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NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

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Organometallic
Chemistry-I
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Module No. 2

Lecture No. 7

REDUCTIVE ELIMINATION

Hello everyone today we will discuss reductive elimination in the last class we have completed oxidative addition and we have seen three different mechanisms of oxidative addition today's class we will discuss reductive elimination also we will discuss as RE now reductive elimination is exactly the opposite of oxidative addition it is like counting 1 to 100. 1, 2, 3, 4 and 98, 99 100 and then reductive elimination will be if that is the forward direction in oxidative addition reductive elimination will be counting back from 100, 99, 98, 97,96, 95 soon to 1.

So you know technically there is really not much new things but again now reversing something is not that easy that is why we need to discuss and the principal specifically we would like to focus we will discuss reductive elimination very briefly once again whatever you have learned in oxidative addition if you can reverse it okay it is kind of microscopic reversibility of oxidative addition okay let us look at reductive elimination so reductive elimination will be tracking from a ligand metal complex.

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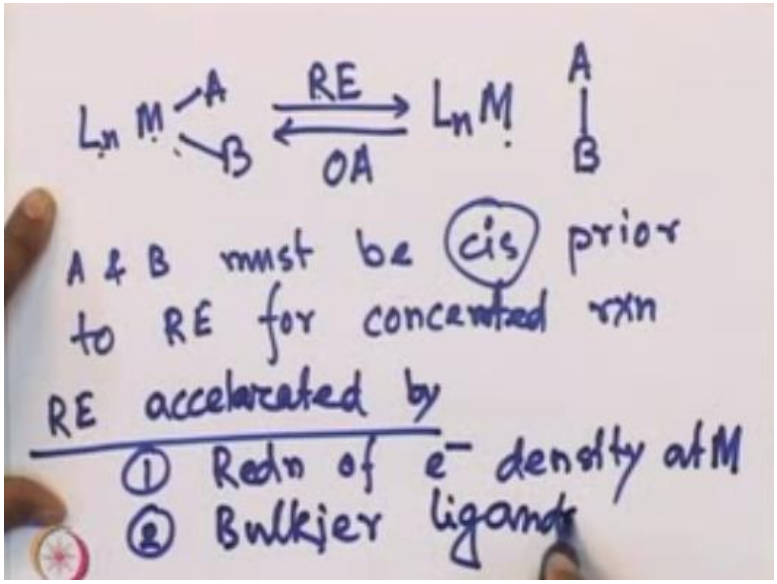

Ligand metal complex having A and B component this is the species you get after oxidative addition or into A and B right so the reductive elimination will be on the forward sense to give you L_nM and A B you can understand that the backward direction of these would be oxidative addition so ligand metal complex interacting with A and B to give you ligand metal A B by oxidative addition by reductive elimination RE we are looking at that oxidative added intermediate or an intermediate where a possibility of a bond formation between A and B can be looked into starting from that complex we are going to generate ligand metal species as well as A and B.

So that new bond formation between A and B that is the reductive elimination from a organometallic intermediate, one of the requirement for this reductive elimination simply is A and B must be ceased to each other must be CIS prior to reductive elimination for concerted reaction, you have seen in oxy oxidative addition we have three different mechanism concerted radical and your sn2 mechanism.

But over here you need to have A and B in a CIS confirmation before they want to reductively eliminate, now also you would understand the change in oxidation state from ligand metal AB is

going to be -2 right if you are starting that electron count for a ligand metal AB complex as 18 electron after oxidative addition that will be 16 electrode, so after reductive elimination it will be 16 electron.

In the oxidative addition you have seen if a 16 electron species is undergoing oxidative addition it is giving you 18 electron so for oxidative addition 16 goes to 18 and for reductive elimination 18 goes to16, now if you have seen very carefully the effect of ligand on the metal complex are paramount are very, very important in oxidative addition similarly for reductive elimination effect of ligand will be crucial.

For oxidative addition you have seen smaller the ligand and electron richness of the ligand will also favor oxidative addition small ligand electron-rich ligand will favor oxidative addition, now since it is a reversal of oxidative addition reductive elimination will be supported by a ligand which is bulky which is very big that means it will not allow A and B to stay with the metal complex very you know very strongly.

So the big ligand will enhance the fists or enhance or facilitate the removal of AB so steric bulk of the ligand will be good for reductive elimination of course another thing will be electron deficiency if ligand is electron deficient then a higher oxidation state such as you know in eighteen electron cases higher oxidation states will not be favorable the airport it will undergo of reductive elimination to give you the product.

Once again for oxidative addition you need a small ligand and electron rich ligand for reductive elimination you need a big ligand or so called statically crowded ligand and electron deficient ligand to make it more facile that is the kind of, you know direct relation. So let us write down that fact reductive elimination RE accelerated by number one as we discuss, reduction of electron density at M means metal and the bulkier ligand.

So of course as we also have tried to discuss reductive elimination usually a you know consulted process that means it is a metal A and B are interacting together it is almost a you know it is a

sigma bond metathesis type of reaction you would see so it is usually a concerted process three centered reaction you can imagine.

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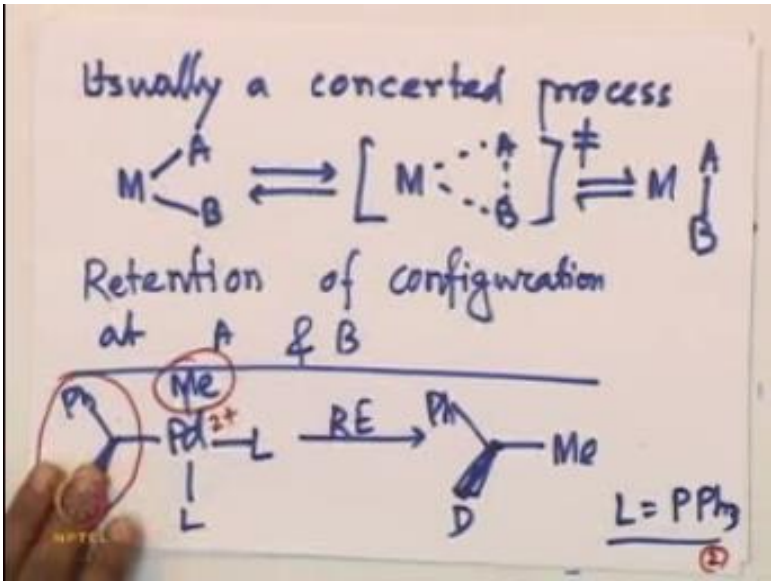

So let us try to write down that transition state for this usually a concerted process therefore if you start with m A and B complex okay. From here you will have them transition state where these three components are interacting and finally you will have M AB formation fine so it is a concerted process and therefore you will have interaction between M A and B therefore finally you will get M and a be back now in the oxidative addition we have seen depending on the mechanism the stereochemistry can be influenced if it is a concerted oxidative addition we have seen retention of configuration of RX or AB if there is any chiral Center present so if you start with R isomer of a species okay.

Then you will not see the inversion if a chiral center will remain basically impact right for concerted one for SN_2 as you see as all the SN_2 reaction you will have the you know inversion of the configuration at the A B or RX whatever we were discussing if they are having a chiral Center then we will get an inversion but for radical reaction of course you have seen that it is the racemization of the of the chiral Center okay, so consulted oxidative addition gives you the

retention and your SN_2 reaction gives you inversion and radical mechanism gives you the racemization of the chiral center.

Now for reductive elimination since we have seen it is usually a concerted mechanism so most often or almost linearly always we get retention of configuration so retention of configuration is for reductive elimination and sis configuration is usually necessary for reductive elimination let me draw with an example retention of configuration at A and B right so we would like to discuss one of the example very simply if you have a play diem complex where these two groups are there now to have a compound like this you must be able to identify A and B very easily this is A let say and this is B.

So there will be bond formation between A and B to form a bee species right after reductive elimination what you will get of course you see that these two species are A and B are cease to each other overall at the end you will get this retention of configuration right so the stereochemistry is retained at this point and in this case ligand equal triphenyl phosphine okay so what you have seen right now is one example of the Palladium this is a palladium to oxidation state this palladium is having 2+ oxidation state A and B are radar up getting reductively eliminated to give you the product with retention of configuration.

Of course another thing it is not very common but another thing is we can make the reductive elimination faster side by adding exogenous ligand from ligand from outside you can add and so that this ligand might will be effective for promoting reductive elimination.

So if you have a ligand metal complex and reductive elimination is not faster the technique here sometime could be is simply add another ligand okay, exogenous ligand from outside which will take out the electron density from the metal center. Therefore, in principle you can promote reductive elimination little bit faster than before of course in every cases you are not going to get you know reductive elimination faster you have to have to in order to promote the reductive elimination by adding another ligand from outside you have to ensure that that ligand outside ligand is interacting with the metal complex with the metal and then taking out the electron density from the metal.

Of course it is not going to be feasible all always but sometime it is possible to take out the electron density from the metal by adding ligand. Again you must remember that it is although in principle generalized technique but you need to have perfect choice of the ligand and without changing way too much of other things at the metal center the ligand should be able to coordinate with the metal and should be able to take out the electron density from the metal.

Therefore almost like five back donation type of thing if that is feasible then you may have a possibility actually then you will have a possibility that reductive elimination can be made faster, okay. Let us discuss with one of the example.

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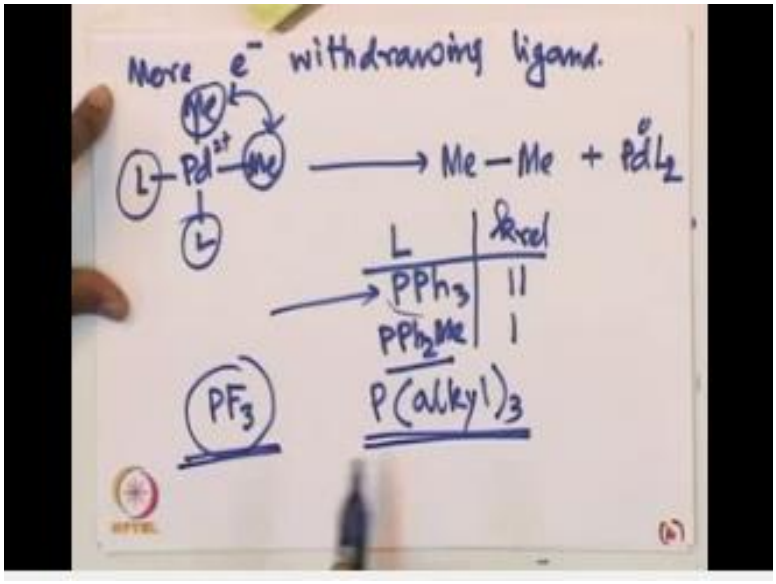

So reductive elimination, okay can be accelerated by addition of appropriate ligand okay, that is what we are trying to discuss right now the example you need to have for these cases or one of the seminal example is the complex with by thriving in all you know it is also known as BP okay this is by period in it will in coordinate with any metal center in a in a five-member chelating fashion in this case nickel and we have to meet high of course this is a this is B so we

are trying to promote reductive elimination so that carbon bond between the be methyl group is formed.

Usually if we try to do this reaction we will see it is a slower reaction of course you can try to heat it up can usually promote it faster but still it is a slower reaction now what you can do is in this particular case you can get the same product formation in a very fast manner or relatively faster manner if you add this an hydride to it okay, so of course again this happened to be the perfect choice in this case it is a it is a etcetera coordinated nickel and then what one would expect that this nickel will coordinate with this anhydride in the fashion and here is your viridian and methyl, methyl.

Since nickel is coordinating with the with this anhydride in this person it will be able to take out pilot phone from the nickel center and therefore this will act as an electron-with drawing ligand and you will be able to promote reductive elimination between these A and B relatively faster okay, and then thereby it is demonstrating that the ducts reductive elimination can be accelerated by choice of a suitable ligand if you choose a suitable ligand you have an opportunity to promote reductive elimination faster.

Once again reductive elimination required bulkier ligand as well as electron deficient ligand so you need to create an atmosphere around the metal centers such as it feels like it is not electron reach and it feels like it is satirically crowded so if you see this oxidative addition and reductive elimination are kind of not mixing oil with each other right they are kind of you know on the two side so that is why often you see the problem that in one reaction let us say in one catalytic cycle you need oxidative addition as well as reductive elimination then the choice of ligand is very crucial.

Because oxidative addition will require each ligand electron-rich ligand and smaller ligand preferably but reductive elimination will need bulkier ligand and the electron deficient ligand, so in one reaction in the same reaction if you want oxidative addition and reductive elimination to be facile it is kind of you know kind of really tricky thing to deal with and this is where you

know extremely important factor for these you know organ metallic species is the ligand design how do you design a ligand.

When it is electron reaching one hand at the same time electron deficient on the other hand how do you design a ligand which is bulky in one hand other as well as less satirically demanding on the other hand you know this is like almost classic and no people have contributed and you know famous faculties from different Institute's has contributed enormously to solve the dilemma but of course now the understanding of the literature in fact a conundrum such a mutually exclusive things can indeed be promoted okay.

Now of course another thing we would like to discuss is some more example or you know the ligand effect let us say. So more electron withdrawing ligand we want to discuss little more so let us take an example since we are discussing palladium little bit or not really we are just taking some example let us say this is a compound of what we are trying to see we are trying to see the reductive elimination between A and B what are you are expecting? You are expecting to get methyl, methyl plus of course the remaining part p dl_2, if it was in+ 2 oxidation state it will be 0 right.

This is the thing you should be very quick in doing, so palladium 22 to Bill to palladium 0 for reductive elimination palladium 0 goes to palladium 2, for oxidative addition right. Now in this case if you have a ligand imagine this ligand, if you have a ligand, which is $PPH_3$and if you have another ligand which is PPH_2 to Amy what do you expect the relative rate to be between these two ligands.

Which one will be faster triphenylphosphine will be faster, or Diephenylmethyl fosston will be faster, okay just let me give you the value triphenylphosphine is faster, this is slower why is that simply first of alltriphenylphosphine is bulkier, and this diphenyl methane phosphine is less bulky.

So triphenylphosphine will promotereductive elimination faster that is fine, number two of course is this is also going to be less electron rage, this is going to be more electron rich right this

is more electron rich, compared to this so you need it bulky elegant as well as you know electron deficient ligand for reductive elimination.

You see that I the relative rate is varying like11 verses 1, in other place for example if you have PF_3 much as if you have let us say P $alkyl_3$ try-try fluro first n versus try alkyl hospital which one will be giving you faster reductive elimination way, that this alkyl group will give promote the faster one, or the fluoride will give the faster road.

If you apply the same principle once again you will see that of course PF_3 is electron deficient as well as smaller inside, all mostly electron deficient okay and this is it depending on the alkyl group of course you will have different in your steric bulk but this is usually of course very much electron rich in this case.

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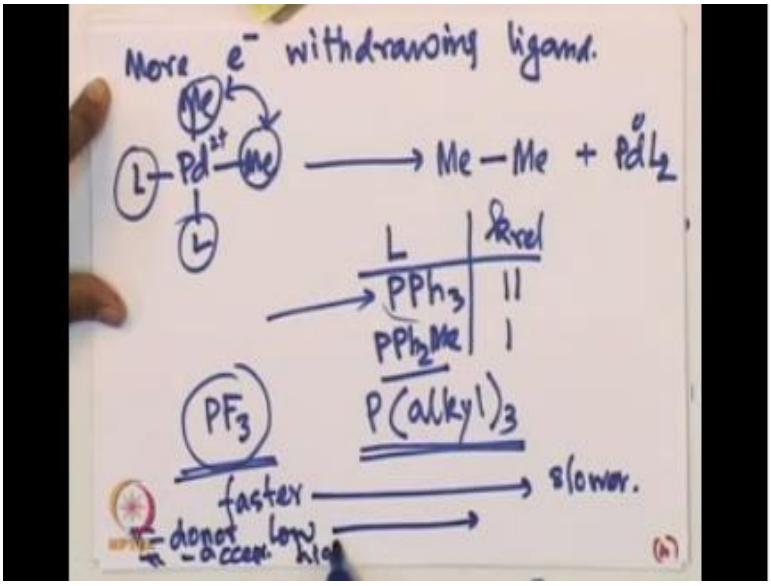

Since, this is very, very electron deficient you will get faster reaction rate overall, you will get slower reaction rate okay. So if you have an σ donor, then you have low or slower reaction rate and if you have a л acceptor, л acceptor you have very high, high reaction rate okay.

So for example, carbon monoxide, carbon monoxide will promote, promote the reductive elimination very faster. We will close the discussion of reductive elimination, yet what we have learned so far today is reductive elimination is almost the microscopic reversibility reversible fact of the oxidative addition, whatever promotes reductive elimination will not be the same factor for the oxidative addition.

For oxidative addition we need you need smaller ligand, electron-rich ligand for reductive elimination, we need bigger ligand and electron deficient elegant. Of course they are kind of non mixing with each other therefore promoting both oxidative addition and reductive elimination in same reaction is always going to be problematic, this is where ligand design has to be perfected we'll look at that in a latter plus and we have also discussed quite a few example and shown that you can sometime be able to add a ligand from outside.

And thereby you will create an electron deficient metal center which can lead to a faster little reductive elimination. With that we conclude today's session and that is on reductive elimination next class we'll discuss migratory insertion and elimination reaction. So we will also discuss in that we will discuss α migratory insertion and α migratory elimination and also β migratory insertion and β migratory elimination, so that's for the next class. Okay, thank you all.

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