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Organometallic Chemistry-I

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Module No. 2

Lecture No. 10

α – MIGRATORY INSERTION
&
α- ELIMINATION REACTION

Welcome back so today we will discuss on α migratory insertion little bit and then when you get into the α elimination in the last class we are trying to show you the examples of α migratory insertion and in lot of examples we have discussed regarding that we will discuss one more time the transition metal carbine which we started discussing in the last one and the we will move to the α elimination so toady's topics mainly will be one α migratory insertion and then α elimination okay.

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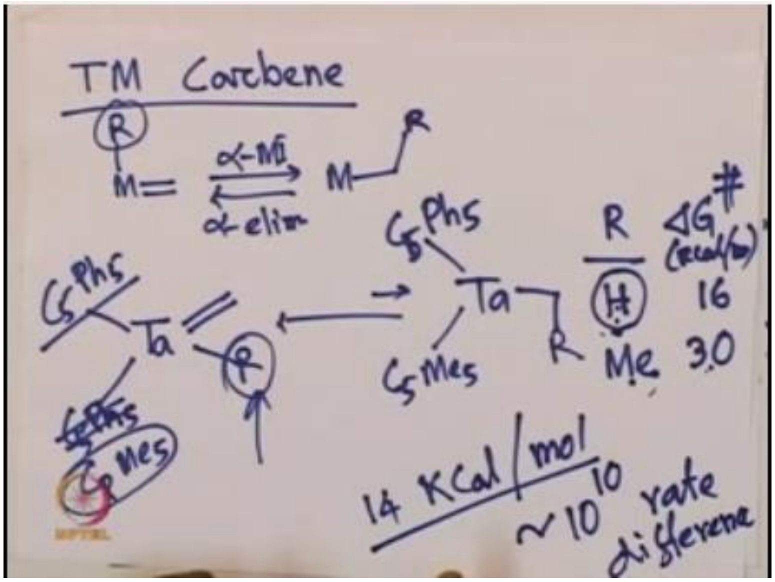

So transition metal carbine as we were trying to discuss transition metal carbine these are complexes of this nature where R groups is there carbine as you know this is the metal carbine spices and there is a R group are these R group can be hydrogen or any other alkyl group so this α migratory insertion we are looking at the reverse will be the α elimination process now if this R group is H or if R group is methyl depending on that we can follow the reaction and we will be able to tell the ΔG G# they get of the reaction and we can experimentally measure the if we do that for example in case of this titanium complex where you have R and C5 Ph5.

And now in this case particularly it would be C5 Me5 and C5 Ph5 this complex was taken this tetra confidante titanium complex was taken and what was found is titanium complex having α migratory insertion happening and in particular we have taken two different R groups okay this R group can be two different one and we can have the product formation okay when R = hydrogen and R = methane what was experimentally found that it is ΔG# value for in KCal/ mol this is 16 and this is 30.

So as you can see it with hydrogen R= H we have the lower activation by a barrier but for the methyl it is having a higher activation barrier how much difference is there that 14 kcal difference theses two how much difference is there again 14 KCal now H versus methyl which one is faster H is faster right this is one is the faster now 4 KCal 4 tine KCal/ mol this energy is equivalent to 10^{10} times rate difference.

So that is why it lot of difference right 14 KCal/ mol rate difference is there between the R= H and R = methyl and this is experimentally given data that means total this 14 KCal/ mol difference would add up to something like 10^{10} time rate difference that is very faster very fast for R= H and comparatively R equals methyl will be very, very slow. Now of course I think you may be aware of how to you know somewhat calculate little bit forth will be the energy difference and there by how much will be the red difference approximately so I am trying to give you a some approximate since, so almost the rule of them you know it is say very generalize thing but not accurate that very accurate and we are trying to give you a ball park figure.

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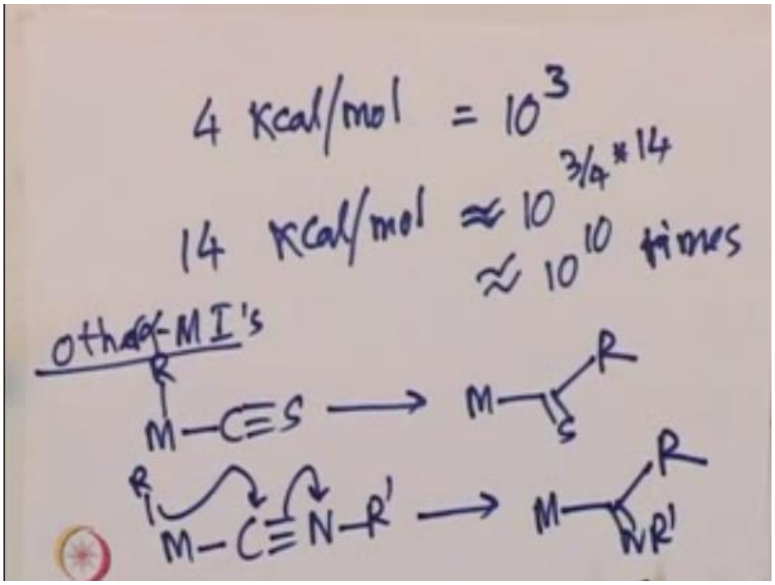

So approximately Kcal for mole equals 10^3 times red different., if there is a difference of 4Kcal/mole the Δg double dagger value then there is you should expected to a 3, in this case 14 Kcal/ mole value difference is there and thereby you are looking for something like this is again very rough calculation, so that would be again 10^{10} approximately 10^{10} times rate difference will be there.

So again this is not really the exact way but this is how the, the experimental chemist kind of quickly calculate how much rate difference is there, the rule of tamp again is 4Kcal/ mole you know Δg double dagger difference that means that 10^{3} times rate difference is there and if it is something like 14Kcal/mole that will be calculated to be 10^{10} times rate difference and you know it is a lot of difference of the rate.

Now let us try to look at what are other possible scenarios for the α migratory insertion, there are other cases where you can expect α migratory insertion and then they would case improved let us say other α migratory insertion then you can have the short of complex again you can get M-C-R you can have this sort of complex as well that would lead to M=N=R'-R okay so these are other α migratory insertion.

That is possible out there you know you can look at the α migratory complexes different complexes and try to judge yourself where the α migratory insertion will be possible but you know mainly I think in common literature you will see mainly the carbon monoxide is one of the major target for this α migratory insertion and then purpose the Carbon examples comes to mind and the others are less slightly okay but of course you should keep your eyes open for such formation, the next we will move on quickly to the α elimination right.

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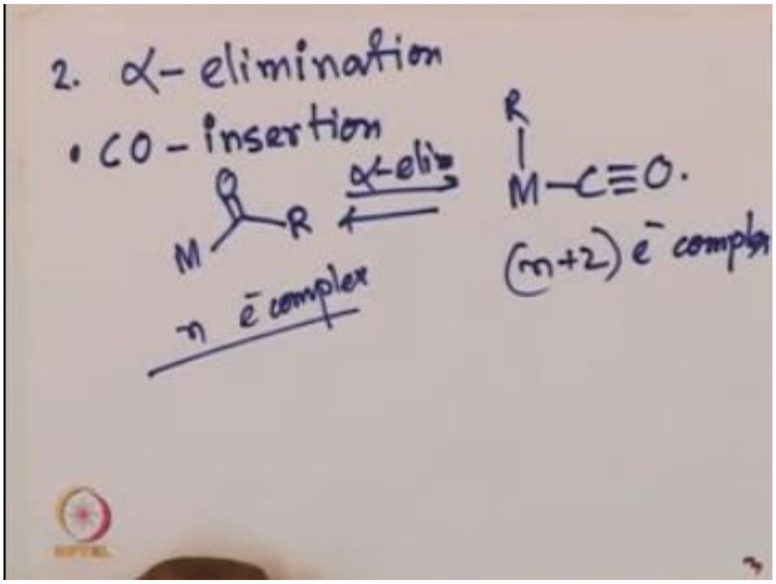
2. α- elimination

• CO - insertion

We will discuss that the reverse closest of α migratory insertion that is α elimination as you have already know this is mainly the CO elimination step we are going to discuss this is what is going to be α elimination then M-R-C=O these are the complex formation and you know if this is n electron complex if this is n electron complex you are going to get n+2 electron complex right.

So these links you should be able to do very quickly and you know you should not have any problem in discussing that so for one second what is the α elimination it is the reverse of α migratory insertion and one second the common fact or common compound where we can see such α elimination is the carbonyl species or the a style species for example MCOR from where the R will be now transferring to the metal center the n electron count of the metal center or metal complex will be giving you n+2 electron count.

Now these are the facts which is true both for α migratory in such α elimination in both this cases we know that the two electron difference will be coming up let us try to discuss one of the example where I am sure you have seen it before this is the de carbonyl reaction okay de carbonyl reaction means let say you have a A metal carbon Asyl species from there or so to speak you have the aldehyde as a complex RCHO from they are by involvement of a organometallic intermediate.

We are trying to form RH aldehyde to let say alkane formation that is the one very simple example that demonstrate α elimination reaction quite, quite beautiful let us look at one of those examples so the.

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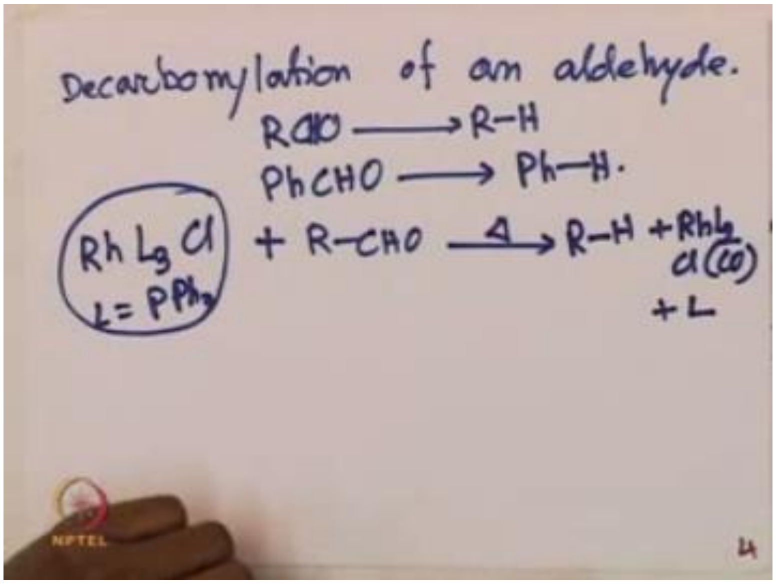

Decarbonylation of an aldehyde.

$RCHO \longrightarrow R{-}H$

$PhCHO \longrightarrow Ph{-}H.$

$\boxed{RhL_3Cl \quad L = PPh_3} + R{-}CHO \xrightarrow{\Delta} R{-}H + RhL_2Cl(CO) + L$

Decarbonylation of aldehyde decarbonylation of an aldehyde but we are having RCHO to RH right so the CO is going out now simple the most common one could be benzaldehyde to benzyme right and you may have known that this is the reaction which has been done of by will using the Wilkinson complex what is we complex that the rhodium complex RH L3 Cl where L equals triphenyl phosphine this Wilkinson complex reacts with aldehyde let say any common aldehyde RCHO if you hit it you will get RH + rhodium L2 Cl Co complex along with the ligand coming out show this reactions are happening this is what we would also like to know where is the alpha elimination or how is the alpha elimination occurring so this is Wilkinson catalyst.

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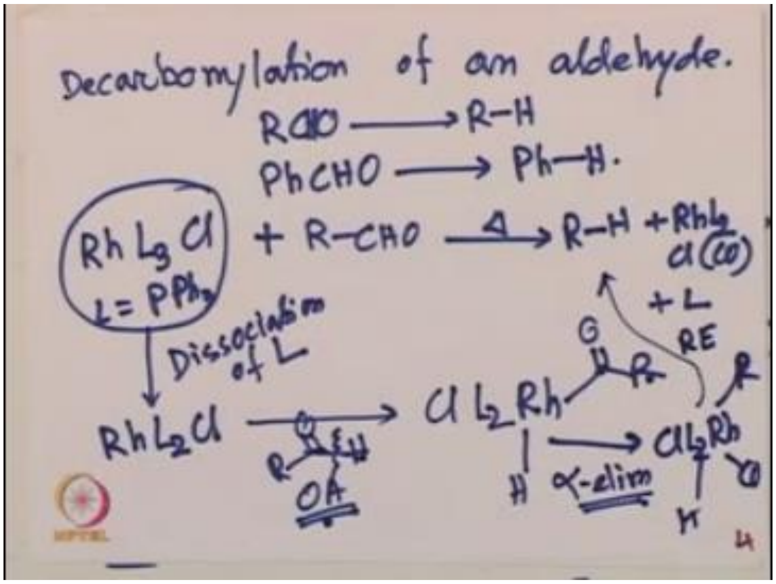

What happens Wilkinson catalyst can react with the aldehyde first step be the dissociation of the ligand of ligand and you will have RhL2Cl one of the ligand goes out this is the triphenylphosphine in this case and you will have RCOH then oxidative addition into it so you, we are going to see the oxidative addition for their and that will give raise to the complex where rhodium hydride and COR is involve from here.

You can see that this is the complex which is the oxidative addition complex the metal is inserted basically into this carbonhydrogen bond to give this intermediate from there is the perfect complex as far you can see there is metal COR group involve then you can have alpha elimination this is the step alpha elimination the previous step was oxidative addition and you can get ClL2 rhodium COH and R, right and then this R and h should be sit to other as you know that by reductive elimination you should get the RH product.

So what we have seen here is very simply the Wilkinson catalyst rhodium catalyst tri or thrice triphenylphosphine come rhodium complex of with chloride can undergo fast ligand dissociation in this case triphenylphosphine ligand will be dissociated to give you rhodium diphenyl triphenylphosphine complex with chloride which then can oxidative undergo addition to the aldyhyde to give you this metal hydride and metal sessile species from there as you know that species is ready to do undergo the alpha elimination reaction to give you the intermediate where R and H will be sitting together and once they are sits to each other they can reductively eliminate to give you the RH.

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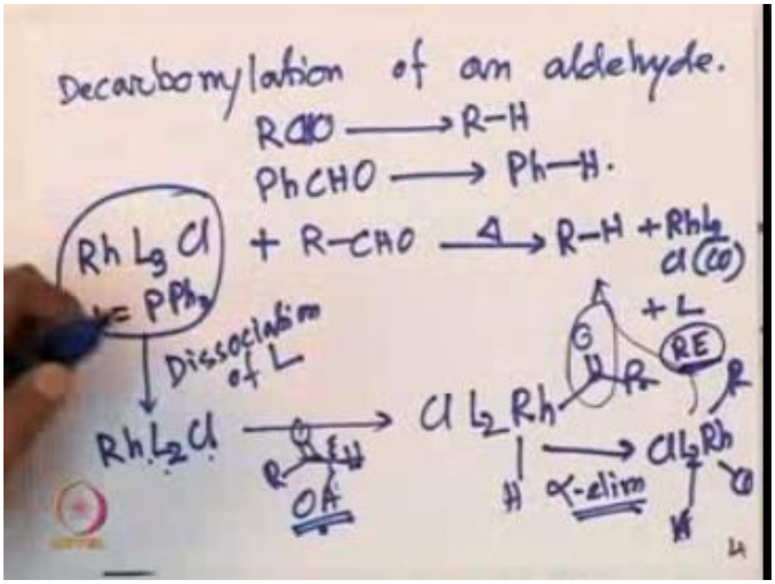

So let us look at the reaction one more time this is the Wilkinson catalyst ligand dislocation gives you RHL2Cl and then it gets into the aldyhyde to give you the oxidative addition complex from there elimination of this CO gives you this complex where R and H can now be sits to each other to give you the reductive elimination and finally you get the RH.

So overall what you have seen in this reaction is your aldehyde effectively is converted in to the alkene so benzaldehyde can be converted to benign let us say you have aliphatic aldehyde that can technically give you the alkane with one less carbon so this is actually one of the really important reaction where you can see that something like bio masks and the converted in to corresponding alkane to give you the fuel grade alkane.

So these are very simple reaction but can have very long term effect, of course in addition to rhodium now we have seen that palladium can do the job radium iridium can also okay but palladium is also very effective for such aromatic aldehyde de carbon less and reactions. Okay now you have seen one of these example let us move on to the alpha elimination of transition metal alkyl species which is again analog of the one what we have discussing. So alpha elimination of transition metal alkyls.

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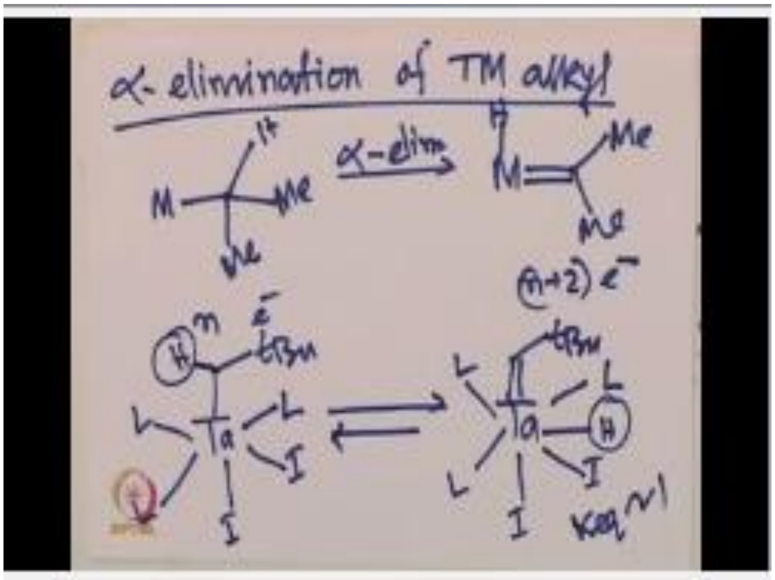

Now in these cases you can have one compound like this where you have A I should profile moiety in there and then you know these are the transition metal alkyl complex if g it undergo alpha elimination you are write that it will give this complex that means the carbine complex once again if this is n electron this should be n+ 2 electron now this is the same if you look at the alpha elimination we have discussed with the CO and R group CA McoR it is exactly of the similar type that here again alpha position elimination is going on and the group is now sitting after elimination it is now sitting with the metal complex.

Of course in this particular case we are going to get metal carbon complex let us take one of the particular example which demonstrate this alpha el9mination of metal alkyl species. This again a very elegant example this is by Prof. Strock proof Richerd Strock at MIT they have shown that this is the tantalum complex can give you this tantalum carbon intermediate okay along with L H I, L, L from this remaining constant from this particular k equilibrium, is nearly one show, this is again one of the very beautiful example that demonstrate that alpha position of this one, this is the alpha position this H is now , migrated over there, this is alpha elimination of transition metal complex.

Now next we will move on to, beta migratory insertion, where we will see that so far we have discusses alpha position are getting converted, or getting eliminated, or come transformation is happening at the alpha position that means the carbon centre which is immediately attach with the metal, are undergoing some changes but it could also possible that, not the alpha position, but the beta position is the second carbon from the metallic centre, is undergoing some transformation indeed.

Such beta migratory insertion or elimination are very, very much happening in the organ metallic complexes, and those are the one which are perhaps more important of this error, let us look at the beta migratory insertion,.

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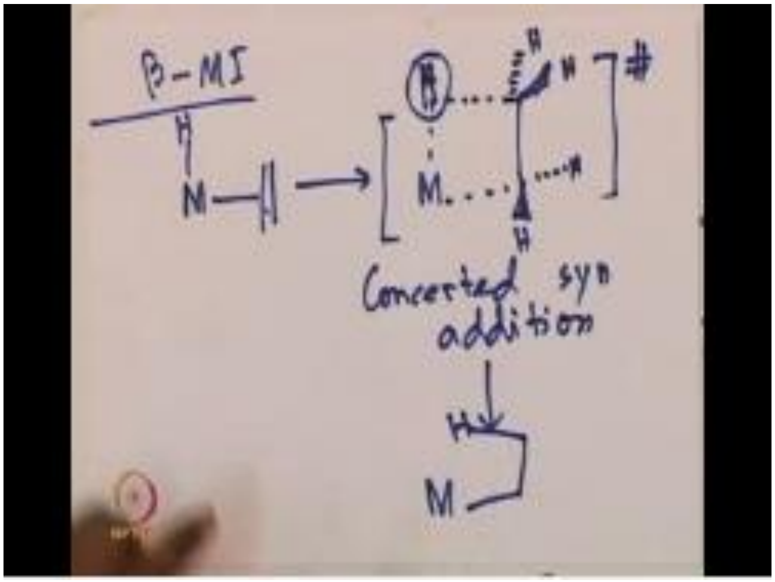

Now most common one for beta migratory insertion, is the one fare, let say you have metal with a olefin coordination and hydrogen coordination, and they will undergo a consorted is in addition, that means, you have metal H, so from there, from there you can have, this consorted reaction where which is fore cantered reaction going on, you can have a transition state like that, this will be a consorted syn addition.

And from there on over all you will be able to have a complex square, this alkyl group is over there, so what we are seen here is metal hydride with a olefin coordination undergoing consorted seen addition in afore cantered mechanism, and from there on we have seen metal alkyl species is getting generated.

Now this is a very common reaction that is absorbent in number of industrial early entrances, where beta migratory insertion, happening the most famous one could be the hydrogenation, hydro formalization and Ziegler and Natta polymer reactions. Now next will try to look at the most critical or most in a compound reaction of which and actually we will be discussing quit a lot on the, β migrating insertion or the elimination reaction, was slowly, let's look at one example at time.

So the first key step, key step in number of reaction, these β migration insertion re involved, so the one that come to the mind is the hydrogenation, any hydrogenation reaction, you have studied here will be β migration insertion hydroformylation. Of course Ziegler- Natta polymerization is another one. Now the first discreet example wa with a, with platinum complex in this case, where we can see the first discreet example of this type are the one where once again in the metal hydride and the oliphine is coordinated to give you, metal, this alkyl intermediate.

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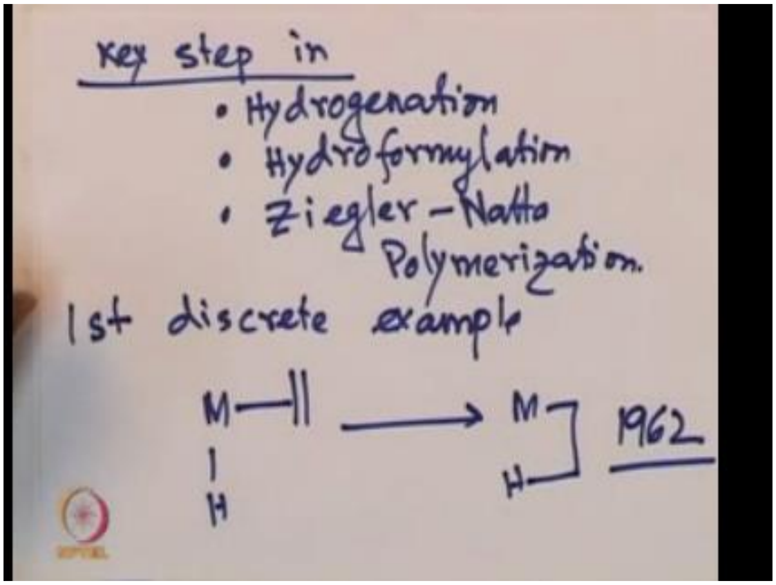
Key step in
- Hydrogenation
- Hydroformylation
- Ziegler-Natta Polymerization.

1st discrete example

This was demonstrated in 1962, where, where we have seen that, the metal oliphine and hydride will be the complex will synthesize and then upon β migratory insertion, we can have the metal alkyl spaces. Let’s take the particular example in mind and that metal hydride ligand, ligand and the chloride ligand in this particular case I triethyl phosphine, under 40atmosphere pressure, when the ethylene gas was fast or reacted and w can see the product formation in this case, particularly less with plate platinum, it give HL chloro and ligand.

So this I one of the first example that we have seen in 1962, way back in 1962, this once discard where metal complex were reacted under pressure with oliphine to get the metal alkyl species. That was the genesis of it completely new and interesting area of which has been commercialized in many, many form in, many, many different important reaction that it’s β migratory insertion step. O we will discuss further on this and how thee, of course the insertion step β migratory insertion also would like to learn, how the migratory aptitude varying from one R group to another one and also n number of synthetically and industrially important reaction, we would be discussing in the next class. Till then keep reading and we will be discussing more on this topic. Thank you bye, bye.

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