Introduction to Organometallic Chemistry

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Lecture - 33
Addition of HX to olefins

This lecture deals with the catalytic processes, where there is addition of the species like HA or HM, HX or HY species where the second atom other than hydrogen is more electronegative than hydrogen or less electronegative. Now, there are several instances where these type of additions turn out to be important.

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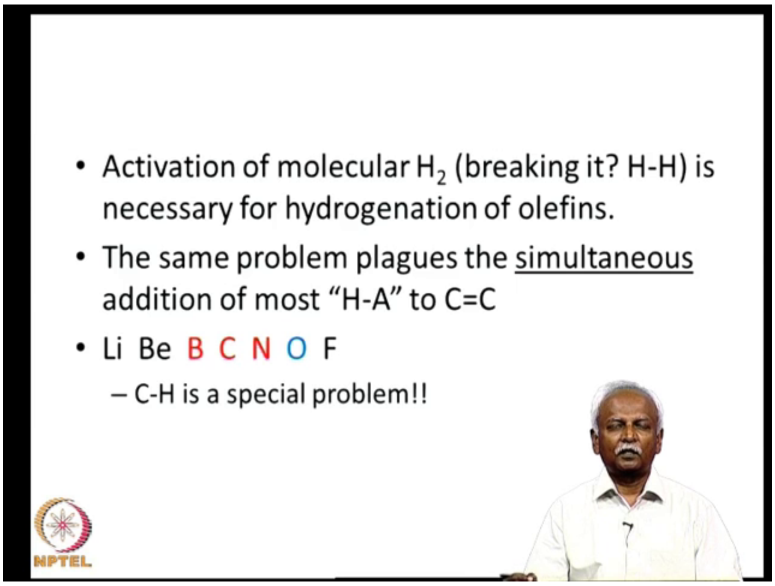

- Activation of molecular H_2 (breaking it? H-H) is necessary for hydrogenation of olefins.
- The same problem plagues the simultaneous addition of most "H-A" to C=C
- Li Be B C N O F
  - C-H is a special problem!!

We looked already at the addition of molecular hydrogen. We went through the argument as to why addition of hydrogen to olefins turns out to be unacceptable or it is not a process which can happen easily at room temperature and pressure and why a catalyst is necessary. The same problem in fact, plagues the simultaneous addition of most species like HA to the carbon-carbon double bond.

So, if you want to add a species HA to the double bond, you need a catalyst, especially when the second atom is not very different in electro negativity from hydrogen. So, in other words, if you look at the 3 atoms, which are marked in black, lithium, beryllium and fluorine, the electro negativity difference between hydrogen and these elements are quite large. So, you do not have a serious problem in terms of addition of these molecules.

So, lithium hydride and hydrogen fluoride do not have a problem. When you take a boron hydrogen species BE addition of BH or addition of NH, then it looks like you need a catalyst because the polarity difference between these 2 species is not very large. CH is a special problem because many of the molecules that we are dealing with have got CH bonds.

So, selective addition of CH or activation of CH is indeed a very difficult problem. We will deal with it in a separate class altogether. Oxygen, in fact, is quite polar. So, the difference between oxygen and hydrogen in terms of electro negativity is indeed large. So, it should be able to add on without difficulty, but as we will see, even that addition of OH bond to the C double bond, C turns out to be as a reaction, which needs a catalyst.

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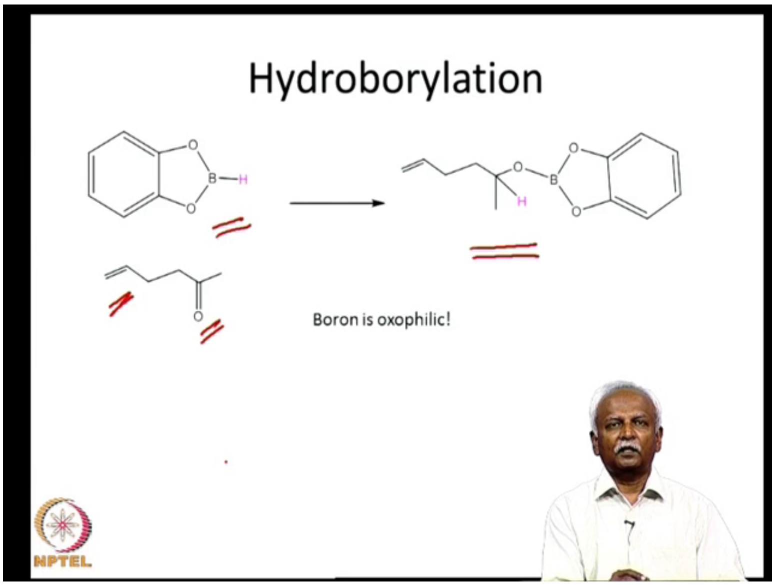
Hydroborylation

Boron is oxophilic!

First, let us take hydroborylation, the addition of a BH bond. Here is a molecule, which I have for you pictured for you here, which is a one and a one. So, the 2 species are in fact separate. There is a double bond and there is a ketone moiety. The 2 are not conjugated. When this species reacts with the borene, the BH bond, the uncatalyzed reaction, where you do not have any other species gives you a reduction of the ketone in such a way that the boron is now attached to the oxygen. The obvious reason or the obvious conclusion is that boron is oxophilic as indeed it is. So, this is the side of the molecule that reacts with the borene.

So, you do not have a surprise in this uncatalyzed reaction. So, what would you do if you want to react the carbon-carbon double bond with the borene hydroborylation is the reaction which happens quite readily in many cases. So, you want to force the reaction to go on the carbon double bond carbon rather than on the C double bond O.

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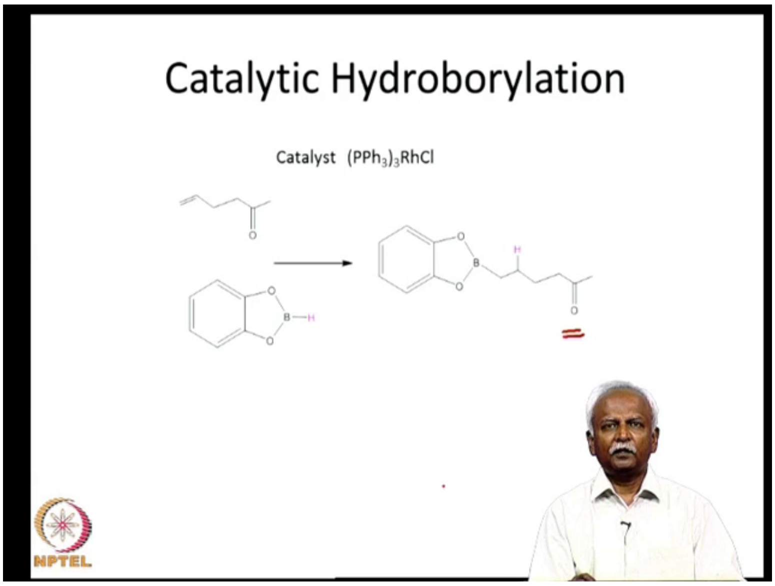

Catalytic Hydroborylation

Catalyst $(PPh_3)_3RhCl$

Here is a catalyst, which is the familiar Wilkinson’s catalyst, which carries out the same reaction that we have just noticed that we have just discussed. It results in the addition of the BH bond onto the olefin carbon rather than onto the ketone. So, here is a reaction in which the chemo selectivity is important. The chemo selectivity is changed markedly with the rhodium catalyst, which we are familiar with. Now, the mechanism of this reaction could be envisaged fairly easily because we know what happens with the Wilkinson’s catalyst.

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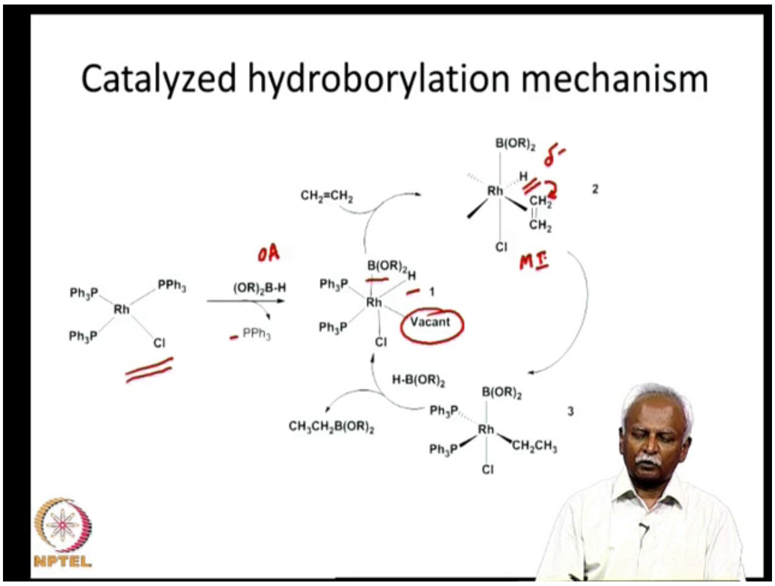

Catalyzed hydroborylation mechanism

I have a catalytic cycle drawn for you here that is very familiar should be very familiar to you. From what we have been looking at, here is a resting state of the catalyst, which on loss of PPh3, is minus PPh3. Loss of PPh3 from the coordination sphere generates a vacant coordination sphere. At the same time, you have oxidative addition of the BH bond. So, the BH bond is oxidative added. If you remember the oxidative addition that we have discussed, this falls in the class of molecules where the polarity difference between B and H is not very large. So, a cis addition is called for.

So, we will have a cis addition of the boron and the hydrogen to the rhodium. Since, we have lost the PPh3 molecule; you have this vacant coordination sphere in which we can coordinate a molecule of the olefin. So, the olefin would be coordinated in such a way that that would also be in a cis position with respect to the hydrogen. We now have migration of the hydrogen noticed at this is delta minus and boron is less electronegative.

So, it would have been be delta plus. So, if you look at the initial molecule also, you have hydrogen which is slightly delta minus. It undergoes a migratory insertion, which is essentially like a nucleophilic attack, internal nucleophilic attack on the carbon-carbon double bond. So, this is the carbon on which it would attack. As a result, you would get a ethyl group coordinated to the rhodium if you started out with ethylene as the alkyne.

So, you have the oxidation state change. The first step is in fact, an oxidative addition process. Then of course, you have a substitution or of the phosphorous by the olefin.

Then you have a migratory insertion. This is a migratory insertion that has happened where H minus or at least a pseudo H minus is migrating from the metal onto the olefin leading to the formation of another rhodium 3 species. The migratory insertion reaction does not change the oxidation state of rhodium.

So, you now have rhodium 3 species, from which the boron and the ethyl group can be eliminated in order to generate the catalytically active species. So, the elimination of this molecule, the organic molecule, the olefin which now has a BH moiety added on to it generates, regenerates the catalytically active species. It can add on another molecule of the reactant, which is the borene. It can carry on the catalytic cycle. So, once again, you have the familiar oxidative addition migratory insertion or some rearrangement followed by the reductive elimination in the last step.

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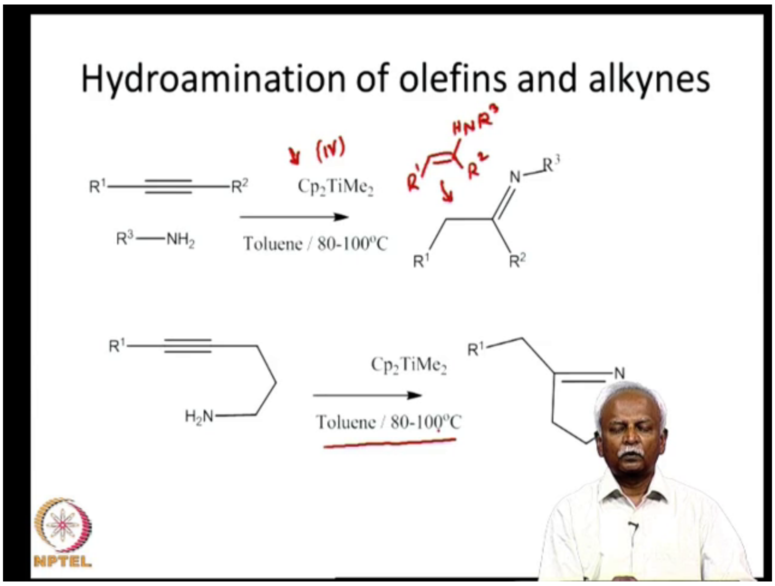

Hydroamination of olefins and alkynes

So, let us now proceed to hydroamination. As I mentioned CH activation turns out to be a special instance, it is carried out by several molecules. It is one of the most difficult challenging tasks because we make a molecule extremely reactive. It will show up the organometallic catalyst. So, hydroamination is an instance, where the hydrogen is slightly electropositive with respect to the other group. So, it is an instance where slight polarity difference is there just as we had in the BH bond.

Now, H is slightly positive. It turns out that these reactions are reactions where the mechanism is not necessarily the same as what we had proposed in the previous case.

This means it is not similar to the oxidative addition and migratory insertion followed by reductive elimination, but a variety of other mechanisms are possible. I have listed out 1 catalyst, which is a titanium 4 species. Obviously, the titanium 4 species is not the one that will carry out an oxidative addition reaction. But, the reaction mechanism is similar to what we had studied for the metathesis reaction itself. So, we will take a look at the mechanism. Just to convince you that this is only an addition of amine, let me just write out the equivalent of this molecule.

So, this is the tautomeric form of that molecule. It just involves the addition of an amine to the alkyne. All we have done is add on hydrogen and RR3NH group to the alkyne. This will readily isomerize to the species, which we have listed. So, it turns out that you can also have a cyclic variant. The cyclic variant is what is listed in the lower half of the slide. This reaction turns out to be a useful reaction. If you want to do addition, add an amine to an alkyne. You could do the same thing with an alkyne. In this case, you will get the saturated variety of this molecule.

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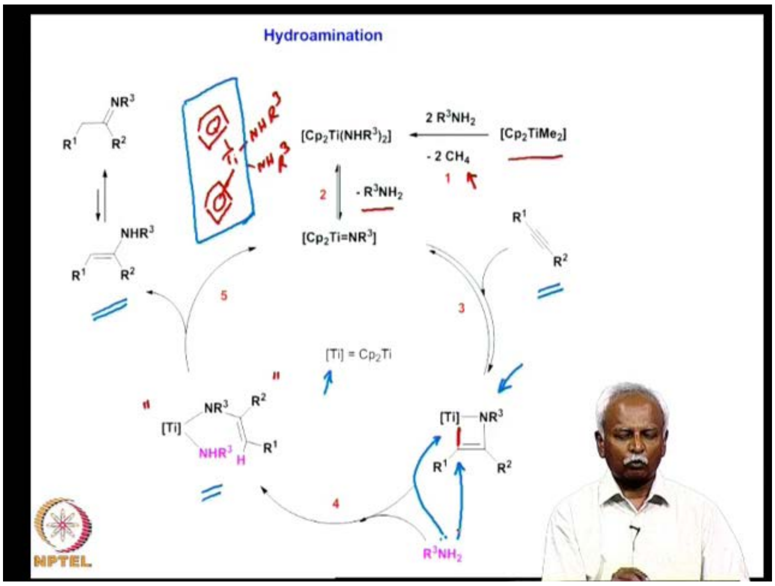

Hydroamination

So, let us just take a look at the hydroamination reaction. Now, the hydroamination reaction because the nitrogen is more electronegative than hydrogen, you realize that Cp 2 time 2, this molecule will readily react with a methyl groups, the alkyl groups and release methane. So, elimination of methane generates a catalytic catalytically active species. I could write this molecule as if it is having NHR3, NHR3, and then another titanium molecule.

So, here is the catalytically active species, but this species loses 1 molecule of R3NH2. It generates an imido species, which means there is a titanium double bond NR3 group. This is because we have to repeatedly write this framework. We are going to approximate this framework. I will do that by marking it in a different color so that you can see what we are talking about. We are going to mark out this species as the titanium species, as titanium within square brackets.

So, the loss of an amine generates an imido species. Now, you will notice that the double bond NR can add on to an alkyne in order to produce a metalocyclobutene. This is a species, which we found is analogous to the metathesis reaction. So, this is the reaction which we had noticed. Earlier, only we had an all carbon variety. Now, we have both the nitrogen and the titanium on the cyclobutene metalocycle. So, if you form this cyclobutene, it can now reopen in a slightly different fashion. That is exactly what they are going to do. We are going to move the species in such a way that we will end up with a molecule, which would have an imido compound.

So, this again reacts with another molecule of R3NH and liberates the species that we are looking for. This means that this is the enol form, enol type enamine type of a molecule. It will isomerize to give you the final product. So, you will notice here that we end up if this R3NH2 reacts with this titanium. I can indicate this as follows. Then I would have hydrogen adding on here. One hydrogen from this amine adds on here. The nitrogen adds on to the titanium. So, you have both reactivity of this bond.

The titanium carbon bond undergoes an ammonol, ammonalysis or aminolysis in order to generate this intermediate. This is going to give your product. So, this reaction is partly like the metathesis reaction. It is generates the catalytically active species, which can undergo ring formation as a metalocyclobutene. Then the ring form that is formed is kind of hydrogen aliased or by this amine in order to generate the final product.

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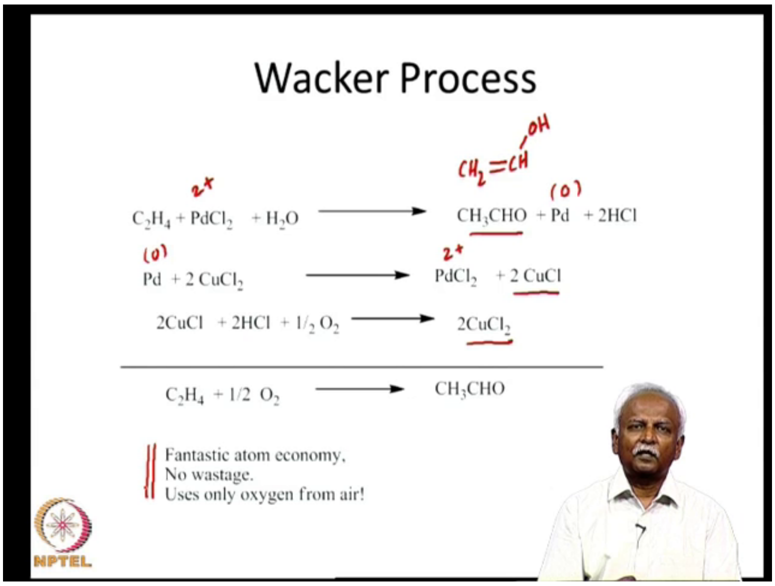

Wacker Process

$$\overset{\text{OH}}{CH_2{=}CH}$$

$$C_2H_4 + \overset{2+}{PdCl_2} + H_2O \longrightarrow \underline{CH_3CHO} + \overset{(0)}{Pd} + 2HCl$$

$$\overset{(0)}{Pd} + 2\,CuCl_2 \longrightarrow \overset{2+}{PdCl_2} + \underline{2\,CuCl}$$

$$2CuCl + 2HCl + 1/_2\,O_2 \longrightarrow \underline{2CuCl_2}$$

$$C_2H_4 + 1/2\ O_2 \longrightarrow CH_3CHO$$

Fantastic atom economy,
No wastage.
Uses only oxygen from air!

So, we will now proceed to the OH bond. This is just the amine was one example and the same thing can happen with a water molecule or any OH bond. For that matter, we will see the celebrated wacker process. It has been the main stay of the industry, especially the wacker chemie, which is in Germany. It was originally discovered. The reaction that we are talking about is a reaction of ethylene with water molecule in order to generate acetaldehyde.

Once again, you will realize that this is in fact, the enol form. If you write the enol form of the molecule, you will realize that ethylene has undergone a partial oxidation. You have instead of adding H and OH across the double bond; you have added H and OH. Then you have removed the molecule of hydrogen. So, here in this case, you have both an oxidation and an addition that is taking place. So, oxidation is carried out in an indirect fashion. Initially, it is a palladium 2 plus, which gets reduced to palladium 0. Then in a second step because you have cupric chloride in the reaction, the cupric chloride oxidizes the palladium 0 to palladium 2 plus in turn it gets converted to cuprous chloride. Cuprous chloride is oxidized in a very first step in eco solution with oxygen to cupric chloride.

So, this is a combination of 2 catalytic cycles. One in which oxygen oxidizes the copper 1 to copper 2. The copper 2 in turn oxidizes the palladium 0 to palladium 2. In a second reaction, in which only the organic species reacts with palladium 2, there is an oxidation of the ethylene to the enol form of acetaldehyde. Now, why I will be classifying or why are we using this reaction, talking about this reaction in the chapter where we are discussing a nucleophilic attack on the ethylene? We will see this is in a particular topic in a few minutes. I just want to point out that this reaction is a fantastic reaction. In the case of atom economy, there is absolutely no wastage of atoms when you convert the ethylene to acetaldehyde. The reaction medium is also water. So, there is a very green chemistry that we are discussing right here.

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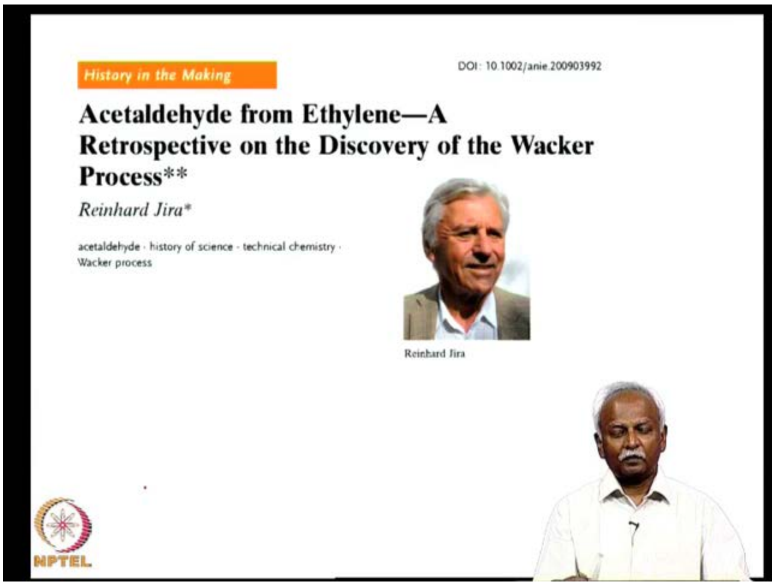

History in the Making

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Acetaldehyde from Ethylene—A Retrospective on the Discovery of the Wacker Process**

*Reinhard Jira**

acetaldehyde · history of science · technical chemistry · Wacker process

Reinhard Jira

In fact, although wacker process is not used by many companies, Wacker Company itself uses this methodology to generate acetaldehyde. Recently, the discoverer of the wacker process, Reinhard Jira era gave small account of the discovery in a journal, which is referenced here. It makes very interesting reading. Let me just tell you a few points from that article, which will allow you to appreciate the whole discovery at the point.

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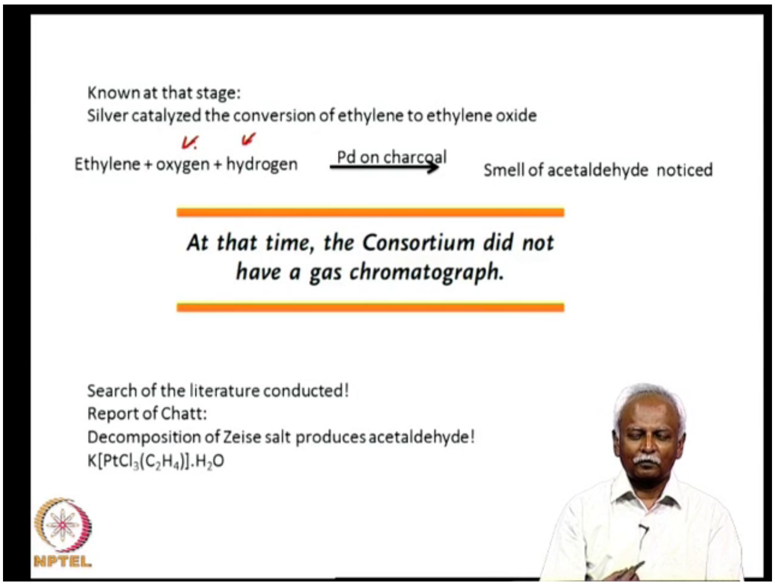

Known at that stage:
Silver catalyzed the conversion of ethylene to ethylene oxide

Ethylene + oxygen + hydrogen $\xrightarrow{\text{Pd on charcoal}}$ Smell of acetaldehyde noticed

At that time, the Consortium did not have a gas chromatograph.

Search of the literature conducted!
Report of Chatt:
Decomposition of Zeise salt produces acetaldehyde!
$K[PtCl_3(C_2H_4)].H_2O$

When Jira started his work, it was known that silver oxidized ethylene to ethylene oxide. He was trying to discover what would happen if you oxidized ethylene with other metal systems? He chose palladium on charcoal as a catalyst system. He added both oxygen and hydrogen. So, both oxygen and hydrogen were in the reaction mixture. On passing ethylene, he found that the reaction had proceeded, but there was no way for him to analyze the reaction mixture in a very modern way. He smelt acetaldehyde in the reaction mixture. That is all that he had as a hint about what had happened to the reaction. This is because at that time, as he in his own words, he says that consortium of the company did not have even a simple gas chromatograph.

So, based on the smell, he decided that he would look up the reactions where acetaldehyde is generated and alone, he found another report of Chatt, which indicated that zeise salt. It is an olefin platinum complex, which had a molecule of water. So, here is a molecule of water coordinated to an ethylene complex of platinum same group is palladium. That also generated acetaldehyde. So, he felt that if you had only oxygen, platinum and palladium, probably you would generate more acetaldehyde. Hence, the rest is history he patented.

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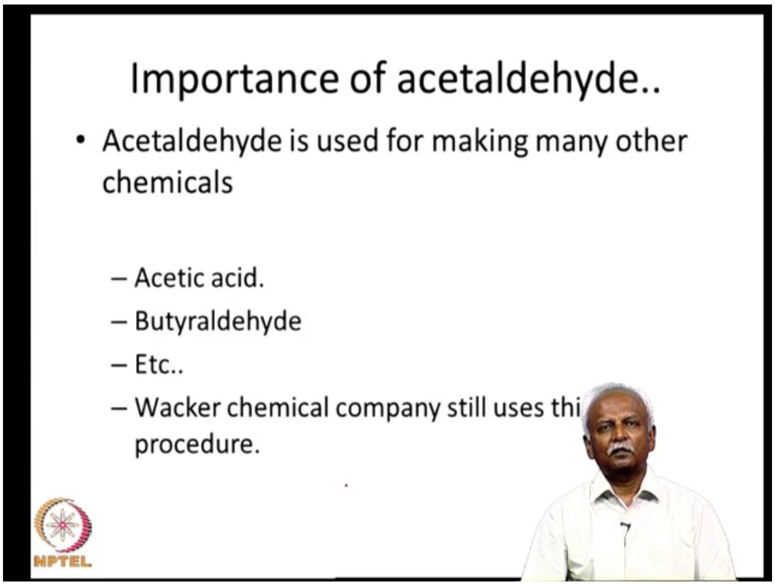

Importance of acetaldehyde..

- Acetaldehyde is used for making many other chemicals
  - Acetic acid.
  - Butyraldehyde
  - Etc..
  - Wacker chemical company still uses thi procedure.

This method for generation of acetaldehyde was very important at that time for making a variety of chemicals including acetic acid and butyraldehyde. It turns out that in recent times; at least acetic acid synthesis has moved over to monotonous process, which is something that we had discussed when we discussed carbon monoxide insertion chemistry. But, Wacker Company still uses this particular procedure in order to make acetaldehyde

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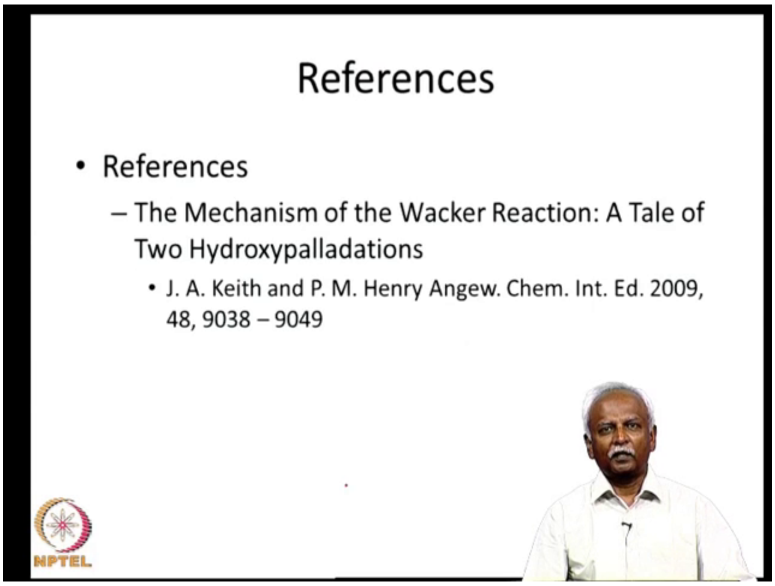

References

- References
  - The Mechanism of the Wacker Reaction: A Tale of Two Hydroxypalladations
    - J. A. Keith and P. M. Henry Angew. Chem. Int. Ed. 2009, 48, 9038 – 9049

If you want to read more on the mechanism of the wacker reaction, you could refer to this article, which is there in Angew. Chem and which also makes very interested reading.

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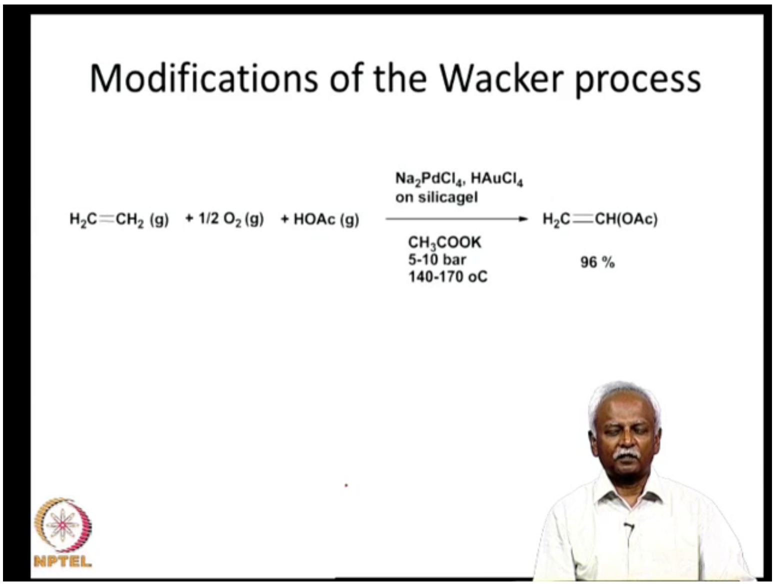

Modifications of the Wacker process

$$H_2C{=}CH_2\ (g)\ + 1/2\ O_2\ (g)\ + HOAc\ (g) \xrightarrow[\substack{CH_3COOK \\ 5\text{-}10\ bar \\ 140\text{-}170\ oC}]{\substack{Na_2PdCl_4,\ HAuCl_4 \\ \text{on silicagel}}} H_2C{=}CH(OAc)$$

96 %

Apart from Jira’s article that I mentioned earlier, let us take a look at some of the modifications of the wacker process. As I told you, if you use acetic acid instead of water, you would be able to generate instead of OH, ON, the enol. You now have vinyl acetate, which is also extremely useful. This reaction proceeds at the best when you have sodium salt of tetra chloro palladium. Also, it is promoted by gold. So, these reactions are still used in a industrial scale to generate vinyl acetate.

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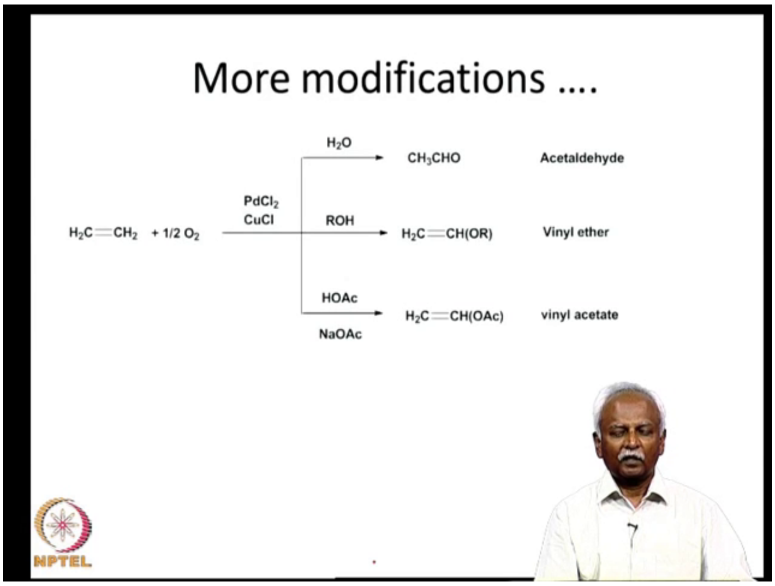

More modifications ....

$$H_2C{=}CH_2 + 1/2\ O_2 \xrightarrow[CuCl]{PdCl_2}$$

$\xrightarrow{H_2O}$ CH_3CHO Acetaldehyde

$\xrightarrow{ROH}$ $H_2C{=}CH(OR)$ Vinyl ether

$\xrightarrow[NaOAc]{HOAc}$ $H_2C{=}CH(OAc)$ vinyl acetate

You can also generate vinyl ether, if you do the reaction in the presence of ROH. So, essentially there is the addition of a nucleophile RO minus or O Ac minus to this double bond. It is instructive to see.

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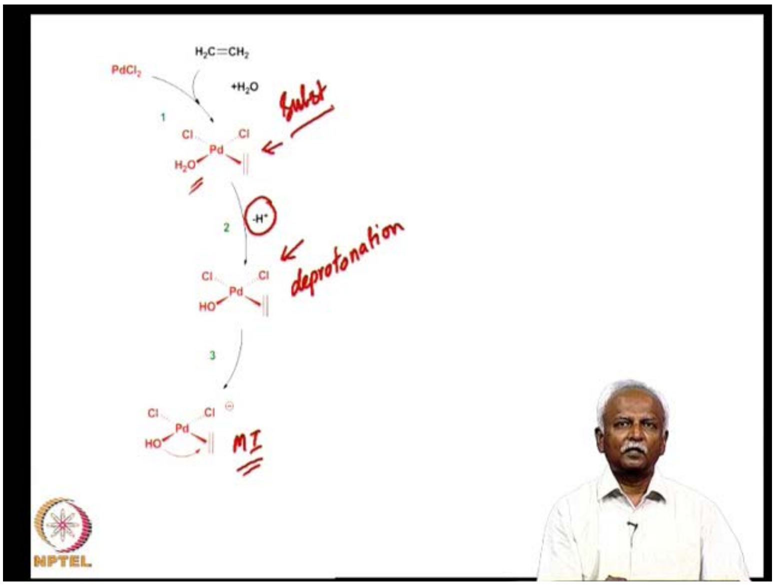

The mechanism of this reaction has been studied in great detail. Here, I have for you the first few steps of the reaction, which involves the addition of a ethylene to palladium chloride in the presence of water in order to generate a olefin palladium 2 complex. So, olefin complex is of a palladium a plenty. So, there is plenty of precedence for such a reaction if you remove a proton from this water molecule, which is very often easily done. You have a metal in a plus 2 or a plus 3 oxidation state; then the ph of water changes. It becomes lot more acidic.

You would lose a proton failure readily. You can generate a molecule, which has got an OH group and an olefin coordinated to the palladium, if this molecule undergoes a migratory insertion. So, notice here that in this reaction, we have not carried out oxidation state chain. We have only carried out a deprotonation. We have carried out a deprotonation. We have carried out a substitution. We have carried out a substitution, a deprotonation and a migratory insertion in this reaction.

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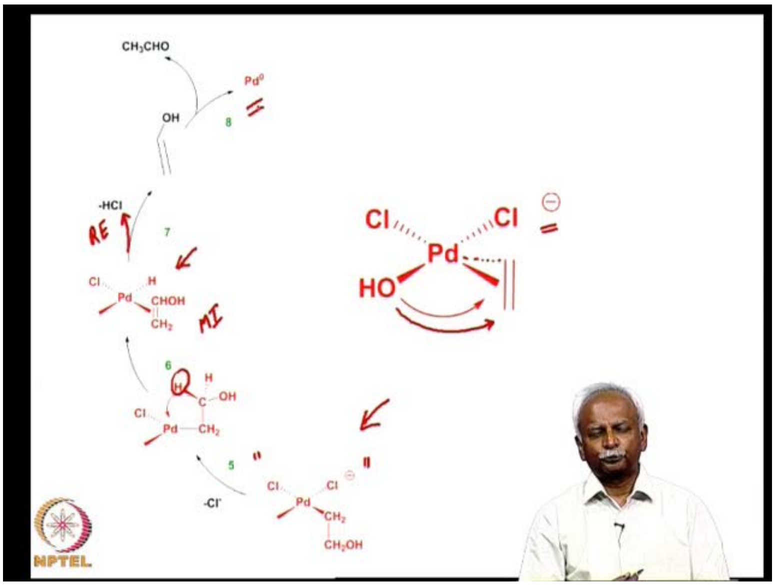

That would give us the species, which I have indicated for you here, where an OH group has migrated from the palladium onto the double bond. So, you have this migration of this OH to this double bond. You have the formation of a single bond between the palladium and the terminal carbon of the olefin. So, you would get a species like this. So, notice that because we deprotonated that neutral molecule, we end up with a negative charge on the whole system. The migratory insertion does not change the process. So, you have a negative charge on this molecule, which I have indicated here it for you at the bottom of the slide.

Now, let us do a couple of things. This molecule can carry out a couple of reactions or undergo a couple of reactions. One of them is the movement of this proton, of this hydrogen from the organic moiety onto the palladium. That will give you reverse of the migratory insertion. So, this is the migratory insertion in the reverse, is a migratory extrusion if you might call it. It leaves you with a palladium 2 complex. The palladium 2 complex has got an enol coordinated to the palladium. It has got hydrogen and a chlorine cis to each other on the palladium coordination sphere. Loss of H Cl would happen if this underwent reductive elimination.

So, reductive elimination gives you the enol and palladium 0. The enol can be converted to acetaldehyde. Now, if you look at this reaction, you started with palladium 2 and ended up with a reductive elimination. So, the oxidation state of the palladium has been reduced through the catalytic cycle to palladium 0. That is why; you needed the copper in order to oxidize it.

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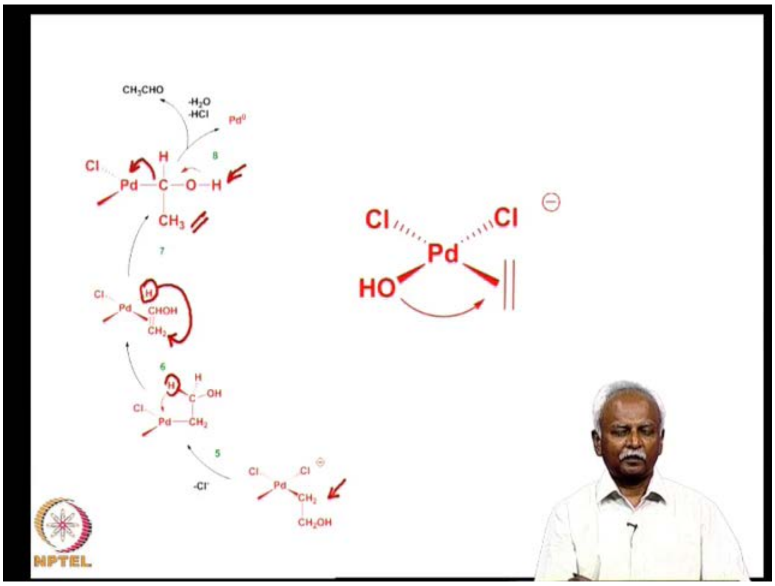

There is also an alternative mechanism for this whole process. That is the reverse of the migratory insertion. If the migratory insertion were to proceed from the hydrogen onto the CH2, then you would end up. If this hydrogen adds onto the CH2, you would end up with this molecule, where you have a CHOH attached to the palladium directly. The advantage of this particular mechanism is that it is easy to see how the reduction of the palladium could happen. This is because the transfer of this lose of this hydrogen as H plus and transfer of this pair of electrons into the palladium would completely reduce the palladium to palladium 0, instead of doing the reductive elimination of H Cl. So, these two parts are difficult to distinguish, but nevertheless, both mechanisms are common in the literature.

So, the two mechanisms are different only because of the way in which we have carried out the transfer of the hydrogen. In one mechanism, we have transferred this hydrogen directly from the organic moiety onto the palladium. In the other case, we have transferred it back to the organic moiety. You have isomerized the alcohol. This alcohol has been isomerized in order to generate a new alcohol, in which the alpha carbon has got an OH group. That led to decomposition or a reaction, where the acetaldehyde is generated directly.

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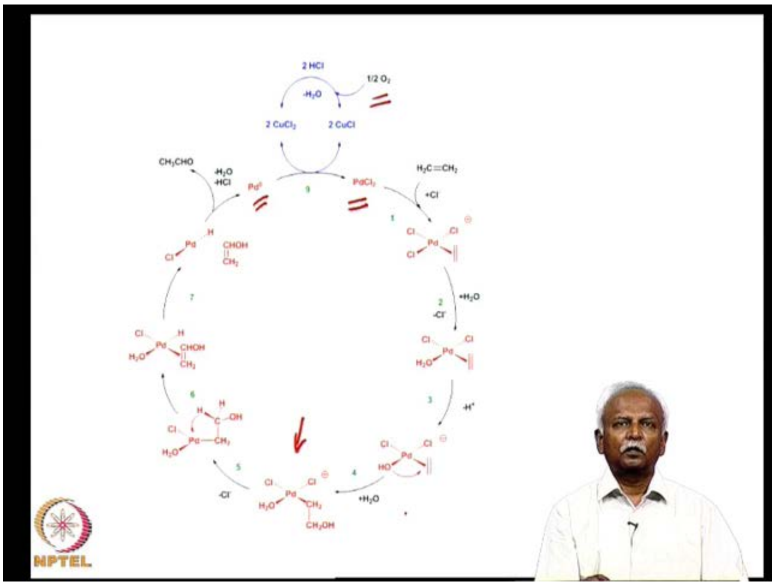

Now, let us put all these things together and look at the full catalytic cycle that is there in front of you. As I told you, the palladium 0 is oxidized to palladium 2 plus. Palladium 0 is oxidized to palladium 2 plus. The coordination of an olefin gives you an intermediate, which can undergo a migratory insertion of a water molecule or an OH group depending on the ph of the medium. That gives you a hydroxyl ethyl group, which is the key molecule in this whole catalytic cycle. It can either undergo hydrogen abstraction or a hydrogen migration back and forth in order to give you the final product. So, the palladium 0 being oxidized to palladium 2 in independent step oxygen from air is also a very important step. This is because if that was not present, all the palladium 2 plus would be reduced to palladium 0. This would render the catalytic cycle completely inactive. The 2 cycles are independent of one another.

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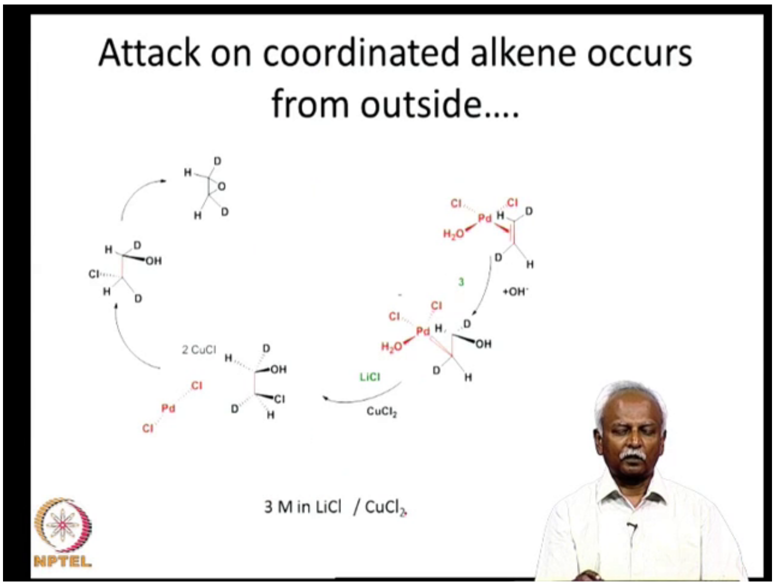

Attack on coordinated alkene occurs from outside….

3 M in LiCl / $CuCl_2$

That is also a very important point to notice. If you avoid the copper, you could do several reactions. We have for you a few, which are of mechanistic relevance. For example, if you do not add copper, instead you add lithium chloride and cupric chloride, this is the reaction cycle. We have done this or we have shown this reaction with iso topically labeled species.

So, you realize that the hydroxide, which we showed in the previous slide, we showed it as an internal attack from the palladium. It can also happen from the outside. So, here is a reaction where you add OH minus and add lithium chloride and cupric chloride. The concentration of these 2 species is quite high in solution. Then you have a strong probability of forming the chloro ethanol. That is a product that is formed because you have hydroxide ion also in the reaction medium. The alcohol is deprotonated. It carries out an internal attack on the second carbon atom ejecting the Cl Cl minus.

So, let us take a look at this stereo chemistry in detail. What you have is OH minus, which is attacking this carbon. Whether this attacks the carbon, you end up with the palladium on the opposite side of the hydroxide ion, which is incoming. So, I have exaggerated the length of bond, so that you can see that the hydroxide is coming from outside from towards a viewer from the side of the viewer towards the olefin. The palladium is behind the olefin away from the viewer.

So, that leads to a molecule in which the deuterium 2, deuterium atoms. If the OH and Cl are present on the same side, the 2 deuterium atoms are trans in this molecule. You would end up with a rotation in order to do an internal attack of the OH minus or the O minus on the second carbon. You would have to rotate the hydrogen around this carbon. The hydrogen and deuterium would change places. That is what we have shown here. The hydrogen and deuterium have changed places. As a result, their epoxide has got cis deuterio atoms. So, this tells us two things. The hydroxide can come from the opposite side of the molecule a and b. It also tells us that it is possible to modify this reaction in such a way that other products can be obtained.

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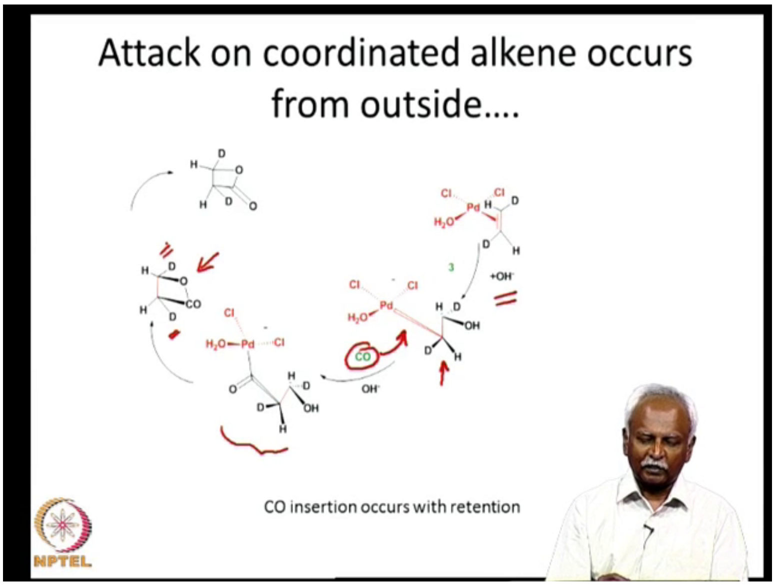

Attack on coordinated alkene occurs from outside....

CO insertion occurs with retention

Here is another reaction. We will go through this rather quickly this time because you have a similar situation. Hydroxide attacks from the outside because OH minus was added. It turns out that adding hydroxide from outside can be combined with insertion of carbon monoxide into this palladium carbon bond, which as I showed you in the last trans last projection. The palladium carbon bond length has been exaggerated so that you can follow what is going on.

If the insertion happens with retention of configuration of the carbon, this is the carbon which is undergoing migration and if that happens with retention, the product that you would obtain would have this following configuration. So, where the 2 hydrogens are now still trans to each other and rotation of this oxygen in such a way in order to generate a lactone. In this case, a lactone can be achieved only if you bring the 2 atoms on the same side, the 2 deuterio atoms on the same side. So, you will notice that the migration has to happen with retention of configuration. So, the OH minus must have come from the opposite side of the palladium.

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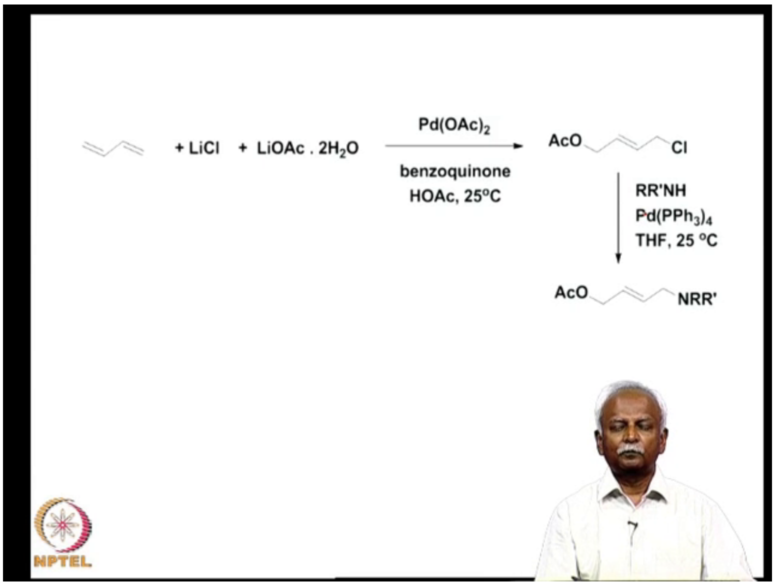

So, these are 2 mechanistically relevant and important reactions that have been studied. Now, the Wacker reaction as I mentioned earlier has been modified in a variety of ways. It has also been modified in such a way that can be industrially useful. Here is a modification where you carry out acetoxylation into a diene. That results in O Ac minus being added on to the 2 terminal positions of the butadiene. This gives us a very useful molecule because reduction with raney nickel, this is raney nickel and hydrogen leads to a diol formation. This diol is a useful molecule because it can be used in the polymer industry in a fairly large scale.

Here is another reaction. If you want to carry out addition of 2 different nucleophiles; it is possible, especially when you have palladium acetate and benzoquinone. Benzoquinone to reoxidize the palladium to palladium 2 plus and in a second step, you can convert the chloroacetoxylated species to an amine. This happens in the terminal positions only. The nucleophiles have come in from the terminal positions. As a result, you can generate this very interesting and novel molecule fairly easily.

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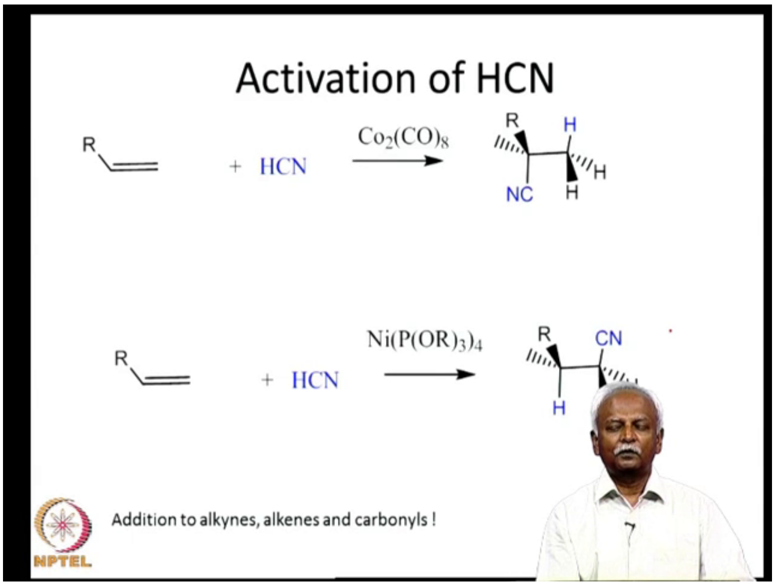

Activation of HCN

Addition to alkynes, alkenes and carbonyls !

Now, although we are not strictly adding bimolecular species in this reaction, here is a molecule which has got a cyano group. Instead of HA, we have pseudo halogen cyanide, which is attached to hydrogen. It turns out that this is a reaction, which can be carried out in two different ways. The nickel catalyzed fashion is a one, which is used in the industry significantly. We look at the catalytic cycle in a minute.

The interesting fact is that if you use di cobalt octa carbonyl, you end up with different region chemistry. We will take a look at this reaction, which can be carried out with alkynes alkenes and even carbonyls. So, you can even add HCN to carbonyls to get a cyano hydrine. So, this is a very useful reaction. You can carry out addition with a variety of species.

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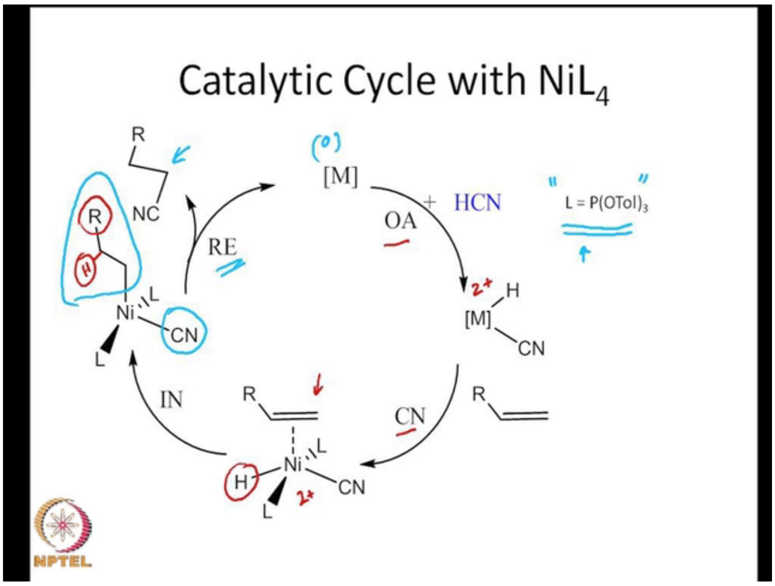

Catalytic Cycle with NiL$_4$

Here is a catalytic cycle. Catalytic cycle is shown with addition of HCN. We now move over to what we had seen earlier an oxidative addition followed by oxidative addition of HCN followed by addition of an olefin in the vacant coordination sphere of the nickel 2 plus. Now, nickel has become 2 plus. At this particular stage, this oxidized nickel 2 plus would prefer a 6 coordinate species or a 5 coordinate species. That is what happens when you in the second step have oxidative addition followed by coordination of an olefin leading to a high coordinative intermediate.

Now, you have migration of hydrogen. This migration of a hydrogen could have taken place in 2 different fashions. If it added onto this CH2 group, it would have ended up with a hindered alkyl group. Instead, it seems to add on to the hydrogen to the carbon, which has got less number of hydrogen. This is like the anti markovnikov of addition of HCN. So, you end up with an alkyl group, where the bulky group is usually away from the metal atom. The hydrogen that you have added is also added in this position.

So, this is the hydrogen. This is the new position of the hydrogen. This alkyl nickel species can reductively eliminate. Let us indicate that with the different color here. This can eliminate a CN group and the alkyl group. Then you would get the product. So, this results in the catalytically active species because reductive elimination brings back the nickel to nickel 0. It is now capable of doing the oxidative addition back to nickel 2 plus.

So, the interesting fact is that the region selectivity in the reaction is very much dependant on the ligand that you use. If you use a very bulky ligand, the region selectivity is very good. You get only 1 product. That product has got the R group away from the cyanide. In other words, the additions of hydrogen will happen in such a way that the hydrogen is added to the bulkier side of the olefin. You get a terminal carbon where you can add on the cyanide. So, this happens only if you have a bulky ligand and a phosphite as opposed to a phosphene. So, the presence of a phosphite is important and the presence of a bulky group is also important.

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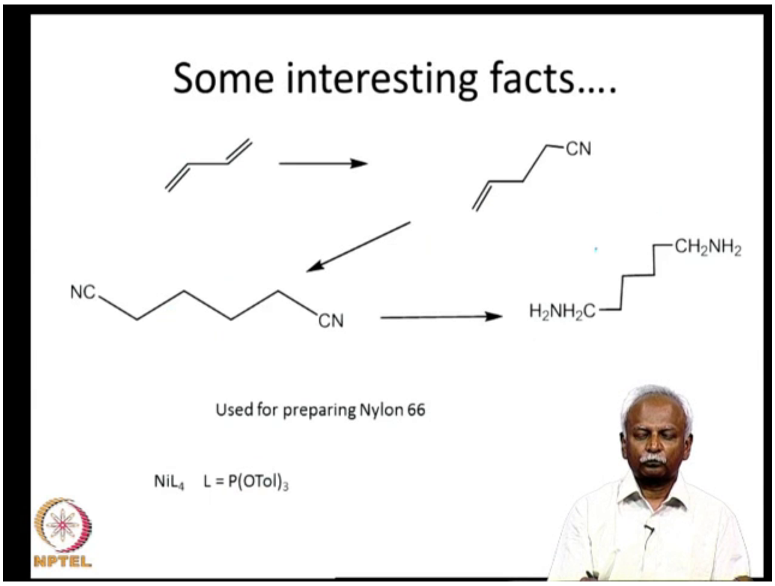

Some interesting facts....

Used for preparing Nylon 66

NiL_4 $L = P(OTol)_3$

So, if we do the same reaction cycle with a butadiene, then you can do the reaction in 2 steps. In the first step, 1 cyanide is added and in second step, another cyanide is added. This leads to the molecule, which has got, which is now ready. If you add on hydrogen in this step, you add hydrogen to this step to this molecule; you end up with a 6 carbon molecule and a 6 carbon di amine. This is exactly the molecule that was used to prepare nylon 66. Nylon 66 can be prepared by oxidizing this to the di acid and reducing it to the amine. That gives you a very easy way of converting butadiene to an extremely useful molecule, which is nylon 66.

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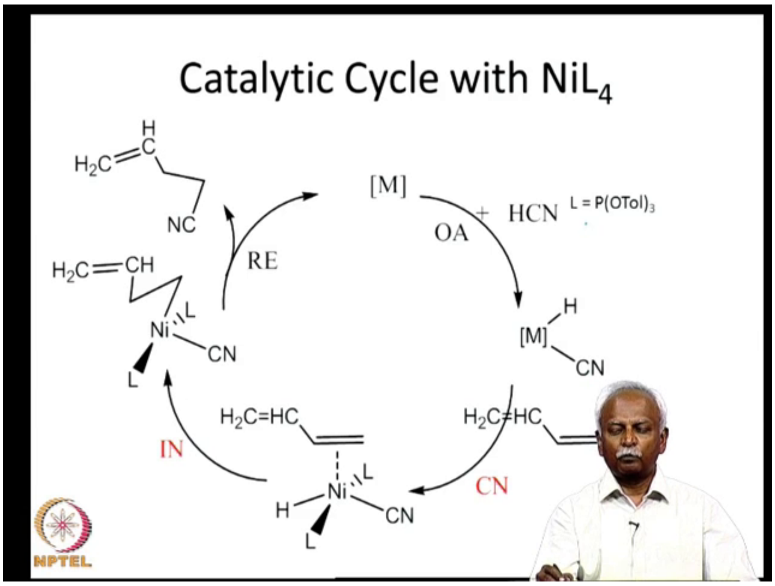

Catalytic Cycle with NiL_4

So, here is the catalytic cycle, which we will go through fairly fast because we have already discussed it with a single ene. Suffice it to say that each ene behaves independent of the other ene so much so that you end up with the CN group added to each end of this diene. So, if the 2 double bonds are cooperated, we would have obtained a different result. So, the importance of the bulky and bulky phosphite is not to be minimized.

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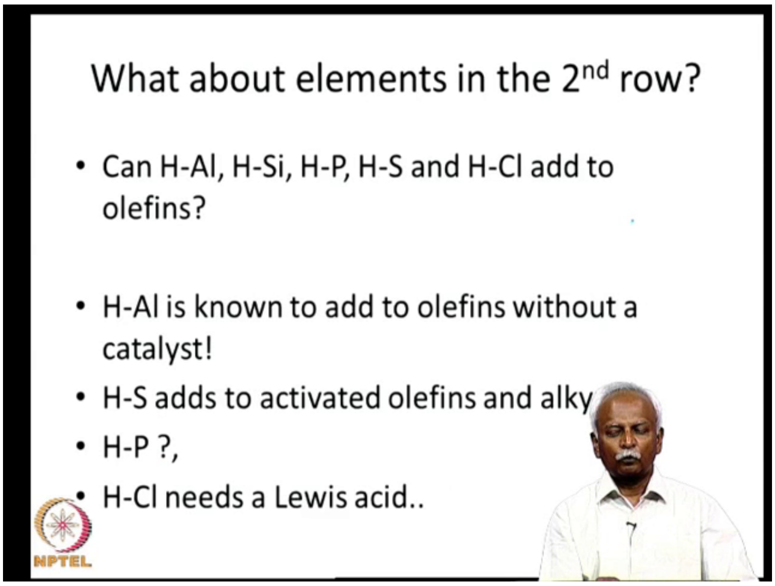

What about elements in the 2nd row?

- Can H-Al, H-Si, H-P, H-S and H-Cl add to olefins?
- H-Al is known to add to olefins without a catalyst!
- H-S adds to activated olefins and alky
- H-P ?,
- H-Cl needs a Lewis acid..

Now, let us just ask the question what about elements in the second row. So far, we have talked about the 3 elements boron, nitrogen and oxygen. What about elements in the second row? Can the alumin or the silane or the phosphine add onto the olefin? Is that possible? In fact, hydrogen attached to aluminum is known to add on olefins without the catalyst. This was in fact studied by Ziegler. We will talk about this in a moment, but the moment you move onto other species, it is interesting that they can either add on without a catalyst or with the presence of Lewis acids. They do not really need a transition metal catalyst. Let us just take a brief look at the hydroalumination reaction.

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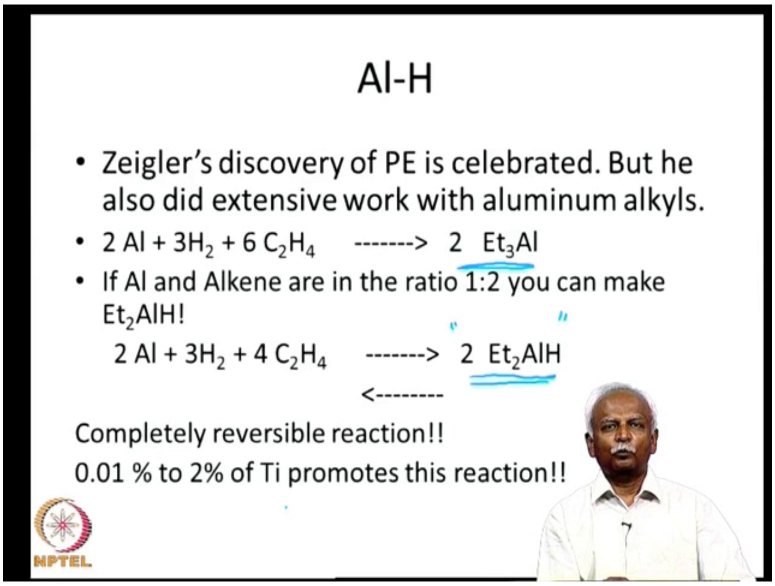

Al-H

- Zeigler's discovery of PE is celebrated. But he also did extensive work with aluminum alkyls.
- $2\ Al + 3H_2 + 6\ C_2H_4 \text{ -------> } 2\ \underline{Et_3Al}$
- If Al and Alkene are in the ratio 1:2 you can make Et_2AlH!

$$2\ Al + 3H_2 + 4\ C_2H_4 \underset{\text{<--------}}{\text{------->}} 2\ \underline{Et_2AlH}$$

Completely reversible reaction!!

0.01 % to 2% of Ti promotes this reaction!!

This is because that is a fairly interesting reaction. It is a challenging reaction to understand as well. Ziegler's discovery of polyethylene is in fact quite celebrated, but he did extensive work with aluminum alkyls. What he showed was that aluminum in the presence of hydrogen and ethylene can lead to triethyl aluminum. So, triethyl aluminum is a species, which is generated in the presence of just ethylene and pure aluminum.

Now, if aluminum and alkene are in the ratio 1 is to 2, you end up making an alumin, which has got an aluminum hydrogen bond. This turns out to be like a stoichiometric reaction. So, you can do this in a batch process and you will see in a moment how this can be extremely useful. So, it looks as if the direct reaction of hydrogen aluminum hydrogen and aluminum is quite feasible. The catalyst for this reaction, auto catalyzed process because aluminum triethyl alumina itself functions as a catalyst. Another interesting fact is that this reaction is completely reversible. It can generate the reaction can go in the backward reaction, a backward direction as well. The last important point is that a small amount of titanium promotes the reaction.

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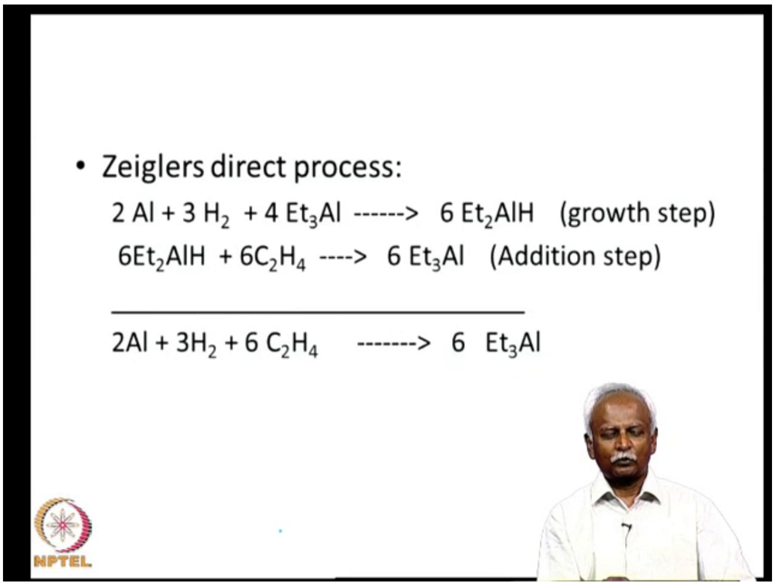

- Zeiglers direct process:

$2\,Al + 3\,H_2 + 4\,Et_3Al$ ------> $6\,Et_2AlH$ (growth step)

$6Et_2AlH + 6C_2H_4$ ----> $6\,Et_3Al$ (Addition step)

$2Al + 3H_2 + 6\,C_2H_4$ -------> $6\,Et_3Al$

So, you notice that the Ziegler Natta reaction is catalyzed by or promoted by aluminum. The hydroalumination that was discovered by Ziegler was promoted by titanium. So, here is a net reaction for this whole process. If you treat aluminum with hydrogen in the presence of triethyl aluminum, which is a catalyst, then you get a growth process, where growths step. You end up making an alumin and this alumin can add on ethylene. So, each of these aluminum hydrogen bonds adds on a molecule of ethylene. It leads to the triethyl aluminum. So, if you have a small amount of triethyl aluminum, it can catalyze this whole reaction. The net reaction of course, is the formation of triethyl alumin.

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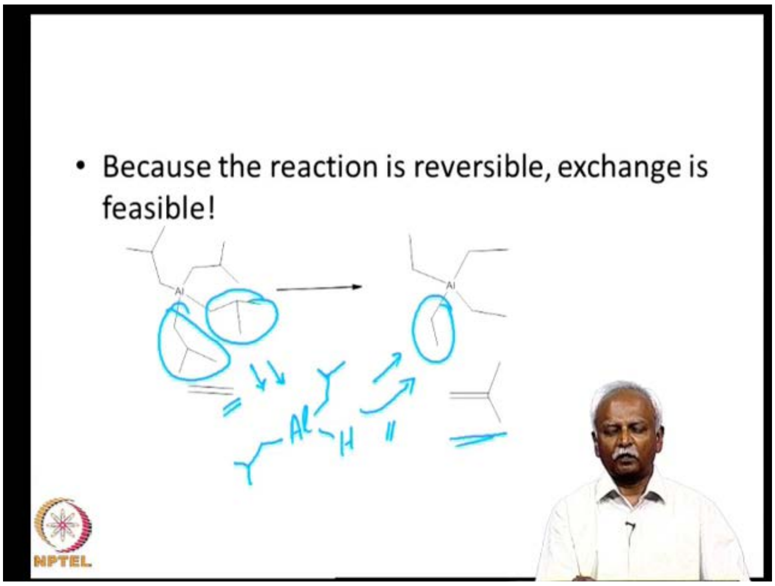

- Because the reaction is reversible, exchange is feasible!

So, let us just take a look at this usefulness of this reaction. If you do the reaction with isobutylene for example, you would end up with a sterically encumbered alumoxin. So, this would be a sterically hindered alumoxin. This has got only 3 groups attached to it. So, we will ignore this. We will ignore this part of the molecule. This is not there that.

So, you can remove 1 arm. Each of these arms on the aluminum with an ethylene molecule and eject this alkyl group as an alkene. So, presumably the reaction goes through aluminum with hydrogen and 2 alkyl groups. So, this can now add on the ethylene and generate this triethyl aluminum. So, if this happens in 3 times, you would end up with triethyl aluminum. So, this is the reaction where you have triethyl.

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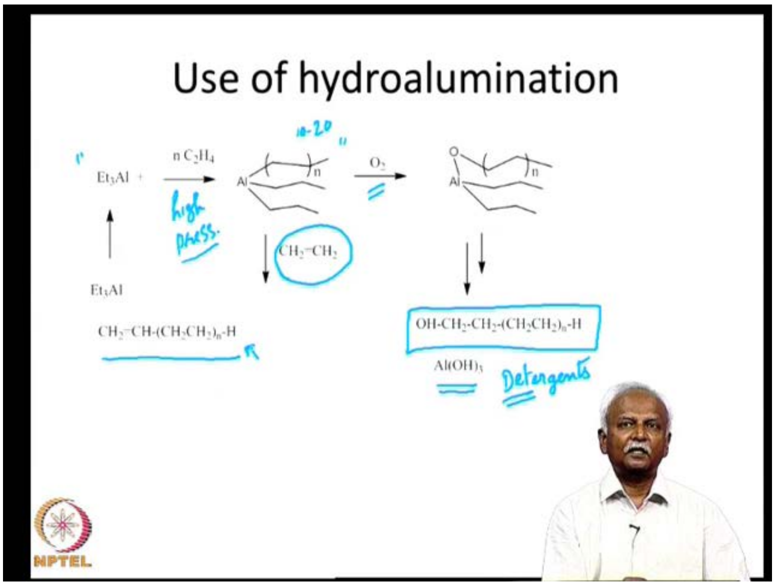

Use of hydroalumination

Aluminum being formed starting with bulky alkyl group on the aluminum. So, the use of hydroalumination is extremely valuable because you can use this growth step to keep adding alumin ethylene groups in order to generate multiple or very long alkyl chains attached to the aluminum. This can be done in a bulk process. So, in a batch process, so triethyl alumin can add on aluminum in multiple steps in order to generate linear species. As I told you, the bulky aluminum atom or the bulky alkyl group on the aluminum atom is unstable.

So, it would exchange with a linear group. So, if it keeps doing it, then a very long polymer not a polymer, but very long oligomeric chain can be attached to the aluminum. As much as 10 to 20 ethylene groups can be attached and after carrying out this reaction with a high pressure of high pressure of ethylene, you would end up with a long chain attached to the aluminum, which can now add on oxygen. If you add oxygen to it, it generates in an alcoxy group attached to the aluminum.

This would be in only one step as shown. Multiple after multiple steps, you would end up with a long chain alcohol where the end that is attached to the aluminum. It is the one that is having the oxygen. So, this would end up with Al OH thrice and the alcohol. These long chain alcohols are extremely useful in the industry for making detergents. So, these are extremely useful molecules. These are extremely useful molecules for generating detergents. So, you can also make simple terminal alkenes with long chains n equals 10 to 20 as I mentioned to you before by treating it with a high pressure of ethylene. So, the whole chain growth is stopped and the bulky alkene is ejected from the coordination site.

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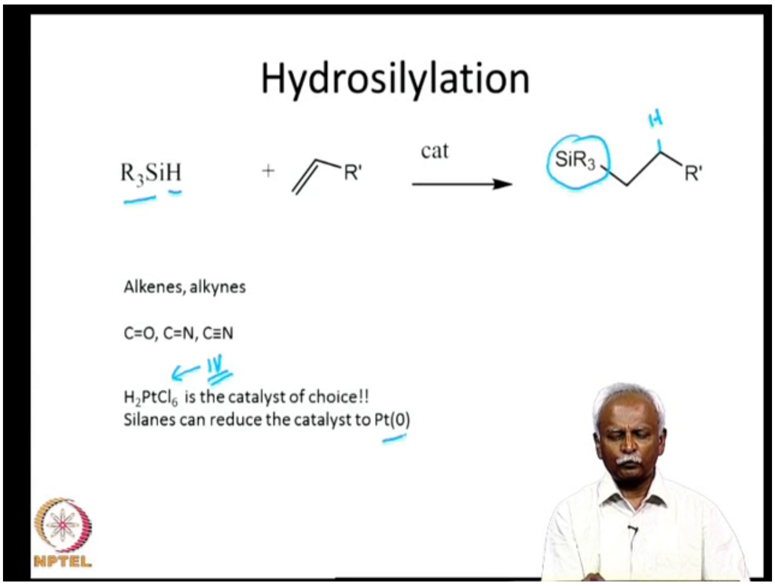

Hydrosilylation

Alkenes, alkynes

C=O, C=N, C≡N

H_2PtCl_6 is the catalyst of choice!!

Silanes can reduce the catalyst to Pt(0)

So, this turns out to be an extremely useful. Hydroalumination turns out to be an extremely useful reaction. If you take hydrosilylation, hydrosilylation is also useful because you can convert the silicon that is attached to the carbon to other groups in a subsequent step. So, alkenes and alkynes add on R3SiH. The interesting aspect of this addition of hydrogen and R3Si group, the hydrogen adds on here. So, you can see that the hydrogen adds on to the sterically more encumbered carbon.

You can do this reaction with alkynes alkenes carbonyls and shift basis in even nitriles. For all these cases, it turns out that platinum is the best catalyst. Now, catalyst of choice is usually in this as shown in this slide. It could be in any oxidation state of platinum because the silane reduces the platinum from whatever oxidation state you start with. In this case, it is shown as a plus 4 oxidation state. It reduces the catalyst to 0 oxidation states, platinum 0.

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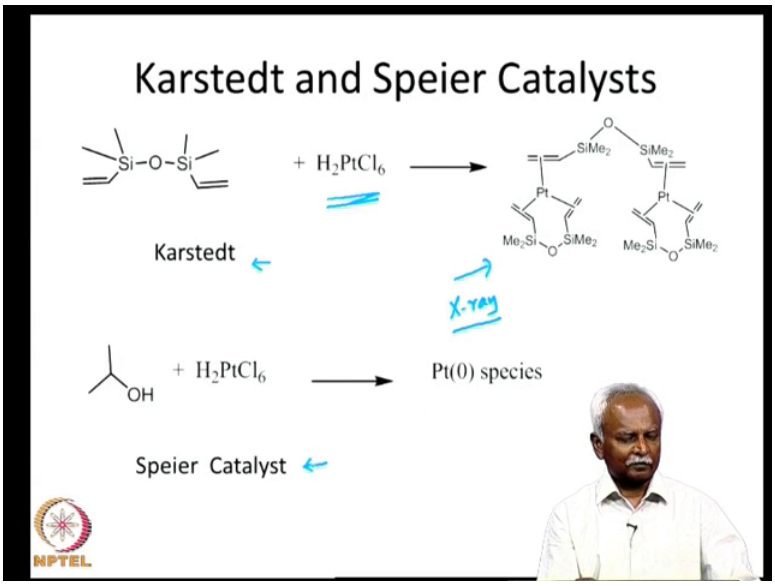

Karstedt and Speier Catalysts

+ H_2PtCl_6

Karstedt

X-ray

+ H_2PtCl_6 → Pt(0) species

Speier Catalyst

Platinum 0 is an active form of the catalyst here. As 2 systems, this compound has been crystallographically characterized by x ray the fraction and the karstedt catalyst system involves the use of a vinyl silane, which stabilizes the platinum 0 resting state of the catalyst. So, H2PtCl6 is reduced by silanes to platinum 0. The platinum is found coordinated to the olefins and resting in the stable state. You can also reduce it isopropanol and that is called the speier catalyst. So, these are 2 catalyst systems, which are popular for hydrosilylation reactions.

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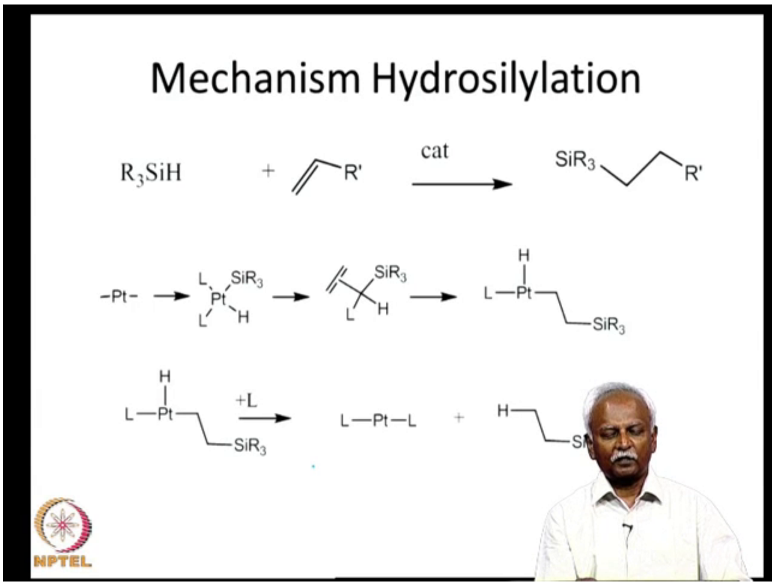

Mechanism Hydrosilylation

The mechanism of hydrosilylation has been invariably discussed in great detail. It turns out that you can add the silicon first or the hydrogen first conceptually. You can either way you can end up with the product, but the reaction mechanism where you have platinum, platinum in the 0 oxidation state undergoes first of all oxidative addition. So, an oxidative addition is essential after the oxidative addition. You do have a step in which there is a migratory insertion. The migratory insertion happens in such a way that the alkyl group now has got silicon attached to the beta carbon of the carbon attached to the platinum.

Now, it can reductively eliminate to give you the product. So, this can now reductively eliminate. This is the reductive elimination step. This is the migratory insertion step that we have. That will give you the final Silane, which can be manipulated either with treatment with oxygen or hydroxylation species so that you can form a variety of interesting molecules.

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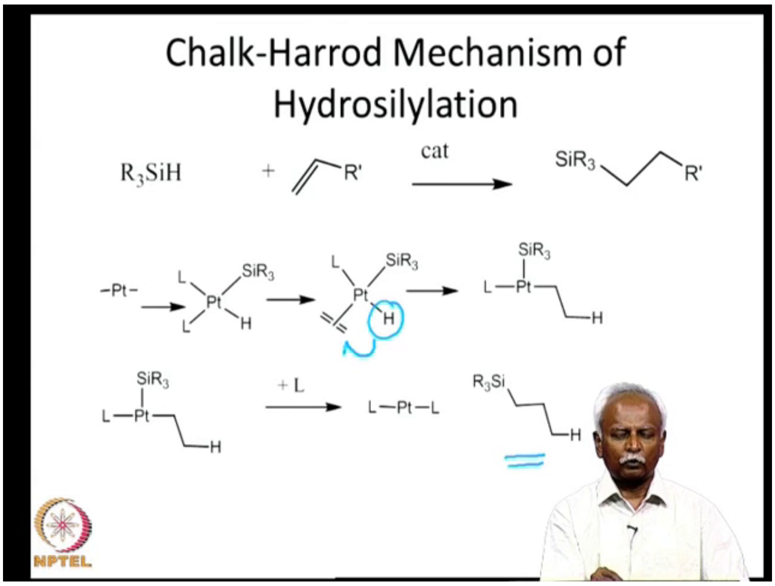

Chalk-Harrod Mechanism of Hydrosilylation

Now, the Chalk Harrod mechanism for hydrosilylation suggests that it is in fact the hydrogen which is added first is the more popular of the mechanisms, which are used in the literature to explain the way in which the stereo chemistry goes. You have the addition of H and Si R 3. Only difference between these 2 mechanisms is that the hydrogen is added on first. The hydrogen migration happens first to the olefin and that leads to an alkyl species, which reductively eliminates the Silane.

So, in conclusion, one might say that as long as there is a significant polarization in the 2 groups that means hydrogen on one side and either it is aluminum as in one. As in some examples that we have seen or fluorine, then direct addition of an olefin to these molecules is possible.

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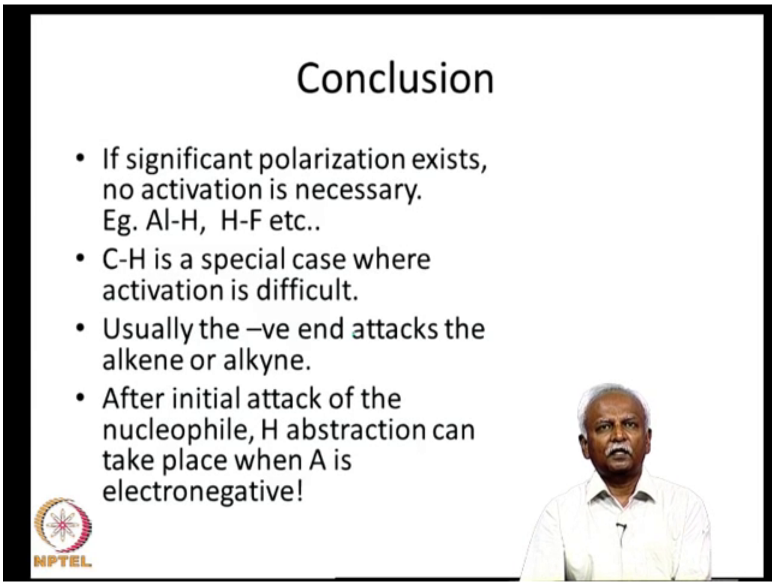

Conclusion

- If significant polarization exists, no activation is necessary. Eg. Al-H, H-F etc..
- C-H is a special case where activation is difficult.
- Usually the –ve end attacks the alkene or alkyne.
- After initial attack of the nucleophile, H abstraction can take place when A is electronegative!

So, there is no activation necessary. There is no catalyst that is necessary for this whole reaction. But, if you have a non polar molecule or less polar molecule, where the polarization between hydrogen and the molecule A is significantly less, then you end up with the need for a catalyst. The catalyst is usually a molecule that can do oxidative addition of this species. Oxidative addition followed by a migratory insertion and a reductive elimination makes up the catalytic cycle.

CH is a special case, where activation is even more difficult. We will discuss this later. Usually, it is the negative end of this species that carries out the attack on the alkene although CN seems to be an exception. When you have HCN, we noticed that there was the cyanide. It is obviously the negative end of this molecule, but still it was hydrogen which carried out the attack on the alkene. So, in general, the nucleophile is a one which attacks the alkene. This could be followed by hydrogen abstraction. So, in the case of wacker, the wacker process, hydrogen abstraction happened.

In other cases, hydrogen at abstraction is not happening. You have just an addition of the 2 molecules, the H and the A to the double bond. Then you have the activation of these molecules. Then we say that we have the activation of molecules to add on to C double bond C or any unsaturated molecule C triple bond C or the C double bond O as well.

So, in future lectures, we will discuss the CH activation, which is even more difficult because it has to be rather specific chemo specific oxidate activation. Chemo specific activation is necessary because the ligands on the organometallic compound are also capable of undergoing a reaction if you do not have chemo specific reactivity.