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Organometallic Chemistry-I

Prof. Debabrata Maiti
Department of Chemistry, IIT Bombay

Module No. 3

Lecture No. 12

β- Elimination Reaction

Hello everyone welcome back today we will discuss β elimination we started discussing in the last class about the β elimination β elimination as you have learned by now it is a microscopic reverse of the β migratory insertion and we have also seen that the intermediate that involves or you know this is a force entered reaction mechanism that involves this reaction now β elimination let us try to look back one more time this is again the microscopic reverse of the β migratory insertion.

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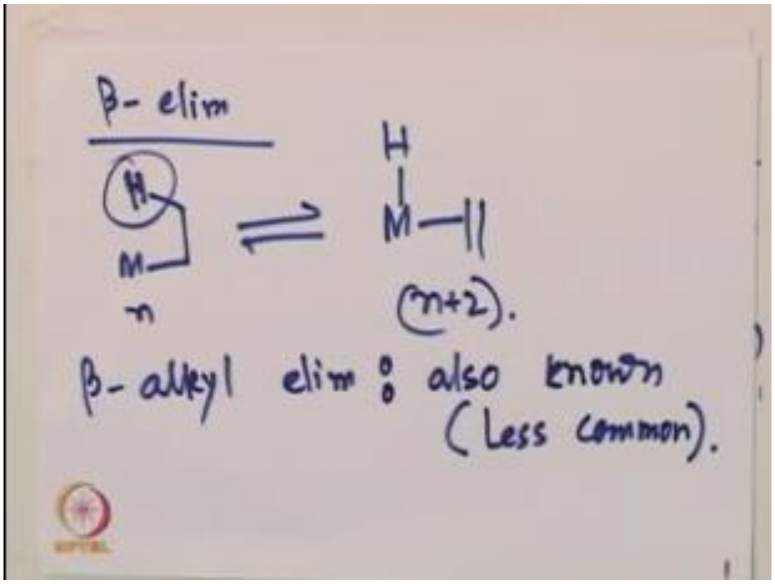

β- elim

β- alkyl elim : also known (Less common).

β elimination involve the metal alkyl species for example the hydride being the major one or the primary one and the alkyl over here is less likely although it is possible alkyl is usually less likely and we have very good examples of the hydride example hydride complexes if this is n electron this is going to be n+ 2 electron complex β alkyl elimination let me write that down because that is you know it is very usual question usual question by the student it is also known but less common okay.

Let us put it that way that is easier to remember now you know one thing we can try to discuss then what would be the preferred geometry what in what scenario this β hydride elimination will be favored of course I try to tell you that the β hydride elimination in so common that it can be nuisance it can create trouble for a desired another reaction right you have a bit alkyl into you have an alkyl intermediate if β hydride elimination becomes for side to side other reaction which you may be expecting with the alkynes may not be occurring that that is so β hydride elimination product gives you a lot of trouble in fact a number of cross-coupling reactions suffers due to the fact that this alkyl intermediate will undergo the β hydride elimination.

So desire cross coupling reaction becomes extremely problematic okay and that is what why one of the reason that sp3 carbon Center alkyl center sp3 center carbon different carbon heteroatom other bond formation becomes bit of an issue I mean it is more than an issue it is it is something remained as still challenging after three four decades of research on this on this field involving cross-coupling reactions we might to discuss that on a different forum but mainly let me try to put you the idea of a geometrical preference how can you determine what type of geometry will be preferred and what could be one of the example for such cases.

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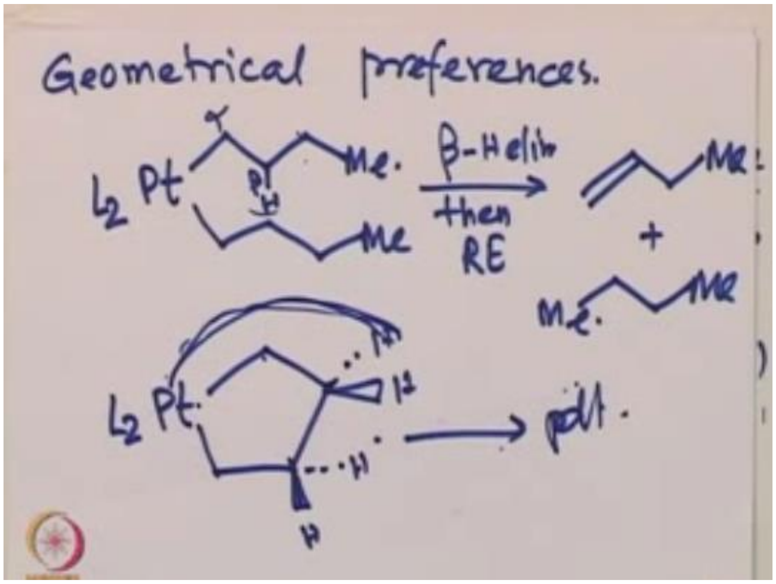

Geometrical preferences right the example we are going to briefly discuss is let us say you have a platinum complex with two ligands and then you have an alkyl species like that where it is an open chain hospices and β hydride elimination and subsequent then reductive elimination will give you the product this one plus if you do it correctly you will realize that this is going to be the other product right so what will happen that this is α this is β from β.

Let us say for example β this hydride it comes to the here so olefin coordinated with the hydride as you are trying to discuss remember to let me show you one more time if you have forget sure if you have a metal alkyl species exactly species and metal olefin and the hydride intermediate in this case we have an alkyl extra so that alkyl let us say is over here.

Now you have metal hydride olefin and then alkyl now this two will reductively eliminate and this olefin will also follow from the intermediate, so overall for this platinum complex as you see it is a die one two three four die butyl complex with a hydride elimination and then reductive elimination will give you an olefin and then long chain alkane species, now that is good if you have another reaction which is let us say of similar type.

But in this case you have certain strain in there and you know of course you have the hydrogen and then the thing is of course you are going to get the products with a hydride elimination product, now in these two cases where you have an open chain starting material dialkyl or di-butyl starting material and in another case you have the cyclic intermediate where you know you have the four-member intermediate.

That means over here you are expecting a four-member intermediate 1 2 3 4, 4 member intermediate actually in this case it is strained for beta hydride elimination, right. So overall what you will see that this four member intermediate 1 is strained and therefore it is very slow to undergo beta hydride elimination because you know you are not going to get that reacts or the first one where the di-alkyl group is there.

And it is going to be very facile and there is no strain involved so that it is going to be very easy to deal with the other one the second one since there is a strain involved that for Center intermediate formation becomes very difficult, so the relative rate if you want to put at relative rate for this reaction k relative for this reaction would be something like 10^4 versus one, so that that emphasizes quite a lot of difference of relative rate.

And that is how we would like to call that in a strange situation in a strange situation we will have a very slow β migratory insertion but in a normal very easy situation that β Hydrate elimination is going to be faster once again that is one of the problem rather than a good thing for a lot of cross coupling reaction of course this is a facile reaction it becomes a nuisance it creates a lot of side reaction.

And we will see why it might further complicate in the next example, the next example we will try to see a very beautiful elegant example which is discussing about the β hydride β migratory insertion and β L migratory insertion, migratory insertion and elimination occurring in together in one of the example and how beautifully it can give you the value of this β migratory insertion and elimination. So application of β migratory insertion and β elimination reaction, so we will deal with the Schwartz region in this case.

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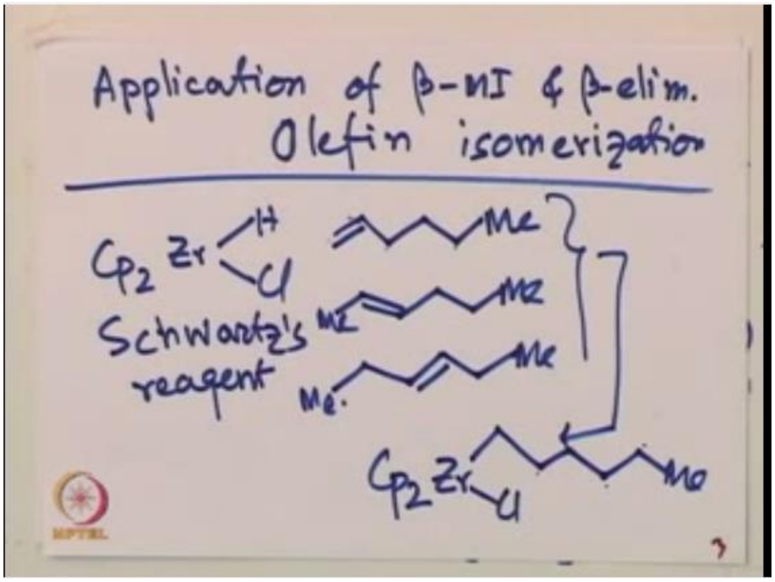

That will be the application of β migratory insertion and β elimination, β elimination of course and this should be about all about olefin isomerization okay so what happen is you start with a organometallic intermediate okay and you know in this particular case you will be able to see with Schwartz region particularly zirconium reagent you will see it is a metal hydride region and then no matter what olefin you take whether it is in turn terminal olivine internal orphan double bond is at the 23 position or 45 position eventually you end up getting exactly the same product that is quite a lot and I mean you know it is very interesting it does not depend on the type of olefin you are taking.

The metal alkyl species that you are going to get is exactly same in this case type of olefin I mean that the isomers of olefin you have a terminal olefin okay let us say CNH and HX now another olefin with the same CN HX but the double bond is now shifted to the β and λ position between β carbon and the two second carbon and the third carbon and then another one between lecture 4th and 5th another one between fifth and sixth all different olefin with the double bond at different position okay exactly same molecular formula same long chain alkane okay.

But the double bond position is shifting all of them will give you the exactly same product that is quite interesting and that I guess is a very beautiful and elegant example for this β migratory insertion and β elimination reaction let us try to look at the cyclopentadienyl zirconium this complex also known as very popularly known as s large real is not this is by the way done by one of the under graduate student at MIT in any case this is let us say you have one of the olefin like this you can have another olefin like that of course another Oliphant as you can draw from the same thing.

Is this right overall what you have is a for all these cases you have CP to zirconium chloro starting with this complex 123456, 123456 so the zirconium hex exile complex in exile complex you are going to get so irrespective of those all the olefin that we have drawn we have drawn three different olefin in this case with six carbon the double bond position is shifting one is a terminal they the internal further internal and shown all the complexes you are going to get exactly same product that is quite amazing right no matter which olefin you take exactly same product is getting.

So this is a thermodynamic complex it is a stable complex irrespective of the positioning of the olefin we are going to get it now of course you have understood why it is happening that is because it is a primary one as we already try to discuss this primary alkyl species is more stable compared to the secondary one and of course compared to the tertiary one secondary is most prefer one the tarsier you one but how exactly that is happening.

Let us try to look at of course we have this example where we have again different olefin in three different olefin giving exactly same product this is the thermodynamic product this is the thermodynamic product where we have again different olefin three different olefin giving exactly same product this is this is the thermodynamic product this is the thermodynamic product of course product since this is the primary, okay since this is primary and primary is more stable. Now how it is exactly happening let us try to draw.

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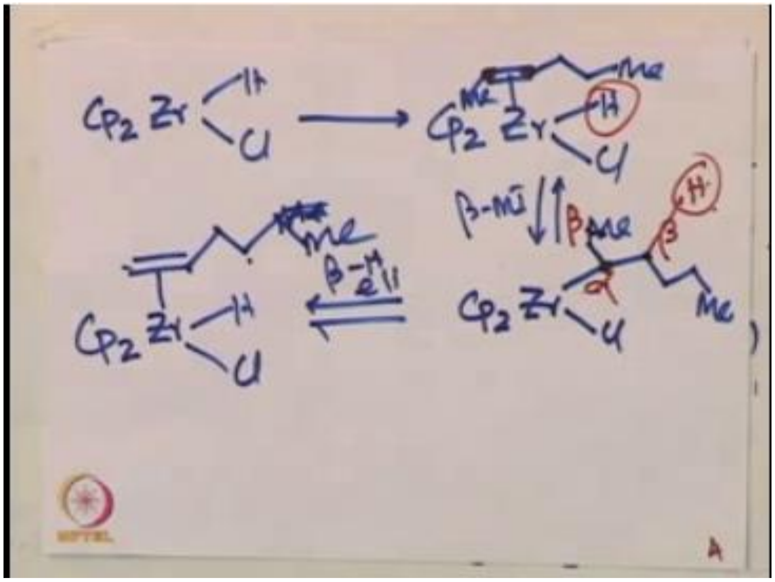

This Schwartz reagent one more time so this is your Schwartz reagents and starting from this one if you let us say take of course now first terminal olefin one you know how it is happening how you can explain, but with the secondary one let us say try to take sepatu zirconium H and CL the olefin will coordinate let us say here over here methyl. Now here first step would be the beta migratory insertion right, beta migratory insertion you will get Cp2 zirconium chloro with a intermediate where this is forming and from there on again further here you can see that this is the most important thing to note.

So this is beta migratory insertion right, so at the at the alpha position at the beta position you have the hydride this hydride is getting involved right, this is alpha position this is the position this is the beta position in this case after product formation at the beta position hydride is going on so that is the beta migratory insertion that is happening. Now if you look at from this intermediate of course this is alpha this is beta but of course this is also another beta if you look at this product this is alpha this is beta.

Now from here as you have seen in the previous general example this is also a beta position from this beta position you can have the beta hydride elimination right, so beta hydrogen elimination particularly from this hydride from here this methyl right, and overall you are getting Cp2 zirconium and this intermediate of course 1,2,3,4,5,6 one more carbon will be there and this intermediate where you have again the opposite the other beta 1 not from this one from this one due to the thermodynamic reference you will get that one and what you overall see is then.

Irrespective of the starting material, irrespective of the olefin positioning you are able to transfer the bond from an internal to a terminal product, right. So that is I guess it is look literally very amazing so starting from an internal olefin you are able to convert the internal olefin into the terminal olefin. Anywhere that double bond is there olefin is there that olefin double bond can be taken at the end or the terminal position as soon as you have that you have a very stable metal alkyl species.

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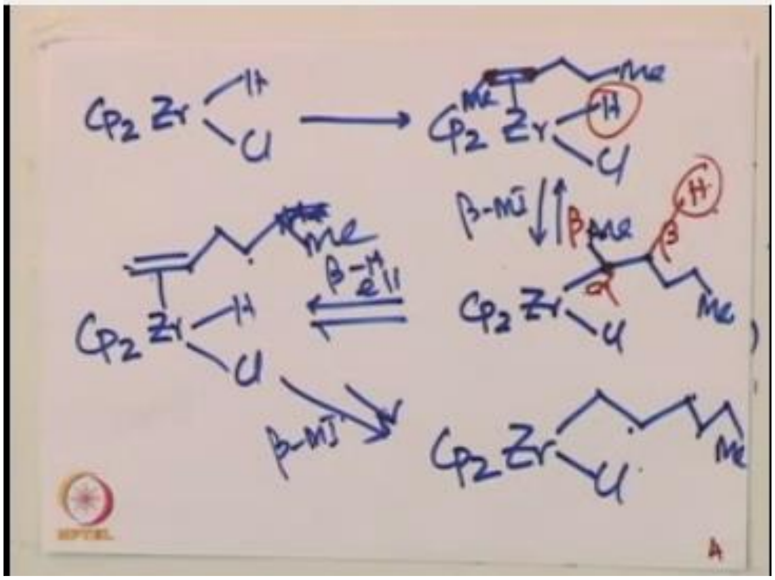

So let us let us look at that product formation from their own of course you are going to have the same product that is Cp2 zirconium chloro and beta migratory insertion in this case 1, 2, 3, 4, 5, 6 right beta migratory insertion you are going to going to get from there on so beta migratory insertion will occur to give you the same product. Remember from the internal olefin you get a terminal olefin and then you get the this primary alkyl, so of course the primary olefin itself will give the same product thus in internal olefin also giving the same product.

Now that that having said that you have perhaps realize that it irrespective of the double bond position, you have the possibility of getting the more preferred metal alkyl species, because the double bond can be isomerised that is how actually double bond isomerisation occurs, this is at here are a lot of example in the literature sometime it is called the Jeepers reaction I mean zip you just zip unzip.

This reaction you can you can see lot of example, with these with these cases right, now we will particularly then try to tell you that that, it is possible to generalize this reactivity pattern and the pattern is very simple, as week we have discussed earlier pattern is primary is more stable then secondary, and then tersely, of course let us try to write down in terms of more of the olefin. We have the generalization.

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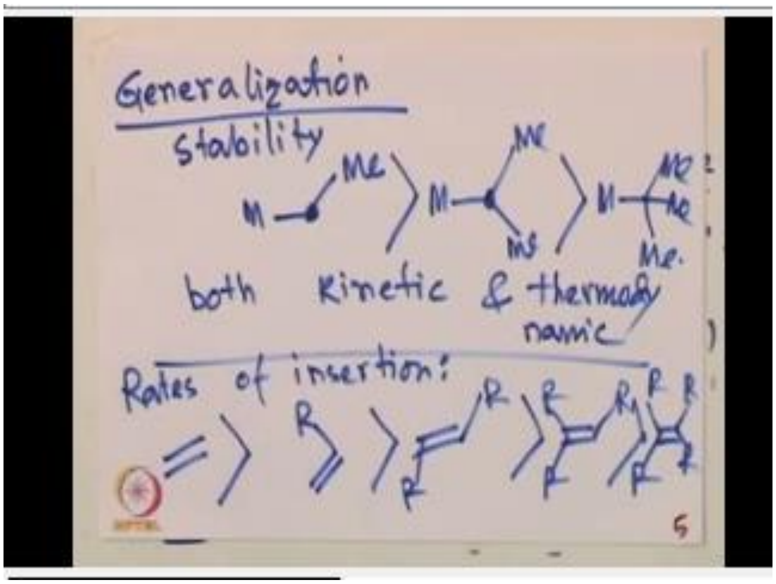

Generalization

Stability

both kinetic & thermodynamic

Rates of insertion:

The stability is very simply as we try to say, metal primary this is a primary one. Okay is more stable than metal secondary, this is the secondary, you have secondary and you have metal alkyl species that is over here. So both this is both kinetic and thermodynamic product, kinetic and thermodynamic stability thermodynamic, mixed able to both kinetic and thermodynamic stability.

Rates of insertion if you see rates of insertion of course I think it is a no-brainer, you understand that of course the non substituted one, is more step more or the faster one and then the mono substituted one, and then die substituted one of course tri substituted one, and finally tetra substituted one, due to the steric region, for the steric regions you would understand it is it is going to be very less stable.

So the un substituted one like ethylene, will be the most reactive then the, then mono substituted one, then die substitute done then tri substituted one, and then finally the tetra substituted one, like now that that would be a the all for these beta migratory insertion, and beta migratory elimination, or beta elimination in general beta elimination.

Now we would like to then of course the other type of reaction that exists over there, where you do not have a migratory group associated with the metal, and but you end up getting almost the same product, or exactly actually the same result in terms of let's say olefin product formation, now it could also happen that that is what I am trying to say that it could also happen that that migrating, this beta migratory insertion or let us say beta migrated elimination, specifically elimination reaction.

This elimination step where the metal hydride is forming or metal alkyl, could possibly form this alkyl group may or may not bind with the metal centre, and therefore what you have left up with is the, net result and that is net razor is the one, where you have the olefin coordinated with the metal centre, but that hydride is missing. In the in the in the alpha elimination or beta elimination both, the cases you have seen that let us say alpha hydride elimination or β a hydride elimination you have seen the hydride is attached or associated with the metal center upon elimination but it could also possible that hydride could directly come out of course this example are not that very common but it is feasible it exists there where the hydride intermediate does not form due to a region that there is no possibility of forming.

Those are the reaction we call it obstruction it obstructs directly so now I think in this category we would like to discuss α obstruction we know the Alpha elimination where the hydride gets associated and the β abstraction that is the that is the one where the β migratory that β group will not be associated with the metal center after the reaction it will be directly obstructed right of course how are you going to differentiate we will try to look at that let us try to discuss the α abstraction briefly today and we will then move to the next class.

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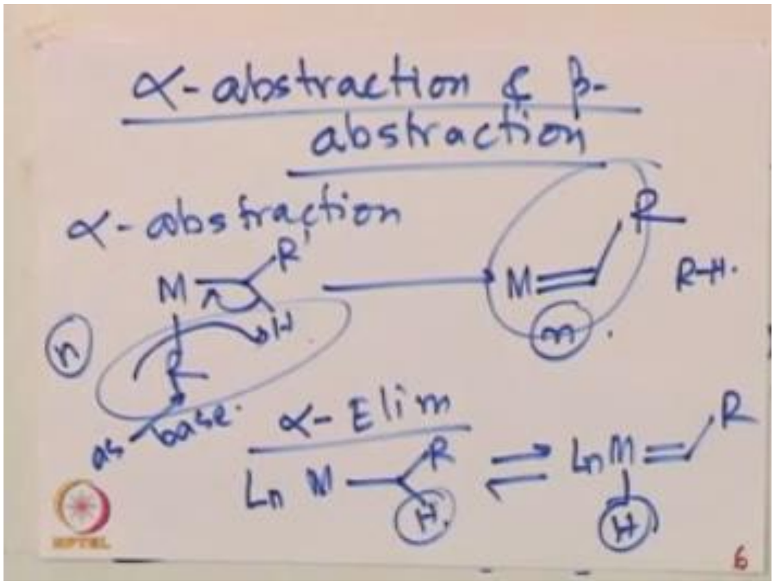

So α abstraction and β abstraction that is what the topic we would like to discuss again these it is extremely crucial to understand that there is a subtle difference what is the α obstruction you have a metal let us say r alkyl it could be hydride as well okay, now this metal is taking and giving directly let us say this sees as base right directly you have a metal carbine species plus r h no change in electron count as you can see no change in electron count if this one was n electron it will be also n electrode.

Just to remind you about the α elimination it is important just to really get the feeling of it you have let us say Ellen metal the same type of species MH over there if you have this compound the become sorry α elimination will give you the product where the same exactly same exactly same product you are going to get but this carbon product that comes with the hydride in this case so this α hydride α position hydride is moving to metal in this case in this case there is no association of the hydride with the metal center.

So it directly comes out as the RH so there as you can see there is a very subtle difference between this α obstruction and α elimination you have seen the example now we will like to discuss in the next class how this example will construct a very good mechanistic view or why we would like to why this β obstruction or α obstruction is feasible why they are elimination and you know α illumination and β illumination cannot happen in certain case so that will be discussed in the next class till then you guys keep on reading and since soon as the question that you may have. Thank you very much.

NPTEL
Principal Investigator
IIT Bombay

Prof. R.K Shevgaonkar

Head CDEEP

Prof. V.M Gadre

Producer

Arun Kalwankar

Digital Video Cameraman

&Graphics Designer

Amin B Shaikh

Online Editor

&Digital Video Editor

Tushar Deshpande

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Teaching Assistants

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G Kamalakshi

Sr. Web Designer

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Riya Surange

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