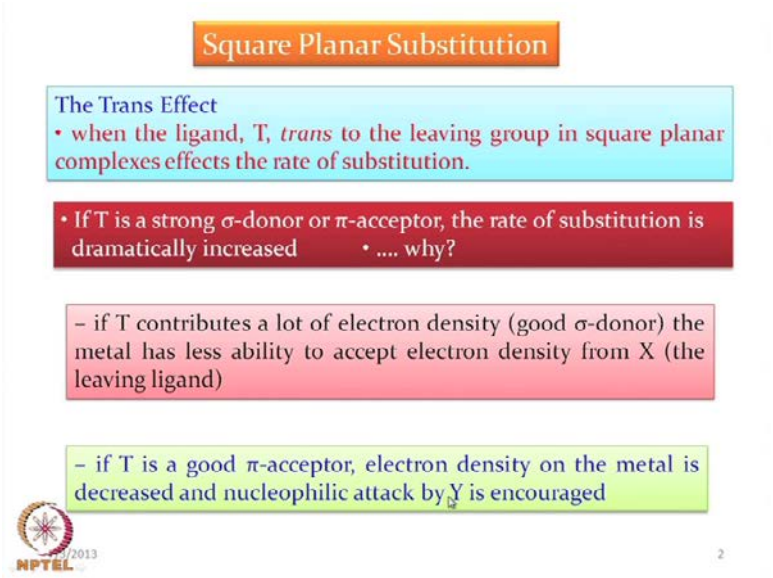
So, this fourth part of these reaction mechanisms what we were just seeing here, we can have two types of molecules what we have seen whether the system is labile or inert and how the labile molecule is going for the substitution reaction and how the inert molecule can go for that. So, this particular thing immediately tells us that if we just simply compared these two molecules where this is the particular molecule which is M L 5 X and after this corresponding activation if it goes from the same M L 5 X or substitution with some Y giving rise to ML 5 Y, then it always crosses the corresponding reaction barrier.

Because if we just moved from here; that means the octahedral geometry to a square pyramidal one we have from the Arrhenius equation what we have seen in our last class that you will have the corresponding energy of activation for this; that means the bond dissociation; that means for the M X bond, the bond dissociation energy will be utilized for the activation of the molecule from this ground state to it is excited state which is square pyramidal in geometry. Then it gets back its corresponding X or the attachment of Y which is the incoming ligand to keep the octahedral geometry back, but it has some different amount of stabilization which is not going to the ground state level; that means there is a typical separation or gap between the corresponding enthalpy of the reaction delta h or that delta h can also be correlated to the delta g value the free energy change for this particular form to the other form.

But these two can simply be correlated by comparing the corresponding ligand field stabilization energy for the octahedral state to that of our square pyramidal state. So, we

get basically the ligand field activation energy. So, if we just simply compare in terms of the corresponding stabilization in terms of the ligand field in a particular environment which is octahedral to that of the other one which is having some square pyramidal environment then LFSE. So, what is that activation? That activation is directly equal to that of our ligand field stabilization energy for the square pyramidal geometry minus the ligand field stabilization energy for the octahedral geometry. So, it is this difference which tells us that how much would be our energy of activation if we just simply consider the corresponding contribution from the ligand field terms for this activation of the molecule from one form to the other.

(Refer Slide Time: 08:48)



So, what we see that in case of one particular geometry if we move to a square planar geometry and this particular geometries are very important because we have considered this particular electronic configuration which is substitutionally inert; that means low spin d 6 what we all know now that how hexaamminecobalt 3 plus can react with H 3 O plus to giving rise to the corresponding hexaaquacobalt 3 plus compound and 6 ammonium ion. So, it is a very substitutionally inert molecule and that particular inert molecule goes for the corresponding reaction with the acid or protonated as the proton which is aquated that means H 3 O plus. So, this rate of this reaction is very slow and we get a corresponding inert species and also we have the other electronic configuration; that means the corresponding d 8 configuration in strong field environment. So, in strong

field environment we get again another species which is substitutionally inert is the corresponding d 8 system.

So in d 8 system, it is basically preferring the corresponding geometry in square planar one which is tetracyanatonickel 2 or Pt Cl 4 2 minus. So platinum centre, palladium centre or the nickel centre can give rise to this particular square planar environment and how this particular environment where the metal is there and we have L L L L for substitution reaction. Because we know that a very important molecule which can function as a molecular drug which is having some two chloride anion and two ammonia groups; that means NH3 groups attached to the cis positions and this particular molecule is known as the corresponding cis-platin. So, how this cis-platin molecule can function as a anti concert drug which is important to know and not only these; that means how it can go for it is reactivity as a anti tumour or anti cancer drug, but also the first thing what we can do how we can synthesize it; that means the preparation.

So, if we know that we have a starting salt like this which can be obtained from platinum dichloride; that means platinum chloride like nickel chloride or palladium chloride we can have and use of these with potassium chloride give rise to the corresponding salt as the potassium salt and how we can get that from particular geometry; that means this is also a square planar one, how we can get this particular substitution; that means the ligand substitution reaction to get the cis-platin molecule or whether we will end up with its corresponding trans isomer that we should know. So, if we only know that how the ligand substitution reaction is taking place in some other geometry; that means it is now square planar geometry. So, we have changed the geometry to octahedral; from octahedral to a square planar one and in this square planar geometry we think that the corresponding metal ligand bonds are pretty strong.

So, we have strong metal ligand bond. How we can labialize the corresponding metal ligand bond and we introduce the other ligand; that means if we just go for the substitution of a X that M X will remove the X from around M and Y is coming into the picture and will bind to M giving a new bond of M Y. So, this is not only for substitution of one particular point but which is also important to get the corresponding second substitution reaction; otherwise we would not get the corresponding cis variety of this molecule. Because we can go for the corresponding one from the tetraammine salt of the platinum also whether it can go for the corresponding trans isomer or cis isomer that is

important to know. So, if we go for the square planar environment and this square planar environment will just follow the trans effect. What is that? This trans effect we can consider as the two positions because we have a square planar environment not like the corresponding octahedral geometry, it can have two trans positions to each other.

So, when if we have a ligand T which is designated as the corresponding ligand remaining in the trans position. So, it is the trans position to the leaving group which is going away from the square planar environment and that is responsible for effecting the rate of substitution reaction. Effects the rate of substitution reaction; that means whether the rate of substitution reaction is very fast or not and in that particular case if we just considered that these ligand which is present trans to the leaving group. So, if the leaving group is Cl minus like that of our tetrachloroplatinate salt or NH3 group for the tetraamine platinum salt, then the group which is present and which is labializing the trans ligand is important. And that is also important when we go for the corresponding hydrolytic reaction; that means water molecules can also substitute either the Cl minus or the ammonia group for its hydrated form or the aquated form which can further bind to the corresponding nitrogen atom from the corresponding DNA basis which is functioning as a good ligand to the platinum centre for it is activity as a drug molecule.

So, if this trans ligand is a strong sigma donor or pi acceptor, so these are the two categories what we can find which are important; that means they can have good trans effect to show for the substitution reaction and in that particular case the corresponding rate of substitution can be enhanced or increased. So, why this is so? This we can find it out because what we find that this particular trans ligand the T has some effect that it is forming a strong bond; that means it is giving a sigma donor electron density to the metal centre and that donation of electron density to the metal centre can change the corresponding metal ligand bond for the other side and what we get that if it is a sigma donor one or a pi acceptor one where the nucleophilic ligand can go and attack the metal centre and if this is a pi acceptor one.

So, this particular attack the nucleophilic attack of the incoming ligand can also dramatically change or increase the corresponding rate of the substitution reaction. So, two types of T ligands we will consider; one is a sigma donor type and another is the pi acceptor type because these two types what we have seen earlier that it can change the

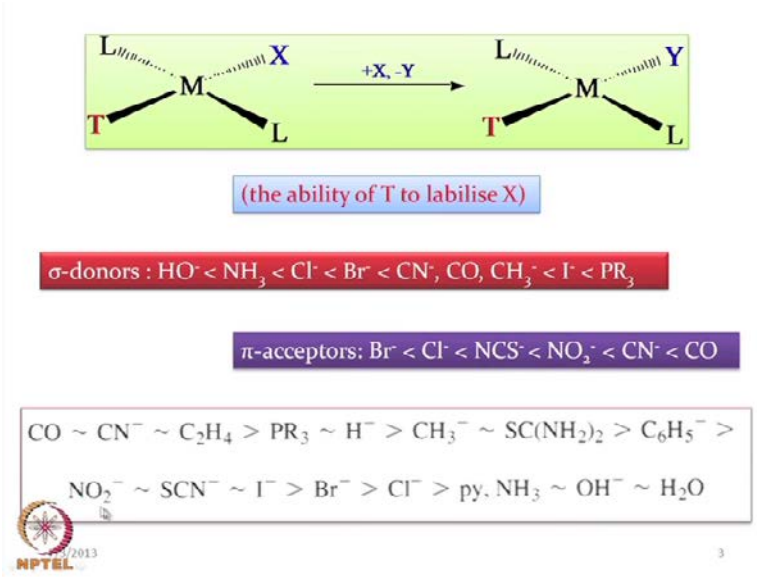
corresponding ligand field stabilization energy; that means the splitting is more and which is stabilizing the corresponding compound in the low spin state and where the gap between this molecular orbital's which is metal centred and which is ligand centred are also bigger. So, now if this particular ligand; that means the T ligand which is contributing a lot of electron density; that means it is providing good electron density to the metal centre which is a good sigma donor. So, if we just simply compare the sigma donor ability of this particular ligand which is trans to the leaving group, the metal will have less ability to accept electron density from X; that means X is leaving out from the metal environment.

So, there will be some competition between the sharing of electron density by the metal centre with that of our T and X. So, if T and X in the same linear line; that means they are trans to each other, then T is maximally providing the corresponding electron density to the metal centre. As a result the metal will engage itself to a lesser extent to the corresponding electron density which is available from the X which is going out from the metal centre. So, as a result X can nicely go out due to the corresponding higher trans efficiency or trans effect of the ligand attaching to the metal centre. So, this is for the sigma donation ability. In a similar fashion the pi acceptance is also contributing a lot to this particular liability of these ligands. So, if now instead of a good sigma donor if our T ligand is a good pi acceptor the electron density on the metal is therefore decreased; that means it is withdrawing the electron density from the metal centre through it is metal T bond.

So, metal is forming a T bond and T is also a very good pi acceptor withdrawing the electron density. As a result the density of the electron; that means the electron density over the metal centre is decreased and nucleophilic attack by Y is encouraged; that means it has some dependence on the incoming group. When we talk about the sigma donor ability we talk the corresponding group which is leaving the system, but when we talk about the corresponding pi acceptance we talk about the corresponding group which is coming and attacking to the metal centres. So, both these two are important; whether our Cl minus is going out from the system and NH 3 is coming and attacking to that particular platinum centre to give us cis-platin or this particular role for this corresponding trans group which is responsible for the formation of this corresponding bond, the new bond with the Y as well as the corresponding removal of X; that means

the trans effect has some double role which can have some role to play for the removal of X as well as attachment of the Y to the metal centre .

(Refer Slide Time: 21:23)



So, if we just see that this is the trans ligand and this is not only this is minus X and plus Y. So, X is removing; we are removing X and we are attaching Y. So, this particular T which can show some effects such that your M X bond is weak and X is departing from the molecule giving rise to some vacancy at this particular point. And this vacancy is not such that if this particular environment which is getting stabilized after removal of X; if the removal of X is going there and if the system is stable without X and no solvent or water molecule is coming there and binding to the fourth position, if there is some reorganization of the coordination environment and these bond angles are going from 90 degree to 120 degree; that means the trigonal environment we can have after removal of x.

But that is not happening in all the substitution reactions some square planar molecules where we see that after removal of X whether the solvent molecule or any other water molecule is attaching or occupying the position of X the three other ligand; that means the L L trans to each other and T which is already there trans to X, they will remain at 90 only and these two L are at 180 degree; that means the vacancy is there such that Y will come and will attack to the metal centre forming a new bond of M Y. So, in that particular case also in the second step the T is also playing some good role to attach the Y to M. So, this particular thing; that means we are considering in the red coloured T

thing; that means this ligand we are also considering how it is responsible for labializing the X group that we will consider as its trans effect.

So, if there are some ligands which will have some good trans effect which will immediately labialize this particular X and as a result we get some substitution at this particular position. So, if this is Cl and if after substitution the group which is attaching is not Cl is NH 3 then Cl and NH 3 are not trans to each other; they might be cis to each other and as a result we can have the corresponding cis molecule for the preparation of the cis-platin molecule. So, the way we know the corresponding sigma donor ability of the groups which we have formed in case of the spectrochemical series. So, during the framing of the corresponding spectrochemical series we have seen that we can arrange the corresponding sigma donor ability of the ligands which are higher for PR 3 the trialkyl phosphine and which is less for the hydroxide ion, then ammonia is greater than Cl minus is higher than ammonia then bromide then cyanide then carbon monoxide then methide ion and the iodide ion.

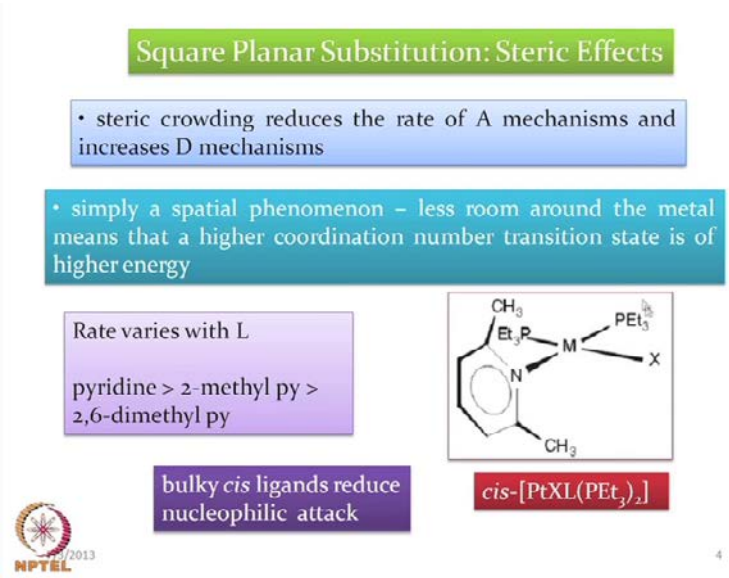
So, in these two position; that means if we just considered the Cl minus at higher trans effect than ammonia; that means during the substitutions of these groups based on the corresponding preparations of cis-platin molecule, it is the Cl minus which can control the corresponding trans labialising effect on the metal centre for the synthesis; that means the chloride Cl minus will control the corresponding labialisation on the platinum centre trans to the Cl minus. It is not the trans of the ammonia molecule, but it is the trans of the Cl minus molecule which can play some important role for the substitution reaction. Similarly for the pi acceptors, the order is typically a different type of order where the position of Br and Cl is different because Cl minus will have higher pi acceptance capability compared to Br minus, then thiocyanate is also higher than Cl minus then nitride then cyanide and then C o.

Here we have clubbed cyanide, CO and CH 3 minus together, but here CO will have higher pi acceptance capability compared to the Cl minus; that is why we have seen in the spectrochemical series, the carbon monoxide molecule have the strongest ligand field splitting for the compounds which is forming like that of our nickel tetracarbonyl or iron pentacarbonyl or chromium hexacarbonyl. So, the pi acceptance is going little bit in a different way compared to the sigma donor ability and if both of these two can play some

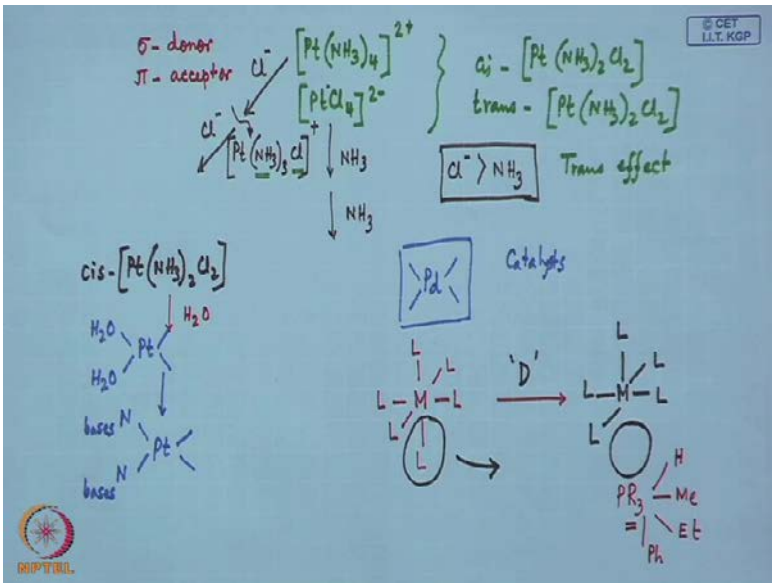
role to the substitution reactions we can have the entire trans effect series. So, this is the trans effect series where we can mix-up these two; that means we have placed that Br minus is greater than Cl minus; that means the sigma donor ability for this trans effect we are considering; we are not considering the corresponding one for the pi acceptance because this two we have also is close together, but little bit on the higher side compared to the Cl minus.

So, starting from water to carbon monoxide we have the entire range for the substitution reactions and interestingly now we can have that we have this labialising effect of Cl minus is hard than NH 3 when we talk about the corresponding synthesis and it is reactivity of the cis-platin molecule. Similarly when we talk about the corresponding substitution by the water molecule we see that these two; that means the Cl minus and ammonia and which is very similar to that of the pyridine molecule. Both of them have higher trans labialising effect compared to the water molecule. So, water molecule will have less effect for labialising the trans group which is present trans to water molecule is same for the corresponding substitution reactions. Similarly the nitrate ion will be stronger in respect to the corresponding substitution reactions compared to the Cl minus and the ammonia molecule.

(Refer Slide Time: 28:21)



(Refer Slide Time: 28:32)



So, we see that whatever we have seen for the corresponding abilities in terms of the sigma donor and the pi acceptor ability and we have the corresponding two starting materials we can consider the tetra ammine salt of platinum and tetra chloride salt of platinum. So, this particular two groups whether we can have, then one of them will give the corresponding cis isomer and another will give the corresponding trans isomer of Pt NH3 whole two Cl 2 and the trans Pt NH 3 whole 2 Cl 2. So, when they are reacting basically; that means the sequences of these two reactions are there; that means when we have these NH3 group, the first one will just substitute by Cl, then again will have the substitution for Cl minus. But in this case we have the substitution by first by the NH 3 and then again by NH 3. So, these two things will also tell us that how this particular one; that means the trans effect for Cl minus is greater than ammonia.

So, how this particular orientation can change the corresponding triviality of the group which is present to the trans group. So, when this is there; that means when all four of them are same immediately we get the corresponding substitution; that means the p T NH 3 whole 3 Cl which we get as plus Cl. So, at this particular point we make this particular molecule immediately and then only we can have the choice for NH 3 and Cl. So, in the second step how the group which will be leaving from the system for the attachment of the second Cl will be dictated by the corresponding trans effect and this particular trans effect sequence for this Cl minus is greater than ammonia will ultimately tell us that whether we can have the corresponding trans molecule or the cis molecule.

Similarly, if we have the corresponding anti-tumour or anti-cancer drug as the corresponding cis-platin, so we can have the corresponding cis one which is the platinum NH 3 whole 2 Cl 2. So, then again this particular trans effect can control the corresponding hydrolytic reaction; that means whether it can go for the corresponding hydrolysis reaction by the substitution for the substitution of the water molecule for any of these two groups; that means for the ammonia or for the Cl; that means we should have certain groups where we have the platinum with two water molecules attached to that and then this platinum centre can go and bind to the nitrogen's of the nucleon bases. So, the nitrogen's of the different nucleon bases can provide this nitrogen's to attach to this platinum centre. So, all these things are related to the corresponding trans effect of the groups on platinum centre.

Similarly it can also show the similar type of effect for the different palladium compounds because this palladium compounds square planar palladium compounds rhodium and iridium compounds also we all know that they are very good catalysts. They are therefore the corresponding very good catalysts. So, the different substitutions and the different groups attaching to the square planar metal centre is important to function as a good catalyst. Now we will consider not only the corresponding electronic effect but also the corresponding steric effect; that means how the steric effect can also play some role for the typical substitution reactions. So, the steric crowding if we can have on the metal centre the rate of the corresponding associative mechanism will reduce and it increases for the dissociative mechanisms. So if there is a crowding, then for crowding the rate for the associative mechanism will reduce definitely because already the metal centre is sterically crowded. So, it is very difficult to put the incoming group the incoming ligand Y on the metal centre still if it is in the square planar geometry.

So, steric crowding will only favour the corresponding dissociative path way; that means if the groups are having some steric crowding like that of the corresponding comparison if we can make on the platinum centre for ammonia or the Cl minus, then if we just move for the corresponding substitution the steric crowding on the nitrogen atom; that means the hydrogen atoms are substituted by some alkyl group, it can behave differently for the corresponding reaction for Cl minus or the new NH 3 groups because it is going for some dissociative mechanism as we increase the corresponding crowding over the metal centre. So, if we just consider a simple spatial phenomenon; that means we can have less

room around the metal means that a higher coordination number at the transition state is of higher energy that means if we increase the corresponding coordination number through some associative mechanism, then it will have some higher energy because it is already sterically crowded.

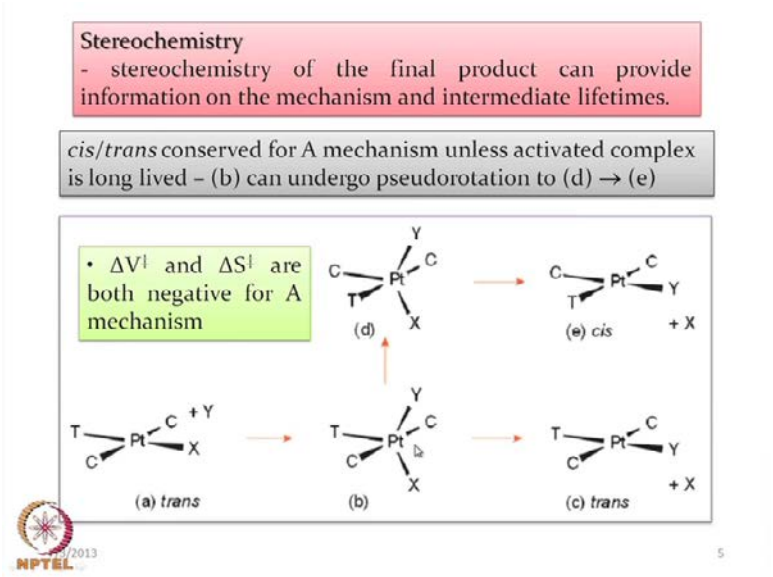
So, there is little space or little room to attach the new group around the metal centre. So, if we just consider a group like this is again some kind of cis and trans isomer but now is triethyl phosphine is the ligand where the ethyl groups had certain amount of bulking environment, then X is there and L is there, how this particular group can form and how it is function there also we can see. So, here this particular PEt 3; this is the PEt 3, X is there and L is definitely is a ligand which has some steric crowding. It is not the simple pyridine molecule but having 2, 6-dimethyl pyridine molecule. It has substitution at position 2 and 6 because already these methyl groups are going above the square plane and this methyl group is below the square plane that is already we are crowding the top of this metal centre and the bottom of the this metal centre; that means this particular steric crowding can control some reactivity pattern with respect to the platinum centre which is the end centre with respect to these two groups because already this particular side is sterically crowded.

So, this phosphine group this triethyl phosphine group is less sterically crowded. So, in terms of only steric crowding. So, this PEt 3 can some amount of reactivity by going for some dissociation and some other type of attachment to some other new group which is coming and replacing this PEt 3 group. So, this particular case the substitution reaction for this molecule, the rate of the substitution reaction can vary and it basically varies with respect to the different types of L groups. So, when L is less sterically crowded; that means only pyridine where we do not have any substitution on these two carbon atoms, these two carbons having hydrogen atoms attached to it which is basically the simple pyridine molecule, then in one case we can have one substitution; that means the substitution at 2 position and then we can have substitution and both these two positions. So, as we increase in a stepwise manner the steric crowding around this nitrogen, so the reactivity pattern is also changing.

So, the rate is highest for pyridine and lowest for 2, 6-dimethyl pyridine for this substitution reaction. So, steric crowding is definitely playing some important role and

we can put some bulky cis ligands. So, if we just put bulky cis ligands around it which will reduce the nucleophilic attack. So, definitely the nucleophilic attack will go; the nucleophilic attack basically will not take place on this X and this PEt3. It can only attack on the other side on the trans side, the cis side is crowded but the trans side is free and it can only show some substitution from the trans side.

(Refer Slide Time: 38:33)



Then we can think of the corresponding stereochemistry; that means the three dimensional arrangement of the groups which are there. So, the stereochemistry of the final product can provide us some information on the mechanism and the intermediates and their lifetimes. So, if we have certain of these things; that means if we have this T groups already we are talking so much about this T groups which is the trans labialising group and if we have this particular trans labialising group; that means if we have it is if it can consider as the corresponding Cl function, then we can have the corresponding three amine groups, then X can be ammine, these two can also be amine. Ss the intermediate ones is forming from the tetraamine platinum compound but what will happen that the T; that means, the trans Cl group can labialise the trans; that means the trans amine group and if Cl is coming and attaching to this particular centre, we get the corresponding trans-platin isomer only.

So, in this particular case Y is the incoming group. If all these three are amine, then this Y is the Cl minus where T is also the corresponding Cl after first substitution. Then this

square planar geometry can have some effect; that means whether it can write the corresponding trans geometry or it can invert to its corresponding cis geometry. So, the typical arrangement; that means the stability of the intermediate how this reaction is proceeding, so when we get this if we have this C bond, if we still take the C bond at 180 which was already present in case of the corresponding square planar environment and we put this T X and Y in the trigonal plane.

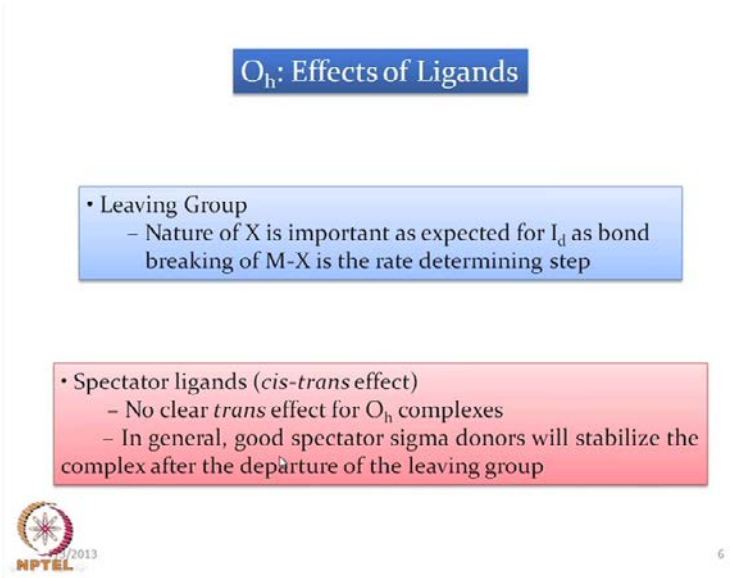
So, this is basically a trigonal bipyramidal geometry which we are getting from a square planar geometry. So, T is there and this T is basically labialising the group X but as an intermediate case where this X has not gone away; that means it is not giving us some trigonal geometry. Because what we have discussed earlier that X can go away giving rise to a tri-coordinated form of the platinum and if all these three groups rearrange and if they come to this angle of 120 degree; that means a trigonal coordination environment can be achieved. But if it is remaining as a vacant position or this entire molecule is forming as a T shaped molecule or some solvent a water molecule can attack to this position or it can go for a trigonal bipyramidal geometry where this particular C-C bond will remain intact; that means this trans geometry is preserved; that means the C-C is the trans orientation.

So, the C-C trans geometry is preserved; we are unable to modulate or modify the corresponding carbon platinum carbonate C platinum C angle from 180 degree; only we are able to make a trigonal plane involving the trans labialising group, the leaving group and the incoming group. Then our X is going away. So, it is the step where X is leaving away from the system. So, when one X is leaving away we are only getting back X is going out. We are getting back the corresponding trans configuration only; that means the trans geometry is preserved for this particular environment. But if the intermediate has some sufficient stability and it has some good lifetime, the intermediate has some good lifetime and in that particular case if that some reorientation of the groups attached to the platinum centre and the two C-C positions are changed from this 180 degree to exchange where we can have the corresponding C-C angle is changed from 180 degree to 120 degree and we have now the T Pt T C is at 180 degree and T is our trans labializing group and in this particular case we can have this corresponding geometries of different type.

But when it is in the trigonal pyramidal geometry, it is going to labialise this X in square planar geometry but when it is trigonal bipyramidal geometry, this T is not labialising the C, but it have the same effect that it is just moving away the X which is in some cis position of T. So, after removal of X-X is going away. The rearrangement of this thing will leave to cis geometry because already we moved this; for this change we already moved this two C groups to the 180 degree position, then to 90 degree position for the cis geometry. So, these two are the possibilities depending upon the stability of the intermediate. So, cis and trans geometry can be conserved for A mechanism. So, cis trans geometry both are conserved; that means if it is trans to trans conservation; that means associative mechanism unless the activated complex is long lived. So, the mechanism is associative; that means one group; that means it is moving from one increasing coordination number, that coordination number is moving from 4 to 5.

And this has less stability lifetime, immediately it is moving towards the product. But if the activated complex the trigonal bipyramidal complex has some long lived species the b can moved to d and ultimately d will give rise to the cis product; that is why the d is transforming to e. So, in this particular case what we can also measure the corresponding volume of activation and entropy of activation for changing from the square planar geometry to trigonal bipyramidal geometry. Both of them are negative which is supporting again the corresponding associative mechanism; that means this mechanism is typically associative in nature not dissociative.

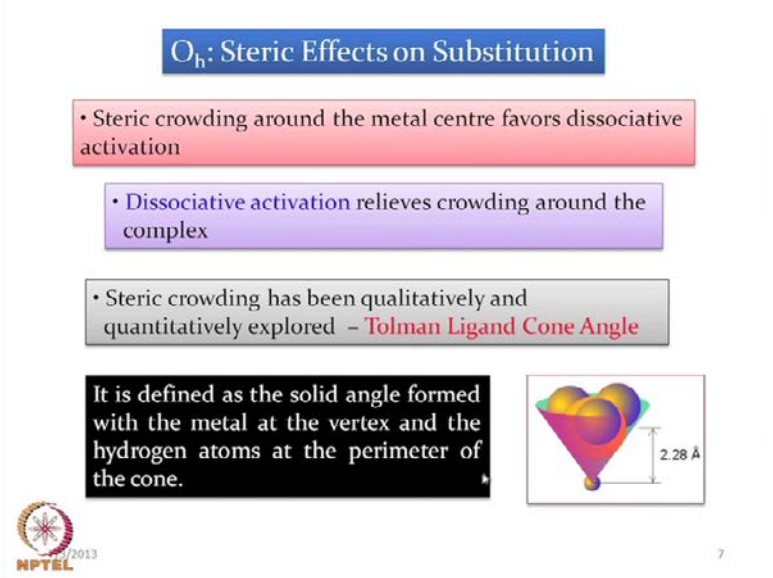
(Refer Slide Time: 45:45)



Then we can see the effect of the ligands on the octahedral geometries, then octahedral geometry how it supports the corresponding effect of the ligand for the substitution reactions. So we can have again, like that of our square planar geometry the leaving groups; that means how the group X is important. So, nature of the X is important as expected from intermediate dissociative path way. So, it can be a dissociative path way but it is of intermediate type. It is not fully dissociative or not fully associative as bond breaking of M-X is the rate determining step. Why it is dissociative because X has some important role to play and the RD step the rate determining step is the bond breaking of M and X. We can have some spectator ligands where we can see the trans effect as well as the opposite of that we can considered as the cis effect. So, we consider the cis trans effect for octahedral geometries.

So, no clear-cut trans effect is seen for octahedral geometries which is observable for only square planar geometries. In general good spectator sigma donors which are having some good trans effect what we have seen will stabilise the complex after the departure of the leaving group; that means when the leaving group is going away the X is going away, the bond is breaking on M-X; the molecule is moving from an octahedral geometry to a square pyramidal geometry and in that particular case a spectator ligand which have a sigma donor ability will stabilize this particular square pyramidal geometry for its stabilization as it is expecting to attach the corresponding group which is coming to attach the centre as Y.

(Refer Slide Time: 47:47)



Then like square pyramidal geometries we can have the steric effects on the substitutions; steric crowding around the metal centre favours the dissociative path way that we have seen also for the square planar geometry. Then dissociative activation if we can consider that one ligand is going away, octahedral is giving square pyramidal geometry, then this dissociative activation relieves crowding around the complex. So, we do not have any crowding on the metal centres. Now extra crowding is required if the path way is associative. So, steric crowding has been qualitatively and quantitatively explored. How we can consider the typical steric crowding that the steric crowding has some role to play for octahedral substitution reactions. And this particular substitution reaction basically control the dissociative path way which has some important role to play or thing to say about the corresponding dissociative path way for the typical types of the different catalysts, what we have seen that our catalyst can be this or our catalyst can based on octahedral geometry.

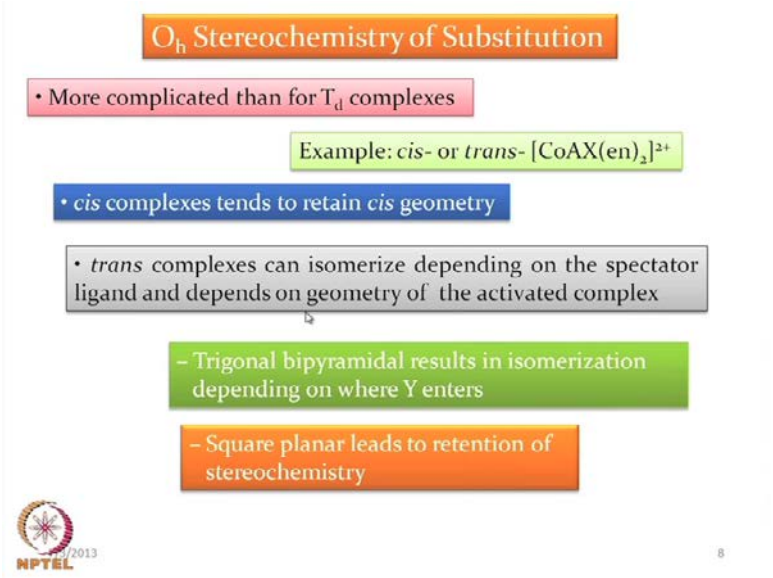
So, how big the group L is there and the path way; that means the corresponding dissociation; that means if the mechanism of the reaction is D type dissociative path way, then we can have the square pyramidal geometry and this particular group is going away and we can quantitatively analyse this particular substitution reaction if we can compare the steric bulk of the ligand which is removing from the system or which can be attached to the metal centre. So, if these are some good phosphine ligands. So, we can vary this R from hydrogen to methyl to ethyl to phenyl, we get triphenyl posphine from phosphine. So, we can explore this with respect to the Tolman Ligand Cone Angle; what is that? It is some Tolman who introduced that while doing his work some company that this is the phosphorous centre which is there; that means the big red orange sphere is the phosphorus centre and which is attaching to three other groups, it can be the hydrogen atom or it can be the phenyl group and this is our metal centre.

So, how we can see that the corresponding distance between this metal and the ligand; that means the phosphorous; that means the metal phosphorous bond is important and in some case it is giving at a 2.28 Armstrong for some octahedral geometry. So, as we change the corresponding steric bulk or the steric crowding around the phosphorous. So, if we increase the phosphorous steric crowding; that means we increase the cone angle. So, basically this cone angle can be close to 90 degree when it is only for spin; that means hydrogen atoms are attached to the phosphorous atom but it can go beyond that

when we can have some substituted phenyl rings on the phosphorous atom, it can go beyond 180 degree. So, this way when we change the corresponding cone angle we have the corresponding change in the corresponding distances and the labialization of the metal phosphorous bond.

So, it can be defined how we can define the corresponding cone angle; it can be defined as the solid angle formed with the metal at the vertex. So, how the solid angle is forming? So, this is the solid angle the solid cone angle and the hydrogen atoms at the perimeter of the cone; so the hydrogen atoms there if they are the hydrogen atoms of the PH3 group. So, since they are at the perimeter of this ring and from that perimeter we draw this cone, the solid angle we draw and then this is the angle which is our theta which is telling us how the steric crowding can be important for the corresponding substitution reactions.

(Refer Slide Time: 52:32)



So, this stereochemistry what is important for this sort of substitution that for octahedral stereochemistry is more complicated than for tetrahedral complexes and we can have this type of substitution reactions on cis and trans groups of ligands. So, stereochemistry of the reaction can play some important role that we can have the cis molecule and the trans molecule and cobalt AX en twice 2 plus; that means the cobalt molecule is there which is the trivalent cobalt centre and this can be some neutral ligand and this can be our chloride group or in some cases CO Cl 2 en whole 2 can also can be checked with a

neutral system; that means we do not have their corresponding charge on it and this particular substitution how it is varying; that means what type of geometry we can have for the substitution reaction with that of our chloride with say water molecule or the hydroxide group when we have the cis complexes, the cis complexes always tend to retain the cis geometry; that means if we start from the cis geometry, always the n product is also the cis geometry whether we can go for the corresponding substitution of the Cl by the hydroxide group.

Then the trans complexes; for the trans complexes we can have the isomerization depending upon the corresponding spectator ligand and depending on the geometry of the activated complex. So, for the trans complexes we will see that how the corresponding activated complex can be different from the cis complex and this activated complex can react differently with the corresponding incoming group.

So, if we just react both the cis and the trans compounds with the hydroxide groups the hydroxide groups the OH groups, then we will find that OH group can react differently with that of the corresponding cobalt complex. In some case it can basically retain the cis geometry or some other case it can also go for the corresponding change in the configuration of the system. And in trigonal bipyramidal geometry, in basically most of the cases it goes for isomerization depending on where the Y enters and in square planar geometry leads basically to the retention of the stereochemistry. So, in our next class we will consider particularly the octahedral geometry how the cis and trans geometry will give rise to the different products depending upon the different reactivity with the hydroxide ions.

Thank you very much.