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Organometallic Chemistry-I

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Module No. 4

Lecture No. 16

HYDROGENATION REACTIONS

Hi everyone today we will discuss hydrogenation reactions. So as we are trying to discuss in the last class we have I think we have discussed quite a lot about the fundamental reactions of organometallics, but it time has come to apply some of these knowledge into the real catalytic cycle and see how best we have understood those simple techniques. I think hydrogenation is one of the simplest reaction of course a very effective reaction as all of you may be familiar with.

But hydrogenation reaction as well utilizes the simple reaction techniques which we have discussed so far. Hydrogenation catalyst are well-known to many of you if you look at very carefully there are two classes of hydrogenation catalyst one is monohydrate another is dihydride. Now monohydrate catalyst are the one which has one hydride with the metal centre to start with.

So the catalyst itself with will have one hydride in it that is the starting material. So metal ligand complex and metal along with it a hydride is there that is the monohydride complex usually or all we see. Now dihydride catalyst by definition should be having two hydride with them when we start in fact it does not have any hydride to start with but in between of course, it will have to hydride which can be utilized further.

Let us try to look at the monohydride catalyst first for the hydrogenation reaction and then we will get into the dihydride catalysts. So the hydrogenation is the today's topic.

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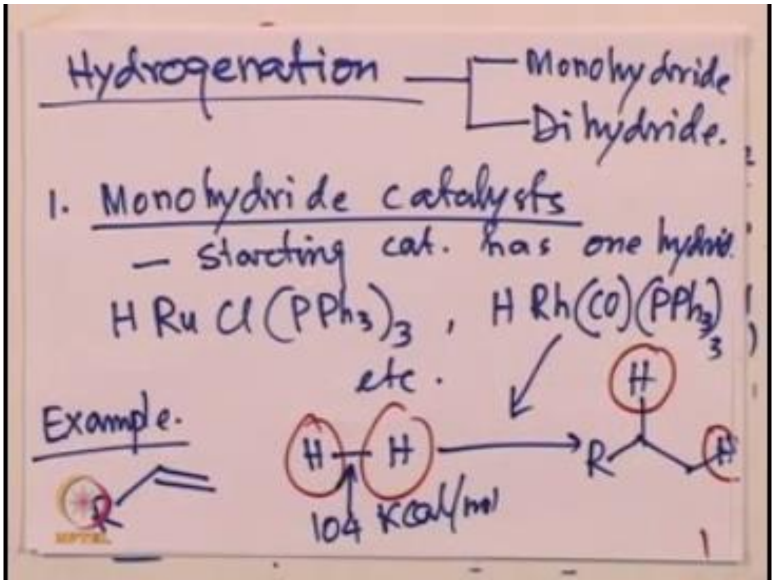

Hydrogenation — Monohydride
Dihydride.

1. Monohydride catalysts
— starting cat. has one hydride.
$HRuCl(PPh_3)_3$, $HRh(CO)(PPh_3)_3$
etc.

Example.

As we were trying to discuss two classes are possible one is mono hydride and another would be definitely dihydride. Now in terms of monohydride catalysts monohydide catalysts starting catalyst has one hydride. For example, this ruthenium complex okay we can have also other rhodium complex similar to that, we can have a series of these different complexes where these mono hydrides are present.

Now example includes these type of example we have seen that a olefin for instance can be reacting with a hydrogen gas where this hydrogen had this bond dissociation energy is 104 kcal/mole that is quite high in presence of this rhodium catalyst we will be getting over all the saturation of this molecule. So this hydrogen, hydrogen both the hydrogen can be inserted into this molecule.

So these are the example of monohydrate catalyst where we have seen very clearly that olefin for example in this case olefin is reacting with hydrogen two hydride or two hydrogen atom are getting incorporated into the olefin from an unsaturated molecule. Now we have a very clean and clear saturated molecule this is done by a monohydrate catalyst the reaction mechanism will now need to look at how these reactions are occurring for the monohydrate catalyst the catalyst we were taking was the rhodium one.

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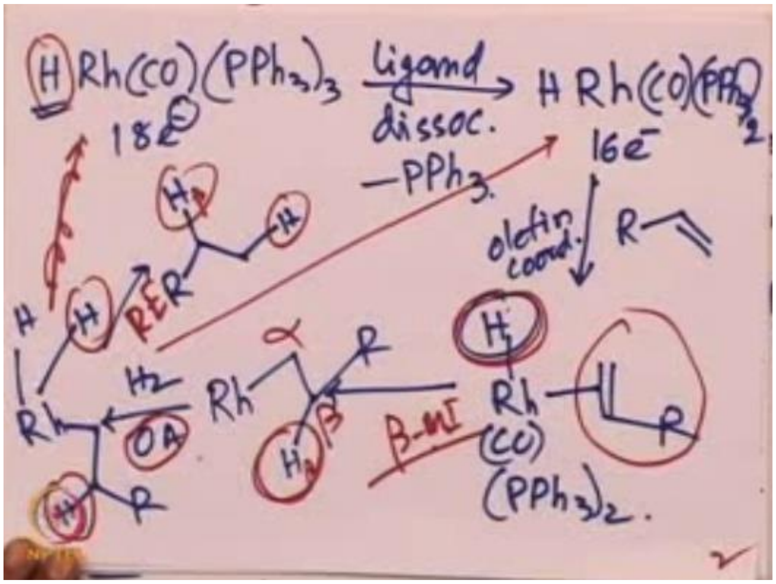

This rhodium catalyst which is a 18 electron complex please try to count it is an 18 electron complex now this piece is undergo first will be the ligand dissociation what we are going to look at is the saturation of the olefin to give you the alkane the first step is ligand dissociation the ligand that can get dissociated pretty easily in this case is Triphenylphosphine from an 18 electron complex therefore you are going to get a 16 electron complex so that the first principle we have used.

So 18 electron goes to 16 electron one ligand dissociation occurs which we have discussed earlier so first principle we have discussed now next would be the olefin coordination okay then again another step ligand dissociation olefin coordination so another fundamental steps occur one followed by second one second fundamental step occurs so we have rhodium hydride to start with rhodium hydride to start with and olefin coordinates and let us not draw all other ligand with it okay.

So of course all other CO triphenylphosphine is present we are not going to draw it too far then subsequently what you can imagine of course now by looking at this you should be very quick in understanding what is happening from there it is β migratory insertion which we have discussed quite extensively previously so you are going to get this intermediate were at the β position α β position this hydride is getting incorporated so this is going to be your β migratory insertion step now from this β migratory insertion step a hydrogen will oxidative add to give you this intermediate where you are going to get a metal alkyl intermediate right.

From their own it is a reductive elimination so this is going to be an oxidative addition we have seen ligand dissociation olefin coordination β migratory insertion oxidative addition and finally, finally we are going to see a reductive elimination to give you the product where these hydride are going to be part of part of it okay so this hydride all these hydrides are now being taken up so that one of the hydride that is the one at the beta position is the one at the beta position so this is the beta position hydride starting from the metal hydride intermediate so this is the beta hydride and that one and the alpha position is coming from the hydrogen gas, of course you know it regenerates then it regenerates the catalyst or so to speak this catalyst it regenerates.

So this is not the material it regenerates this catalyst and the catalytic cycle goes on, so what we have seen again in this case is very clearly starting from a rhodium material starting from a rhodium complex which is 18 electron species therefore you cannot have a direct association of olefin usually you need to do a ligand Association 18 electron species undergoes 16 electron species formation now you have the space available for an olefin to interact with this metal center.

Subsequently olefin coordination occurs after ligand association olefin coordination occurs and then the hydride the metal hydride which we have started from the monohydrate catalyst the hydride attacks on the olefin and to give the beta migratory insertion step and subsequently an oxidative addition of hydrogen gas occurs to give you an intermediate which upon reductive elimination can give you the final product that is the alkane product.

So olefin is getting saturated one hydride at a time first hydride came from the metal hydride we started from the second hydride came from the hydrogen gas in effect we generate regenerate the active catalyst to recreate the catalytic cycle, so catalytic cycle keeps on moving and we keep on forming the product starting from olefin then olefin and hydrogen gas by the help of rhodium hydride intermediate.

We can get a very efficient catalytic cycle where olefin is getting effectively saturated by hydrogen gas and that is going to be a beautiful process in making and it has been utilized quite efficiently for industrial at all as well as academic use and these tip this is a monohydric catalyst once again because the starting material is having one hydride itself we will discuss the di-hydride catalyst soon.

Then you will be able to see the difference between the monohydrate and the di-hydride catalyst, monohydrate catalyst delivers one hydride to the olefin first and then the second one is getting delivered by the hydrogen gas in effect in longer run both the hydrogen you can say that it is getting contributed by the hydrogen gas itself. So the ligand dissociation, olefin coordination beta migratory insertion, oxidative addition and reductive elimination.

All almost a lot of steps which we have discussed earlier is coming into effect in this catalytic centre we will see again and again and again that all these fundamental steps what we have discussed so far will be part of the beautiful reaction some of them are really, really popular these are very simple as long as you can understand the fundamental of fundamental reaction mechanism of the organometallic chemistry.

Now let us try to look at the di-hydride catalyst, now before going into that let us try to look at one more time at the monohydrate catalyst, this is the monohydrate catalyst one to start with one of the ligand gets dissociated and from there olefin coordination occur beta migratory insertion Alpha Beta Alpha Beta, Beta migratory insertion occur hydrogen gets oxidative addition into it and finally the reductive elimination between this hydride and this alkyl this part to give you the product formation Alcon product along with if the rhodium catalyst that is getting regenerated is the 116 electron species which is ready for the next catalytic cycle.

Of course our next topic would be the dihydride catalyst okay now dihydride catalyst you have seen a lot these are the actual the one which are more popular in terms of hydrogenation chemistry or there are named name catalyst like in a stock Osborne catalyst Wilkinson catalyst and of course Crabtree's catalyst which are all of the dihydride catalyzed by nature let us let us try to discuss dihydride catalyst.

Dihydride catalysts right, so we have a 16 electron species for example rhodium chloro Tristriphenyl phosphine species also known as Wilkinson catalyst of course Wilkinson's catalyst other one it could be a 12 electron species rhodium l2 plus this is a Schrock-Osborn all Osborn catalyst Schrock-Osborn catalyst and we also have other one for example iridium l2 class of course this is a rabtree’s catalyst rabtree's catalyst now for example there is simple one rhodium chloro Triphenyl phosphine one the one we call it hydrogenation catalysts this is very good for mono and disubstituted olefin.

What is important to understand that all the hydrogenation catalysts are not going to be effective for all the type of substrates there are some catalyst which is going to be very useful for a variety of substrate but then certain other problem could be there but then there are other catalyst which will be useful for a particular type of substrate and because I mean because mainly because it is very expensive or very difficult to deal with for example some catalyst will be used only when a diesubstituted or a trisubstituted olefin is there.

So if it is sterically crowded we use one type of catalyst if it is not statically demanding very simple olefin then we use another type of hydrogenation catalyst it is all about robustness and reactiveness and then of course then other factor would be how cost-effective these catalysts are all of them what we are going to discuss are going to be the hydrogenation catalyst so they effectively hydrogenate the olefin to give you the corresponding alkane species but mechanism will be quite similar.

But nonetheless they are not used in academics or industry at all the time all the catalyst only a particular catalyst usually people try to use for a particular type of substrate and of course there are few catalyst which can overcome all the limitation of the reaction and therefore can be widely used like Universal hydrogenation catalyst okay. Now let us look at the reaction mechanism with our Wilkinson catalyst for the hydrogenation reactions.

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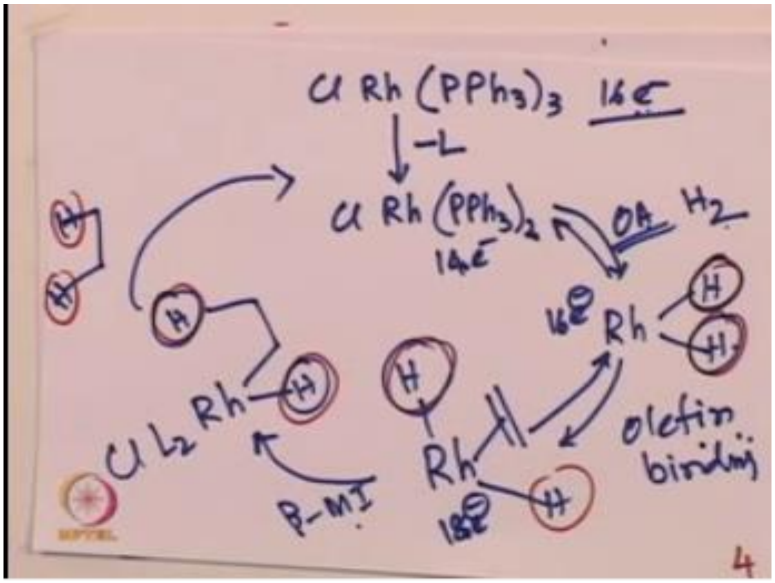

So mechanism for Wilkinson catalyst we start with the rhodium species rhodium chloro species with triphenylphosphine as the ligand of course ligand dissociation is the first step although it is a 16 electron complex still ligand dissociation is the first step and to give you the 14 electron species and which is actually going to be the key one of the key intermediate involve for this process. In this particular case you get oxidative addition with hydrogen gas first just to tell you that neither of these starting material, this is the starting material it had any hydride in it.

But under after ligand dissociation that means one of the triphenylphosphine comes out these hydrogen gas comes into the picture to give you the active catalyst this is the one which is the dihydride catalyst the name dihydride catalyst is coming because the oxidative addition happens in the first step. In the monohydrate catalyst you have seen that the mono hydride one which is coming with the starting material is getting inserted with the metal centre first and then oxidative addition is happening into the hydrogen.

Yes, in this case we see that oxidative addition is happening quite efficiently at the beginning and subsequently rhodium this hydride intermediate interact with the olefin so this is now then olefin binding olefin binding occurs subsequently again so this was 14 electrons species this was a 16 electron species then this was an 18 electron species you can imagine why these 16 electron starting material undergo 14 electron then 16 electron then 18 electron in this ligand dissociation was not there this step then this intermediate would have been 20 electron right, which is not going to be feasible. Therefore although it is a 16 electron species it will undergo a ligand dissociation in the overall process to give you the very good reaction.

Now then from there on this hydride will attack so that we were discussing as earlier beta migratory insertion this is going to be your beta migratory insertion oxidative addition olefin binding beta migratory insertion to give you the rhodium alkyl and hydride intermediate where we see very clearly this is forming the final product and that is going to be your hydrogen over there so two hydride is getting incorporated into the molecule these are the two hydride these are the two hydride all these hydride are coming from the hydrogen gas okay.

Now none of this step what we have seen so far is none of this step is spectra scopically characterized okay of course one should also remember that if there is a observed intermediate into the into the catalytic cycle that is not necessarily one is one of the step for the reaction so what in this particular case in Wilkinson catalyst case although none of these steps are spectroscopic ally characterized still this is a feasible these are the feasible steps.

But in some cases what happens is let us say you are doing a catalytic cycle one of the step you are able to get the crystal structure of you are able to interact or you are able to find that you can characterize perhaps one of the intermediate but that intermediate not necessarily has always to be the one which is which is associated with the main catalytic cycle it could be the off cycle intermediate it may or may not be relevant to the catalytic cycle.

So even if you have a crystal structure from a reaction mixture there is no point in thinking that that is the one which is participating in to the catalytic cycle you need to test the catalytic competency of the reaction that means whether that intermediate is giving you the product what you are getting and kinetic competence that means that that intermediate should be at least as fast as the original reaction if these two criteria are fulfilling both the chemical competence and the catalytic chemical and the kinetic competent then perhaps you can say that this is the intermediate that is likely to be involved into the main catalytic cycle.

And one of the component of the main catalytic cycle the one must be very careful in assigning that but coming back to the hydrogenation reaction, so we have seen monohydrate catalyst and now right now we have seen the di-hydride catalyst and the classic example is the Wilkinson catalyst it does not start with two hydride but after ligand dissociation it undergo oxidative addition which it gives its to hydride.

So the name came from that step that it undergoes the oxidative addition to give the di-hydride species but in the monohydrate species we start with a one hydride intermediate but the di-hydride species we do see very clearly that after ligand dissociation oxidative addition olefin coordination and beta migratory insertion and subsequent reductive elimination will give you the product.

So it is a once again it's these are very simple and fundamental reaction mechanism, and it Walker's quite efficiently for these cases. Now we will look at the stereochemistry of these reactions, if you are particularly looking at.

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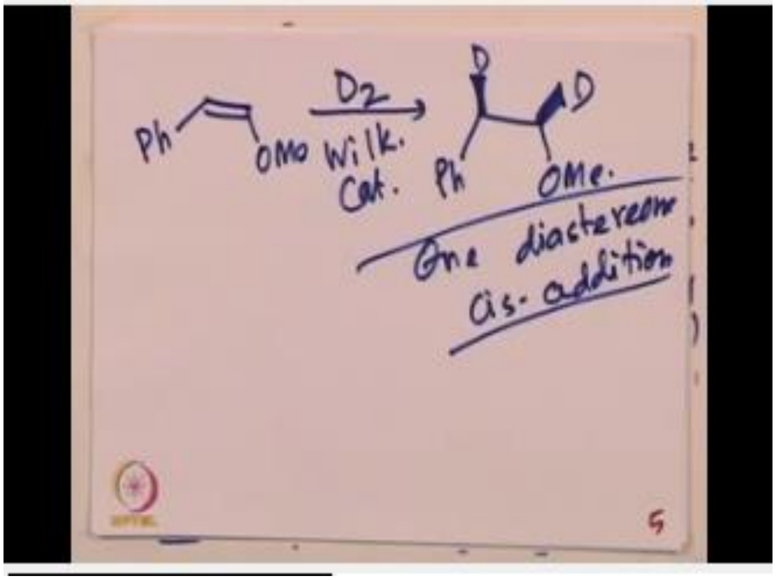

One diastereom

cis-addition

One of the example in this case, this one and you react with d2, with Wilkinson catalyst what you get is, a sis Isomer from their own right, so this is a cease isomer so 1 dashed view Mars is forming one diastereome forming, this cis addition is going on and therefore we are going to get only one product in this case, and this clearly demonstrate that this edition is happening in these graces, of course other type of catalyst we will be discussing subsequently, like stock or bond catalyst, and of course the Crabtree's catalyst.

So the take-home message for today's class is very simply we started with the hydrogenation reaction, this hydrogenation reaction is actually the application of all the fundamental reaction that we have discussed so far, so far we have discussed oxidative addition reductive elimination, all if ligand dissociation and coordination of certain unsaturated molecule, and then internal attack beta migratory insertion and shown.

All these fundamental steps are utilized in this in these hydrogenation catalysts, and therefore we both in the monohydrate catalyst and the dehydrate catalyst, whatever mechanism we have seen so far, it utilizes these fundamental steps of organ metallic chemistry to give you the product, the net result in these cases is the saturation of the unsaturated olefin molecule, to give you the alkynes compound.

And as you see particularly for the dehydrate catalyst we have discussed for the Wilkinson catalysts, we have seen that hydrogen addition dehydrate addition, or is cis in nature, so it is a going to give you the cis product, from the dehydrate complex in the next class will discuss more about these hydrogenation catalyst specifically about the dehydrate catalyst rock, Osborne and Crabtree' sand other catalyst and, we will discuss further from their own, till then I would like to ask you to read more about the hydrogenation catalysts, and get back to me if you have further queries thank you very much.

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