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Organometallic Chemistry-I

Prof. Debabrata Maiti
Department of Chemistry, IIT Bombay

Module No. 3

Lecture No. 11

β- MIGRATION INTEGRATION

Hello every one welcome back today we will discuss β migratory insertion we stared discussing in the last class β migratory insertion was first reported in 1962 since then it has revolutionized or it has evolved in a way perhaps no other reaction has been evolved in organometallic chemnsity in that fashion you know quite a number of reactions like hydroformylation hydrogenation and chillar not a polymerization rely on as the ket step.

Let us look back at the β migratory insertion and today we will discuss little more in-depth about β migratory insertion, so we try to discuss in the last class.

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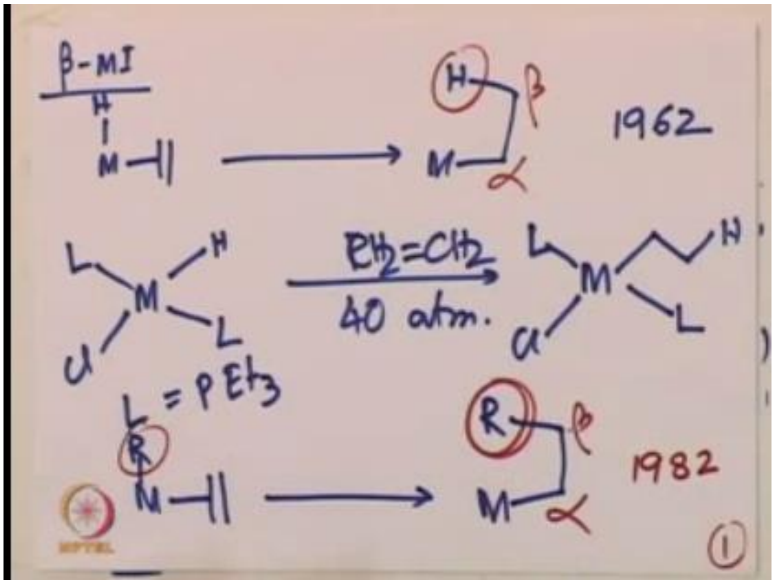

β migratory insertion involve this metal with hydride and olefin coordinates for example and then we will get a metal alkyl spices as you can see H is at the β position okay now this reaction you know can be of different type let me give you one example you have metal hydride with two ligand and a chloride this ligand could be let us say tri ethyl phosphine and under 40 atmosphere pressure you have this ethylene very 40 atmosphere pressure you will get the product that is over there it could be with platinum as the metal right.

Of course first example of any metal hydride species doing getting into the metal hydride and olefin interaction and thereby it is β migratory insertion with the hydride was reported in 1962 but first metal alkyl insertion at the β position was reported in 1982c of course as you can imagine we can draw the exactly similar thing for this metal alkyl one where metal R is coordinated with the olefin over all you get metal alkyl or intermediate where R is now at the β position.

So this is β position R is involved so this one first reported in 1982 of course then we can quite a lot of discussion on this but most importantly we need to understand when you have a terminally substituted olefin where the β position is going to be which β position the alkyl group let us say for example we terminate whether it is the less substituted position or the more substituted position the alkyl group will go because both the more or less substituted one you can call as the β position depend it actually depends on where the substitute or the you know the H or R is getting migrated.

Let us try to look at one of the example perhaps which can determine which center whether the more substituted center of the olefin or less substituted carbon centre of the olefin will have the migratory goal for you know explaining this we have one of the very important example this was reported with cyclopentadiene.

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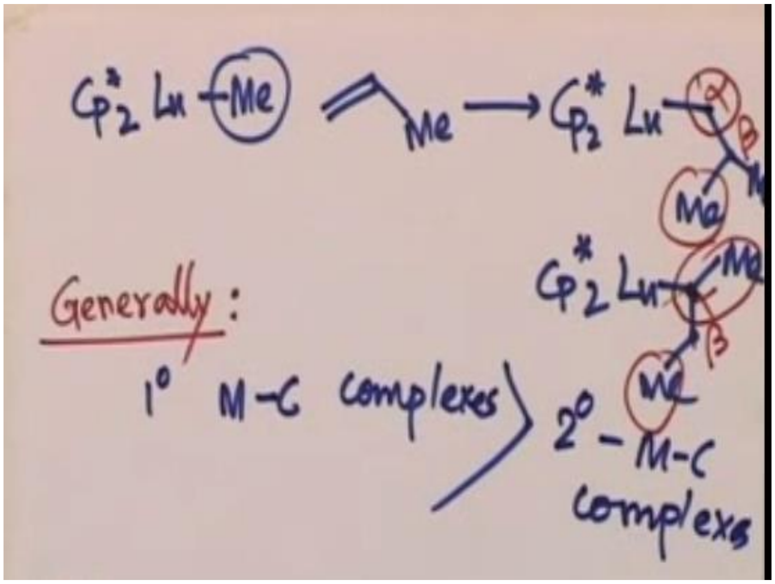

As a supporting ligand with plutonium and with a methyl, so of course you have an alkyl group in there you want to react it with this propene let us say for example, now let me draw the product two product possible two products are possible one of them could be this one for example then you have α β of course β migratory insertion product the other one would be your Cp* the same compound.

But here you have the methyl group at let us say over there now in this case again this is the α1 this is the β1, so it all depends how the olefin is oriented and where the alkyl group is getting migrated, now if you look at these two products it is both of them are β migratory insertion product, the first one as you have seen the R group that is the alkyl here alkyl to be particularly this case has been transferred at the β position.

Of course both the products and the β product but it is having the center which is more substituted one the carbon center having the more substituted one possessing the methyl group in the other one the second product that we have drawn is the one where the methyl group is a present at the less substituted position of the olefin but again that is also a β migratory insertion product.

Both of them being the β migratory insertion product which one is going to be more in amount or the major product or let us say exclusive product in lot of cases which one is going to be the one, if you look at the past product the first product is the one where the you know the overall methyl alkyl species that getting generated is having least spherical events at the metal carbon center, so the α carbon center which is attached with the metal.

Is having least steric demand in the first product, in the second product you can see the α carbon centre is housing with let us go back and look at the product again, we have the α carbon center, okay. α carbon center is least substituted ors least Sterically demanding but over here you see the α1 is more Sterically demanding, now if you look back therefore the actually the first one this first product which is having the metal carbon center least Sterically demanding is the one that going to be preferred.

The first product is going to be preferred of course in some cases you can get nearly exclusive product for medicine, this is mainly due to the fact that metal alkyl species are stable if the α carbon centre is less Sterically demanding that make sense right, so let us try to write down that fact, so we have generally of course you know there could be different other factor involve generally we have primary metal carbon that means primary 1 with primary metal carbon complex is called metal alkyl complexes.

Is preferred over secondary metal carbon complexes, so that is in terms of the stability, this is the secondary one this is the primary on, primary secondary, primary is more preferred of course you know that train will follow primary secondary tertiary as you been see more and more steady demand is happening and therefore we will get less and less product for now as we try to discuss with that the hydrate migration or achyl migration which one if you have a competitive situation which one is more like which one is fas I.

Let say now that is a very tricky experiment to do you have to make sure that everything is remain as constant as possible and similar as possible then only you will be able to make some just mean about with that hydrate transfer is faster or alkyl transfer is faster right that is literally a tricky experiment to do but of course some scientist has got around this problem.

And they have come off with the really beautiful design of the experiment let me try to discuss that particular one with you so that is will be on migratory aft quid which group that hydrate or alkyl look migrates faster if when there is a competitive situation or how will you proof that one is faster one the other and they working in a similar fashion exactly same rate of course you can imagine that they are not but let us try to see the example one example with this so the migrated aptitude.

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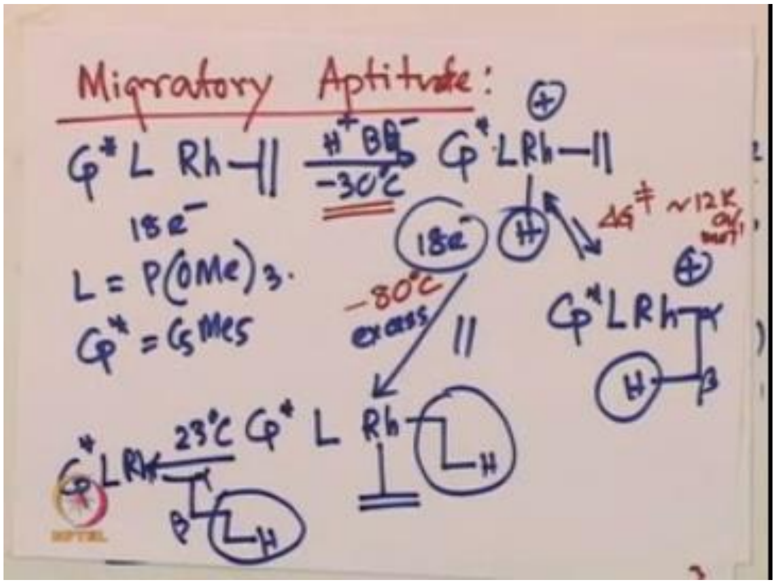

So in order to again in order to you know prove this mechanism of course it is going to be little tricky out there but the thing scientist have very clever in design is this experiment this is rhodium complex okay, now let me write down the experiment and I will try to explain let along with it so this is the rhodium complex with olefin coordinated now you have a protonation okay of course you know proton will bind with the metal center and overall you will have Cp*L rhodium and olefin coordination along with the hydrate species in there and this is a plus complex right.

Now of course from this intermediate you can expect that you know your product formation will be going on and in this case the product would be the one where rhodium is having the alkyl group so one second α β at the β position this hydrate this hydrate is getting migrated right so again this will be at complex now if you do the electron count you should have done that initially this should be 18 electron count and this ligand could be this enthoxi phosphine and C_p* as you know is a C5 Me5 that.

So this is the β migratory insertion where you have the hydrate transferring to the β position of this olefin so α β, β for this an hydrate educating transfer again these region 18 electron complex and now once you have this olefin exists okay now this reaction can be done at - 30° see this is important to note this reaction can be done at - 30°C now ΔG for this reaction is going to be nearly approximately.

To ~12k/mol so this is 12k/mol very nice but if you do this reaction in presence of excess you know excess olefin what you could expect that you know let say you are doing further slowing down the reaction or further for that doing the reaction at a low temperature where you will be able to bind with another excess user ligand olefin then the product as you can imagine will be so after -30˚C you cool down faster to -80˚C the product you are going to expect or you are going to get is either one where you have the qualified coordinated with this alkali intermediate.

Now of course from there on if you try to heat it at room temperature the reaction will be then Cp*LRh and you are going to get these beta migration insertion this whole group become alkali then this is alpha beta and the whole group migrates. So what we have seen so far in this reaction we have started with a rhodium complex, we have started with rhodium complex that has olefin coordination in it we try to do the reaction faster -30˚C which will ensure that olefin will coordinate with the rhodium, okay.

And also the prolongation will occur so the prolongation will give you the intermediate where beta migrated insertion is possible, now that intermediate if you try to do the reaction further it will be of course the reaction will go on further you will get the beta migratory insertion of the hydride and the delta energy the whole diagonal for this reaction is found out to be something like 12K/mol lighter -30˚C.

Now from that intermediate at -30˚C which is a metal alkali intermediate if you further cool down the reaction mixture and if you are doing the reaction let us say you are doing the reaction in presents of excess olefin, what will happen that the metal alkali species will have coordination with olefin, so olefin coordinated metal alkies species will be generated at -80˚C subsequently if you hit that half, okay at room temperature then so 23˚C.

Let us say for example is the room temperature that at room temperature you will be able to get the alkali group the whole alkali group ethane group it to be particular migrating into the another olefin that is coordinated at -80˚C giving raise to the product in this particular case it will be a large in product like you know a butyl intermediate metal butyl intermediate will be able to get. Now let us look at the scheme once again.

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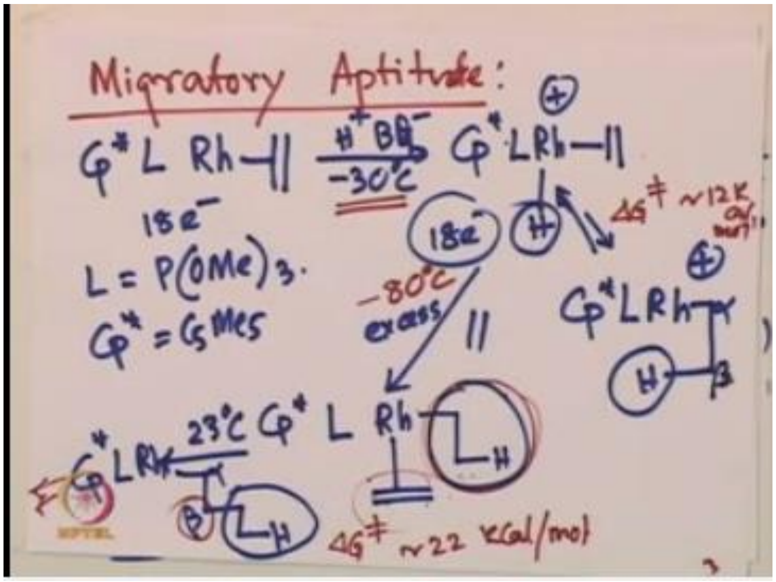

So we have this step of course this is a β migratory insertion, this is the β position. Now this is also a β migratory insertion as you see that at the β position this whole alkyl group is getting transferred. Now this reaction ΔG for this reaction is going to be something like 22 Kcal/mole. So if you look at what we are now having is a very interesting situation where we can follow the energy profile or energy demand for the alkyl group insertion into the olefin ethyl to be particular.

Ethyl group insertion into the olefin, everything else remains exactly same over here we have this hydride migrating at the β position. So if you compare and try to look at this step and the step over here the last step, of course, from here on you can further carry on next reaction if you want, but of course you have to again cool it down, bind with olefin, you can do further reaction, if you do not do it further let us say you stop it over here.

So you have an intermediate, you have a reaction where the hydride can be transferring into the β position of there, of the olefin same way in this olefin exactly remain everything remain the same on the, in place of hydride, you have the alkyl group. Now alkyl group is migrating at the β position of it. So I think it is a very, very good experiment we have is now a clear cut example, that can compare these two cases right.

We have a very clear cut example that can compare these two cases, one is hydride migration, β migratory to the insertion of an hydride, another is β migratory insertion of an alkyl in this particular case ethyl. Now as you have seen the reaction required for the alkyl group the reaction required to into 3°C, whereas at low temperature you can do the hydride migration, the energy difference. Now if you look at the energy difference let us try to look at if there is energy difference little bit closely.

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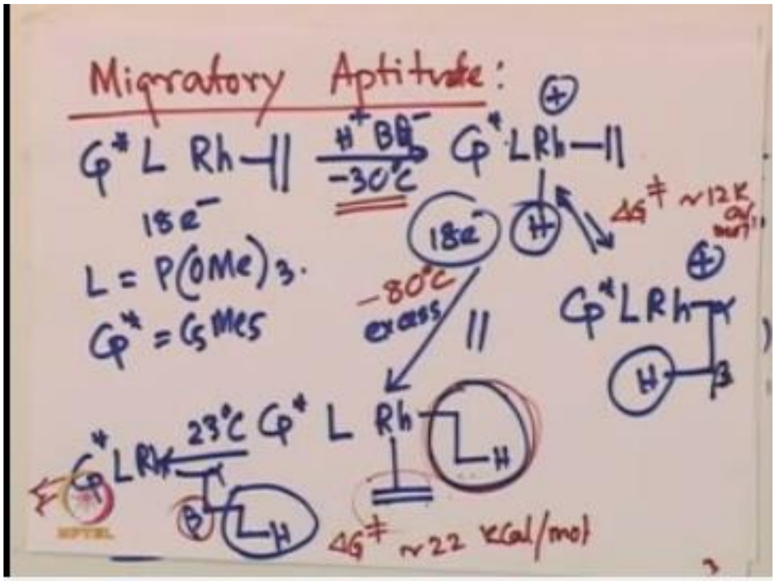

So the 22 Kcal/mole and 12 Kcal/mole overall then what we have a situation is overall we have a situation it is going to be.

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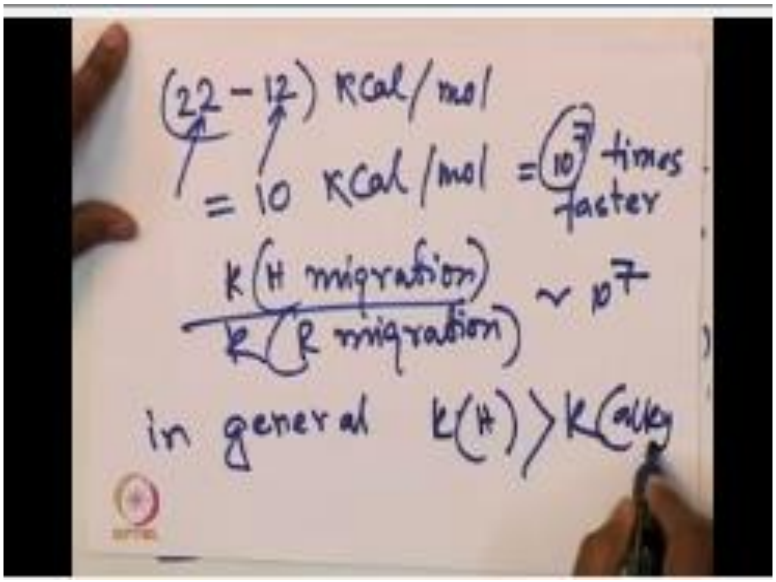

$(22 - 12)$ KCal/mol

$= 10$ KCal/mol $= 10^7$ times faster

$$\frac{k(\text{H migration})}{k(\text{R migration})} \sim 10^7$$

in general $k(\text{H}) > k(\text{alky}$

Now the energy difference between these two step is 22-12 KCal/mole of course, hydride transparent faster, alkyl in this case ethyl transparent is slower which is equivalent to 10 Kcal/mole and then that actually what it hands up is nearly 10^7 times faster. So hydride migration is 10^7 times faster, that is quite interesting right, one would not imagine that value would be so much right. now of course this is happening because after prolongation the first form intermediate as you have seen, after prolongation it is positively charge, so ethylene can bind and form the ethylene, efficiently.

In the first case as you have seen, after at -30^0C you have a one ethylene binding at lower temperature, you have further ethylene binding, another ethylene binding, this is possible only because the metals centre is becoming more and more positive and there, olefin coordination becomes more and more feasible, so let’s try to write down the, equation very clearly.

So you have H migration, migration versus R migration, and that is going to be your nearly 10^7 times, in general if you like to out, in general you will have K(H)>K(alkyl) , okay, so that is the general formula, now i hope this is a very simple example, and you have realized that this example can give you an idea, hydride migration versus alkyl migration, and of course in general, in chemistry usually we don't want to generalize too much.

But you know that's is the usual fount rant but one may not take it for granted all the time, right you have to see the situation if under the same situation, yes! You can perhaps call that hydride migration in first at over the alkyl migration, okay, so I guess a so far we have discussed, alpha migratory insertion, and beta migratory insertion.

Next of course you have seen the alpha and beta migratory insertion in a number of cases, next we would like to start with the beta elimination, right now of course beta elimination is just opposite of beta migratory insertion, right, we have seen oscillatory by addition , detective elimination, alpha migratory elimination, alpha migratory insertion, And elimination.

Beta migratory insertion and beta elimination will now see the beta elimination, of course we will try to discuss with one example as always and try to discuss further if, you know today permits, let see, so beta elimination in general that is what is called.

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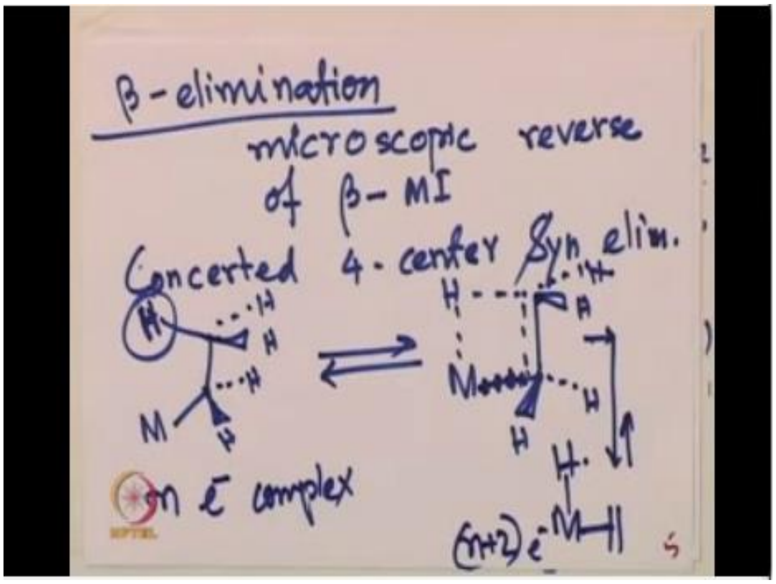

β-elimination

microscopic reverse of β-MI

Concerted 4-center Syn elim.

n e complex

(n+2) e

Now of course the first step is microscopic reverse of β migrated insertion that goes down saying at these point and it is the, on sorted 4 centers in elimination, concerted 4 center, okay that I think you guys will be able to find by now, syn elimination. Now let’s give you one example, it will be just opposite to the β migrated insertion, that we’re trying to discuss today, let say the product that in this case particularly that this one you try to pick up and as you go, it's going to be a reversible reaction.

4 center reaction, you control very nicely over here and that will give you the intermediate here this is nicely drawn 4 center intermediate, of course sorry, this would be dotted line, dotted line here and you have of course hydride or other species. Finally you are going to get the product where metal polyphine and hydride. It coordinated, if this I the electron complex, okay, of course there should be no doubt in +2 electron complex.

Now, so this is generic example as you can see, previously we have seen the general example of β migrated insertion, it is the opposite of β migrated insertion, that is the β elimination, we tried to give the example where we have hydride elimination, β hydride elimination. Now, of course it is possible to have β elimination, just like, you know insertion, elimination is also possible, but it is extreme rare, you do not see that often but of course on the special condition you can, on the special cases you can still promote β alkyl elimination but the most common one is the one that you see almost routinely and that is β hydride elimination.

Sometimes it, this step would be any sense, it can be problematic for a dijad reaction, let say, you don't want β hydride elimination to be occurring and it ends happening, so that potentially causes the problem for your dijad, other product formation both more valuable product formation, we hopefully able to discuss little later.

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

Jr. Technical Assistant

Vijay Kedare

Teaching Assistants

Arijit Roy

G Kamalakshi

Sr. Web Designer

Bharati Sakpal

Research Assistant

Riya Surange

Sr. Web Designer

Bharati M. Sarang

Web Designer

Nisha Thakur

Project Attendant

Ravi Paswan

Vinayak Raut

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