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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. 8

MIGRATORY INSERTION
&
ELIMINATION REACTION

Welcome everyone today we will like to discuss migratory insertion and migratory elimination reactions so it is called MI and ME right.

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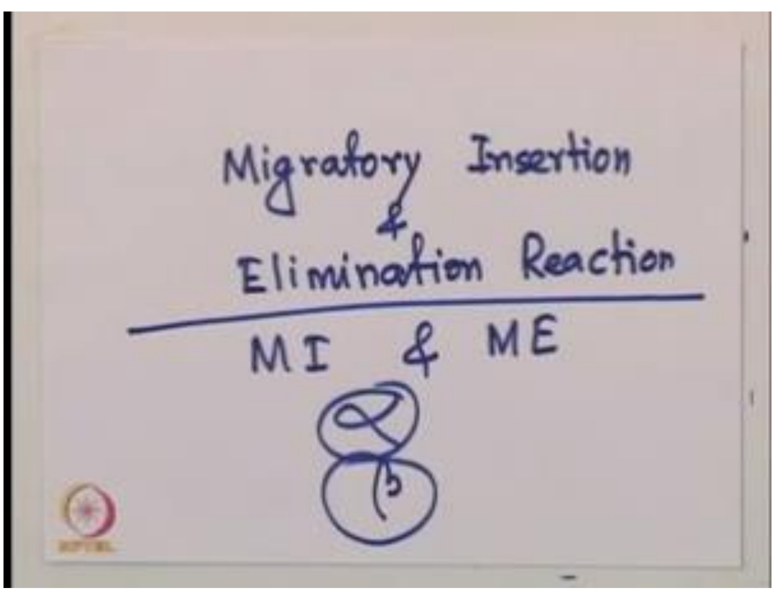

We have two different types of MI α migratory insertion and β migratory insertion these are most common migratory elimination once again also of two different type α migratory insertion and α migratory elimination with some example we will discuss the basics of it and we will be focusing mainly on α and β version of MI and ME right let us get started once again we will have a metal complex.

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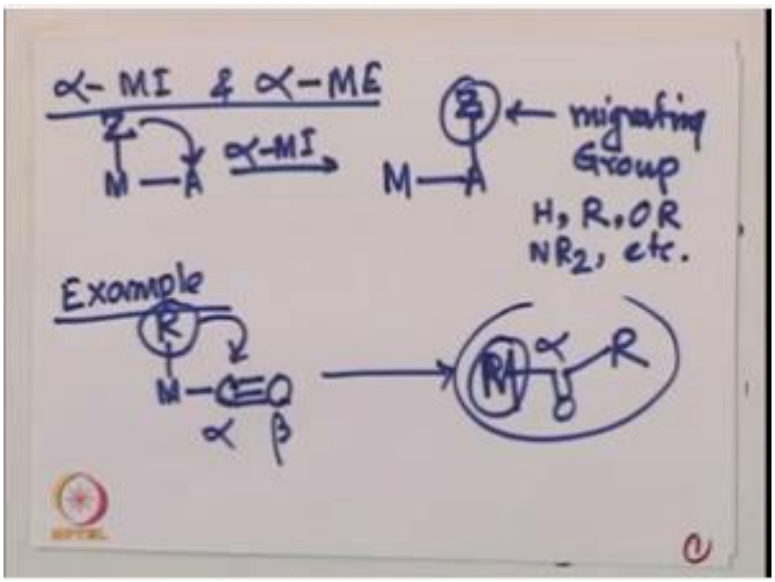

These are going to be the metal complex of organometallic type we have metal where a and Z are involved now if we are talking about α migratory insertion it is the forward reaction where MA and this Z bond formation MAG bond formation is happening now this Z is the migrating group so you have seen Z is migrating to A usually the Z are something like H are hydride are alkyl alkoxide NR_2 etc..

Now let us take one example then it will be clearer a if you have a metal carbonyl species with R group let us say R is alkyl group you are familiar with the MCO our bond formation so technically speaking R is getting migrating on the carbon so this is the α position this is the β position since our is migrating selectively at the α position in this case it will be called α migratory insertion.

Now of course there is a β migratory insertion when you will see that R group is migrating at the β position of course one can argue whether it is you know insertion into the MR or the migration of R so R can migrate or CO can go and insert so we will discuss specifically with an example what is the usual way of doing things in this case once again it will be the migration of R not the insertion of CO but with a very elegant example done by researcher we will discuss why it is a migration not insertion.

So migration of R is happening not CO getting inserted of course both migration and insertion will give you the same product so once again this is the α carbon or α position β position α is directly coordinated with the metal and the R group is migrating on the α position not on the β position so you get this species sorry this should be M okay you get the species where MCOR species is form.

Now let us look at the β migratory insertion β migratory insertion as you can imagine at the β position of the coordinating coordinated species the R group will be migrating, okay. It is perhaps the more common version of these migratory insertion and elimination.

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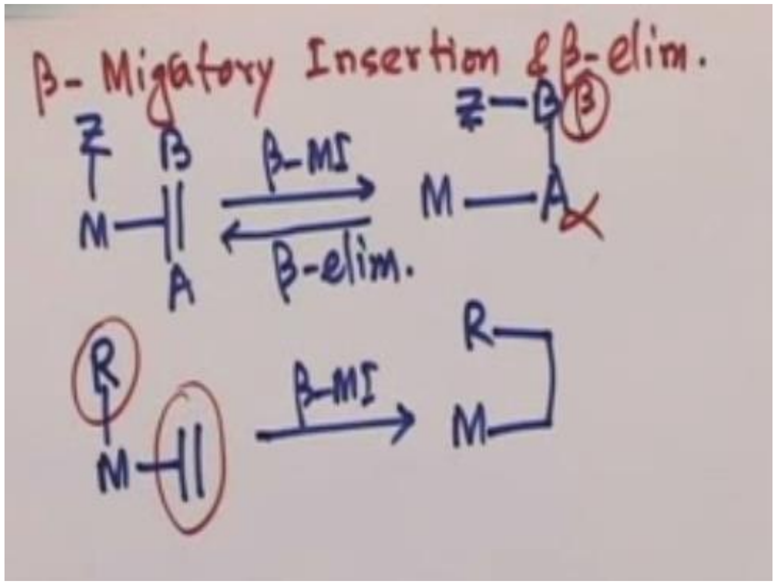

So we are trying to discuss or see one generic formula of β migratory insertion, insertion and β elimination. Now we have a species a once again a metal species metal Z and we have AB let us say an olefin β migratory insertion would be something where M-A-D and Z this species is formed once again you can see this is the α position this is the β position selectively at the β position this z is migrating.

The reverse of it the reverse of this process will be β elimination, so it is it is very crucial that you understand the you know the type of type of thing you will be getting in these cases where the examples may vary from α to β and you should be very careful about judging whether it is α migratory insertion or β migratory insertion, let us take one of the simple example for these cases so if it is a R metal olefin species by β migratory insertion.

You get something like what we were calling like that, okay. So the most important factor for these cases is that these two groups are and this species should be ceased to each other should be CIS to each other okay and thereby that is the prerequisite for migratory insertion reaction. Now the α migratory insertion we will be discussing now with a with few more examples these examples you know are very well known examples you are definitely aware of it.

But may not have realized that it is in fact the α migratory insertion some of the industrial scale synthesis are done by utilizing these migratory insertion let us say α migratory insertion and the product formation for these cases could be you know tons of millions of tons, right. It is a lot of product formation that goes on by migratory insertion I think in a minute we will show you the example then you will realize that yes indeed you are familiar with it let us look at some more examples of α migratory insertion.

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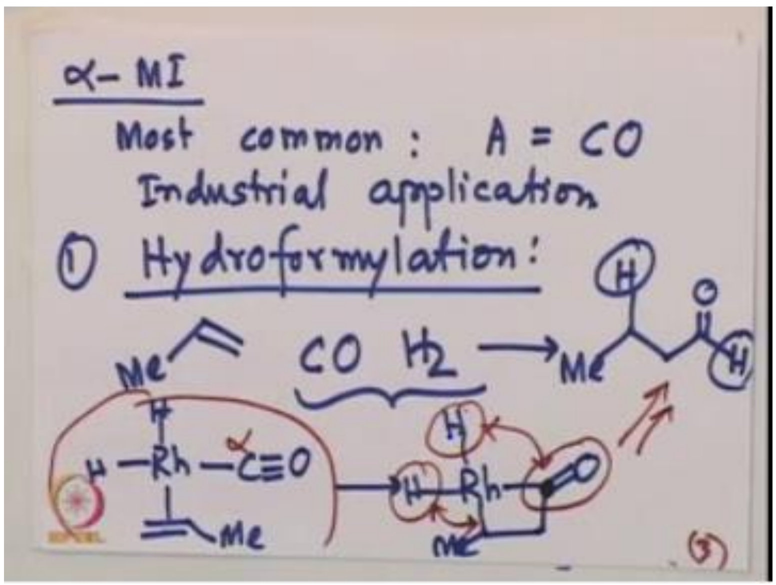

So we are discussing α migratory insertion most common of course most common of these processes are when your A equal carbon monoxide right and usually you know you have a lot of industrial application with such spaces, one of the most famous reaction in these case is the hydroformylation reaction I am sure you have heard of it you have studied about it before what is the hydroformylation reaction. You have a olefin and a CO and hydrogen.

So carbon monoxide and hydrogen together usually it you form a linear aldehyde in these cases where you have two hydrogen one CO into the olefin now for these cases we know that it is a very well-known industrial process you know 100 millions of tons are getting prepared of these aldehydes are prepared by this process and we have rhodium or mobile catalyst for these sort of transformation nowadays used industrially now of course you know by looking at this reaction you may not be appreciate the fact that there is a alpha migratory insertion involved.

But if you look at the mechanism of this reaction very briefly I think it will be clear although I will not discuss the mechanism in stepwise fashion in a you know in a very elaborate form I will just take you to the key step where alpha migratory insertion is happening let us try to write down the reaction so you have let us say rhodium species it could be rhodium and cobalt usually rhodium or cobalt catalyst so you have rhodium species it is a dehydrate species let us say you have again I am not discussing the mechanism in detail.

So you have this intermediate are you have carbon monoxide olefin and hydrogen's are attached with the rhodium then what you will see in the next step is usually a rhodium intermediate where you see the olefin is inserted into the α position of carbon monoxide so this is the step where the α position of carbon monoxide α and these olefin is getting inserted so α migratory insertion is happening and then you can appreciate a reductive elimination between H and this carbon center and a reductive elimination between H and this carbon center you can see the product formation right.

Of course this is a very rudimentary way of showing this mechanism but most important step is here you see the α migratory insertion at the carbon center so at this carbon center migratory insertion is happening and as you all know this is a very, very facile process and this is utilized by the industry worldwide to produce the aldehyde from some very simple starting material such as polyphen you know propane in this case or other olifen propane and carbon monoxide and hydrogen can give you this aldehyde in presence of a rhodium or cobalt catalyst and producing selectively the linear product aldehyde product.

Most often you get the linear product of course there is there is a chance of forming the branch product where aldehyde will not be at the terminal projection but at the branch position in here we might we'll discuss later that one but hydro formylation reaction is a really great example for α migratory insertion another reaction would like to discuss which is once so utilized you know widely in the industry that is Monsanto acetic acid process let us try to look at the Monsanto acetic acid process and shear again all of you are familiar with it but may not be realizing that a α migratory.

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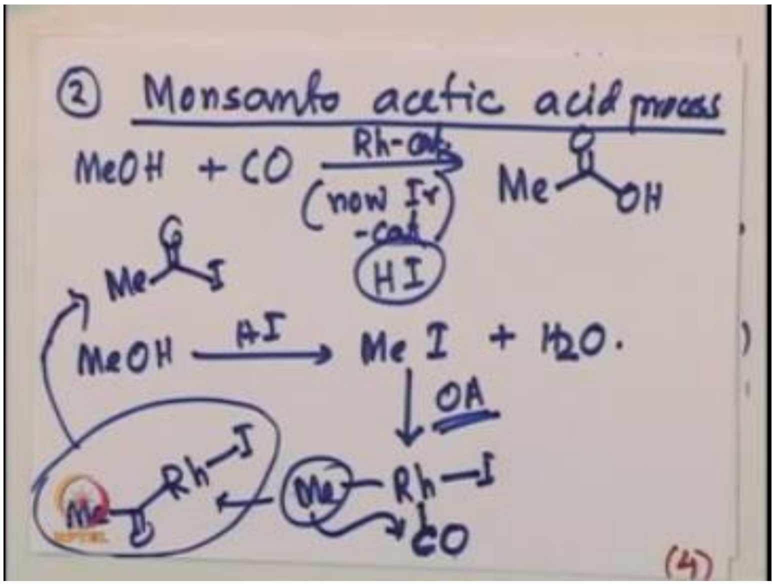

Insertion is involved in it so Monsanto acetic acid proceeds what is it as you all know methanol simple methanol and carbon monoxide usually with rhodium catalyst traditionally or historically with rhodium catalyst but nowadays it is replaced with Iridium catalyst so nowadays industry use Iridium catalyst but if you look at the history of the development for the Monsanto acetic acid process if the rhodium catalyst that has been utilized essentially you get the acetic acid formation, right.

So methanol and carbon monoxide give you acetic acid that reaction looks really funny right, well I mean of course it is not going to be insertion of CO or you know methyl, methyl from methanol directly into the forming there what you need here is you need a iodine okay, source so what you need in addition is a HI therefore the mechanism is little bit you know interesting at one glance it may be CO just getting inserted here no, that is not you know on but it is not really the case.

First of all methanol will be converted in presence of a HI to give you methyl iodide plus water, right. Now this methyl iodide will undergo oxidative addition into let us say rhodium you have methyl and iodide I am not drawing the ligand on rhodium what then you have of course Co coordination, methyl iodide this is almost this is a oxidative addition and coordination of CO you get methyl and CO sits to each other from where you will get Me CO alpha migratory insertion so and the alpha position methyl is getting inserted here to give you rhodium this intermediate.

From this intermediate, from this intermediate you will get Me CoI okay, and then hydrolysis of this intermediate will give you the acid. It is a very simple reaction but elegant example of alpha migratory insertion, what you have seen in this example is methanol is converted into methyl iodide in presence of HI and that methyl iodide undergoing oxidative addition as well as the CO coordination with the metal centre occurs.

The methyl migrates at the alpha position of the carbon monoxide to give you MCO metal intermediate then a reductive elimination from that intermediate where you have the rhodium I do and this Asyls species they will be six to each other and thereby you will be able to have a reductive elimination to form ch3coi will then undergo hydrolysis to give you the acetic acid.

So once on to acetic acid process as you know it is a very you know well-known process it is used industrially and it utilizes the Alpha migratory insertion beautifully to produce the acetic acid will discuss few more example of alpha migratory insertion because this is again this is a few process that happens quite often let us let me look at few more examples.

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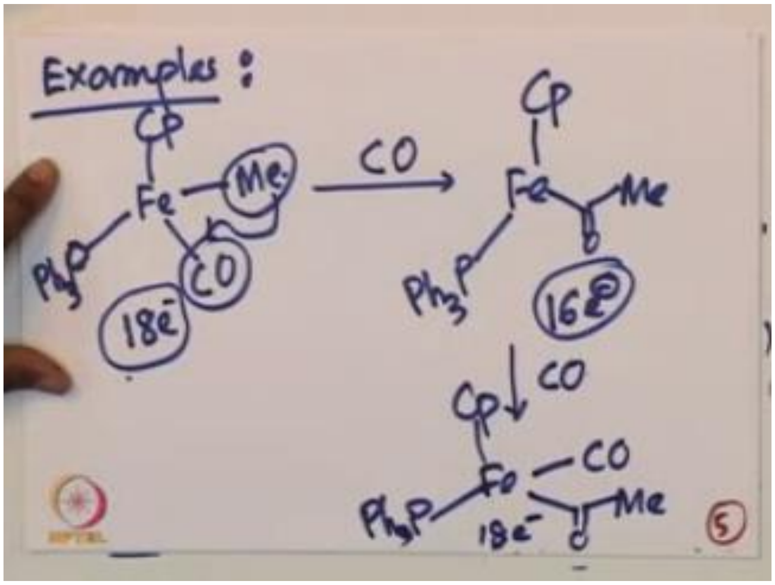

Now if you are looking at an iron complex such as this you have di-carbonyl or sorry mono carbonyl intermediate if you count the electron it will be 18electron species right now you want to do a reaction in presence of co with this iron complex, the first step you would expect it is a 18 electron species it is not going to interact with the CEO to give you know the di- carbonyl species but what will happen is this methyl and the co so alpha migratory insertion will go on okay.

So from there you have now 18 electron to 16 electron species right now alpha migratory insertion has happened so you have from it tetra coordinate iron you have now try coordinated iron this is a 16electron species since this reaction under CEO, now co can interact with iron to give you iron co this inter mediate again it is back to 18 electron now this is your final product in this case.

So what you have seen in this case is RN complex organ metallic inter mediate having 18 electron and you are reacting this with a carbon with carbon monoxide nothing happens at the first place with the carbon monoxide from outside, but methyl will migrate, at the meta centre to the carbon monoxide and the Alpha position to give you that, aisle intermediate so, 18 electron species will undergo a 16 electron species formation, and from there the CO can interact to give you now another edition of carbonyl, to give you the final complex.

So 18 electron species goes to 16 electron, comes back to 18electron, in between beautiful alpha migratory insertion reaction occurs, let us look at yet another example which will be again very interesting one, it's a zirconium one we would like to discuss, so we have a zirconium complex, is very interesting.

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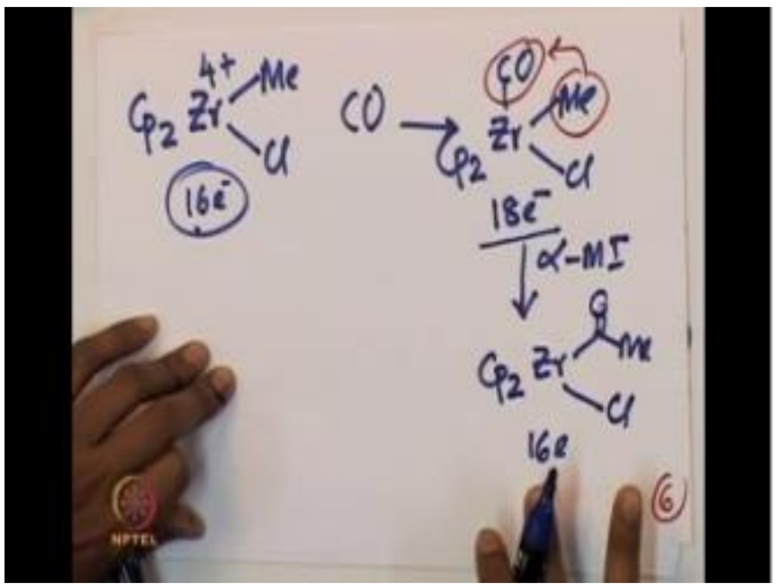

Usually CP_2 is conium, what is the oxidation state of zirconium in this case, quickly if you look at oxidation state will be 4+ right, 4+ oxidation state if you do the electron count for this species it is going to be 16 electron, once again what you want to do you want to deal with your favourite Liggett CO, for these alpha migratory insertion okay.

What will happen? simply you will get an 18electron species this is a 16 electron species, you will get a 18 electron species where carbon monoxide is getting a charged with the zirconium, right, so 16electro species goes to 18 electron species very well, and then from this 18electron species as you perhaps fenced by now, there is a CO there is a me now migratory insertion will occur to give you CP_2.

So this is the one α migratory insertion CP, to J_r C_o me and cl, of course if since this was a 18 electron now you have a 16electron species right, you should be able to do this electron count literally, very, very easily 16 electron, CO addition18 electron and migratory insertion 16electron right.

Now one thing to notice here is, why this18 electron species? Right the first intermediate will undergo the migratory insertion it's 18 electron species, in this case 18 electron species is specifically undergoing migratory insertion, because you do not have a D electron it is a d0 species the zirconium intermediate was d0 one and it is extremely difficult for d0 species to stabilize a, a ligand such as carbon monoxide where, where a л back bonding is usually preferred but, there is no D electron there for л back bonding will not be possible and therefore the migratory insertion, α migratory insertion in this case becomes very facile.

So starting with a 16 electron species, you go to an 18 electron species, but this 18 electron species in this particular case are not, is not going to be stable because, it is a d0 electronic configuration. Since, back bonding is missing you will not be able to have its stabilization so the methyl will migrate on to Co to give you the Co mo intermediate of course, this is a 16electron species what you see in here that is a finally this lone pair from this will be donated here to give you the zirconium C_{P2} species.

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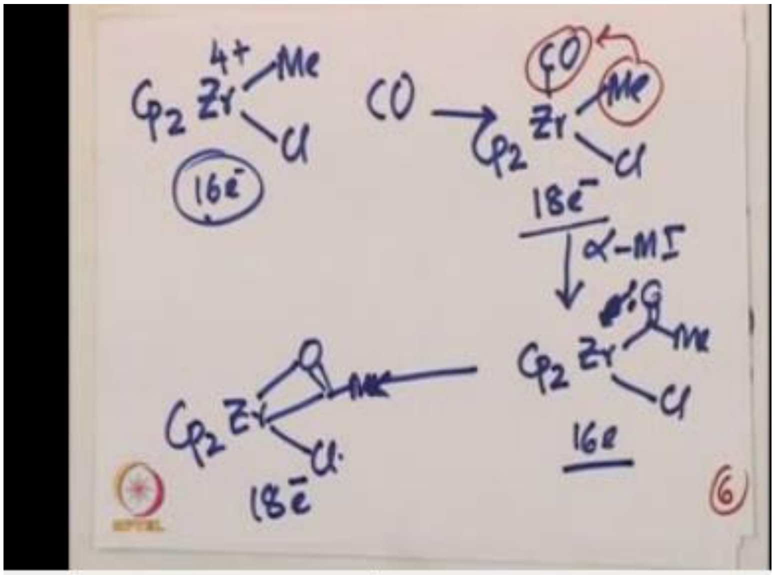

Now this will be 18 electron species, such d0 metal you know it is very difficult to stabilize Co complex, Co complex is going to be unstable as we try to discuss due to absence of back bonding and actually there is almost no example of d0, d0 Co complex, d0 metal center with carbon monoxide bound with it specifically crystallo graphically characterizes explanation is extremely difficult because, you do not have much stabilization.

Okay, even with or without methyl if you have a species which is d0 and carbon monoxide bound to it I think it's extremely difficult to stabilize it and getting a crystal structure out of it will be kind of next to impossible all. Of course it is a very good research problem if one can figure out how to stabilize d0 metal spaces with carbon monoxide bound with it okay.

So we will conclude today's session here we have seen migratory insertion and migratory elimination, we have briefly discussed α migratory insertion with some example we have discussed insertion and elimination being the you know reversible process, we have also seen alpha and beta but we will have more and more example of these even α migratory insertion ,we will see some more interesting example in the next class okay, till then you guys keep on reading on this and we will continue discussing these migratory insertion and migratory elimination.

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