Hydrogenations Reaction
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Lecturer - 32
Introduction to Organometallic Chemistry

Transition metals have been used for hydrogenation reactions for a longtime. After the renaissance of organometallic chemistry in the 1950's, it became obvious that a single site catalyst or a well characterized organometallic catalyst for hydrogenation could be discovered and used.

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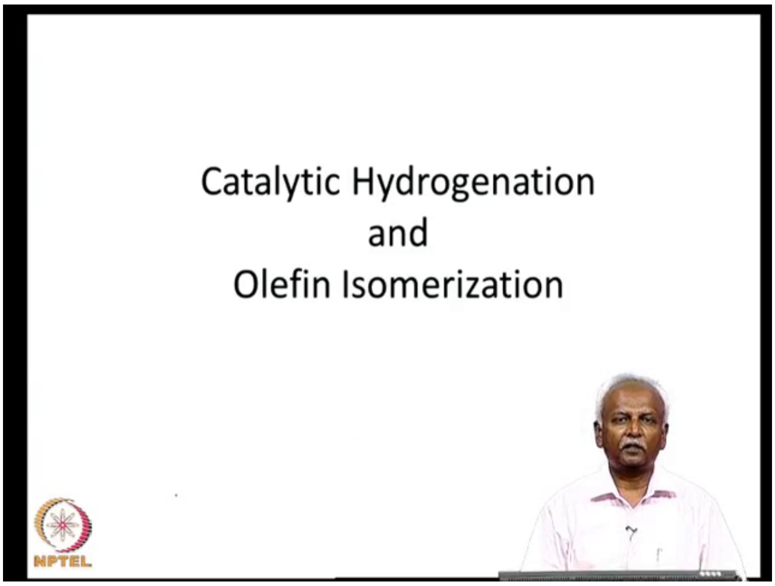

Catalytic Hydrogenation
and
Olefin Isomerization

And this became a reality quite soon after the renaissance due to the discovery of harassing. So, today in this lecture we will discuss the catalytic hydrogenation reaction and a closely related reaction which we may call as catalytic isomerization of alkanes.

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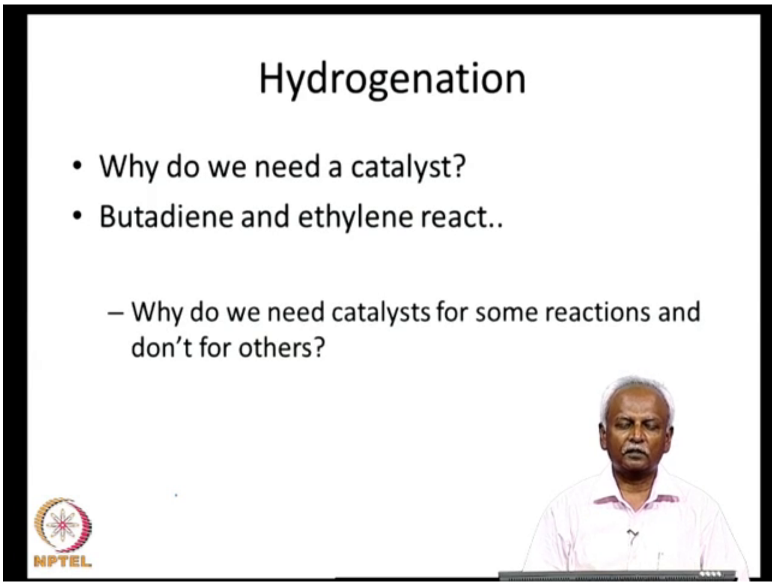

Hydrogenation

- Why do we need a catalyst?
- Butadiene and ethylene react..
  - Why do we need catalysts for some reactions and don't for others?

Now, why do we really need a catalyst for hydrogenation, if you think about the reaction. For example, a two bond formation in the case of butadiene and ethylene reacting together that is the classic reaction, where you have a four plus two cyclo addition reaction you do not seem to be requiring this catalyst. And in fact there are several reactions, which do not require a catalyst and would produce and would proceed under fail in normal conditions. But hydrogenation is one reaction where the reaction will not proceed unless we have a catalyst and usually, this is a transition metal catalysts.

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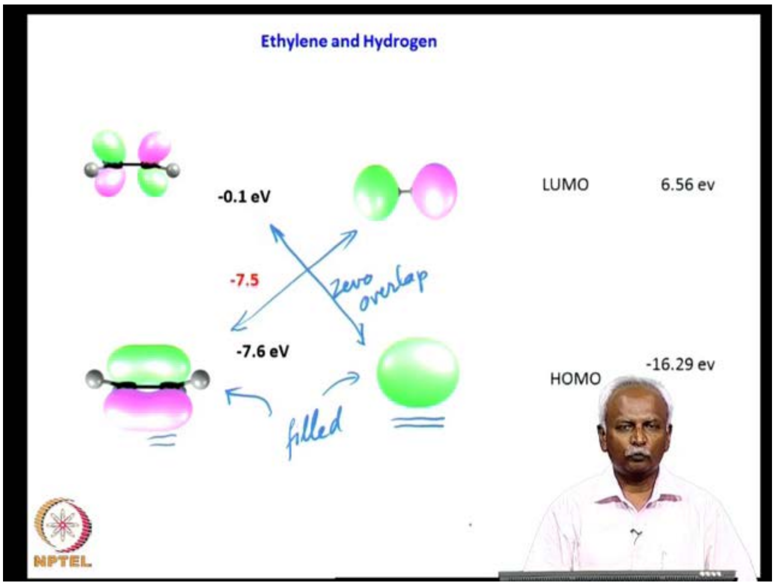

Ethylene and Hydrogen

Now, if you look at the molecular orbitals of hydrogen and ethylene this becomes familiar becomes easy to understand. And here I have shown for you the highest occupied molecular orbital of hydrogen and the highest occupied molecular orbital of ethylene. And you can see that these two can be overlapped rather easily, so that you can have a nonzero overlapped interaction. And in this case both are filled orbitals. This both orbitals are filled.

And as a result the overlap of these orbitals would actually lead to a repulsive situation. What you need is to have an overlap between the filled orbitals of one reactant with unfilled or empty orbitals of the second reactant and vice versa. And this is in fact not possible because if you look at these two orbitals that is the LUMO of ethylene, and the HOMO of hydrogen you can see that there will be zero overlap and the same thing holds good for the filled orbital of ethylene and the empty orbital of hydrogen. So, you can see that this reaction cannot proceed in a simple fashion by a cyclo addition type reaction unless you have a catalyst.

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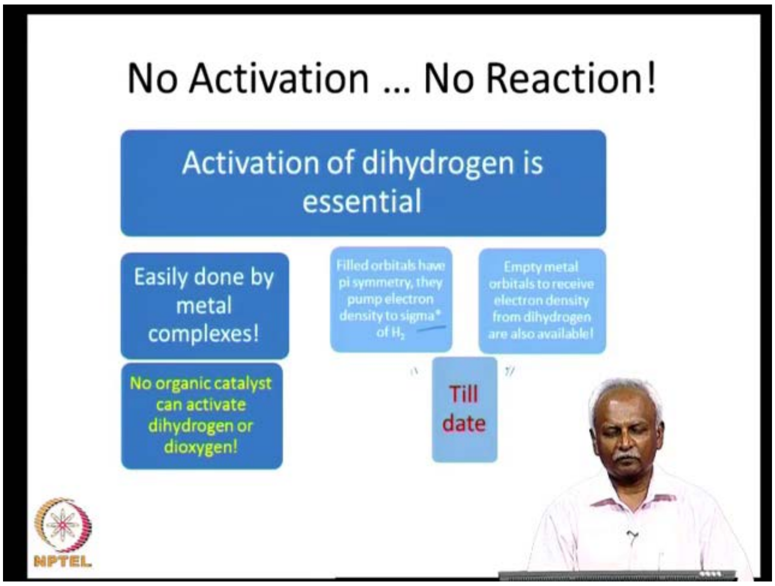

No Activation … No Reaction!

Activation of dihydrogen is essential

Easily done by metal complexes!

No organic catalyst can activate dihydrogen or dioxygen!

Filled orbitals have pi symmetry, they pump electron density to sigma* of H_2

Empty metal orbitals to receive electron density from dihydrogen are also available!

Till date

And so what is a catalyst do. Dihydrogen has to be activated and that is what we are shown just now. And the catalyst basically has filled orbitals which have five symmetry they have electron density in the orbitals which are capable of pumping in electron density into the sigma star orbitals of hydrogen. So, the sigma star orbitals are the empty orbitals of hydrogen and they are populated and that in turn leads to weakening of the hydrogen bond and the metal hydrogen bond is formed leading to activation of hydrogen.

There are very few catalysts which are non-transition metal, which are capable of activating hydrogen. For that matter even dioxygen is more readily activated by a transition metal than by a simple organic compound. That I should say is till date and this can obviously change if one discovers a more suitable catalyst which is completely organic.

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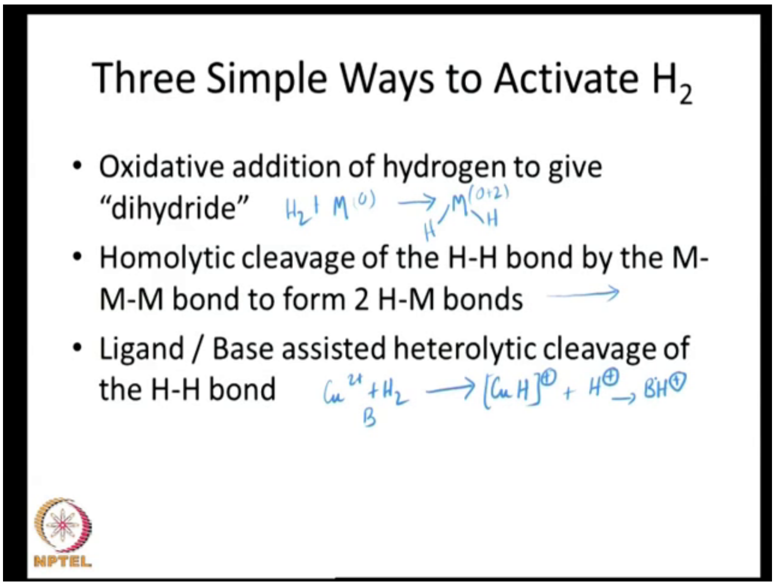

Three Simple Ways to Activate H_2

- Oxidative addition of hydrogen to give "dihydride" $H_2 + M^{(0)} \rightarrow H{-}M^{(0+2)}{-}H$
- Homolytic cleavage of the H-H bond by the M-M-M bond to form 2 H-M bonds $\longrightarrow$
- Ligand / Base assisted heterolytic cleavage of the H-H bond $Cu^{2+} \underset{B}{+} H_2 \longrightarrow [CuH]^{\oplus} + H^{\oplus} \rightarrow BH^{\oplus}$

Let us backup a little bit and talk about the ways to activate hydrogen. There are three ways in which we can activate hydrogen using a transition metal complex. The first one of course, is the oxidative addition of hydrogen to give a dihydride. In this case the metal which is in the zero or in the m oxidation state goes to a plus two oxidation state and then it has got to bonds to hydrogen. So, you just have to change the oxidation state of the metal to plus by plus 2 and make it a dihydride. It is also possible to do a hemolytic cleavage of the H 2 bond by using a M-M bond to carry out this reaction.

Here, the M-M bond is a weak bond and the H-H bond is a strong bond, but because the MH bonds will compensate for the formation for the reaction, for the loss in the bond strength between the two hydrogen is possible to push this reaction from the right left to the right. It is possible to take compounds which are metal metal bonded and make the metal hydrogen bonded systems. And the third class of activation belongs to those where there is a heterolytic cleavage of the H-H bond the dihydrogen molecule.

This is usually carried out by an electrophilic metal system which reacts with H 2 and generates MH plus and the hydrogen is reactant is the other dihydrogen is then reacted with base to produce BH plus. A classic example of course, is copper to plus and if it reacts with H 2, you can see that it can generate CuH plus and a H plus ion which can be mocked up with the base. So, if you have a base in this reaction medium this would then generate BH plus. So, you can see that there are a variety of ways by which you can activate hydrogen.

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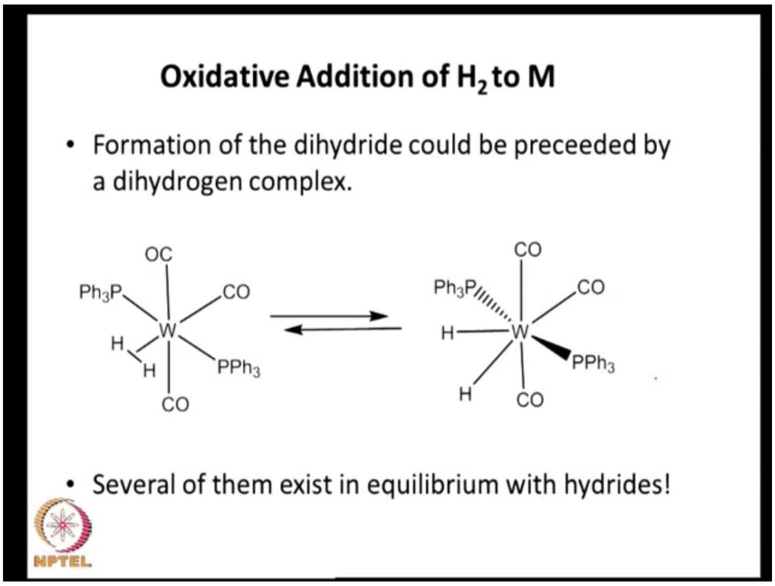

Oxidative Addition of H_2 to M

- Formation of the dihydride could be preceeded by a dihydrogen complex.

- Several of them exist in equilibrium with hydrides!

Now, the formal oxidative addition of hydrogen as we mentioned in the class on oxidative addition is in fact a change in the oxidation state, but not in the charge on the metal itself. We should keep this in mind throughout this lecture also because we will be frequently shifting the oxidation state of the metal, but that does not necessarily imply that the metal bares the increase in the charge on the that does not mean that the metal increases the charge that is present on the complex. Now, several of these complexes are in fact any equilibrium with hydrogen complexes. So, here is one example where there is an apparent activation of hydrogen and you have a tuncson complex which is an equilibrium between a dihydride and an H 2 complex.

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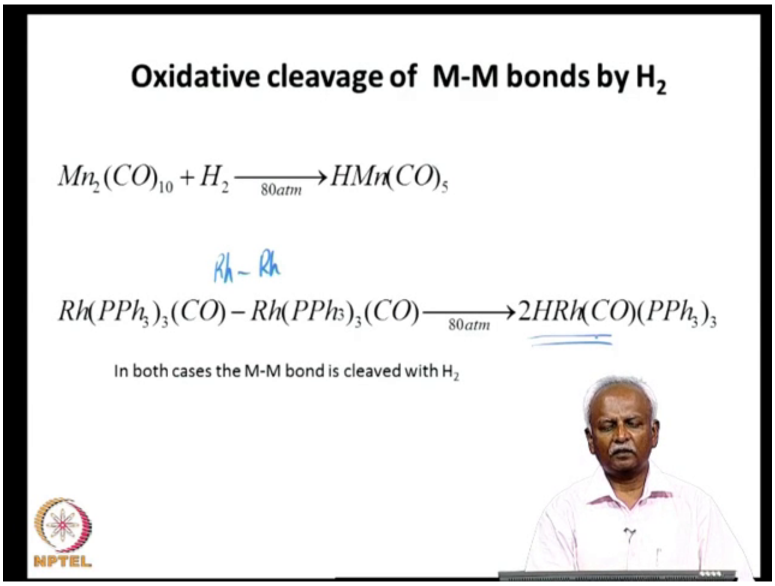

Oxidative cleavage of M-M bonds by H_2

$$Mn_2(CO)_{10} + H_2 \xrightarrow[80atm]{} HMn(CO)_5$$

Rh – Rh

$$Rh(PPh_3)_3(CO) - Rh(PPh_3)_3(CO) \xrightarrow[80atm]{} 2\underline{HRh(CO)}(PPh_3)_3$$

In both cases the M-M bond is cleaved with H_2

So, the second class of molecules which undergo oxidative cleavage of the M-M bond. And one of them is shown here where you have a manganese manganese bond cleaved with hydrogen, but these reactions require slightly higher pressure of hydrogen. In this case about 80 atmospheres of hydrogen is required in order to carry out this reaction. So, HMnZ CO 5 is monohydratic metal complex which can carry out reactions which the simple system cannot carry out.

So, that is another molecule rhodium rhodium bonded system awaits it and it does not appear there is rhodium rhodium bond, but it is two rhodium atoms that are bonded together. And this rhodium rhodium bond is cleaved and rhodium hydrogen bond is formed. So, these molecules can carry out reactions which dihydrogen itself will not carry out.

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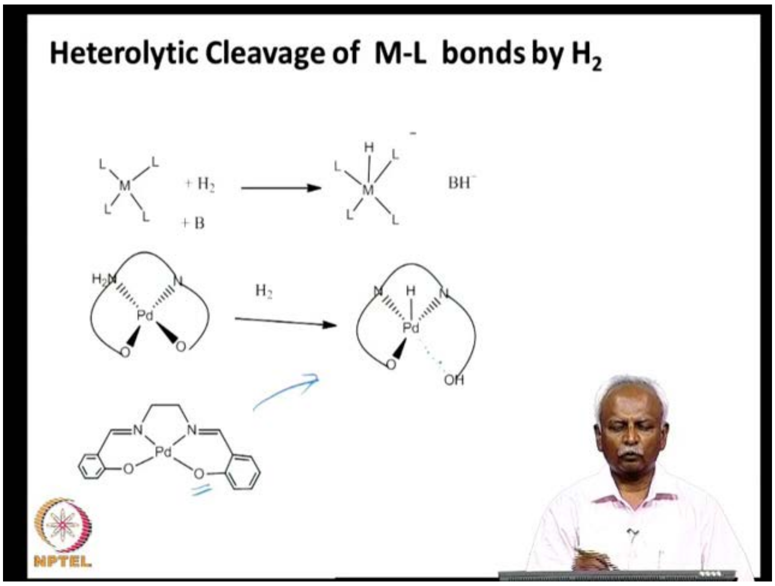

Heterolytic Cleavage of M-L bonds by H_2

Third class of activation is a heterolytic cleavage of the M-L bond. And is a heterolytic cleavage is actually carried out with the help of a ligand or a base. Sometimes it is the ligand and sometimes base and which is present in the medium. And it is shown here in this example for a palladium complex which is a silent derivative. And this can readily add on hydrogen one hydrogen is attached to the metal and the other hydrogen, which is a proton is attached to the finalate of this system. So, much so that you have a four coordinate molecule in the end, but one of these original metal oxygen bonds has been broken and the OH bond has been formed instead, and there could be only weak interaction between the palladium and the oxygen.

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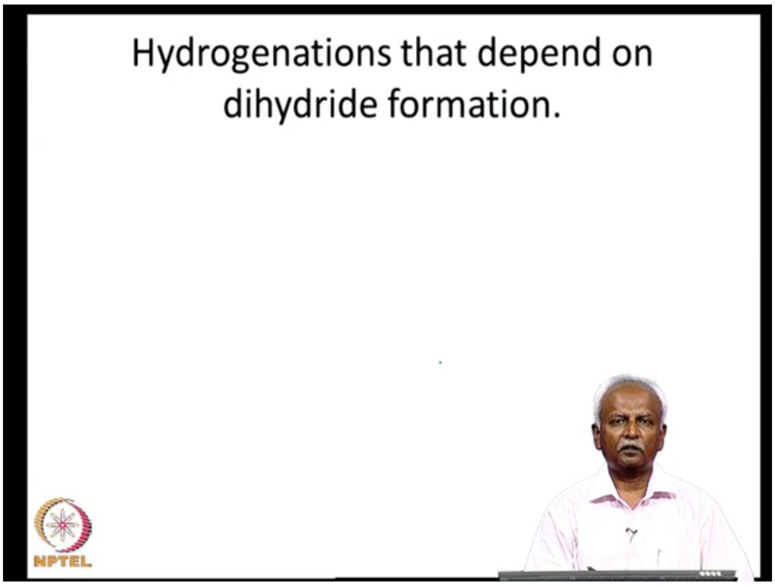

Hydrogenations that depend on dihydride formation.

So, let us talk about reaction that depend on the formation of a dihydride. These all these are systems where the oxidation state of the metal changes by plus 2 units. So, you have an 0 going to plus 2. And many cases these dihydrides carryout hydrogenation reactions very readily.

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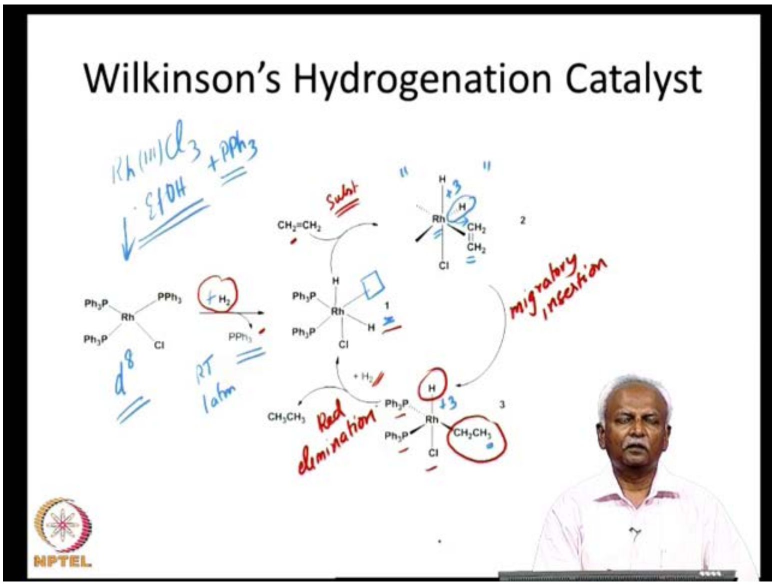

Wilkinson’s Hydrogenation Catalyst

The classic example of course, belongs to the Wilkinson’s catalyst, which most of you might be familiar with because this is the most popular example. Probably the first example for hydrogenation catalyst that was discovered, but more importantly this catalyst can be used to carry out asymmetric hydrogenation. And that is the reason why it is extremely popular. Now, the basic Wilkinson catalyst is also readily prepared in the laboratory starting with rhodium 3 chloride and ethanol.

Just refluxing this two compounds together generates the rhodium one complex which is pictured here. And so in the presence of the pph 3 you just have to reflux the two and the rhodium three becomes rhodium 1 because of a reduction reaction which we will show in the subsequent slides. And the pph 3 stabilizes the rhodium 1 species, which is formed and you have his d 8 system stabilized in square planner geometry. Now, this molecule readily adds on hydrogen.

So, even if you mix if you take a solution of those Wilkinson’s catalyst and expose it to dihydrogen at room temperature and atmospheric pressure 1 atmosphere pressure of hydrogen you end up with a color change in the solution. And you have the formation of a dihydride. Now, this dihydride can lose one of its ligands the pph three and have the vacant coordination site on the rhodium atom. So, multiple steps are compressed in order to make this fit in a single slide what you should realize other two steps which involve loss of pph 3 and addition of hydrogen leading to the oxidative addition of dihydrogen.

As we saw in the lecture on oxidative addition molecules like dihydrogen add as sis fashion. So, you have sis addition of dihydrogen, which is pictured as intermediate one. This intermediate one has a vacant coordination site, which can take up a molecule of the ethylene. Ethylene when it is coordinated to rhodium, this rhodium atom which is now in a plus three oxidation state formerly. And the insertion of a hydrogen or a hydride species from the rhodium onto the ethylene if you have the reverse of a migratory insertion reaction.

So, you remember what happens when you have a insertion reaction, you have the nucleophilic component going from the metal onto the organic component and then new metal carbon bond is formed. And so you have the formation of a metal rhodium carbon bond between the two species that are just underlined and at what you have here. And the need hydrogen as adder onto the terminal carbon so your natal group attached to the rhodium now and this species which is also rhodium plus three you will center.

So, you are not change the oxidation state you only done a migratory insertion reaction which is converted the neutral ethylene molecule into an alkyl molecule. This molecule is now well set up to do a reductive elimination. So, elimination so elimination of excess indicate that with a different color now. If you eliminate these two groups from the rhodium plus three center you will end up with a rhodium one center which is got two pps three units. And one chloride with that underlined fellow.

So, this would lead to rhodium one center which can readily add on hydrogen dihydrogen to give you a game that catalytically important intermediate which have labeled as one. So, the first step is a simple substitution step where the pps three has been replaced by ethylene. So, that is a substitution reaction. The second step is in fact the oxidative solid the first back the first step is the oxidative addition of hydrogen to this catalytically active intermediate which gives you intermediate want.

And then there is a substitution reaction were ethylene goes on to a vacant coordination site and this system undergoes a migratory insertion reaction, this is a migratory insertion reaction and following that there is a reductive elimination reaction. So, you do have an oxidative addition and a reductive elimination. Usually the oxidative addition is the first step and the reductive elimination is the last step.

In between you would have a substitution and a migratory insertion or just a substitution and a subsequent productive elimination. So, this is the general pathway for most catalytic reactions. And we will see that in the subsequent slides also. However, the addition of the ethylene could be preceded could precede the addition of hydrogen.

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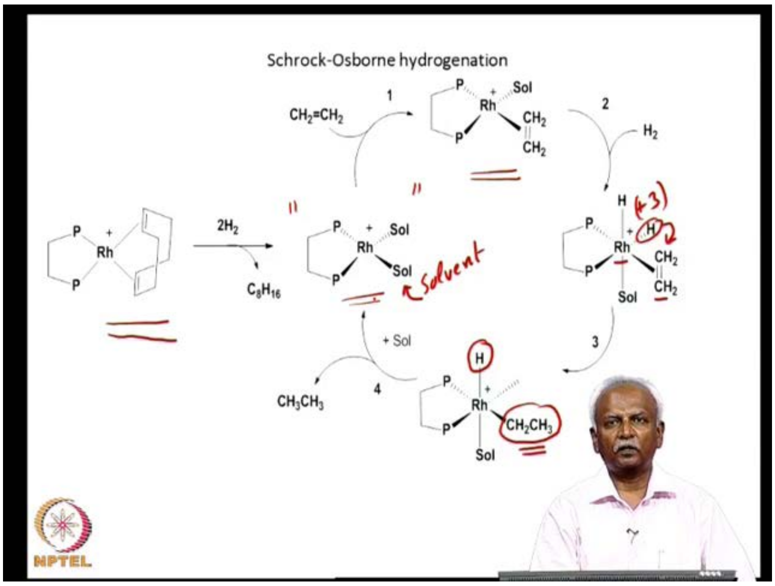

Schrock-Osborne hydrogenation

So, here is another catalytic system which is also based on the rhodium one catalyst, but in this particular instance the olefin coordinates to the metal first before the oxidative addition of hydrogen. This complex is formed as the one that is available in the laboratory or payment in chemical companies which you can purchase. And the advantage of this complex is that if you add hydrogen to it. It is capable of being hydrogen the ligand and is being hydrogenated in the first step in order to generate a very active form of the catalyst.

And Sol really refers to the solvent. So, this is your solvent here and the solvent is something which is easily substituted by the ethylene. And order to give you the olefin complex in the first step. This olefin complex is then reacted with hydrogen and it is in the second step that the oxidative addition happens. In the Wilkinson's catalyst, the oxidative act addition happen in the first step and in the subsequent step you hand the substitution reaction.

So, these two have been interchanged and the shock was born hydrogenation catalysis. So, if you now add on the hydrogen you end up with a rhodium three intermediate this is also rhodium three intermediate this is also the next charge of plus want which has been indicated on the rhodium. So, this plus three oxidation state is because of the two hydrogen and the plus one charge on the complex itself. Now, this complex can also undergo a might migratory insertion. So, that you can form a new carbon rhodium bond and that is what you have here.

And the same ethylene group can now be eliminated as ethylene came by elimination of this hydrogen and this ethylene group. So, you will regenerate the catalytically active species which is got solvent in its coordination sphere. So, that you can do subsequent substitution reactions fairly readily. Now, hydrogenation is which are carried out there especially with rhodium one are typified

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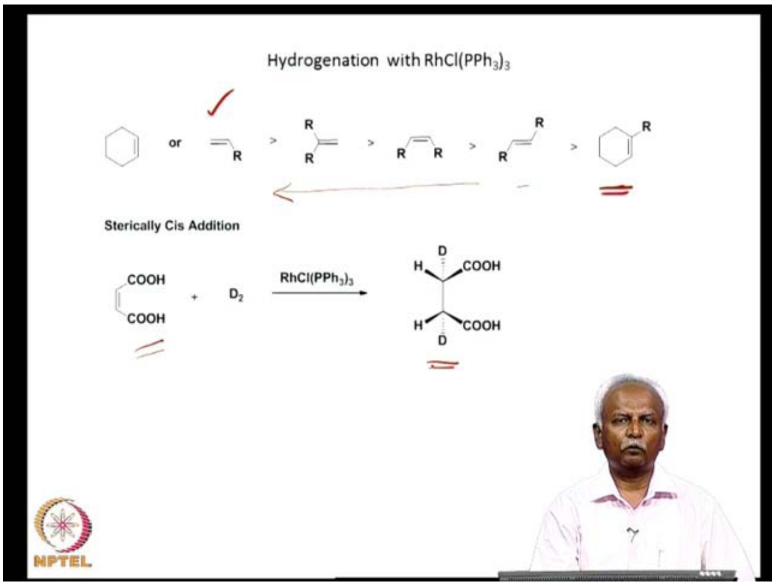

Hydrogenation with $RhCl(PPh_3)_3$

Sterically Cis Addition

by these characteristics. First of all these reactions work very well if you have if you have a unsubstituted or as a olefin which is very small substituent. When you have large substitutions on the olefin then the reaction becomes very sluggish.

And the rate at which hydrogenation happens in various complexes is shown here. And the rate increases in this direction. If you have only mono substituted olefins and the reaction is extremely fast if you have one die substituted olefins, then the reaction is faster than when you have one two disubstituted olefins. And if you have trans or one two 3 substituted olefins reaction becomes extremely sluggish. Now, the rate differences are significant enough that you can in fact hydrogenated very simply a mono substituted olefin in the presence of a tri-substituted olefin which is at the bottom of the series.

This is very advantageous when you want to do hydrogenation in a selective fashion. So, that is why rhodium catalyst hydrogenation is are extremely useful in the laboratory. Another important factor that in mind one has to bear in mind is the fact that cis hydrogenation takes place. So, here is a case where you hydrogenated using deuterium and cishydrogenation gives you the product exclusively. And this is extremely useful if you want to carry out reactions in hysteria specific fashion.

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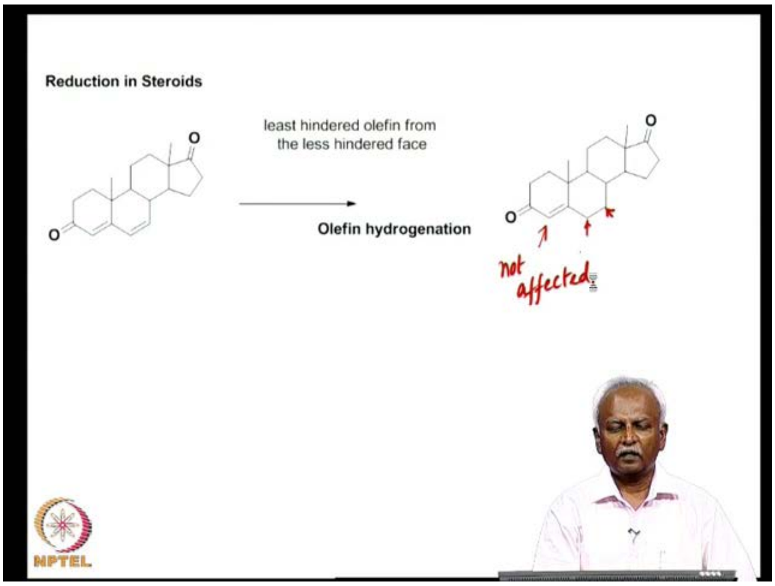

Reduction in Steroids

least hindered olefin from
the less hindered face

Olefin hydrogenation

not affected

So, let us take a real-life example here is a steroid which has to be hydrogenated. And there is more than one reducible group and if you used to rhodium catalyst that we are just discussed in the previous slide you end up hydrogenated only these two places. In other words the double bond which is here is not affected. So, the double bond which is here is not affected in the during the reaction. So, this is a very useful catalyst because of the selectivity.

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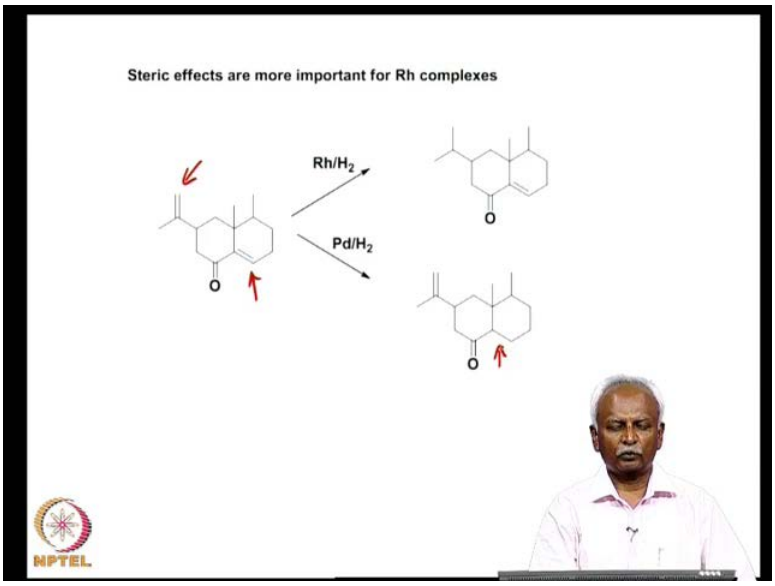

Steric effects are more important for Rh complexes

Rh/H_2

Pd/H_2

And it can be used for carrying out the many complicated synthesis. Here is another example where you have a unhindered double bond and a tri-substituted double bond. And the tri-substituted double bond is left unaffected during this whole reaction. We use palladium and dihydrogen for carrying out the same reaction you end up selectively hydrogenating the double bond which was in this position. And that is because the conjugated double bond is selectively hydrogenated by the palladium whereas a rhodium because of steric reasons it is hydrogenated only in the terminal position where there is less hindrance.

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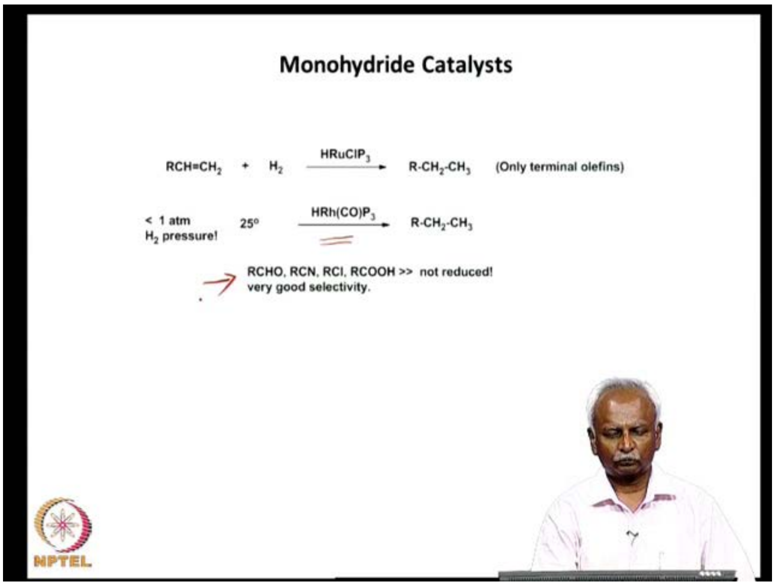

Monohydride Catalysts

$RCH=CH_2 + H_2 \xrightarrow{HRuClP_3} R\text{-}CH_2\text{-}CH_3$ (Only terminal olefins)

< 1 atm
H_2 pressure!

25° $\xrightarrow{HRh(CO)P_3}$ $R\text{-}CH_2\text{-}CH_3$

RCHO, RCN, RCl, RCOOH >> not reduced!
very good selectivity.

Now, let us move on to hydrogenation switch catalyzed by monohydrate catalysts. Now, though monohydrate catalysts are typified by a few examples where the H metal though the hydrogen metal bond is existing in the reaction before the olefin is added. Now, I have shown for you two examples one is a rhodium example and another is a ruthenium example. The rhodium example has in fact a very slight difference compared to the example that we studied earlier.

The only difference being the third rhodium hydrogen bond is already there and instead of the chlorine that was present on the Wilkinson’s catalyst. Now, these complexes are extremely active and the room temperature and pressure you can carry out hydrogenations of a terminal olefins. And the advantage is also highlighted here. Many of the reducible groups, which are present on the molecule will be left unaffected at the end of this reaction.

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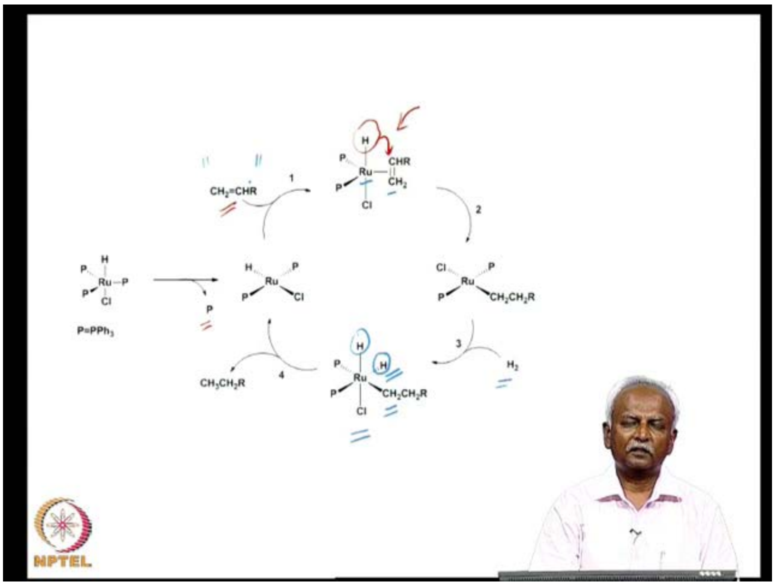

So, here is a catalytic cycle. If you take the ruthenium complex which is the monohydrate then you can carry out a substitution reaction and the loss of a phosphorus ligand and addition often olefin leads to this phy coordinated intermediate. This is the phy coordinate intermediate here and is capable of adding doing a migratory insertion of the hydrogen onto the olefin, migratory insertion of the hydrogen onto the olefin. So, that is this group which is added onto this olefin and a metal carbon bond is formed so the metal carbon bond is formed between these two center’s leading to this alkyne monitoring.

And subsequently you now have an alkyne complex which can undergo oxidative league. And undergo reaction with hydrogen which leads to this molecule which is got a dihydrogen attached to ruthenium. And you can relatively eliminate these two species the hydrogen and the alkyne group in order to regenerate the catalytically active intermediate. So, the difference in the catalytic cycle is minimal the main advantage of the main difference is the fact that you need to coordinate the olefin in the first step even before you do the oxidative addition. And this leads to a strong steric influence on the whole reaction. Unsubstituted olefins are reacted or react much better and substituted olefins.

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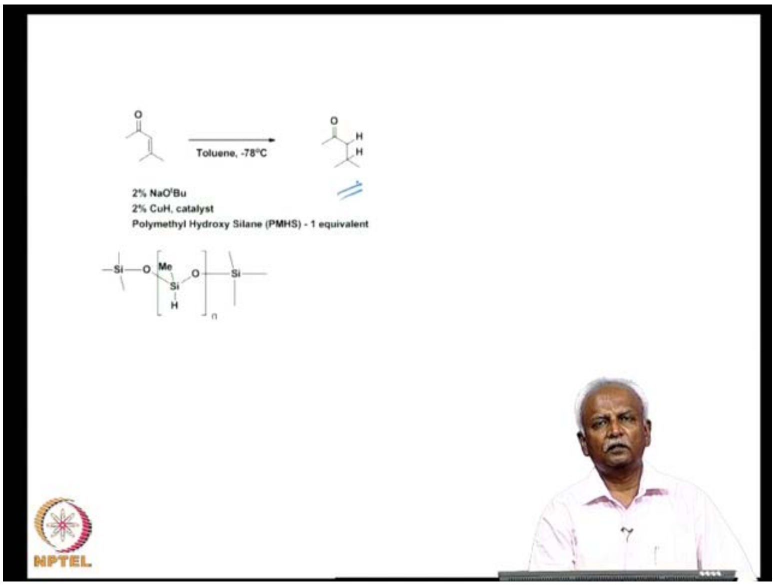

Toluene, -78°C

2% NaO^{t}Bu

2% CuH, catalyst

Polymethyl Hydroxy Silane (PMHS) - 1 equivalent

Now, the catalytic cycle that we have gone through just now is a common for many systems will just illustrate or give two more examples of how monohydrate might act as catalyst. Here I have shown you a copper hydride which specifically hydrogenated is conjugated in own and converts it into a simple ketone. So, the way in which this hydrogenation is carried out is by using poly hydroxyl saline as the reducing agent because it is capable of generating copper hydride. And a copper hydride adds on to this he known in into one loaf in the beta position, so that you generate this molecule exclusively.

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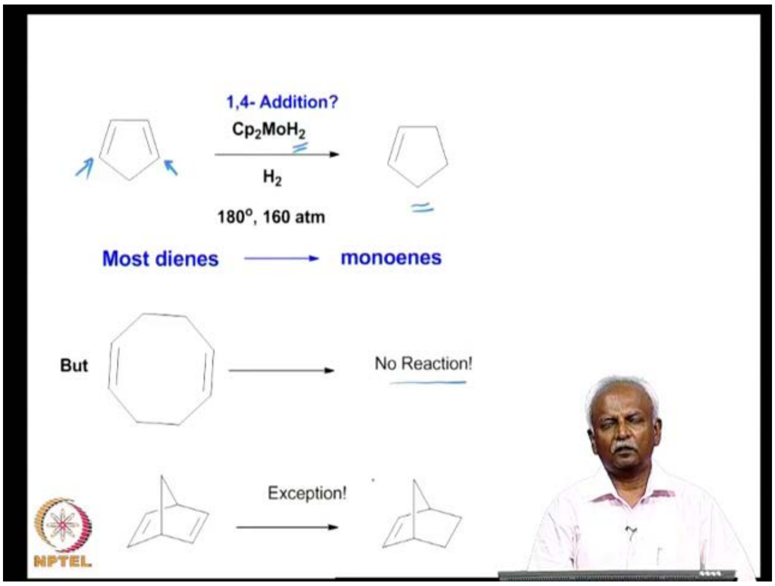

1,4- Addition?

Cp_2MoH_2

H_2

180°, 160 atm

Most dienes → monoenes

But → No Reaction!

Exception!

One more example which is a different, but fairly unique and that is the 1, 4 addition of a dihydride. This time it is a dihydride which is added on to the dine. And this the hydrogenation is carried out at a higher pressure of hydrogen than what we had to do in the previous two instances and hear the dehydrogenation of a dine generates a monoeneses exclusively. At the end of the reaction the other alkene is isolated. And the addition the two hydrogen that have been added have been added in 1, 4 fashion.

So, it is these two positions that actually receive the hydrogen from the dihydride. So, the dihydride addition that we are just seeing will work only if the dienes are conjugated and they will not work with isolated double bonds as an shown. Here there is no reaction so when you want to carry out reactions with the headlights them were dienes. Then this dihydrogen complex is extremely useful. That there appears to be an exception and that exception is now one diene which is converted into no bone mean as a result of this catalyst.

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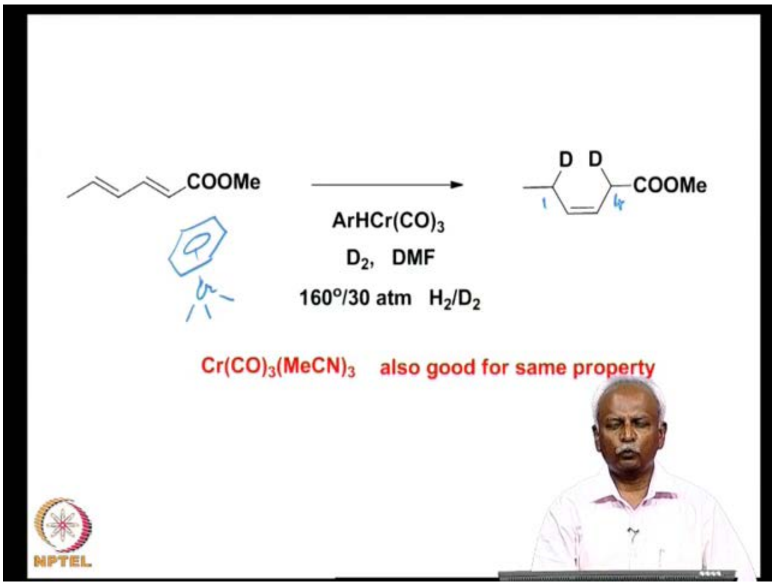

$ArHCr(CO)_3$

D_2, DMF

160°/30 atm H_2/D_2

$Cr(CO)_3(MeCN)_3$ also good for same property

There are a few more catalysts which can carry out this one four addition. And here and shown for you by aromatic the piano stool complex, which we have seen earlier which has the structure with a benzene ring coordinated to the chromium and the chromium attached to three carbon monoxide molecules. So, these molecule are capable of adding hydrogen dihydrogen in the 1, 4 position exclusively. So, these are very interesting reactions and are valuable for making specifically in this case due traded molecules.

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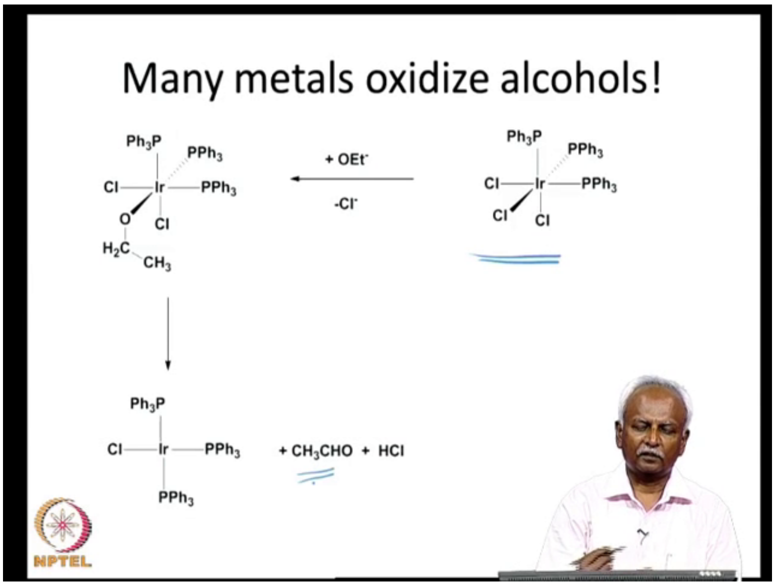

Many metals oxidize alcohols!

So, in the beginning of this lecture we had mentioned that the rhodium three species can be selectively converted to rhodium one species by an alcohol. Now, before we talk about at the reaction called a transfer hydrogenation I want to tell you how the alcohols our capable of reducing battle systems or conversely how the metals oxidize the alcohol. This is an interesting reaction because it has a parallel to what we have just learnt about hydrogenation reactions. This is a simple dehydrogenation of alcohols.

Now, if you have an alcohol you can generate alcohol ate anemone is in this case it oxide. And it oxide is substituting this iridium trichloride molecule in such a way that you have an alchoxide coordinated to the iridium 3. And this it is this alcove alchoxide coordinated species which oxidizes or which reduces the metal and get converted to acetaldehyde in this instance.

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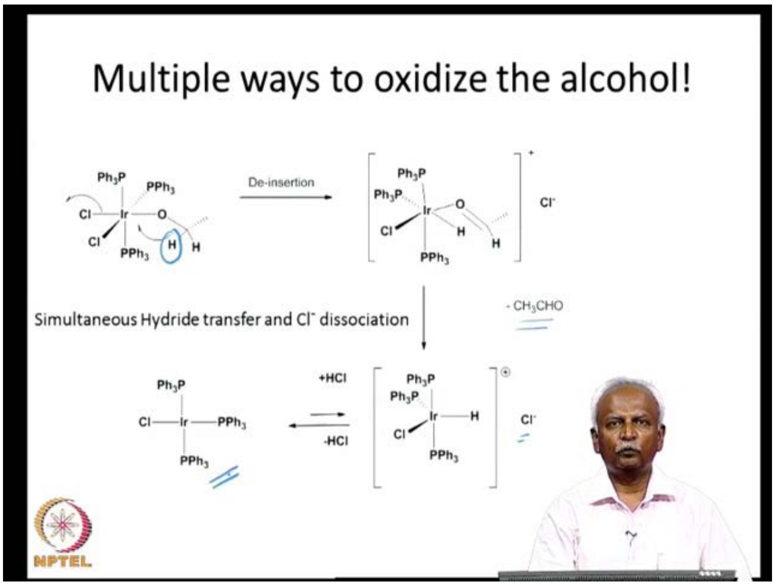

Multiple ways to oxidize the alcohol!

So, let us see how these alchoxides are capable of carrying out this reaction. Suppose, you have an iridium 3 center and this iridium 3 centers are shown here you can carry out the reaction in such a way that you have the insertion, the reverse of the migratory insertion reaction where the hydrogen migrates back to the iridium. And a key tone is for foreign aldehyde is formed. In this instance remember you took an alkyne and added a hydrogen in a migratory insertion step.

This is exactly the reverse of that reaction where a hydrogen is migrating back to the metal center and the alkyne or the equivalent of that. In this case the aldehyde is formed. Now, if you carry out this reaction in this fashion you just you can see that the reaction is capable of forming the aldehyde in the coordination sphere of the metal. And you now have the elimination of aldehyde from the coordination sphere. In order to generate this iridium iridium center, which can lose h plus and Cl minus which was outside this elimination of HCL leads to the iridium one complex. This is the exact analogue of the Wilkinson’s catalysts so there are other ways in which we can imagine this reaction to take place.

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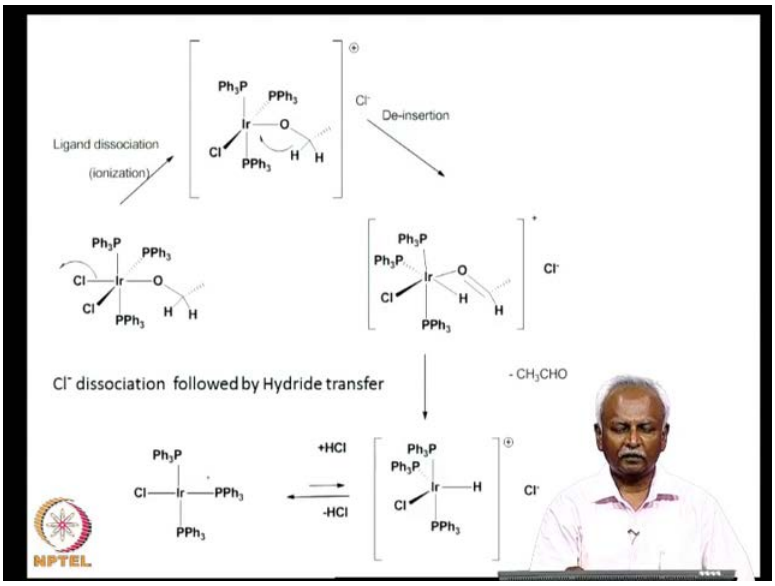

Ligand dissociation (ionization)

De-insertion

Cl$^-$ dissociation followed by Hydride transfer

- CH_3CHO

+HCl

-HCl

And these are difficult to distinguish because these are difficult to distinguish because the net result of this whole reaction is the same. So, in this case be talked about the elimination of a chloride and that the insertion reaction instead

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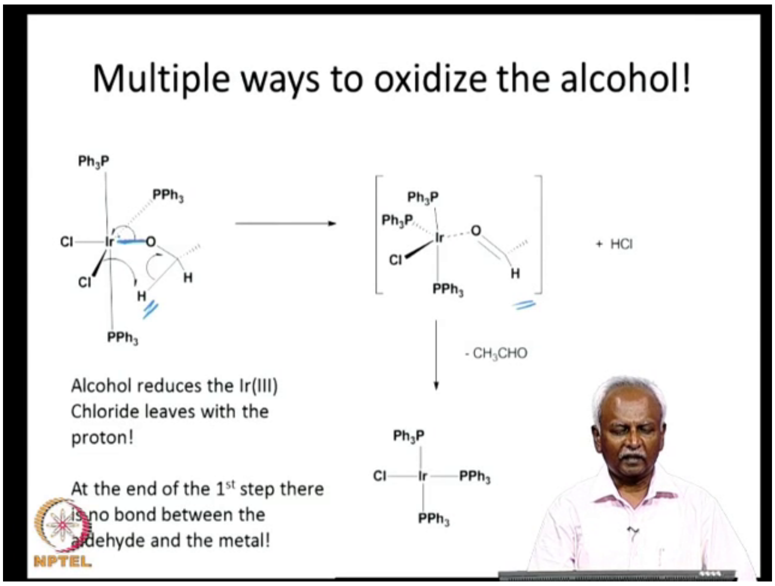
Multiple ways to oxidize the alcohol!

Alcohol reduces the Ir(III)
Chloride leaves with the proton!

At the end of the 1st step there is no bond between the aldehyde and the metal!

we can also think of a reaction where the chloride leaves with the proton on the alpha position of alcohol. So, you have elimination of hcl direct elimination of hcl and formation of this aldehyde coordinated to the iridium one. So, what we are carrying out is the reduction of the iridium one center using the pair of electrons which was used to form the iridium alchoxide bond so this pair of electrons is transferred to iridium so that it becomes iridium one so the alcohol is a real reducing agent

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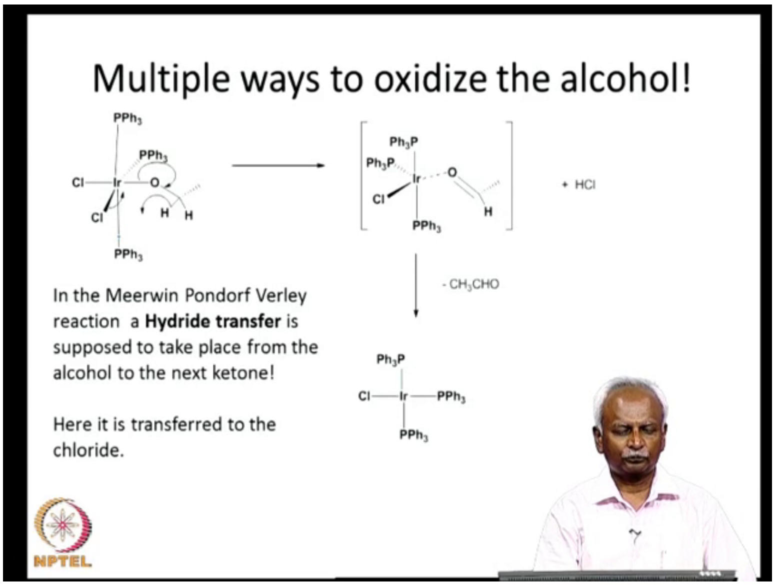

Multiple ways to oxidize the alcohol!

In the Meerwin Pondorf Verley reaction a **Hydride transfer** is supposed to take place from the alcohol to the next ketone!

Here it is transferred to the chloride.

one can in fact write the movement of electrons exactly the opposite direction.

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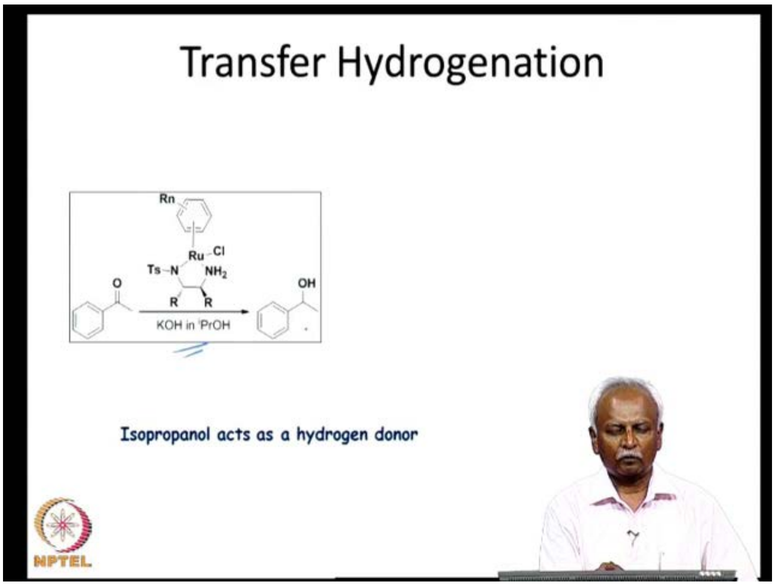

Transfer Hydrogenation

Isopropanol acts as a hydrogen donor

These reactions give us the basis for the transfer hydrogenation reaction. The transfer hydrogenation reaction is basically a reaction in which an alcohol is used to reduce a key tone or an aldehyde to alcohol. And in general isopropanol access a good hydrogen donor, but the other molecules. Also which are capable of carrying out this hydrogenation reaction. So, if you see in this particular projection, here you find that isopropanol in conjunction with potassium hydroxide as reduced isopropanol to this alcohol the secondary alcohol pictured here.

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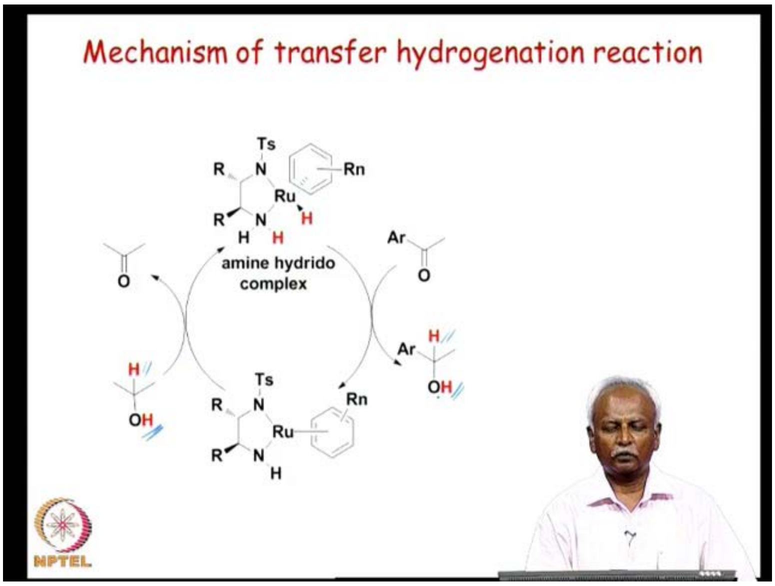

Mechanism of transfer hydrogenation reaction

Now, you can try this reaction in a site in a catalytic cycle you see readily that all the reaction simply involves the transfer of two hydrogen, which is which are present in isopropanol to start with and the transferring them to a aromatic aldehyde or a key tone. And the metal is basically used as a carrier for those to a hydrogen atoms.

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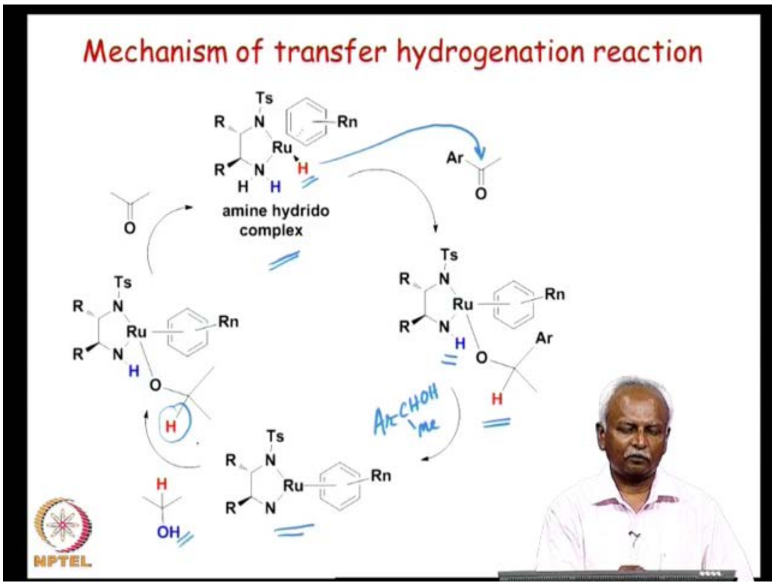

Mechanism of transfer hydrogenation reaction

Now, let us take a look at the mechanism of the actual transfer of this two hydrogen. If you have a ruthenium hydride which is formed as a result of the reaction that we just discussed with the iridium you have a ruthenium hydride here. And in the adjacent coordinated ligand you have a NH compound. Then you can think of a direct transfer of the hydrogen which is present on ruthenium to the aromatic CO unit. So, this hydride can be transferred here and in such a way that you end up with an alchoxide.

And you will see that this is the exact reverse of the dehydrogenation that we talked about in the previous set of slides. So, the ruthenium metal hydride reduces the aldehyde here the key tone and generates an alchoxide. Subsequently, the NH group is capable of transferring the proton to the alchoxide and so much, so that you would end up with elimination of this of this group and generation of a ruthenium complex. The ruthenium complex now has got to nitrogen switcher and unique.

And so it is a neutral species. So, this particular set of a hydrogen transfer is one from the metal which is a hydric hydrogen and another which is a proton which is attached to the nitrogen is capable of reducing the aldehyde or the key tone to an alcohol. And once that is carried out the isopropanol comes in and the exact reverse of this reaction takes place. The hydrogen which is the more protic hydrogen which is attached to the oxygen is transferred to the nitrogen.

And the hydrogen which is attached to the carbon is transferred to the ruthenium center to regenerate the amine hydride or complex which is a catalytically active species. So, you can see that this reaction can now proceed in a cyclic fashion and reduce an aldehyde aromatic aldehyde or a key tone, which is more capable of receiving this hydric hydrogen compared to the alkyl type hydride, which is present on isopropanol.

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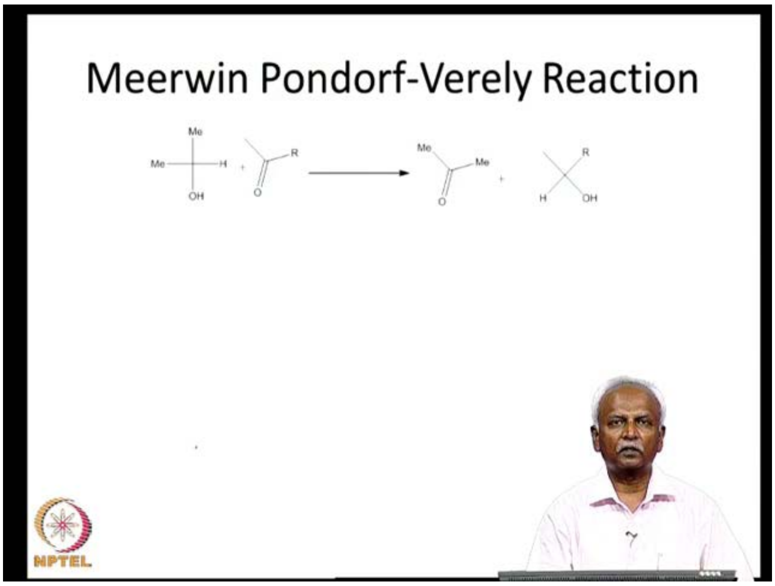
Meerwin Pondorf-Verely Reaction

You will be reminded of the Meerwin Pondorf - Verely reaction, which a similar transfer happened from isopropanol to other easily reduced aldehydes are ketone.

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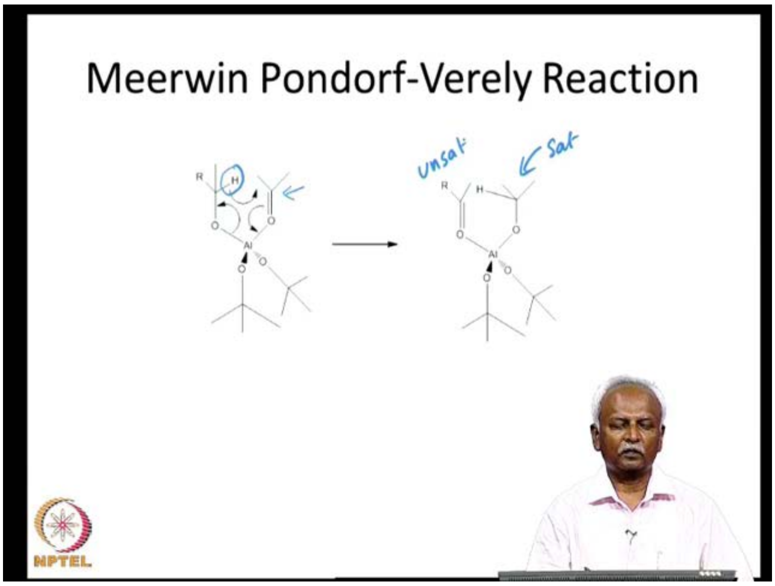
Meerwin Pondorf-Verely Reaction

And this reaction is basically happened because you have a cyclic transition state or it is supposed to go through cyclic transition state, where an aldehyde be reducing alcohol were both coordinated to alumina when you have this type of a movement of the hydride. So, here the hydride is moving from the alchoxide species directly onto the key tone of the aldehyde is directly transferred to the aldehyde. And what was initially an unsaturated molecule has become a saturated molecule and what was originally a saturated molecule has become an unsaturated molecule.

And basically the hydride transfer has happened directly from the two from one organic substrate to the other. And hydrogen was not transferred to the metal. On the other hand in the case of these transfer hydrogenation reactions, there is one hydrogen attached to the metal which we are marked in red and the other hydrogen, which is attached to an organic species of the ligand which is marked in blue.

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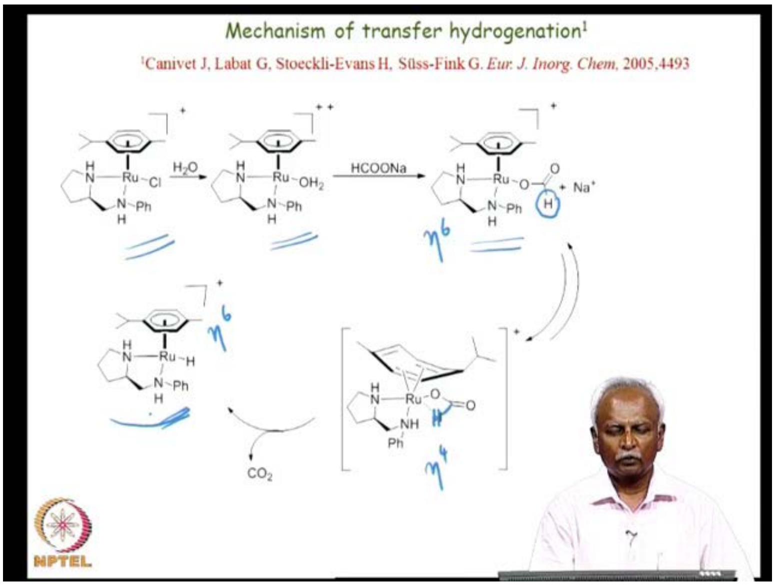

Mechanism of transfer hydrogenation[1]

[1] Canivet J, Labat G, Stoeckli-Evans H, Süss-Fink G. *Eur. J. Inorg. Chem.* 2005,4493

So, the transfer hydrogenation is a very useful reaction because one does not need the high-pressure hydrogen cylinder in order to carry out the reaction. There is another reason why these reactions are extremely useful and that is because you can specifically use species which are. For example, here we have used sodium forming or formic acid as a source of hydrogen. Formic acid can simply can get converted to carbon dioxide and release a molecule of hydrogen, but in the coordination sphere of the metal that hydrogen is transferred to the substrate very readily.

And so without the need for the transfer hydrogenation from the formic acid to the organic substrates take place without getting converted into hydrogen. And then hydrogen being activated and subsequently transferring it to the organic substrate. Let just go through this catalytic cycle into steps. First, let us see how the formic acid transfers the hydrogen to the ruthenium. So, the initial step this is a half sandwich complex and we have illustrated this with a demine ligand. And if the demine ligand and loses a molecule of cl chloride, then you end up with this di cationic species. Which can react with sodium formate.

And now you have this reducing hydrogen which is attached to the sodium in the sodium formate and this can be transferred to the ruthenium, but unfortunately if this has to happen. If the formic acid is coordinated to the ruthenium and it would be difficult. Thankfully, for us we have a aromatic ligand which is capable of changing its coordination with changing the number of ligand electrons it is giving to the metal. So, from eta six coordination here we have moved to eta four coordination.

So, that one can coordinate the hydrogen also. It is not really the hydrogen, but the pair of electrons which is there between the for between hydrogen and the carbon dioxide that is coordinated to the ruthenium. Now, if that happens then the hydrogen is eventually transferred to the ruthenium and tats what we're pictured here. And carbon dioxide is readily ejected from the coordination sphere of the ruthenium to give us the eta six mode comes back and six coordinate complex is attained with the ruthenium hydrogen bond. Now, this ruthenium hydrogen bond bonded compound has got a hydrogen adjacent to the ruthenium on nitrogen. So, that can also be transferred to the key tone or any other species which needs to be reduced.

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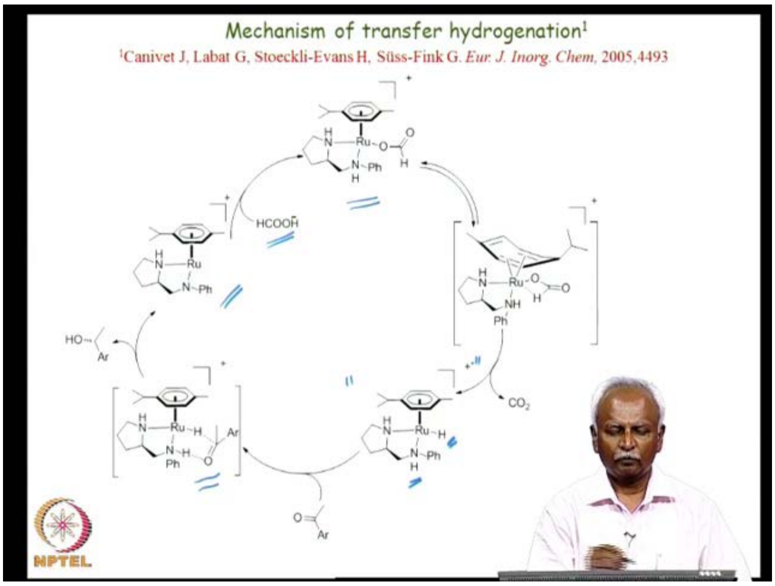

Mechanism of transfer hydrogenation[1]

[1]Canivet J, Labat G, Stoeckli-Evans H, Süss-Fink G. *Eur. J. Inorg. Chem*, 2005,4493

So, when the second cycle what we are shown here is the formation of diene of this species where two hydrogen are situated in such a way that they can be transferred to the key tone very easily. So, this is a catalytic cycle that we are really talking about where two hydrogen are transferred to a key tone or an aldehyde and an alcohol is generated. And notice that in this type of a transition state we are transferring, the hydrogen directly onto the key tone without making an aldehyde ruthenium bond, but even if you want to o make a aldehyde ruthenium bond it is possible.

If the aried rain cooperates and moves from eta 6 to eta 4, but nevertheless a direct transfer can also be done in a simultaneous fashion leading to the formation of an alcohol. And this regenerates the compound which can react with formic acid and generate the compound which we have indicated here. And that is ruthenium to center which is capable of generating the ruthenium hydride. So, once the ruthenium hydride is generated we have a catalytically active species or a reducing species which can react with the substrate which needs to be reduced.

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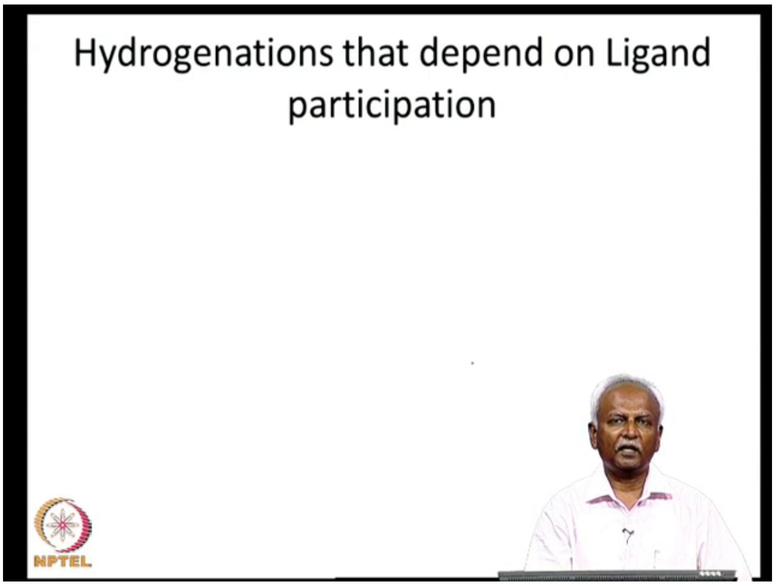

Hydrogenations that depend on Ligand participation

So, we have noticed in the part in the last example that we discussed that hydrogenation is can be carried out with the help of the ligand. So, one hydride actually came from the metal and the other hydrogen came from the ligand.

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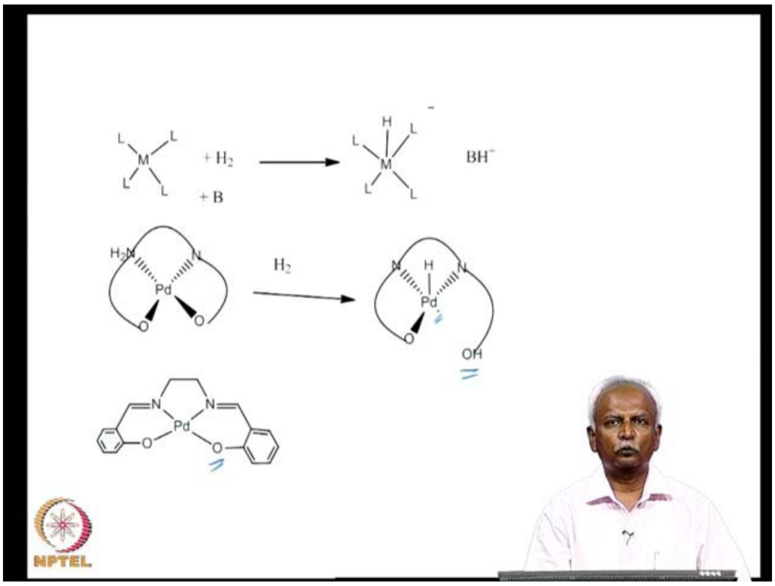

Now, this is a common theme it is possible to activate molecular hydrogen also in this fashion. And here I have shown you when one example where a molecular hydrogen is being activated using an palladium salon compound where one hydrogen has been transferred to a basic oxygen to generate oh group and a hydrogen has been added on to palladium to generate palladium hydrogen bond. So, these molecules also are capable of carrying out reduction reactions.

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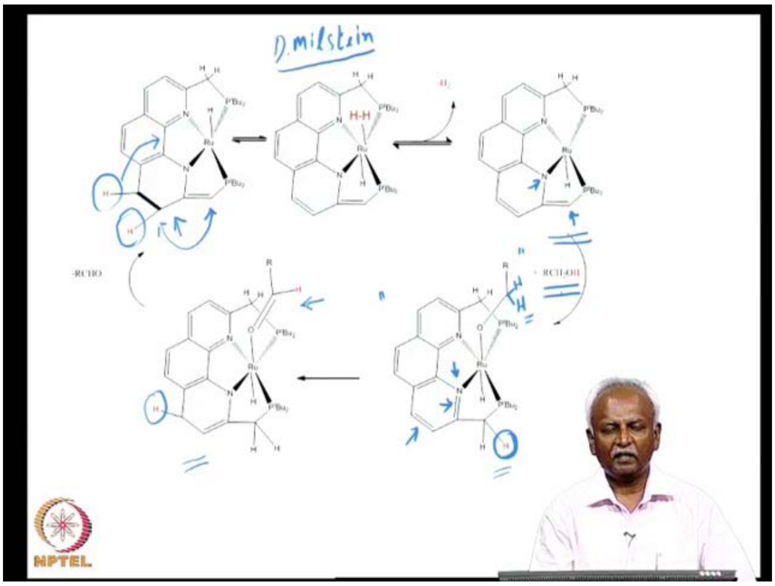

Recently a more interesting example has been discovered by Milstein. David Millstein has discovered this example where a dehydrogenation takes place just the reverse of the hydrogenation reaction. The dehydrogenation takes place in a molecule where the hydrogen is actually transferred to a organic ligand on the metal complex. And subsequently to the metal and liberated as dihydrogen the reaction sequence that we need to first understand the key steps are pictured here.

And you have two hydrogen which have been transferred from the substrate onto this aromatic ring, which because it is in conjugation or fused with two other aromatic rings is not aromatic to the extent that benzene is aromatic, and so it can readily accept these two hydrogen. So, the dearomatization of the ring here is easy and that is what is happening. You transferred these two hydrogens onto the ruthenium to transfer these two hydrogens onto the ruthenium so that you form a dihydrogen complex.

So, this dihydrogen complex loses h two and forms the monohydrate complex which is not having an aromatic ring system. Now, will notice that these hydrogens appear far away from the ruthenium, but in fact because their allylic in nature you do have the possibility of transferring these two hydrogens to another carbon atom, which is close to the ruthenium center. So, eventually these two hydrogens are transferred to the ruthenium.

And a dihydrogen complex is formed or at least that is the postulated reaction mechanism. Now, let us combine it with another source of hydrogen. And in this case the source of hydrogen is an alcohol the alcohol I have written it into different colors. So, that it is easy to follow it is an RcH 2, which here are the CH 2 groups. This is the CH two groups and the hydrogen that is written in red ends up in this position. So, again it might be mysterious to transfer this hydrogen all the way from the oxygen to this position, but you will remember that the nitrogen which is pictured here is capable of receiving that hydrogen.

And that is allilicly related to the position that we have when we have transferred it to. So, we had a double bond which is allelic related to the nitrogen. So, if a proton is transferred in this position it can be readily transferred to the allelic position here. So, that is what is happened, you transferred a hydrogen from this nitrogen to the allelic position. The generated this molecule where an alchoxide is coordinated to the ruthenium. Remember these hydrogens are capable of being abstracted and that abstraction again happens in a position that leads to the formation of this molecule.

Now, notice again it looks as if the hydrogen has been transferred to a faraway place, but it is a game related through the set of double bonds. The double bonds which I am marking here with an arrow to the ruthenium in 1, 5 transfer. So, the hydrogen can be transferred in 1, 5 fashion from the alchoxide all the way to the position which is marked here. So, two hydrogens are transferred sequentially and this leads to the formation of an aldehyde that is a dehydrogenation has taken place two hydrogens have been removed from this alcohol to form this aldehyde. Alcohols can react with this aldehyde to form a hemi-acetyl.

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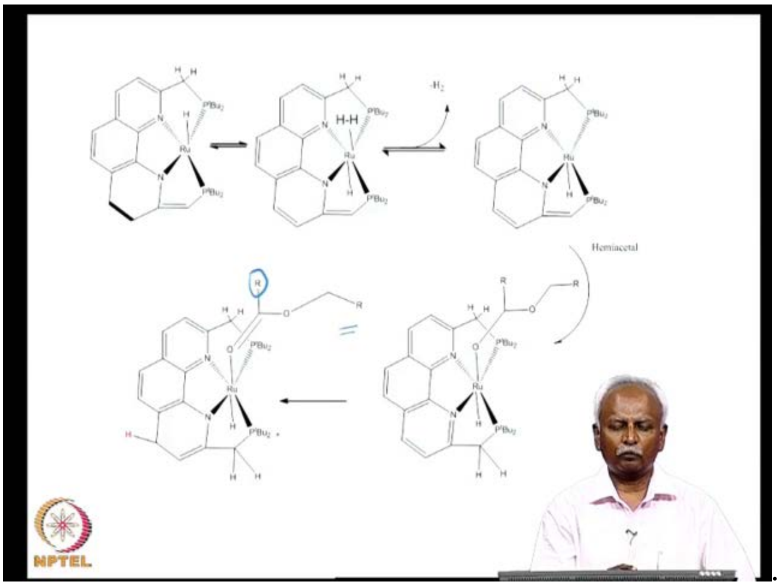

Now, that is the next step that we need to note the hemi acetyl is formed for this aldehyde. And that hemi acetyl can be the dehydrogenated again to lead to give you an ester. So, formally it looks as if a RcH two which has been converted to Rc0H because you have the R group here which is attached to a COO group. And that has reacted with an RcH two, which breaches of reactant to give us an ester. So, this dehydrogenation is capable of generating the ester of the alcohol that we started out with.

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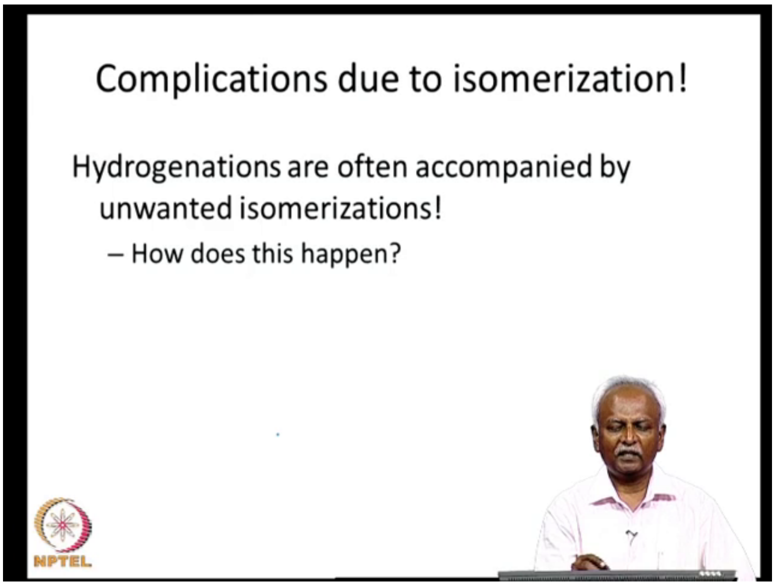

Complications due to isomerization!

Hydrogenations are often accompanied by unwanted isomerizations!

- How does this happen?

So, let us just take a look at some of the hydrogenation that have been described. All three modes of activating hydrogen can be used one is oxidative addition the other is mono oxidation or oxidation change of plus one unit. And the third is an oxidation that depends on a base which is present in the medium. Now, many of these reactions are complicated because of a isomerization reactions and hydrogenations many a time are accompanied by unwanted hydrogenation.

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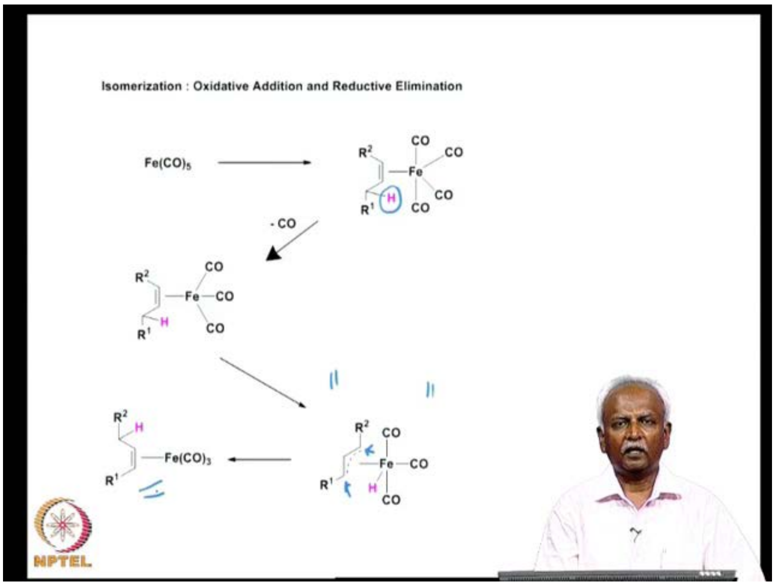

Isomerization : Oxidative Addition and Reductive Elimination

And that is because metal hydrides is capable of carrying out isomerization in this fashion. The two major ways and we will summarize these two major ways in the next two slides. The first one involves the abstraction of hydrogen in the allelic position of an alkane. When you want to carry out hydrogenation you have the possibility of forming an alkane or you always form an alkane metal complex. And if the alkane complex has got an allelic hydrogen this hydrogen can be abstracted. And it can lead to the formation of a allelic metal hydride complex, as it happened it is basically a reverse of a migratory insertion reaction.

Now, you end up with an allied species and the hydric species present in the reaction medium. So, this unlike species at the hydrogen either to the carbon R 1 or which is wearing R 2 the carbon which is building the group R 1 or if it adds it onto R 2 it gives you the starting material, if you added onto our R 2 as I have shown here, then you isomerization, the alkane from one position to the two position.

So, isomerization reaction is very readily carried out by metals which are capable of abstracting hydrogens in the in the alpha position to the olefin. You also have the possibility for an additional elimination reaction. And additional elimination reaction what I have shown here you have a hydrodo cobalt complex. Hydrodo cobalt complex can add onto an olefin and form an alkane.

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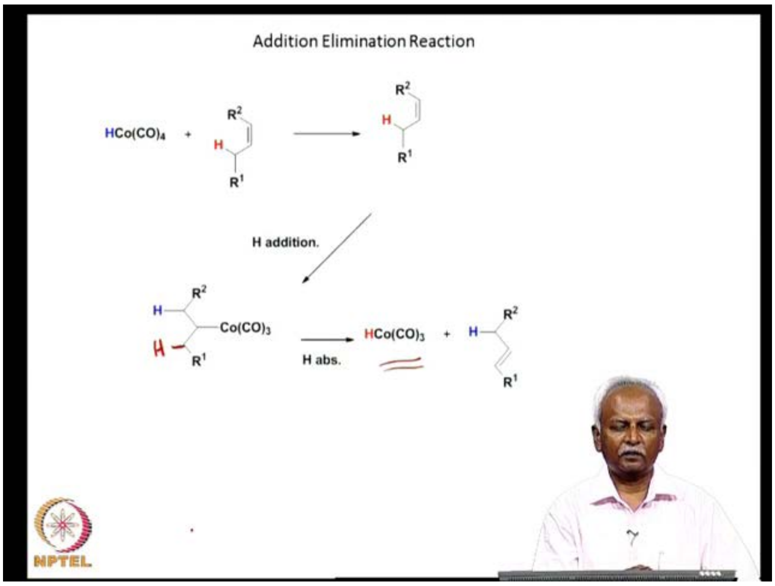
Addition Elimination Reaction

Any species now and for the sake of convenience have marked the hydrogens. Here in such a fashion that you can see that you have now of molecule which is got a hydrogen in two places. And it can either abstract a hydrogen which is red in color attached to carbon atom having the R 1 group or the blue hydrogen, which is attached to the carbon bearing the R 2 group. So, if the reaction proceeds by abstracting the blue hydrogen then you would end up with the starting material.

If it abstracts a hydrogen which is red in color then you end up forming the isomerized olefins. So, isomerization of olefins often aside reaction that one has to bear in mind when you have a monohydrate catalyst the additional elimination reaction happens. And if you have the dehydrogenation catalysts is more common reaction is hydrogen abstraction reaction.

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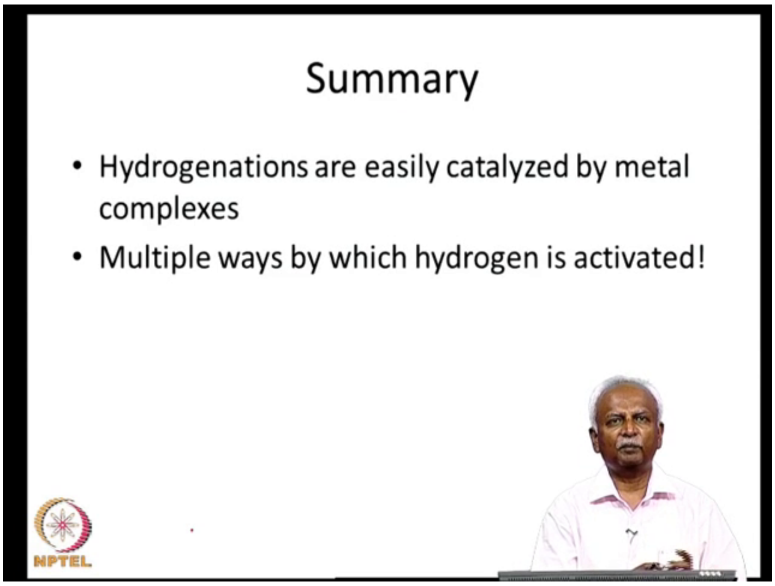

Summary

- Hydrogenations are easily catalyzed by metal complexes
- Multiple ways by which hydrogen is activated!

So, in summary hydrogenation is easily catalyzed by metal complexes. And these hydrogenation is carried out through multiple ways by which the hydrogen is activated. So, you can in fact carry out a variety of reactions both the hydrogenation of unsaturated substrates like alkanes and key tones. And make very useful molecules using organometallic catalysts and that too in the specific fashion. And as we shall see later we can carry out these reactions in asymmetric way leading to very useful products.