Introduction to Organometallic Chemistry
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Lecture - 23
Metal-allyls- eta cube complexes-fluxionality reactivity

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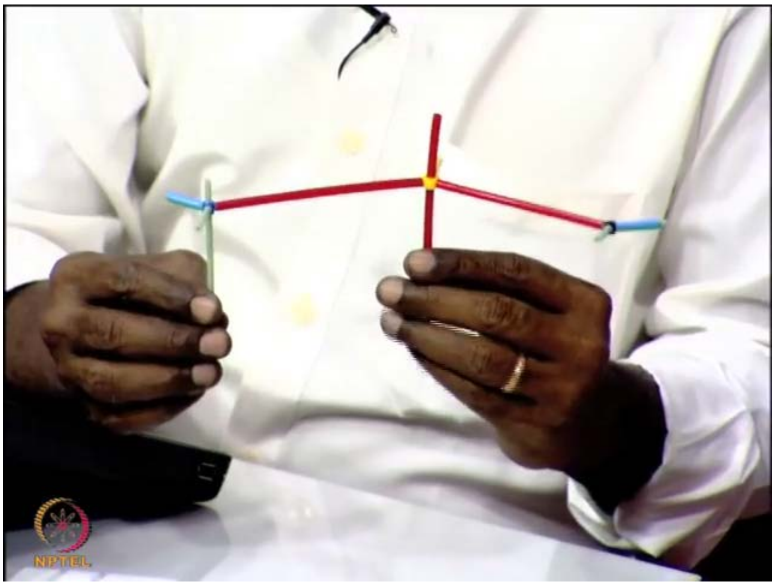

So, we start today’s lecture with a small three dimensional model and the demonstration of how allyl species can be fluxional. The allyl species has got 3 carbons, and carbons are 1, 2 and 3. And these 3 carbons are oriented in such a way, that the central carbon has a unique hydrogen, which is marked with yellow, which is shown in yellow colour, and the 2 hydrogens, which are on the terminal CH 2, on the terminal carbons there are 2 hydrogens 2 alkyl groups, which are on the terminal carbons.

And these are marked in different colours depending on whether they are cin with respect to the central hydrogen. So, for example if the yellow hydrogen is pointing towards me, that it is pointing towards me, and the blue hydrogens are also pointing towards me. So, these are the 2 hydrogens which are called the cin hydrogens, the anti hydrogens are the ones, which are pointing towards the camera. So, these are the 2 anti hydrogens and they are pointing towards the camera towards the camera.

And so there two types of hydrogens on the terminal carbons or two types of positions. One is called the cin position, which is closer to me, and the observer is closer to the anti hydrogens, which are marked in light green. Now, what happens when you have a dynamical behaviour of these allyl groups, the central metal atom, the metal atom is usually in the central position. So, it would make a like my fist, which is where I am holding this allyl group, that is where the metal is situated usually. And it is almost equidistant from all 3 carbon atoms.

Now, during the time that the allyl group becomes fluxional, it moves from the central carbon atom or the central position to the terminal position. So, here I am showing you the my hand which has the ring is the one, which is holding the central carbon, and this hand with holding the terminal carbon. Now, if the metal is closer to the terminal carbon, then the 2 carbons, which are held here have the double bond have the pi bond.

So, this carbon is the one which is free to rotate, and I explained how it is possible to move this carbon in simple a rotation, which would take the metal from the position, which is below the plane of this allyl group to the plane, which is above this allyl group. So, the metal can go from one plane to the opposite plane. During this rotation what happens is that, the position of these two hydrogens, what was cin with respect to the central carbon hydrogen is now becoming anti to the hydrogen.

So, the cin and anti-hydrogens become equal in strength to have a simple rotation of this metal from one plane to one side of the plane to the other side. Now, one can imagine the same thing to happen either through a flip, which is happening by the metal by changing the position of metal or by changing the position of the allyl group. So, I can rotate the allyl group in such a way, that the allyl group now goes from this position from the position where it was earlier to the other position.

So, rotation around this axis rotation around this axis, which would be rotation of the vinyl group or rotation of the metal, both of them are equivalent. Now, we will see this with the 2 dimensional pictures now. This is just a three dimensional model to illustrate, how the flipping of the metal or flipping of the allyl position allyl group. The vinyl group in the allyl, both of them are equivalent, and lead to change of the cin and the anti hydrogens on the terminal position. So, this has serious consequences for understanding the N M R spectrum of the molecule. Now, let us take a look at the written text what we have shown in 2 dimensions.

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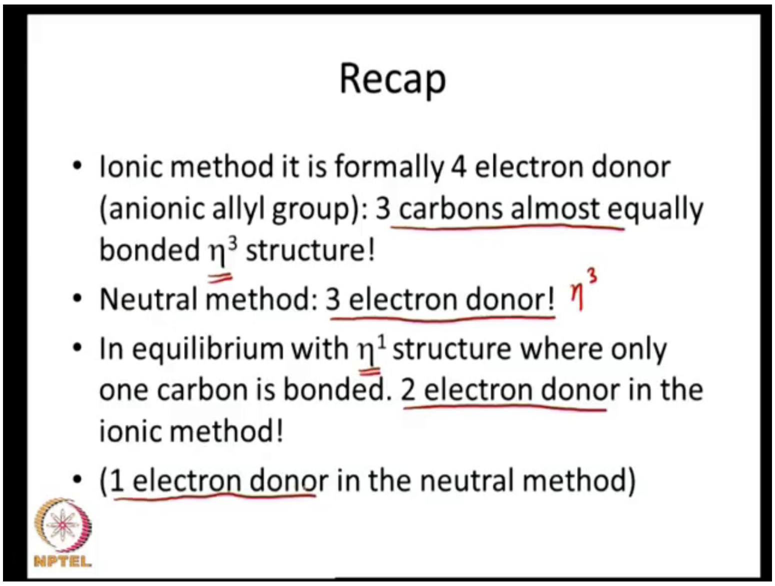

Recap

- Ionic method it is formally 4 electron donor (anionic allyl group): 3 carbons almost equally bonded η^3 structure!
- Neutral method: 3 electron donor! η^3
- In equilibrium with η^1 structure where only one carbon is bonded. 2 electron donor in the ionic method!
- (1 electron donor in the neutral method)

So, allyl complexes are formally 4 electron donors. They are in the anionic method, if you use the ionic method, the carbon is anion. So, you have a 4 electron donor and all 3 carbons all 3 carbons are equally bonded to the metal atom. And, so you have a hapticity of 3, and is indicated by eta 3. In the neutral method, we consider that is neutral group, as an allyl radical, so it becomes a 3 electron donor.

And in this case also, the hapticity is 3, so it is eta 3, whether, it is to use the ionic method or the neutral method, but in the neutral method, you considered as it as a 3 electron donor in ionic method you consider it as a 4 electron donor. Now, what we just discussed is that, in the fluxional state allyl molecules are in equilibrium with the eta 1 structure, when it is only bonded to 1 of the carbons of the 3 carbons, which formed the allyl group.

So, when it wants only through 1 carbon then, in the ionic method it would only be a 2 electron donor. The ionic method requires, that it is only a 2 electron donor. And in the neutral method this would be a 1 electron donor. So, it is important to remember these change in electron counts, as you go from the eta 3position to the eta 1 position.

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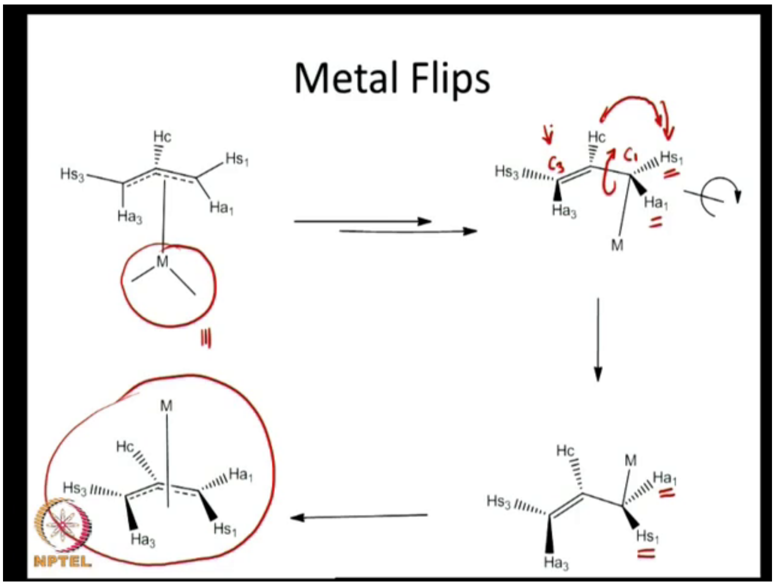
Metal Flips

So, here are the two flips that I talked about, one is a case where when the metal atom which is indicated here, the metal atom moves from central position to one of the terminal positions. And here I have indicated it as if it is moving towards carbon 1, which bears the Hs1 and Ha 1.The s 1 is indicative of the fact that it is cin with respect to the central hydrogen. So, it is this relationship which we are talking about, and then it is called s hydrogen.

If it is anti then we call, it if it is in the opposite direction, we call it anti hydrogen, and then we label it at a 1. Now, when the metal flips, when the metal moves from the bottom plane to the top plane, as we just illustrated in the three dimensional model, then the position of the s and the a get interchanged. Now, Hs1 is present in the position where Ha 1 was present. And, you can move the metal from the terminal carbon to the central carbon again, and you will get a completely equivalent structure.

So, these two structures are identical, the structures that are present on your right hand side or on your left hand side, are two identical structures. The structures are only different because of the position of the metal, either they are above the plane or below the plane. But, when the metal flips from one side of the plane to the other side, what we do is to change the position of the hydrogens. Now, what happens in the following flip is that, only one set of hydrogens are changed from the anti to the cin position. The carbon atom 3 which is indicated here the carbon atom 3 has no change in the position of the two hydrogens. But, nevertheless you will see that in more spectroscopic details the 2 carbon atoms are almost equivalent, so let us see what happens when you flip the vinyl group.

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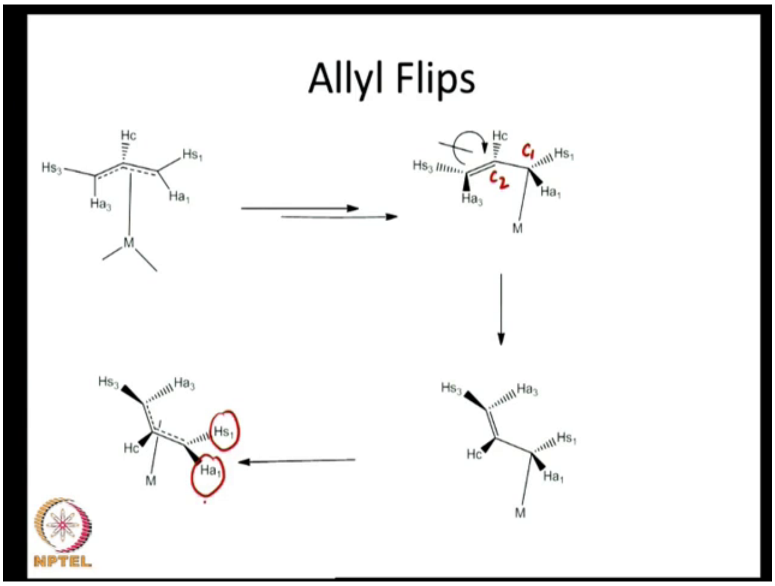

Allyl Flips

If the allyl group flips and this is indicated by rotation around the c1, c2 axis, so this is the c 1, c 2 axis. And if you rotate around the c1, c2 axis the metal retains the position and in the with respect to the plane of allyl group. But, nevertheless you will notice that the 2 hydrogens, which are on the carbon atom 1 are the ones which are changed now between the anti and the cin positions. So, if the metal is attached to c 1, then it is the s 1 and a 1 which get interchanged.

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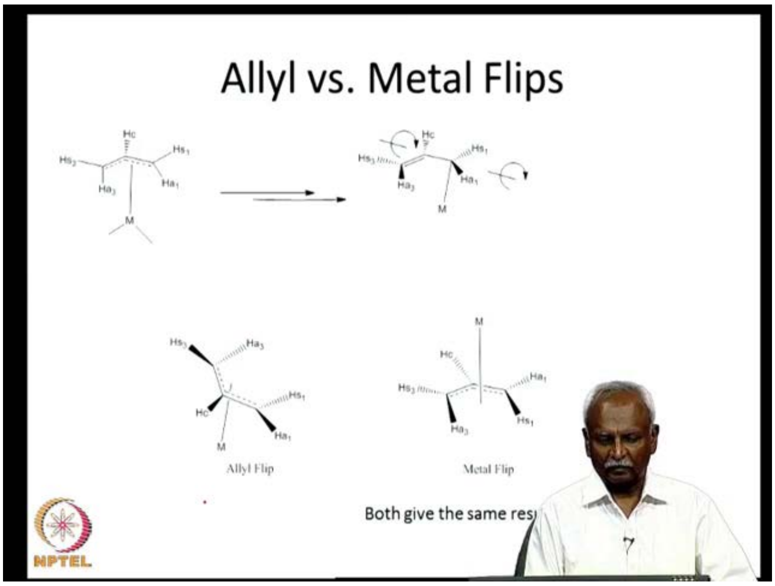

Allyl vs. Metal Flips

Allyl Flip

Metal Flip

Both give the same res

So, it is possible either through an alliance shift or through a metal flip or an allyl flip metal rotation or an allyl rotation. You will be able to interchange the position of the cin and the anti hydrogens. What is important is that, we need to keep track of to we need to keep track of the carbon to which the metal was attached. It is that carbon which will have the change in the cin and the anti hydrogens, let us proceed further now.

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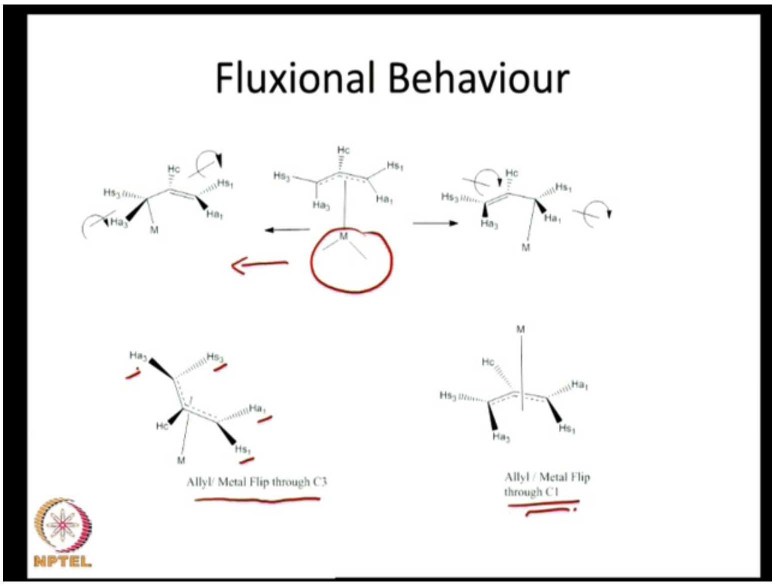

Fluxional Behaviour

Allyl/ Metal Flip through C3

Allyl / Metal Flip through C1

Let us take a look at what would happen, if you change from c1 to c3. Now, it is possible that, the metal instead of moving from the centre position to the right side, instead of moving from the centre position to the right side, as we just discussed. It could have also equally moved to the left side, provided there are no substituents on the c1 and c3 which are different. So, if it moves through the left, then you would end up with an allyl or a metal flip through c3 or through c1.

If it moves to the through the to the right if it moves to the right, you have a flip with the C1. If it moves through the left, you have a flip through the c3. So, what will happen is that, if there are no substituents on the allyl group. All 4 hydrogens Ha 1, Hs1, Hs3, Ha 3 will all become equivalent, as a metal flips back and forth from the top of the plain to the bottom of the plane or from left to right. So, this complicated flipping arrangement flipping that goes on with position of the metal equalises the 4 hydrogens.

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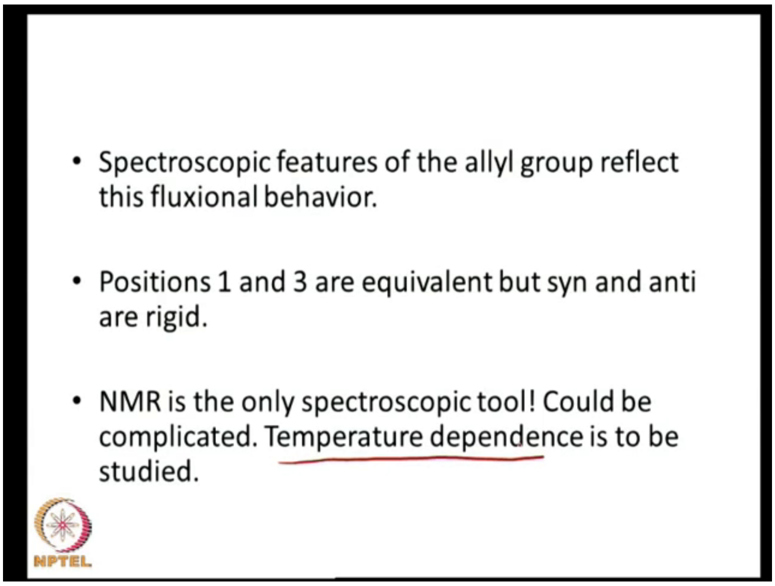

- Spectroscopic features of the allyl group reflect this fluxional behavior.
- Positions 1 and 3 are equivalent but syn and anti are rigid.
- NMR is the only spectroscopic tool! Could be complicated. Temperature dependence is to be studied.

So, let us take a look at the spectroscopic features of the allyl group, that are affected by this fluxional behaviour. Both positions 1 and 3 are equivalent, because the metal can move either to the left or to the right, at cin and anti can be rigid, now that is possible. So, the NMR spectra is only tool, that can distinguish between the different fluxional behaviours of the metal, and the rotations that are involved. And very often one has to do a temperature dependence of the spectrum in order to understand, what is going on in the allyl complex.

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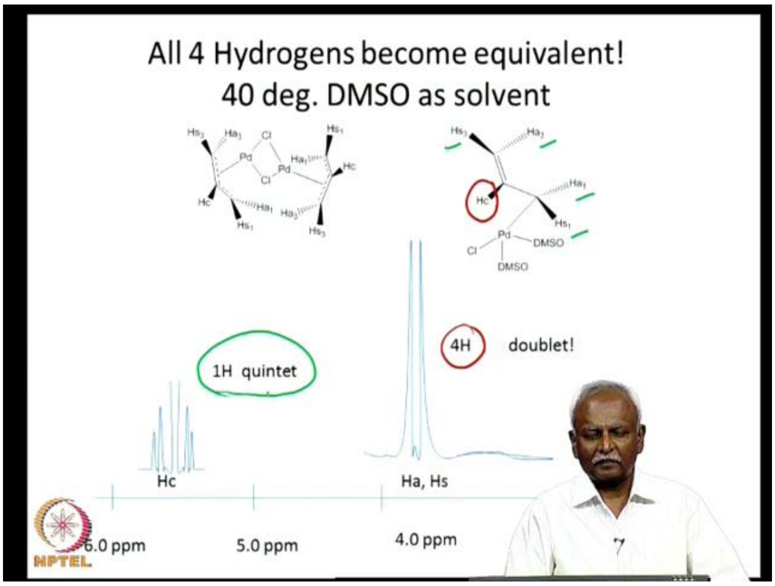

All 4 Hydrogens become equivalent!
40 deg. DMSO as solvent

So, here is a hypothetical NMR spectrum of simple allyl complex. Now, what we have done is that, we have dissolved it in DMSO and warned that the compounds to about 40degree. Now, when you warm the compound about 40 degree, what happens is that, the two positions the position of the metal keeps changing very rapidly. So, instead of recording the temperature spectrum at room temperature, we recorded at slightly elevated temperature. And the metal keeps moving between c1 and c3 the two positions.

And then what happens is, that a 1, s 1, and a 3, s 3 all become equivalent. When they become equivalent, there are 4 hydrogens and these 3 hydrogens, 4 hydrogen these 4hydrogens are split into a doublet by the single hydrogen ,which is that in the centre or which is a unique hydrogen, which is labelled as Hc. So, the central hydrogen Hc appears as a quintet, because there are 4 equivalent hydrogens, which we will mark a slightly different colour for you to follow.

So, these are the 4 equivalent hydrogens, and these 4 equivalent hydrogens split the central hydrogen, which is marked in red, and the central hydrogen appears as a quintet, because of the 4 equivalent hydrogens splitting it. So, you can see that the spectrum will be in a slightly different fashion.

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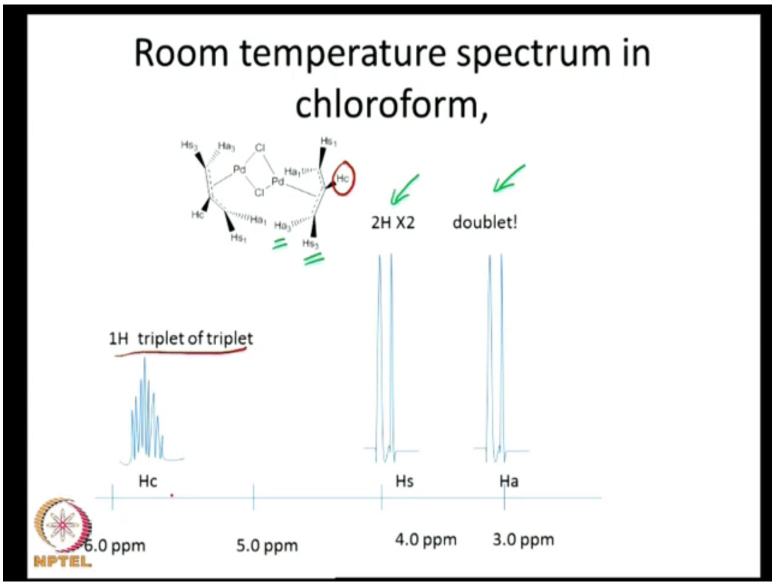

Room temperature spectrum in chloroform,

If you have a low-temperature spectrum, and in the solvent which does not coordinate with palladium. So, here is the same compound dissolved in chloroform, so that is the flipping is reduced. We will just explain in a few moments, why the flipping is reduced.

And because of the temperature the moment of palladium is restricted. So, there are 2 effects that are going on, so when the palladium movement is restricted, you will have the anti and the cin hydrogens in unique positions.

So, the anti and cin hydrogens are in unique positions, and appear as 2 doublets, 2 doublets. The anti hydrogen in a higher field and the cin hydrogen at a lower field, and both of them are split into doublets, because of the unique central hydrogen. So, the central hydrogen, the central hydrogen, which is here is responsible for making this anti hydrogens as doublets, and the cin hydrogens as doublets.

Now, what happens is, because these 2 hydrogens have a different coupling constant with the central hydrogen. The central hydrogen appears as a triplet of triplets, very often that a significant amount of overlap in the triplets. So, you would see much less than the nine lying spectrum that you theoretically expect. So, this is a hypothetical spectrum that you get for an allyl group, which is bonded to the metal, when the system is not aequilibriating in a very fast fashion.

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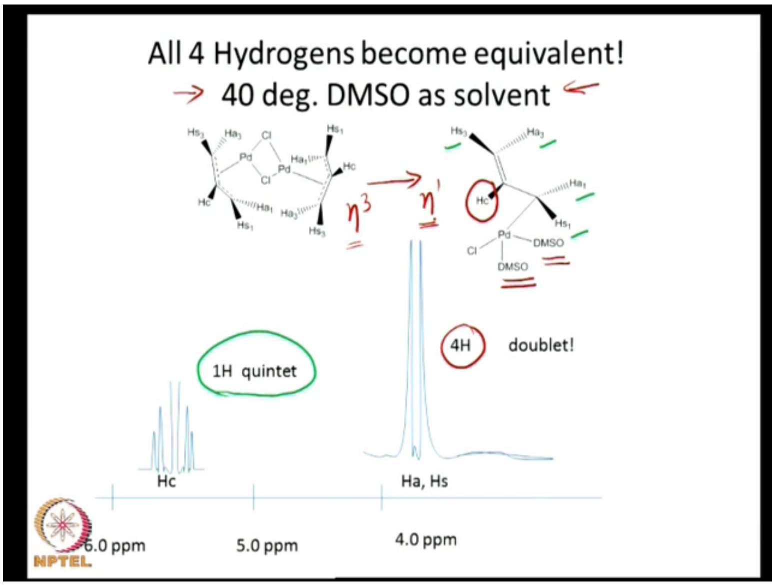
All 4 Hydrogens become equivalent!

→ 40 deg. DMSO as solvent ←

Now, what happened when you dissolved it in DMSO was that, the sigma allyl complex was slightly stabilised by the coordinating DMSO solvent. So, this facilitated the equilibration of the eta 3 to the eta 1 form. And eta 1 form is the one which allows the rapid rotation of the palladium and equalising of the anti and cin hydrogens. So, there are two effects that were going on, one was the temperature fact, that we heated this allyl complex solution to slightly elevated temperature. And the second is, the presence of a coordinating solvent which facilitated the formation of a eta 1 structure.

So, allyl complexes are well-known for their fluxional behaviour for the fact that, they can go from eta 3 to eta 1forms, which we have just demonstrated here and also for the fact that, they can equalise their anti and their cin hydrogen through rotation around the carbon-carbon bond or the flipping of the metal, from one position to the other position.

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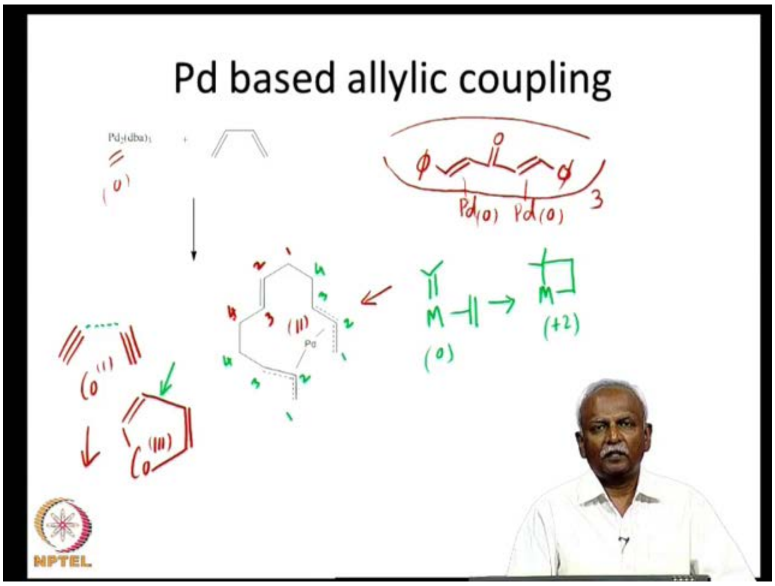

Pd based allylic coupling

So, now proceed to some reactivity of the allyl complexes. And today we will see time permitting three different types of reactions of the allyl group and the metal. Now, here I have illustrated to you one reaction, where palladium which is bonded to dibenzylidene acetone. Now, dibenzylidene acetone is ligand, which stabilises palladium 0, and this ligand is bonded to 2 atoms of palladium. It is a fairly complicated structure, and I am so surpised to say that 2 atoms of palladium are interacting with the 2 double bonds of the dibenzeneidene acetone and there are 3 ligands which are present.

So, we will put a bracket and put 3 of these ligands, which are bonded to the 2 palladium atoms. So, this is a interesting structure which is formed by palladium and palladium is in the zero oxidation state. Now, this compound is capable of converting butadiene in a stoichiometric reaction to the a complex, which is indicated here where there are 2 allyl groups. Now, what has happened is that there has been a change in the oxidation state of the palladium.

Palladium was initially in the zero oxidation state, and in this compound formely it is converted to a plus two oxidation state. So, oxidative addition of the groups the organic groups has happened, and also carbon carbon bond formation has happened. So, this is a typical case, where you have oxidative coupling of 2 carbon base ligands. Remember we have already seen two different examples, where you can have oxidative coupling. One was a case where you have a cobalt one, and the cobalt one was bonded to two acetelene units.

And this got converted to a cobalt three system, and this cobalt three system had a metallocyclopentadyne structure. So, the new carbon-carbon bond was formed. The new carbon carbon bond is indicated by this new position here. There is a carbon carbon bond forming here, and at the same time you have a change in the oxidation state of cobalt from plus 1 to plus 3. So, this is one type of an oxidative addition, an oxidative carbon carbon coupling reaction that we saw.

Another system was the metathesis reaction itself. In the metathesis reaction we had a carbine, and an olefin and these two combined together to form a metallocyclo butane. So, this was a metallocyclo butane, that was formed because of the formation of 2 carbon of the carbon carbon bond. And at the same time oxidation state change of the metal from a let us say 0 to plus 2 in this case. So, there are several examples of oxidative carbon carbon coupling.

And today we will look at the allyl waste carbon carbon coupling reaction which will lead to very interesting molecules. So, here is a example where we have let us just number the carbons because it is difficult to keep track of them, here is 1, 2, 3 and 4. These are 4 carbons, here is another set 2, 3 and 4 and lets mark the third one with a different colour altogether. So, here is 1, 2, 3, 4 carbons, so we have a total of 3 butadiene units which have been combined together, and some carbon-carbon bonds have been found.

So, let us take a look at this reaction in detail. It is interesting that, it is only the nickel group which is very commonly seen to promote this particular reaction, where butadiene units are stitched together. So, this is the product that is formed in a stoichiometric reaction between palladium two DBA three and three equivalents of butadiene.

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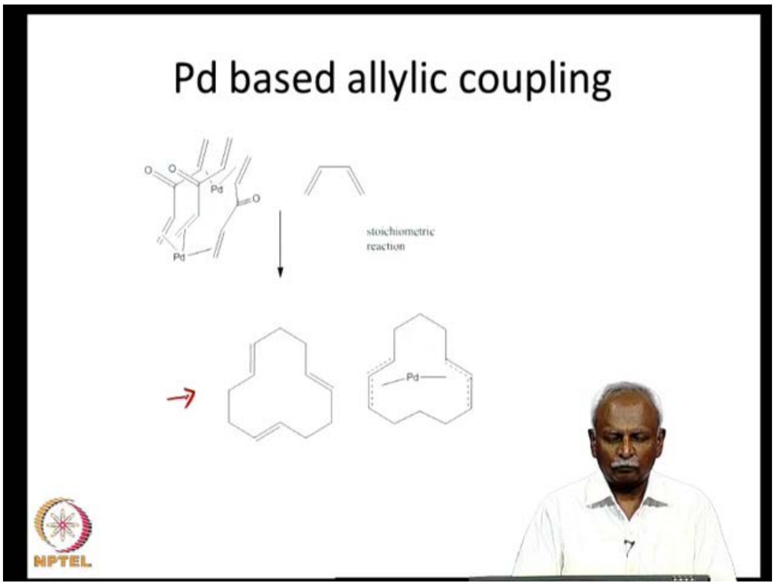

Pd based allylic coupling

stoichiometric reaction

So, the same reaction if the reaction is not done in a stoichiometric fashion, it could be done in a catalytic fashion, and one can isolate the cyclododecatriene. So, this cyclododecatriene is formed by the carbon carbon coupling action, that we just discussed and it is formed as a result of stitching together three molecules of butadiene.

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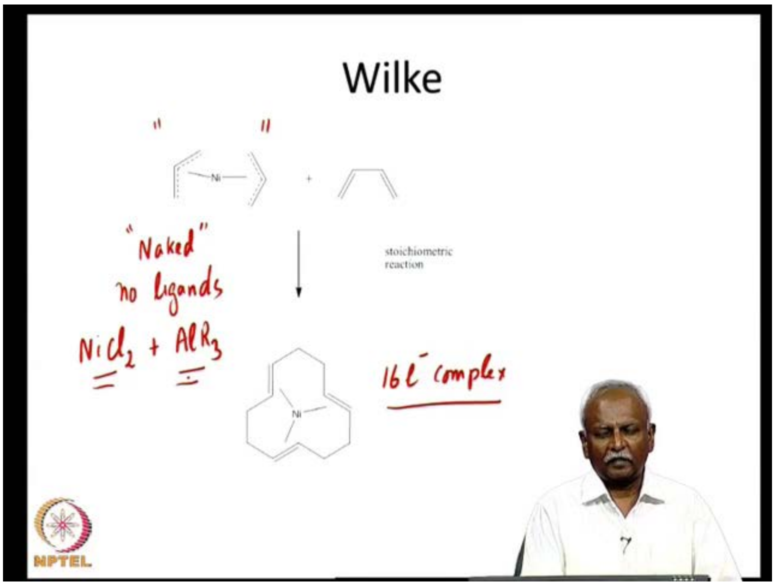

Wilke

stoichiometric reaction

"Naked"

no ligands

$NiCl_2 + AlR_3$

$16e^-$ complex

So, having said this let us just proceed to the famous nickel based reaction. The same reaction can be carried out by nickel, and this was extensively studied by Wilkie and co-workers. And Wilkie was able to generate a very efficient catalyst for this process, which he called as naked nickel. This naked nickel was called naked nickel because, it seemed to have no ligands. There were no ligands around the metal atom or apparently no ligands around the metal atom.

And what he did was, to generate a nickel compound in NiCl2, which was then reduced with, it was then reduced with AlR 3. Which was the reducing agent and that reduced to nickel 0. And this naked nickel was capable of converting butadiene to the cyclododecatriene complex. In the palladium complex, we isolated either the cyclododecatriene or an allyl complex. But, in the case of nickel the complex that was isolated by Wilkie had three olefins coordinated to nickel.

So, this is a 16 electron complex is a 16 electron complex, which was synthesised by Wilkie. It was not thermally very stable, but it could be isolated and characterised. And what was interesting was that, 3 molecules of butadiene have been stitched together in a sequential fashion in order to form a very symmetrical complex. Which is bound to the nickel and nickel is again in the nickel zero state. So, he could either take this ally nickel, which will as we will show that correctly. It can decompose to give you naked nickel, or used nickel in the plus two state and reduced it with tri alkyl allumina.

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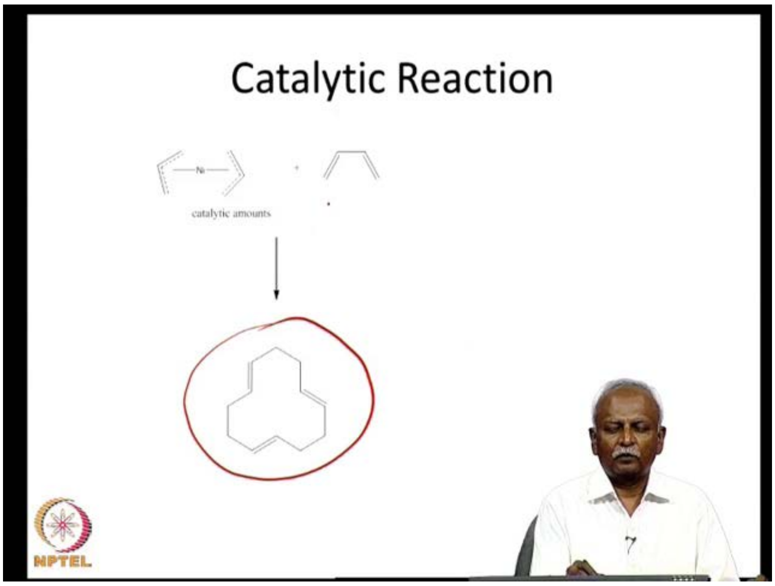

Catalytic Reaction

So, in the same reaction could also be done in a catalytic function. In which case you do not isolate the nickel triene complex, which we just showed earlier. But, you isolate only cyclododecatriene. So, this is one step synthesis of cyclododecatriene which is C12 with

3 double bonds in a cyclic symmetrical fashion starting with a simple butadiene molecule. So, let us see how this catalytic reaction happens.

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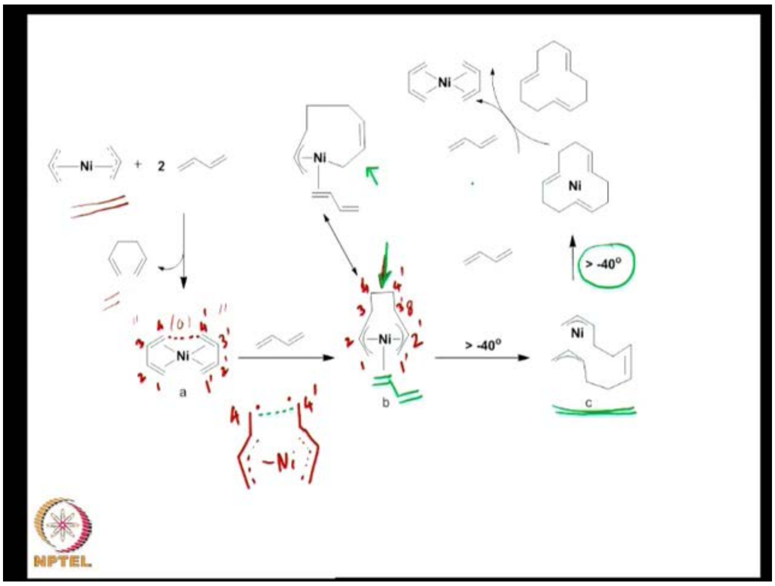

Let us imagine in the first step, we can easily picture the elimination of hexadiene one five hexadiene starting with this allyl molecule. Now, this just results from a reductive elimination of the 2 allyl groups, the 2 allyl groups combining together. So, that you form the cyclo 2 allyl groups combining together to form one five hexadiene, and that is this molecule right here. Now, this will as I mentioned earlier it introduced the very reactive form of nickel, which we can write in tentative fashion, and as 2 butadiene molecules attached to each other in such a way that, it forms the nickel 0, 18 electron complex which is pictured as a.

Now, if you treat this molecule if you treat this molecule with another molecule of butadiene. It induces a coupling reaction, where if you watch this reaction closely, you have a total of 8 carbons you have a total of 8 carbons. And what you done is that you have oxidatively added the nickel allyl group formed the allyl group in the coordination sphere of nickel, and at the same time formed the carbon-carbon bond between the terminal carbons.

So, let us imagine that you form a bond between these 2 carbons, and that is this bond right here. So, you have 4 carbon atoms and we will we will mark them as 1, 2, 3 and 4. And this is exactly what we have here, and atom number 4 dash and 4 have combined together, to form a carbon carbon bond. And it is 1, 2 and 3, which make it an allyl group. You can imagine the transfer of an electron to from the nickel to the butadiene units, such that it forms 2 allyl groups on you either side electron on either side. And that results in the formation of an allyl group, and at the same time results in the formation of a radical species.

So, if you want to write this stepwise, this is what we would write. This is a radical which is formed, and this is the second radical that is formed and this is the 4 dash carbon that we are talking about. This is the 4 carbon atom number 4, which we are talking about. And we now from a bond between the 4 and 4 dash, that is the bond which we have indicated with an arrow here.

So, it is possible to now form the oxidatively added species, and this is induced by the addition of a butadiene molecule, which we have pictured right here. So, this is what is going on what you end up with is an oxidative coupling reaction, when you converted 2 neutral molecules to allyl groups, and at the same time formed a carbon carbon bond. It is interesting that you can now add on this butadiene unit, to form a 12 carbon chain that 12 carbon chain will have the 2 allyl groups interacting with the nickel atom again.

So, here you have the 12 carbon atom chain which is interacting with nickel, and you can also do the same thing in a slightly different fashion. And you can generate this intermediate, which is shown here. Now, the cyclododecatriene complex can be formed by a reductive elimination reaction, which happens when you hit this reaction mixture towards slightly more than 40 degree, and then it forms the cyclododecatriene.

The same reaction could becatalytic in nature, and it can generate your naked nickel. And that is the reaction which is shown here. Now, in order to show the reductive will the various steps that are involved. Let us just go through this reaction against once more, but we will highlight the oxidative additions and the reductive eliminations.

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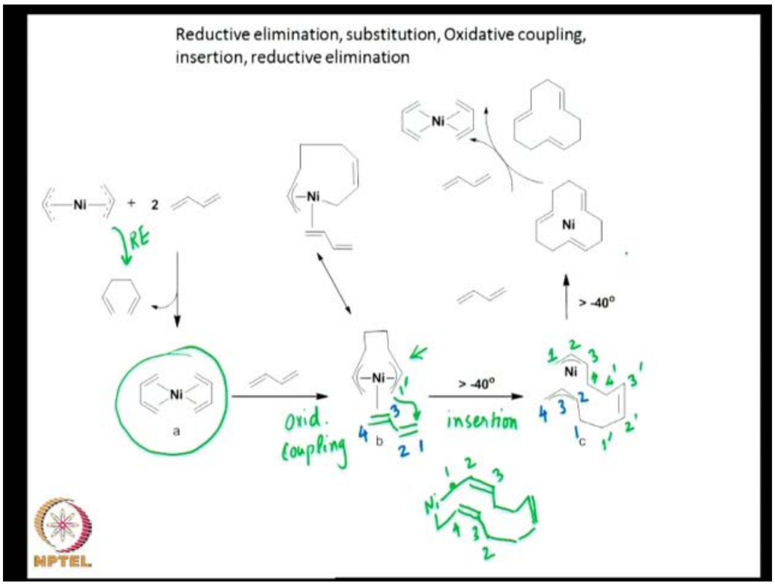

Reductive elimination, substitution, Oxidative coupling, insertion, reductive elimination

In fact the first step is the reductive elimination, and that is this step that you have shown here, this is the reductive elimination step. So, where you have combined together 2 allyl groups and formed the diene. And at the same time you have done a substitution reaction, which is resulted in the formation of a diene molecule. Which is coordinated to nickel 0. So, the diene unit now combines together in a oxidative coupling reaction, this is the oxidative coupling reaction. And this coupling reaction is the one, which gives you the 8 carbon units, which is shown here, this is the 8 carbon unit. Now, this 8 carbon unit we can do an insertion reaction.

The insertion reaction merely converts this allyl group to another allyl group by adding these carbon atoms here, which weirdly labelled as 1 dash. And we are combining it to the terminal carbon of the butadiene. Which is let us convert that into yet another colour. So, that we can follow that, so this is atom number 1, 2, 3 and 4. So, what you would end up with is 4, 3, 2 and 1, the atoms that are labelled in blue now.

Now, the newly formed, newly formed newly introduced butadiene, and so the new bond has been formed between 1 and 1 dash. This is the green 1 dash that was present at, we will indicate it is 1 dash, 2 dash, 3 dash and 4 dash. So, he we earlier had 4, 3, 2 and 1. So, this is how the reaction proceeds, we first have a reductive elimination combined by a substitution and an oxidative coupling followed by an insertion reaction.

And then that gives us a molecule which can do a reductive elimination. And the reductive elimination can happen through a variety of ways. And one of them is to retain the double bond between atom numbers 2 and 3. The blue 2 and 3 can now become, if I write it in a slightly different fashion I can. So, we can have this written in this fashion.

Now, we have the reductive elimination between these two positions. This will have a double bond and this will have a double bond also, so you will end up with the formation of cyclododecatriene. So, this helps us to follow how we can, this helps us to understand how we can carry out a variety of oxidative additions.And reductive eliminations including insertion reactions to stitch together these 3 molecules of butadiene.

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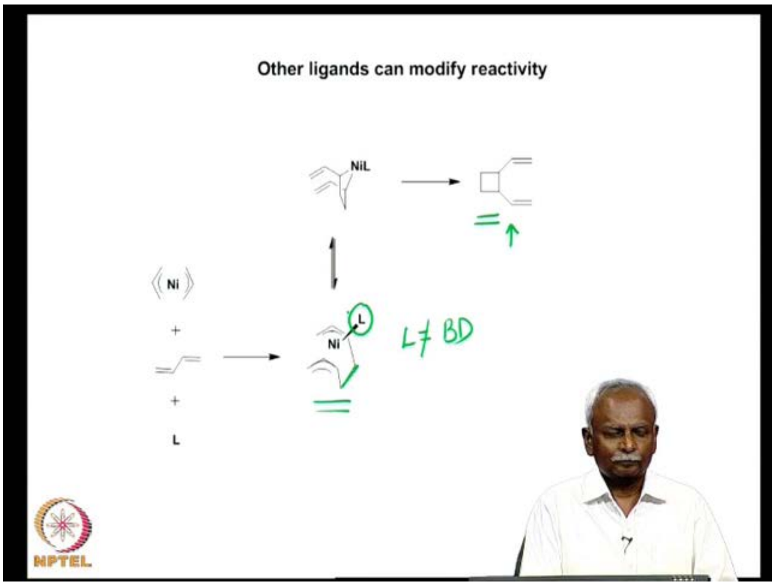

Other ligands can modify reactivity

Now, what followed after these reaction was discovered what followed was the discovery that, you can add some other ligands apart from butadiene in such a way, as to turn the reaction to steer the reaction into a different channel altogether. Now, what we are seeing so far is the oxidative coupling reaction. And the first step in these reactions are also the oxidative coupling reactions. And what we end up with is coupling of 2butadiene units. And that is what we have done here 2 butadiene units have been coupled together to have the allyl group. And the new carbon carbon bond with the new carbon carbon bond that has been formed.

And if you have a ligand that will reduce the reactivity of this system, then you do not have the reaction with another butadiene unit. Earlier this L was this L was a butadiene, now it is not butadiene. So, this is not a butadiene, and what it does is to slow down this reaction to the coupling with a third butadiene molecule. And if you do the coupling with or if you do the reductive elimination in such a fashion that, you eliminate it to form a cyclo butane ((Refer Time: 35.57)). Then you get one four divinylcyclo butane. This is one for divinylcyclo butane which is pictured right here, and this can be generated with depending on the type of ligand that you put in this particular position, but in the same reaction depending on the ligand.

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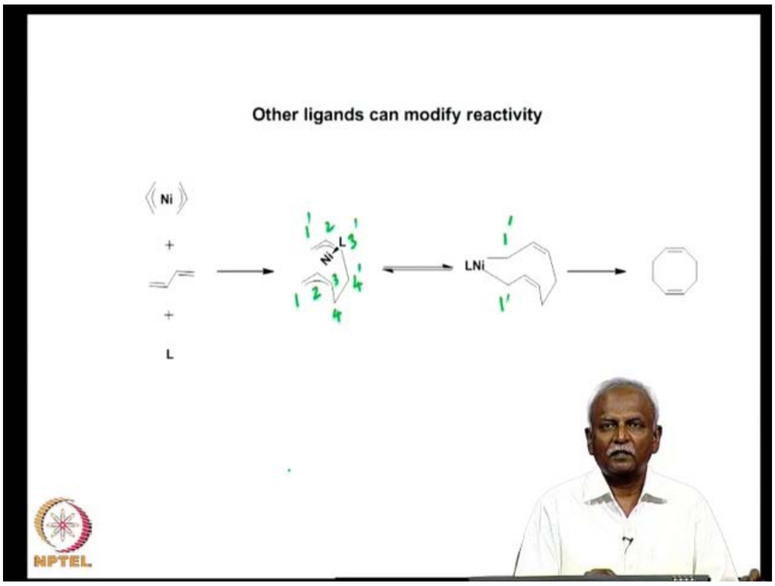

Other ligands can modify reactivity

You can also generate a slightly different reactivity, and that is instead of forming the bond, instead of doing the reductive elimination between atom numbers 3 and 3 dash, you can do between the 2 atoms 1 and 1 dash. The two butadienes that are combined are combined in such a way that, you do a reductive elimination between atom numbers 1, 2, 3 and 4.

So, these if you now do the reductive elimination in or the coupling between 1 and 1 dash, you will end up will end up with cyclooctadiene. So, cyclooctadiene is formed by coupling of 2 butadiene units. Two butadiene units combine together in such a fashion that, you can form cyclooctadiene. You can also do it in such a way that, you can combine it to form, you can form a bond between 3 and 3 dash then you would form divinylcyclo butane.

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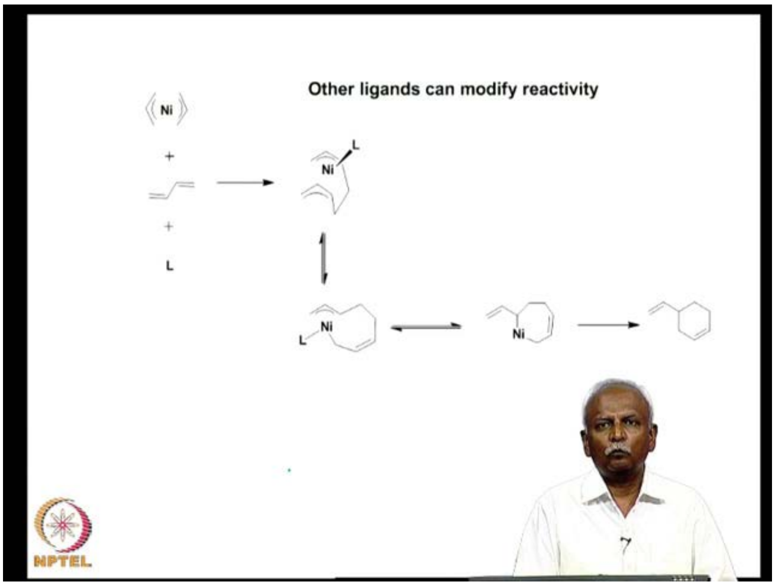

Other ligands can modify reactivity

And yet another modification is to do it between 3 and 1 dash, and in which case you have end up with a cyclohexane. The cyclohexene can be generated if you do the coupling between atom number 1 and atom number 3. So, this is the type of reaction change that happens when you have a ligand, which slows down the reactivity. Now, you might be wondering, what would be a ligand, which will slow down reactivity.

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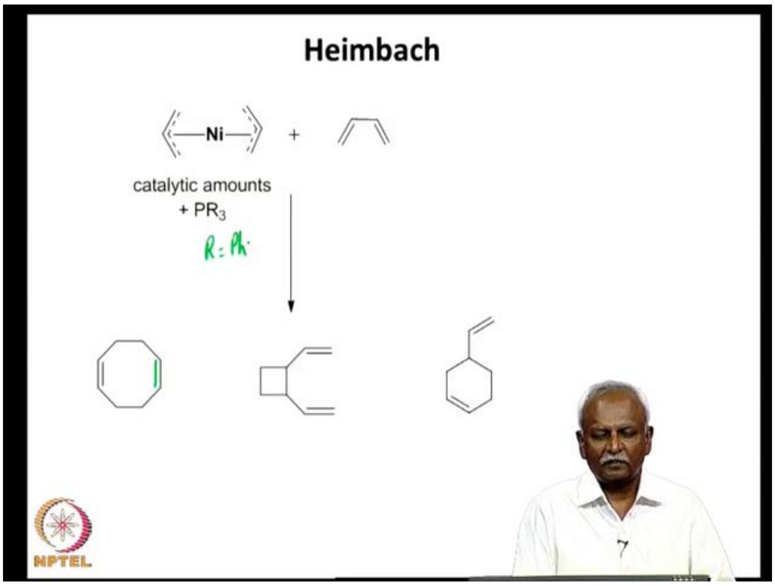

Heimbach

catalytic amounts

+ PR_3

R = Ph

And the reaction was a slowdown in the presence of phosphines. When PPh 3 was used, it was possible to isolate different amounts of cyclooctane, cyclooctadiene. This should be an octadiene and cyclooctadiene, one four divinylcyclohexene, cyclobutene and also vinyl cyclohexene. So, all 3 products were formed in the presence of the PPh 3. So, here are those Ph group, so the PPh 3 was able to capitalise these 3 reactions.

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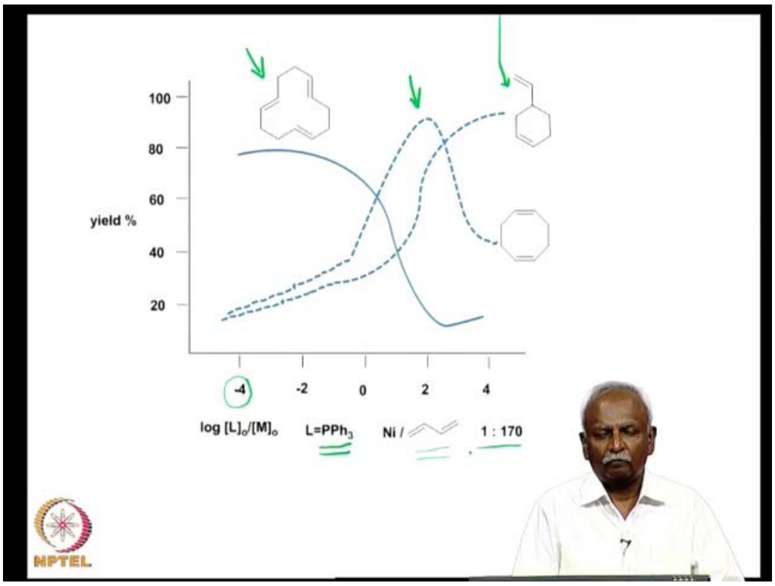

Hyde parks contribution was the fact that he generated, what are called ligand reactivity control maps. So, he showed that depending on the ratio of the ligand, the metal depending on the ratio of the ligand and the metal. It is possible to form different amounts of the 3 products. In the absence of the ligand that means, in the absence of triphenyl phosphine in this graph, what we are discussing is a triphenyl phosphine. If you have a triphenyl phosphine if you havetriphenyl phosphine, which is very small that means almost 10000 molecules of the metal catalyst with respect to the ligand. That is why log of these two is minus 4.

So, if you have 10000 molecules of the metal catalyst, the nickel catalyst with respect to the PPh 3, then you would end up exclusively with the formation of cyclododecatriene. If you increase the amounts of the ligand, and let us say you have 100 moles of PPh 3 per mole of nickel, then you end up with mostly the cyclooctadiene. So, cyclooctadiene is formed when you have 100moles of the PPh 3.

If you now increase the amount of PPh 3 to10000 with respect to the nickel, then you end up with vinyl cyclohexene. So, vinyl cyclohexene is formed when you have very large amounts of the PPh 3. The PPh 3 by nickel ratio is ten power4, then you get only cyclohexene. If you have if you want cyclooctadiene, you have to carry out the same reaction in the presence of close to hundred equivalents of the PPh 3, little less than hundred equivalents of PPh 3 with respect to the nickel.

So, nickel is present only in catalytic quantities, and the butadiene is present in a very large amount. In fact it is less than one percent of the nickel catalysts with respect to the butadiene. 1 is to 170 is the ratio between the nickel and the substrate, which is the butadiene unit. So, this is a very interesting ligand reactivity control map, which allows you to synthesise or isolate one product with respect to rather than a second products.

One of the reaction channels is facilitated, when you have very large amounts of the ligand or you can eliminate one product altogether by removing the presence of the ligand, as when you want to synthesise cyclododecatriene. So, what he also showed was the ligand was critical when you want to synthesise a particular molecule.

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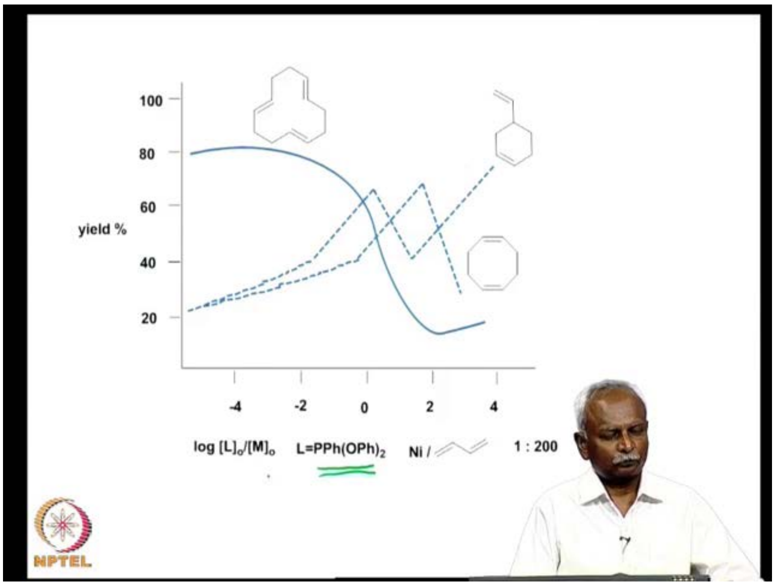

So, if you change from the PPh 3to the phenoxyphosphine. So, here you have two this phenoxyphosphine units. So, this is the PPhOPh 2 have been replaced by phenoxy groups. So, this phenoxyphosphine is capable of changing the way in which the same reaction happens. And here the ratio you can see that, the ratio of the metal to ligand is different for the generational cyclohexene and the cyclooctadiene.

Needless to say one has to painstakingly do the reactions at various concentrations of ligand to metal in order to generate such ligand reactivity control maps. But, this gives you a very clear idea that, the nature of the metal, the nature of the ligand and the ratio of the ligand to metal, is critical in order to generate the product that you want.

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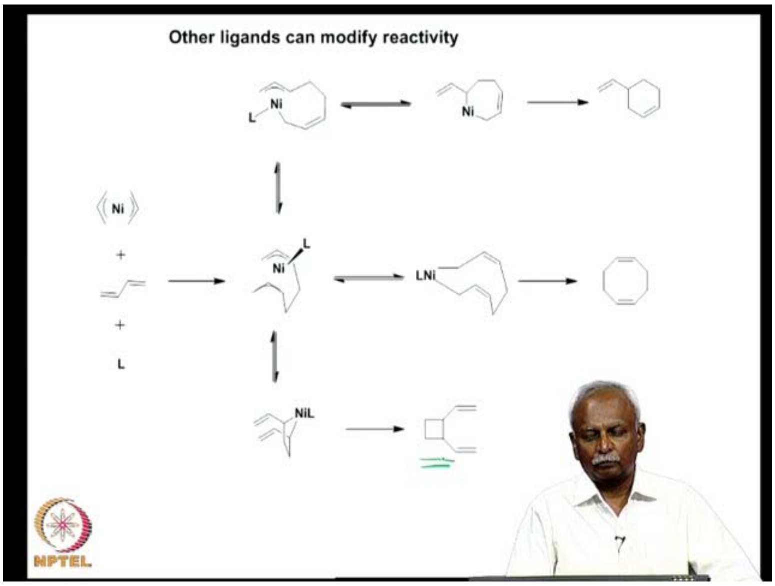

Other ligands can modify reactivity

So, here we have also indicated the 3 products in perspective. So, I have shown you all 3, if you only want to join the 2 the 2 butadiene units together, and form a cyclic compound. Then you need to stop the reaction in the first stage itself, and that is what you do. You have to combine it in such a way that, you form a bond between 3 and 3 dash, and that is what gives you divinylcyclobutane. And you can also do it between 1 and 1 dash, then you get cyclooctadiene. You can also combine it between 1 and 3, then you get vinyl cyclohexene. So, depending on the carbon atom which does the reductive elimination, you would be able to control the size of the ring and the product that you want.

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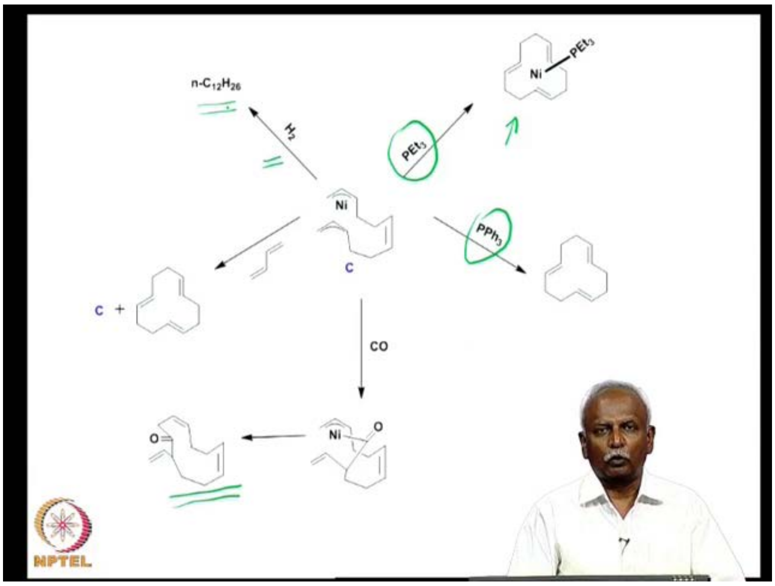

If you use carbon monoxide, he showed that you can in fact do a reductive elimination where you have one CO, which is inserted in during the insertion process. Then that seems to be fairly understandable if you use a high-pressure carbon monoxide, you can introduce a carbon monoxide instead of adding another molecule of butadiene. So, that is what is happening here, so you get a ketone and as one of the products.

You can stop the reaction literally poison the reaction and stop it from proceeding further by very simply adding triethylphosphine. Triethylphosphine is a very strong ligand and it stops the reaction at the stage where you get the cyclododecatriene, and the nickel which is coordinated through three double bonds and cyclododecatriene in symmetrical fashion. PPh 3 when it is present in small amounts can do just the cyclisation reaction. In the same reaction he also showed that, if you added hydrogen a high pressure of hydrogen.

You can hydrogenate the 3 double bonds which are present in the molecule. And you can form in fact the linear molecule. Where all 3 double bonds are also double bonds, that are completely hydrogenated. So, it is possible to make a variety of interesting molecules starting with simple butadiene, and intermediates involved are formed through a carbon carbon coupling process, where the allyl group has literally behaved like a radical. Which is what we showed when the 2 butadiene units are combining together. You form this allyl complex and a radical on each of the terminal carbon atoms. And these two radicals can combine together and from the carbon-carbon bond.

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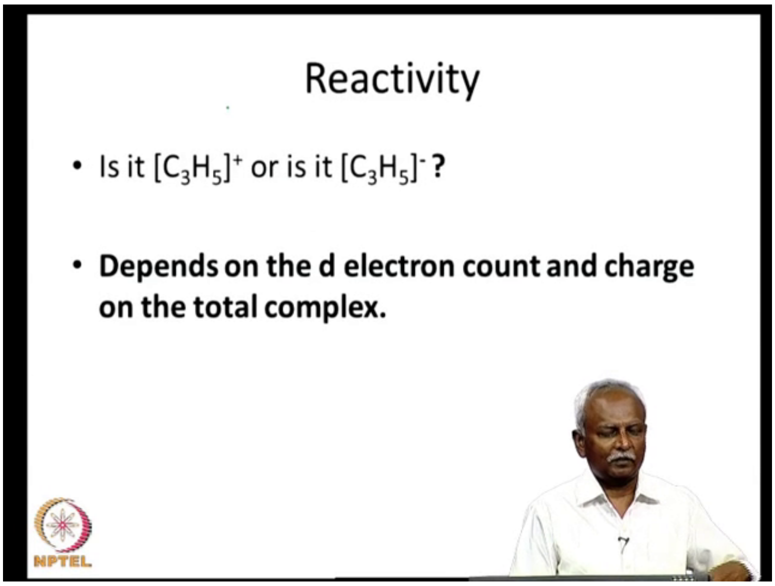

Reactivity

- Is it $[C_3H_5]^+$ or is it $[C_3H_5]^-$?
- **Depends on the d electron count and charge on the total complex.**

So, instead of having a radical type reactivity as what we have shown just now, is it possible to make the allyl radical or the allyl species behave as a cation C H35 plus or as a C H35 minus. This really depends on the d electron count and the total charge on the complex, both of these seemed to be playing a role. And we will illustrate a few examples where you can have such changes of the allyl group.

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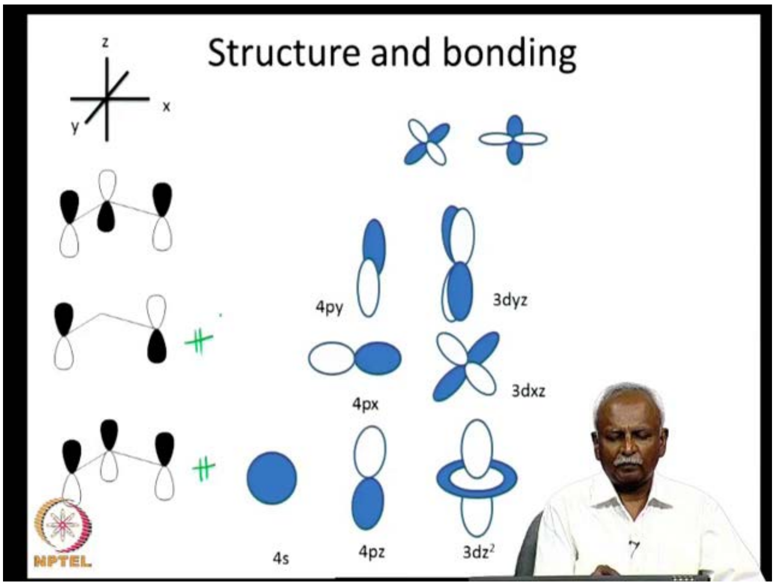

Structure and bonding

And briefly we will just go back to the molecular structure, where we have shown the various m os of the allyl group. If the allyl group is filled up to the second m o then, what you have is an allyl anion. Now, the electron count on the metal can by pumping in electron density into the second m o, you can have the behaviour as if it is an allyl anion.

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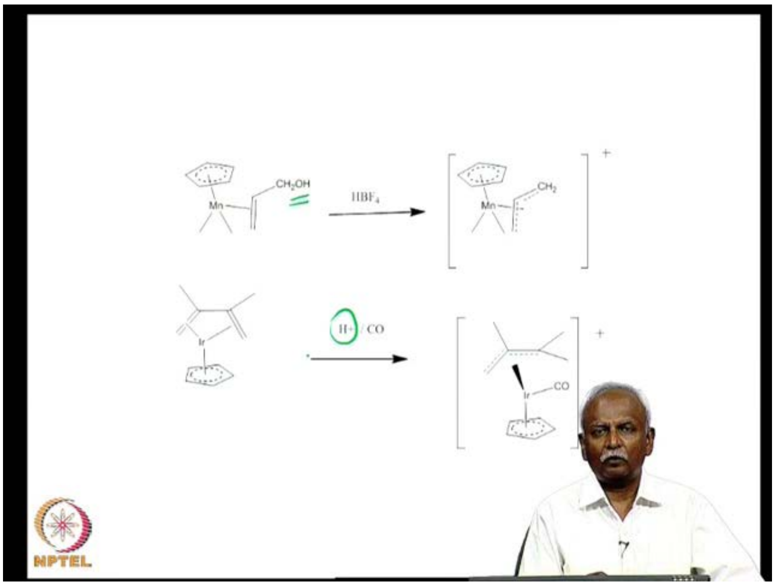

Now, we if you remember the preparation of allyl molecules we used two different types of preparations. Two major classes of preparations one of which was a case, where we took the allyl alcohol coordinated to a manganese for example, and treated it with HBF 4, HBF 4 is a strong acid. It converted the OH group to a positively charged system, and it generated a water molecule and an at least an allyl cation. Which is coordinated to the many is, but because of our electron counting nomenclature.

We would think of the species as if it is a allyl group, which is coordinated to the manganese, where the allyl is got, where the allyl is a 4 electron donor. A similar situation happened, when he took the butadiene molecule coordinated it to iridium 1. And this iridium 1 species can be perpetrated again, and it also generates an allyl species. It is clear that in these two reactions, the allyl group would like to behave or is electron deficient and would like to behave as an allylcation.

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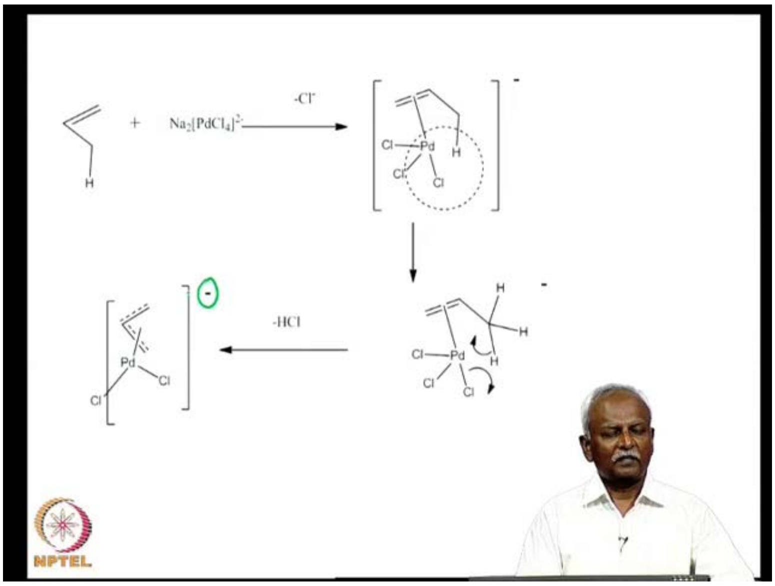

There are other examples example which I have shown right here, where the metal atom is in fact a palladium 2 plus unit, with the palladium electron count is d 8 and it pumps in electron density into the allyl group. And, so you have in fact the generation of a species here for example, you have a PdCl2 allyl with a net negative charge. So, here the allyl group will probably behave as aallyl anion. Now, we can and change the reactivity of this allyl anion by substituting one of these chlorides with the PPh 3.

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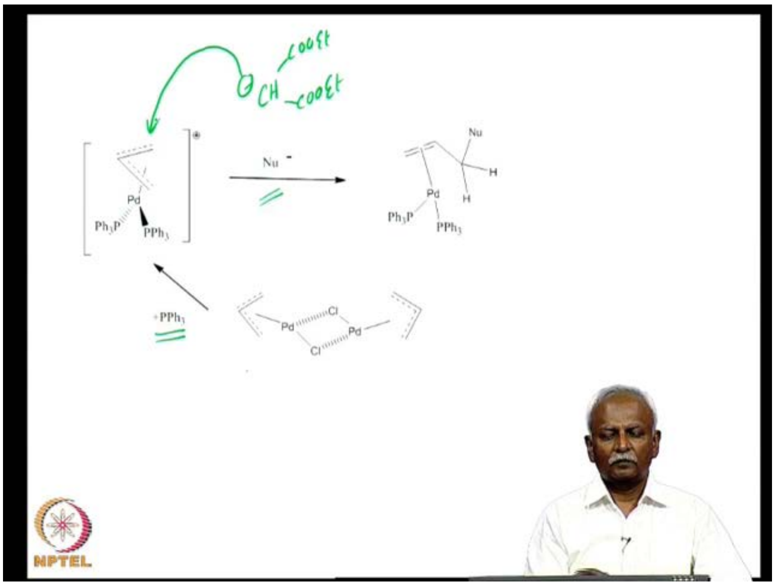

And what we have to do is, to take this allyl molecule and eliminate a chloride and add a triphenyl phosphine. And when you add triphenyphosphine it forms a complex, which is having a net positive charge, because you lose the 2 chloride ions. Which are coordinated through it, and when you do that then you can treat it with a variety of nucleophiles. A typical nucleophile, which you can add is a diethyl malinathe, which has been deprotinated to form the a sodium salt. And this typically adds on as a nucleophile to these allyl groups. So, it will behave as if it is a allyl cation which needs an electron rich centre to react with.

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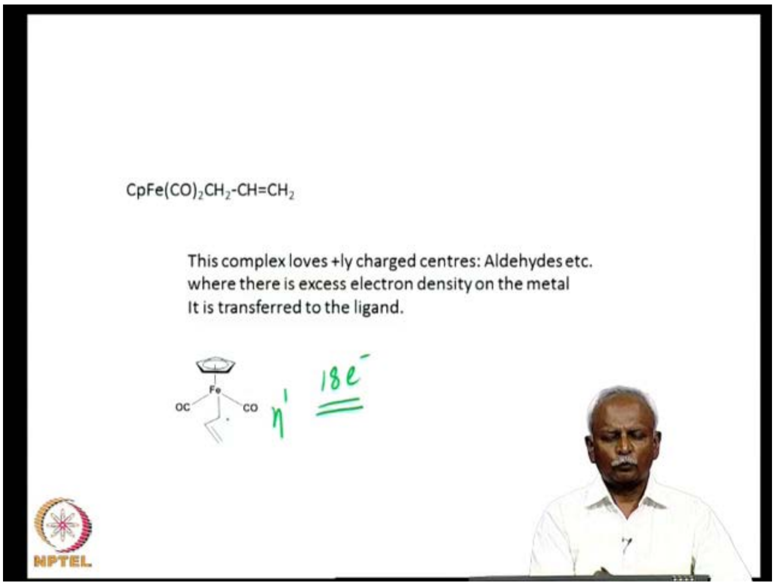

$CpFe(CO)_2CH_2\text{-}CH{=}CH_2$

This complex loves +ly charged centres: Aldehydes etc. where there is excess electron density on the metal It is transferred to the ligand.

So, here you have a different type of reactivity and the same situation happens, when you have CpFeCO2CH2 allyl. Here again the allyl group is eta one in nature, here it is pictured here the picture shown this is a eta 1allyl. And it behaves as if it likes positively charged centres. So, just as the palladium chloride compound was a system, where you have a lot of electrons in the metal in the iron case also.

This is an 18 electron system, and it has excess electron density, which is pumped into the allyl group. And, so this allyl will behave as if it likes positively charged centres. In fact this can react with aldehydes and with the other electron deficient carbon centres. So, you can alkalite species using this allyl group.

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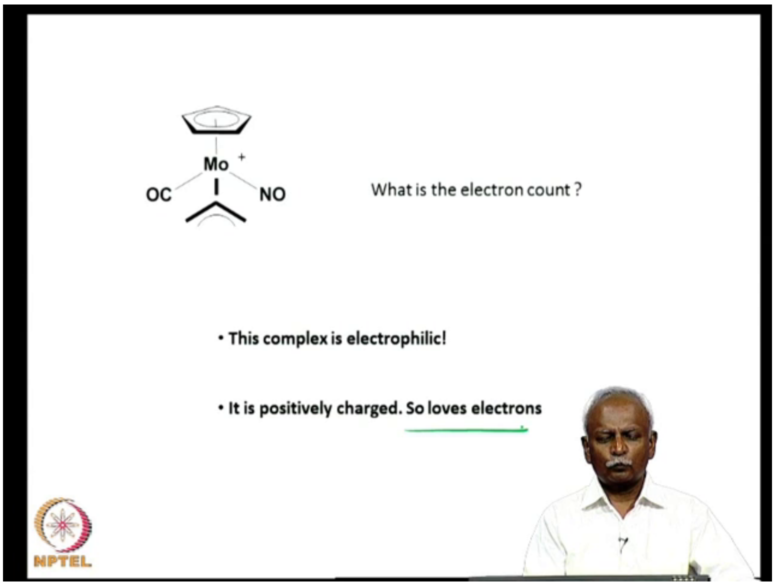

What is the electron count ?

- This complex is electrophilic!
- It is positively charged. So loves electrons

Now, here is another example where the allyl group will behave as a positively charged centre. Now, it is clear that the molybdenum complex that have written here is hostility charged. And it also has a nitric oxide, which is coordinated to the molybdenum, and this compound is electrophilic.

In fact it will allow to react with a species which has extra electrons. And this will this loves electrons, so it would like to react to this species which has extra electrons. In the previous example I shown have shown you a complex which is best which loves positively charged centres, here is an allyl group which is positively charged. In fact it is interesting that you can now react these two species together.

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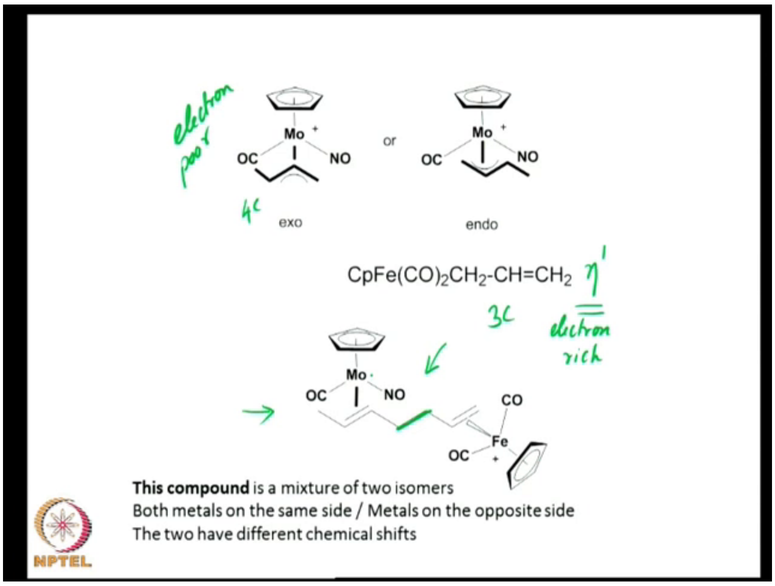

$CpFe(CO)_2CH_2\text{-}CH{=}CH_2$

This compound is a mixture of two isomers
Both metals on the same side / Metals on the opposite side
The two have different chemical shifts

And, if you react these two species, the actual reaction was carried out using a methyl substituted allyl group on the molybdenum. And you could have either the exo or the endo compound of the allyl group, which is present in the molybdenum. Now, you can react it with an eta 1, the eta 1 species that we talked about, and what is interesting is that you, now have the formation of a 7 carbon systems system. Here you have 4 carbons and 3 carbons here, and these 2 centres combine together to form a carbon-carbon bond.

What you end up with is a 7 carbon diene system, which is formed as a result of interacting these 2 allylic complexes. One was a eta 1 electron rich, this was electron rich, and here was an electron poor, this is electron poor and positively charged centre, and this is an electron rich 3 carbon centre. These two combine together to form a diene molecule. Where carbon carbon bond new carbon carbon bond was formed, and this is the carbon carbon bond that was formed as a result of interacting these two units.

And this molecule now has got two isomers, because the two metals can be present on the same side of the diene or on opposite side of the diene. You should remember that the molecule the alkene system is flat, although the other carbons which are attached to the alkene here are s p 3 centres, but the 2 double bonds can be in a plane. And the molybdenum can be in one side and the iron can be on the opposite side. So, you have both cin and anti forms of this cis and trans forms of this molecule, and you can both of them were isolated together in the reaction mixture.

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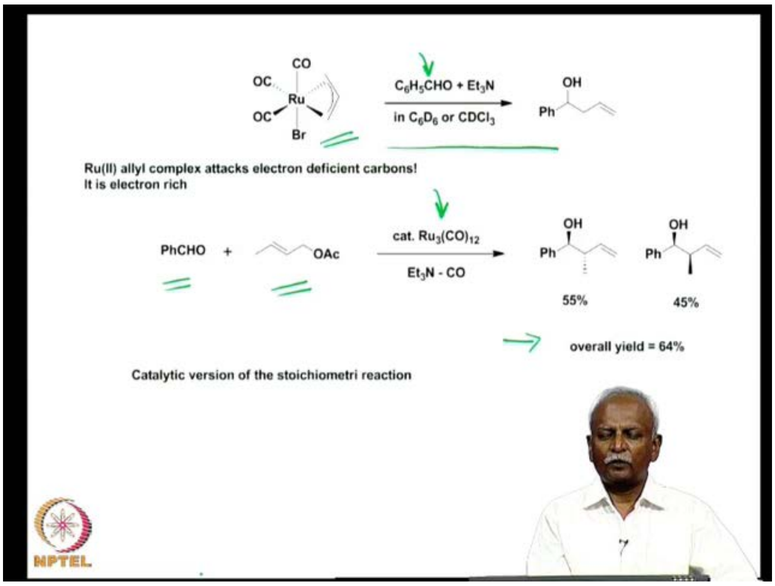

Ru(II) allyl complex attacks electron deficient carbons!
It is electron rich

overall yield = 64%

Catalytic version of the stoichiometri reaction

So, what we have shown up to now is the fact that, you can have a variety of different reactions between the allyl group and electrophyles or nucleophiles. Now, we will take one metal complex which seems to or one metal centre rhutenium here. So, this compound is capable of carrying out both electrophilic attacks and nucleophyllic attacks. Now, here is an example, you have a rhuthenium two allyl complex which is formed by treating rhuthenium carbonyl molecules.

Rhuthenium carbonyl molecules with an allyl acetate, you can generate an allyl bromide, you can generate this allyl complex, which can be which can be isolated and characterised. Stoichiometric reaction is what I have shown on the top of this transparency here is a stoichiometric reaction, where you end up with allyl group adding an electron adding to an electron poor carbon centre, which is the aldehyde. So, this behaves as if it is electrophilic, and this CHO is electrophilic, and it reacts with this allyl group.

Now, the same reaction can be carried out in a catalytic fashion by using a very small amount of ruthenium carbonyl, and adding an aldehyde and allyl acetate allyl acetate reacts with ruthenium to form the allyl complex. And that allyl complex, now adds onto an electron poor centre because it is electron rich. Now, this is a ruthenium 2 centre, which makes the allyl group electron rich. And you can see that, this reaction is something that produces two different isomers. And people have been able to control the stereochemistry of this carbon carbon bond formation, by using modifying ligands on the rhuthenium.

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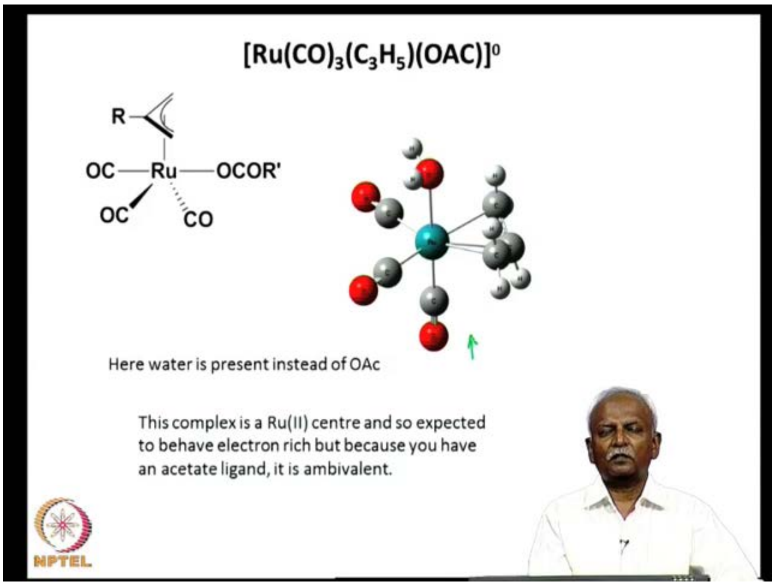

$[Ru(CO)_3(C_3H_5)(OAC)]^0$

Here water is present instead of OAc

This complex is a Ru(II) centre and so expected to behave electron rich but because you have an acetate ligand, it is ambivalent.

So, here is the structure of a of the ruthenium allyl compound, which in which there is a water molecule in the crystal structure instead of the acetate group.

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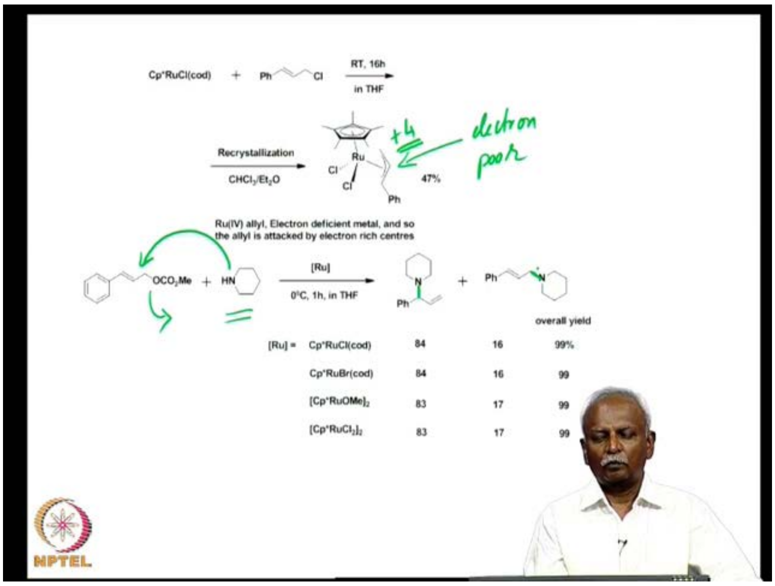

Ru(IV) allyl, Electron deficient metal, and so the allyl is attacked by electron rich centres

				overall yield
[Ru] =	Cp*RuCl(cod)	84	16	99%
	Cp*RuBr(cod)	84	16	99
	$[Cp^*RuOMe]_2$	83	17	99
	$[Cp^*RuCl_2]_2$	83	17	99

So, this is just to show you how the structure might be present, we can also have the same type of the same in this reaction. We can also have the addition of a nucleophile onto the allyl group. And this can be done with ruthenium cyclopentadiene dimethyl molecule, in which case the ruthenium goes from the ruthenium is in a plus 4 oxidation state. So, this allyl group behaves at the as if it is electron poor, because it is attached to a ruthenium 4 centre.

So, the ruthenium 4 centre now reacts with a nucleophile, which is heterocyclic ring system which attacks the allylicmoiety. So, this attacks this carbon, and eliminates the acetate, but this whole thing is facilitated because, the ruthenium 4 allylmoiety is generated in c 2 during the course of this reaction. And you have a new carbon nitrogen bond being from, and this carbon nitrogen bond is formed in the allylic position because of the formation of an allyl molecule.

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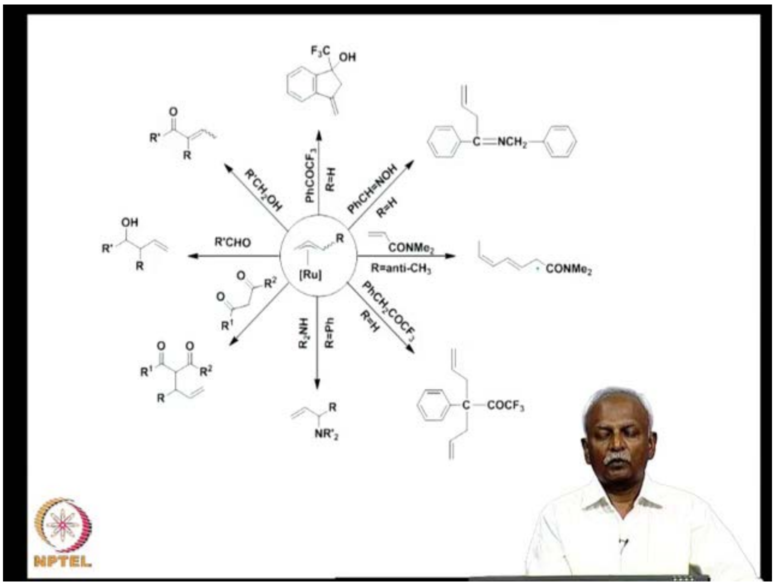

So, you can have a variety of reactions, which are which are possible because of the coordination of the ruthenium.

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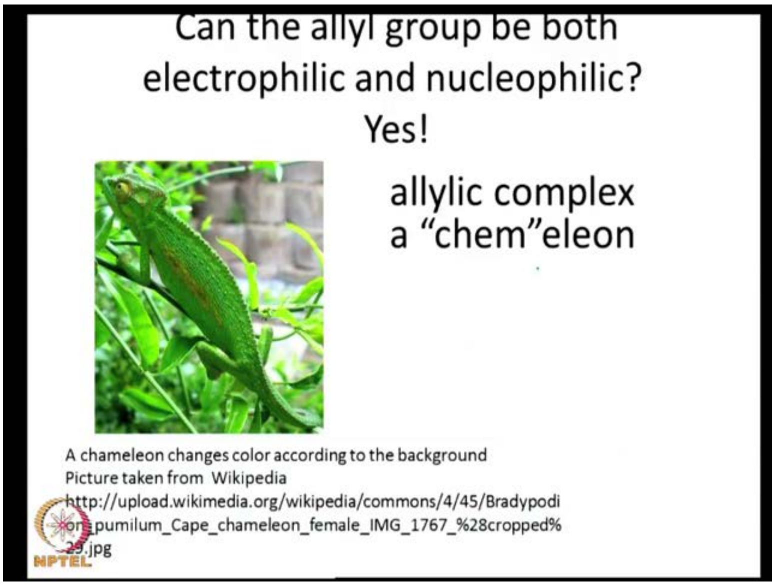

Can the allyl group be both electrophilic and nucleophilic? Yes!

allylic complex
a “chem”eleon

A chameleon changes color according to the background
Picture taken from Wikipedia
http://upload.wikimedia.org/wikipedia/commons/4/45/Bradypodion_pumilum_Cape_chameleon_female_IMG_1767_%28cropped%29.jpg

Basically the allyl group behaves both as an electrophilic centre, and as a nucleophilic centre. The allylic complex is almost like a chameleon, where just like a chameleon changes colour depending on its surroundings. The allyl group changes colour changes its electrophilic or nucleophilic nature depending on the metal which is attached to it.

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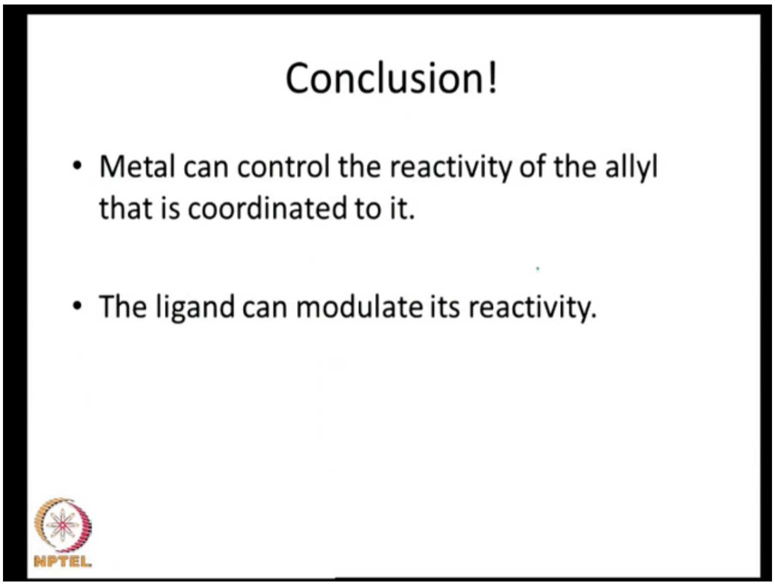

Conclusion!

- Metal can control the reactivity of the allyl that is coordinated to it.
- The ligand can modulate its reactivity.

So, to conclude today’s talk we can just say that, the metal controls the reactivity of the allyl group, and the ligands can modulate its reactivity. So, the based on the type of ligands that, one can add onto the metal and also oxidation state of the metal, one can change the reactivity of the allyl group.