

**NPTEL**

**NATIONAL PROGRAMME ON  
TECHNOLOGY ENHANCED LEARNING**

**IIT BOMBAY**

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**Module No. 4**

**Lecture No. 17**

**HYDROGENATION REACTIONS  
[DIHYDRIDE CATALYSTS]**

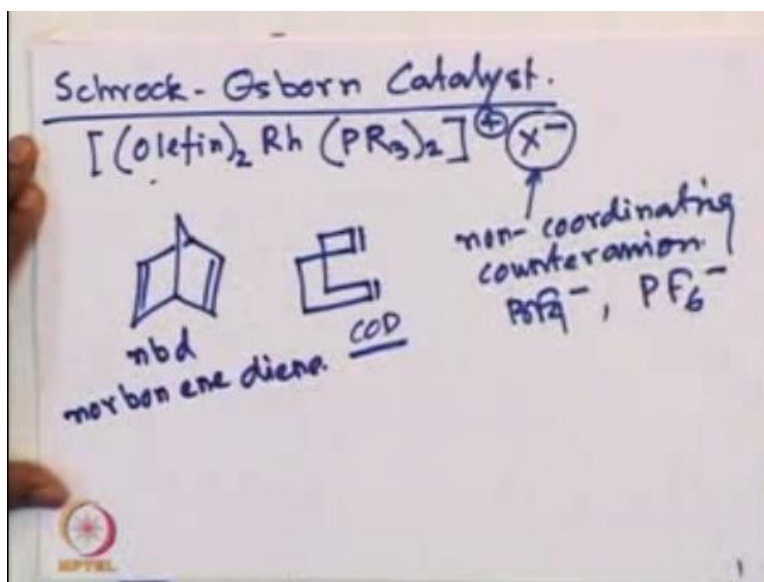
Welcome everyone, today we will discuss on hydrogenation which we were discussing in the last class, well the focus will be on the dihydride catalyst, we have seen in the last class that monohydride catalyst are usually having a hydride one hydride in the starting material. So the hydride catalyst are the one which has known hydride to start with, but after initial activation we will have two hydride with the metal send.

So therefore, the main thing from the fact that it has no hydride to start with and then often oxidative addition to hydrogen it has two hydride in it. Last class we have also seen that the dihydride catalyst can be of various types, some of the very popular catalyst such as Wilkinson catalyst we have seen that rhodium catalyst, we have also discussed briefly about the stock of boron catalyst and as well as the other iridium base catalyst sometimes though the quite familiar and famous such as goal is known as crubcreed catalyst.

Now of course we are not going to discuss each and every catalyst in detail, but we will give an overview of this catalyst so that one can understand when do you switch. For example, the Wilkinson catalyst we were discussing in the last class mainly used for mono-substituted olefin

and disubstituted olefin. For example, the Schrock-Osborn catalyst we will be discussing today will be used for mono, di, tri even tetra substituted olefin. So that makes it quite general in terms of its view. Let us try to look at the Schrock-Osborn catalyst.

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So Schrock-Osborn catalyst as you know is a rhodium based catalyst. Schrock-Osborn catalyst and it is the starting material which is more important to understand, we will have olefin two of them and the rhodium catalyst it is the rhodium center is there and the phosphine it could be two of those alkyl phosphine plus X<sup>-</sup>. Now this is the counter anion which is a non-coordinating counter anion.

So what are those could be you know  $\text{PF}_4^-$ ,  $\text{PF}_6^-$  and so on it is also important to understand that non coordinating counter anion are very important for lot of catalytic activity for example in ligands and catalyst we have a very coordinating counter anions such as chlorides right, chloride is very coordinating therefore if in coordinate is the metals in that title some other non coordinating counter anion such  $\text{PF}_6^-$   $\text{DF}_4^-$  and like bar some is called  $\text{PC}_6\text{F}_5^-$  or different fluorine it will have some benzene ring.

These are the huge counter anion and that makes the metal center more of a electro positive because this counter anion are not going to coordinate with the metal center tightly may be lot of positive charge from the metal center so making the metal center more of electro positive in nature is important for lot catalyst because those you know weakly coordinating substance can be coordinated due to the fact that the metal center is not neutral or having more of a quantity set so counter anion may be curial role in a number of catalytic cycle where weakly coordinating substitute may be coordinating in the metal center by what you having not so coordinating anion okay.

Now let us look back at the Schrock Osborn catalyst now this olefin of course olefin two of then we are saying you can have 1 olefin which one substance which we will have two olefinic count partner such as norbonenediena or sub norbonenediena okay so this should be norbonenediena okay we can as you know we can have cod cyclooctadiene COD so both of these are dicoordinating or two olefins are there as you can see over here we need or we have written the general formula as 2 olefin now of course this is as we are trying to discuss the catalyst is this catalyst particularly is good for hydrogenation.

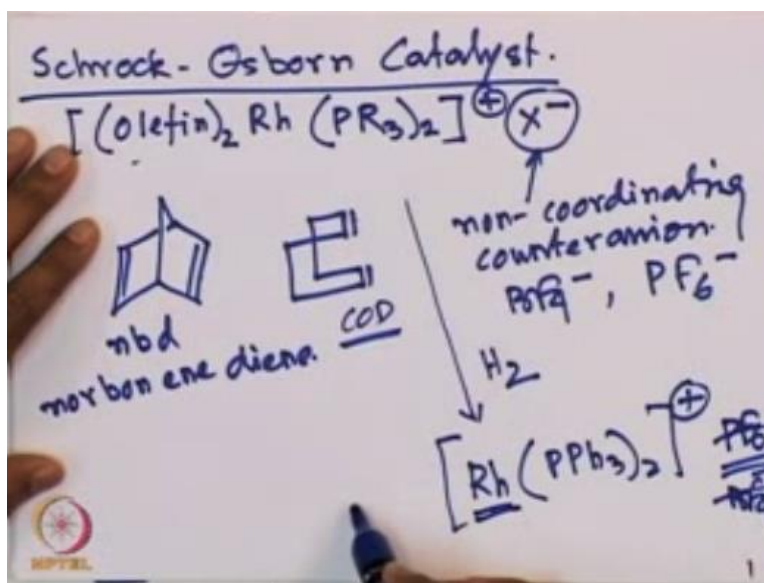
Now if we are taking olefin to start within the catalyst itself then that means that of course you know it is olefin at the one which will undergo the hydrogenation at the beginning now why this olefin are required to start with because it provides the support to the metal center so that is other unwanted reactions are not happening its acting as a uniquely coordinating ligand which at the beginning of the reaction will fall off from the metal center therefore it let the coordination and saturation so there will be space now for the exogenous of external olefin combine at these places and these places where norbornadiene or cyclooctadiene once coordinated.

So let me repeat it again, repeatedly so squad that cyclooctadiene which is having two olefin norbornadiene which is again having two olefin center these are coordinating to the metal center it just starting with Fayal who have been di- olefin center so that they can sacrifice themselves during the catalytic cycle, what is why did it require to sacrifice them because if they are coordinated your olefin.

Which you are interested in doing the hydrogenation reaction of will not have the required position required back in sight at the metal center to coordinate, in anyway the sodium catalyst are very good hydrogenation catalyst going to subscript are associated with them such as norbornadiene to start with or cyclooctadiene to start with, these are the fragment which will undergo hydrogenation very quickly.

Often hydrogenation of these norbornadiene or cyclooctadiene will have a vacant coordination side now these vacant coordination sides are the one where you will have the olefin of interest which could be a very important olefin you want to be the hydrogenation reactions of will coordinate so the role of the olefin norbornadiene and cyclooctadiene is to provide the support the initial support and then sacrifice themselves in the process so that the most important reaction which very interested in the another the hydrogenation process, okay.

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Now let us back one more time at the Schrock of born catalyst and as you were discussing of an hydrogenation first thing we will generate is rhodium P let us say R equals phenyl  $(\text{PPh}_3)_2$  and the dynamic species this is again important to understand as we were discussing the counter anion  $\text{PF}_6^-$  or  $\text{BF}_4^-$  okay, so any of these counter anion and be there which is the non coordinating

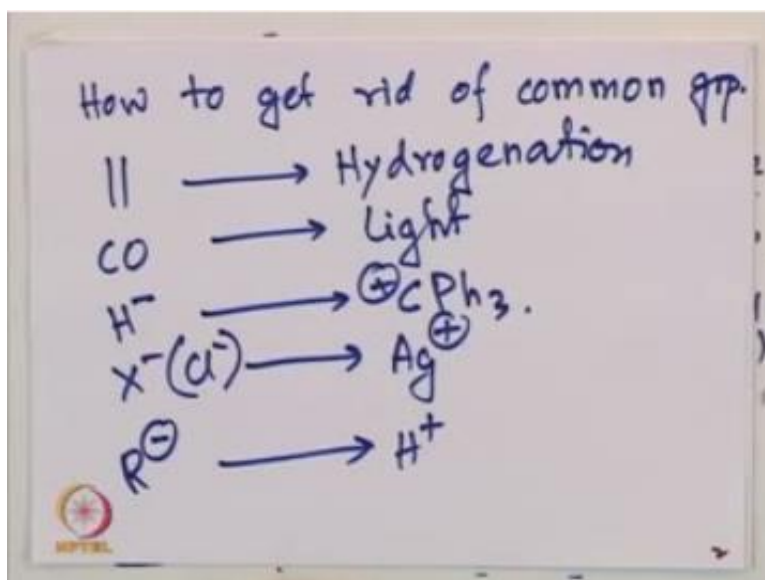
one therefore rhodium centre is ready now it has vacant coordination side it has only two phosphine associated with it, it is ready to bind with the olefin.

Of course in which cases you will get this saturated in partner so from carbon in and you will get this one completely saturated one or from cyclooctadiene will get the corresponding saturated one without double bond so these are the initial products of course you know since the catalyst is required in very, very tiny amount the amount of this product formation will be very less and they do not usually interfere with your main hydrogen right.

So now we have generated that L active catalyst this is the one which is the real active that this is the one which is the dummy one and this is the one which we will get it commercially because commercial source has to be stable this one someone want to be sell it is very difficult to sale because it is not bad very stable they are in most of been therefore storing it will be difficult we need a person which is you know solid which is a stable for quite long time and therefore just at the beginning of the reaction before than entering into the main catalyst cycle you will get your PL acting that that is important did you understand.

Also another thing is important to understand is how to really how really to get rid of some of these are you know ancillary ligands are thought supporting ligands that you have seen we have bounded iron we have cyclooctadiene the iron or how can you get rid of this supporting or that you know secondary supporting substrate from your main active catalyst so there are similar things available for example over here we have utilize hydrogen essence for promoting your hydrogenation of cyclooctadiene but then there could be other form in other let say alkyl fragment or you know suitable like halide which can be get rid of by different methods now let us look at the process if you have.

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Some substrate if you look to get rid of how to get rid of common group get rid of common group so what are the common groups let say olefin so you know that the process to get rid of this will be hydrogenation right, CO carbon monoxide if we have we can rid of the CO by light okay if you have a hydrate you can get rid of by this one okay if you have X- let say for example chloride you can get rid of by silver if you have R - of course you can get rid of by silver.

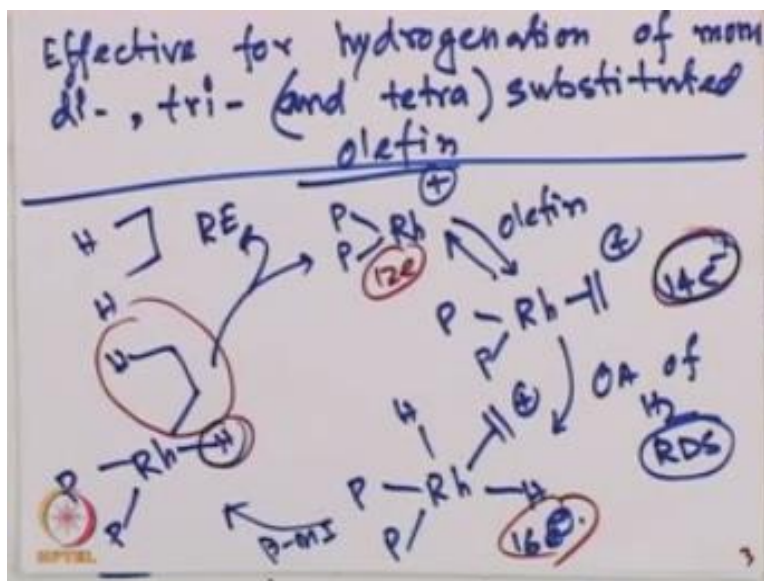
If you have R- of course you can get rid of by  $\text{H}^+$ , so there are as you can see different partners which we can get rid of depending on our need and they exist a number of different regions that we can use, of course in the last class we have seen for you, you know Wilkinson catalyst where having system where the first step of the catalyst was really the hydrogen gas addition to the metal center that means the oxidative addition is going on first and then olefin coordination is happening.

If you remember in the last class, olefin coordination really is not proposed to be happen in before oxidative addition or hydrogen, so first step is the oxidative addition of hydrogen then olefin coordination then beta migratory insertion of one of those metal hydride subsequently

detective elimination between the remaining hydride and the alkali fragment to give you the hydrogenous in of the end care olefin to give you the alkali.

Now in these case of stroke Osborn catalyst so that was we were discussing about the Wilkinson catalyst but in case of Schrock-Osborn catalyst what is important to understand is the first step is going to be the olefin coordination, so in the Wilkinson catalyst first step was the oxidative addition in Schrock-Osborn catalyst first step is the olefin coordination and the second step in the Schrock-Osborn catalyst is going to be the oxidative addition which is the oxidative addition of hydrogen gas and then of course same beta migratory insertion and reductive elimination follows to give you saturated product. Let us try to look back at the catalytic cycle of Schrock-Osborn catalyst.

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So again it is important to understand that this is the catalyst which is effective for hydrogenation of pretty much everything you can give hydrogenation of mono if you do not want to try where two many catalyst different catalyst for different hydrogenation of course this is the one of the paper one you can go for monotri try and even the tetra substituted one, substituted olefin you can get the hydrogenation olefin, okay that is fine that is quite okay.

Now we would like to look at the catalytic cycle, let us say phosphine is P triphenylphosphine as you were saying you are not going to draw it, it is a cationic species, okay rhodium cationic species now the first step will be the olefin binding, right so olefin should come as we were discussing as you remember again for the, for your Wilkinson catalyst fast step was the oxidative addition in this case first step is the olefin coordination as you can see and the second step is the oxidative addition of hydrogen and this is the one which is found the rate determining step RDS thus the slowest step and the most important of all and then that will be view the olefin coordination along with the hydride intermediate again you have a catalyst species.

So this is going to be your 16 electron species if you try to count this is going to be a 14 electron species and you know this is the 12 electron species to start with 14 electron this is going to be the 16 electron species overall then what will happen is data migratory insertion one of the hydride will in set in to the olefin, so finally what will get is that rhodium hydride and then alkyl intermediate along with your this first in amount as you know remaining step is left is the reductive elimination between this two groups where this whole moiety and this whole moiety will undergo reductive elimination to give you the corresponding alkyl product okay.

So what we have seen so far in this catalectic cycle simply is the why coordinated rhodium is which is a 12 electron species to true phosphine and rhodium in one plus oxidation state it is a 12 electron count and from there on what we see that olefin coordination occurs that gives you a 14 electron species and again a cationic intermediate from there of course a concord ion is there Ps 6 of 4 for example and from this 14 electron species you will have oxidative addition of hydrogen to give you the 16 electron species now this is the species which will undergo the  $\beta$  migratory insertion in to the olefin to be give you the alkyl intermediate as well as metal hydride mono hydride intermediate.

This mono hydrate intermediate with the alkyl undergo the reductive elimination reaction to give you the alkane product so this is the catalytic cycle of course in the process you regenerate rhodium species will be phosphine associated with the which is the 12 electron species, let us look at the catalytic cycle drawing one more time so this is the 12 electron species olefin



coordination occurs so give you 14 electron species then oxidative addition of hydrogen to oxidatively added or hydrogen auto oxidatively added.

So this is the rhodium hydride this is the rhodium hydride and now you have a 16 electron species this was rhodium one plus now this would be rhodium of course  $C^+$  overall it is a cationic species  $3+1-1-p$ , this  $n$  is cationic this  $c$ , the one you started with the cationic, this is  $1+$ , this is of course  $1+$ , so overall phosphine neutral, rhodium  $1+$ , cationic intermediate, 12 electron species, rhodium  $1+$  neutral first in the neutral over all let say, cationic species  $14 e^-$  species.

Oxidative addition into the hydrogen gas, that is  $H_2$ , you get addition oxidative addition into that, you get rhodium hydride, and rhodium hydride  $1-1-$ , but this is now  $P^+$ , so over all again, it is  $1+$ , from there hydride for the example, this one will undergo beta migrative insertion, both of them go actually.

Beta migratory insertion, to give you the from  $CH_2$ , you get,  $CH_2$ ,  $CH_3$ , alkyl group, now this alkyl and the hydride both of them undergo the reductive elimination, now these are the two hydride or hydrogen that is coming from this hydrogen gas, over all you get from olefin, this olefin, you get the alkyl species, okay.

So, so far you have seen there is a skittle difference between, win tension catalyst, and the staccato catalyst, as you have seen right now, first step of the staccato catalyst is the olefin catalyst, of course of course there is a pre first step before the first step happens there is a step where the sacrificing the agent, such as norbanodyle or cyclo oxydile, getting hydrogenated.

After that you get 12 electron di-phospine coordinating intermediate, now from this intermediate you see that, olefin coordination occurs and then oxidative addition of hydrogen occurs, but in case of your Wilkinson son catalyst, phosphate is the oxidative addition into the hydrogen, and plane olefin coherent, of course many steps are similar exactly same.

When you compare Wilkinson, staccato catalyst, another thing important if you try to look at to remember, specifically, in the last class you trying to discuss that a, the Wilkinson catalyst none

of the steps in the Anson catalyst system, is spectroscopically correct, from the other hand staccato catalyst, actually of course AB and C, are saying this is A, this is B, this is C, and this D AB and D, these three steps are spectroscopically characterized.

So that gives of course the good feeling, that these are the one which is really existing over there, of course this is the one which is how to be the red determining the step, and overall then there is a very little difference, between these catalytic difference, if you are then looking for follow substituted olefin, un substituted or mono substituted, olefin hydrogenation, I guess Wilkinson's catalyst, but if you are looking at, specifically higher substituted like Di, tri substituted or even tetra substituted, olefin catalyst. Staccato catalysis embedded effusion.

For hydrogenation of olefin, where the next class we will discuss the asymmetric hydrogenation and little bit more on hydrogenation, till then you read about the double bond and the Wilkinson catalyst and differences and what type of substituent, they can be effective for with that a, see you for the next class, take care bye, bye.

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