Advanced Transition Metal Organometallic Chemistry
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Module - 10
Lecture - 47
C-Heteroatom Coupling: Hydroboration

Welcome to the course entitled Advanced Transition Metal Organometallic Chemistry. In this course we have been looking at the utility of transition metal complexes, particularly from the catalytic viewpoint. And we had seen that how this transition metal complexes some of them, some important ones have broken the barriers or confines of the laboratory and have gone beyond the reach in the utility space and gone on to become a blockbuster catalyst in terms of producing important chemicals or compounds in a catalytic fashion in large scale of processes.

So, from that perspective, what we had been looking at is the success of various organometallic catalysts, particularly in their application utility in large-scale processes. Now, one of the main factors which we found common for most of the successful catalyst is the fact that this catalyst carry out the reactions under mild conditions and also in high turnover and throughput. So, this high efficacy of this catalyst is what make them so special for their application or utility in large scale industrial processes.

So, in that perspective, we had been discussing about various catalytic reactions, particularly the palladium mediated C-C coupling and cross coupling reactions. We have also looked at the nickel mediated hydrocyanation reactions uh. And then, we have been looking at this carbon-heteroatom bond forming reactions. And in that context, we have looked at C-N bond forming reactions particularly from arene amination reactions and hydroamination reactions in the last class.

And today, we are going to move on from this C-N bond forming reaction to another important C-B or carbon-boron bond forming reaction, when we take up this topic of hydroboration reaction.

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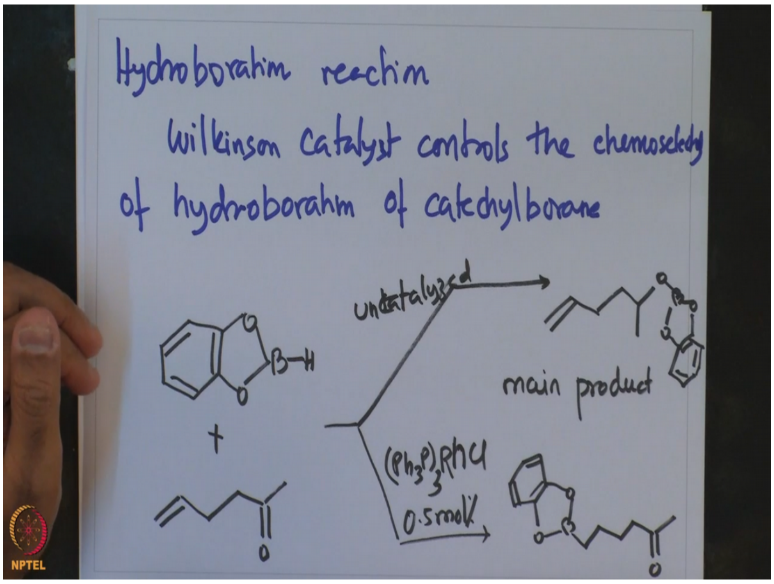

Hydroboration reaction

Wilkinson catalyst controls the chemoselectivity of hydroboration of catechylborane

Now, boron hydrides have been useful reagent ever since for carrying out many important reactions in organic synthesis and has been known to chemist for long. And from that perspective, this hydroboration reactions which is an addition reactions to olefin is of prime importance. And also the fact the catalytic hydroboration reaction being able to perform using organometic catalyst is also an important discovery with regard to this hydroboration reaction.

So, ones can sees that hydroboration reaction, the catalyst controls the chemoloselectivity of catechylborane. Wilkinson's catalyst controls the chemoselectivity of hydroboration of catechylborane. So, let this sort of see the influence of the catalyst and how this is affected by this hydroboration reaction for these 2 reagent. B H + this olefin ketone compound, when uncatalysed, this B H reduces the carbonyl compound and leaves the olefin intact to give this as the major product, this as the main product.

However, when Wilkinson's catalyst is used, whole 3 P rhodium chloride at 0.5 mole % leaves this carbonyl intact and hydroboration happens in the olefinic end to produce this compound. So, what one can see that the chemoselectivity of hydroboration of catechylborane can be controlled when the reaction is performed in absence of the catalyst versus the reaction performed in presence of the catalyst. And as a possible mechanism for this hydroboration reaction;

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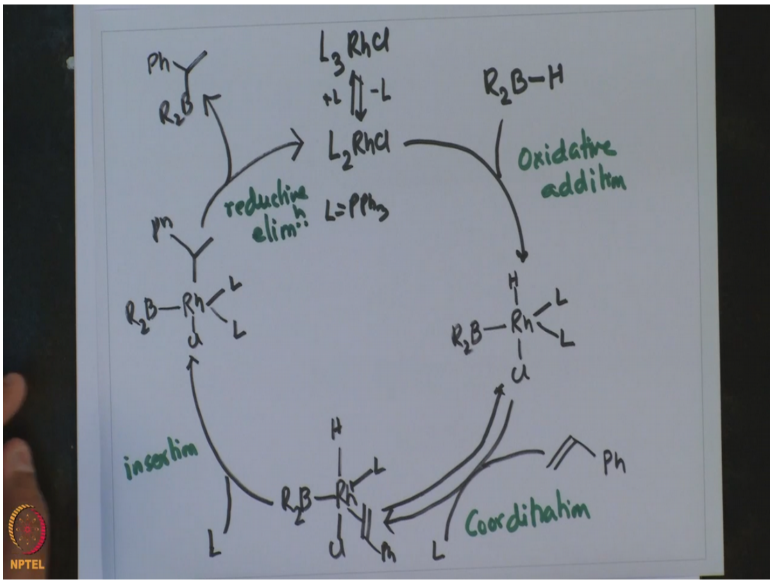

As L 3 chloride would loses in L to give L 2 rhodium chloride L = P Ph 3. This would react with R 2 B H. And this step is the oxidative addition step that one is familiar with to give the corresponding rhodium 3 compound Rh, H, B R 2, chloride, L, L. Now, this then undergoes a coordination from the olefin and this step is called coordination to give the corresponding olefin coordinated complex with the elimination of L.

One of the L is lost. And one can get rhodium, L, Ph, Cl, H, B R 2. And that, then undergoes this rhodium hydride, then undergoes insertion into this olefinic bond to give the rhodium alkyl species of the type R. And then, in presence of the ligand L which comes out over here to give Cl, L, L, Ph, B R 2. So, this is the insertion step. And if one were to look at how this insertion step happened, the hydride is inserted from the hydride attack on the olefin happens from the exo side, outside making it converting it into a methyl group.

And rhodium is bound to the inner carbon over here. So, in this second. So, this kind of addition is a anti, is a Markovnikov kind of addition. And then, finally, so this hydroboration on this olefin when it is catalysed by a catalyst, then the addition is a Markovnikov type addition. Whereas hydroboration of olefin in absence of any catalyst goes by the anti-Markovnikov kind of addition.

So, once this is formed then it undergoes reductive elimination to give the desired anti-Markovnikov product which is Ph, B R 2. And this process is called reductive elimination. So, what we see that hydroboration reaction it is indeed is a 4 elementary step process in which the first one is oxidative addition, second one is coordination, the third step is insertion and the fourth step again is reductive elimination. One should note that this insertion happens in a Markovnikov fashion.

And that the hydride moiety from the rhodium attacks the olefin from the, on the outside carbon converting it to a methyl group. And the inner secondary carbon is bound to the metal and followed by reductive elimination to give this Markovnikov addition. So, this is an important reaction as we see that these hydroboration reaction to olefins, when catalysed by Wilkinson's catalyst then the reaction happens in a Markovnikov fashion whereas the product obtained in absence of the catalyst is and to Markovnikov addition product.

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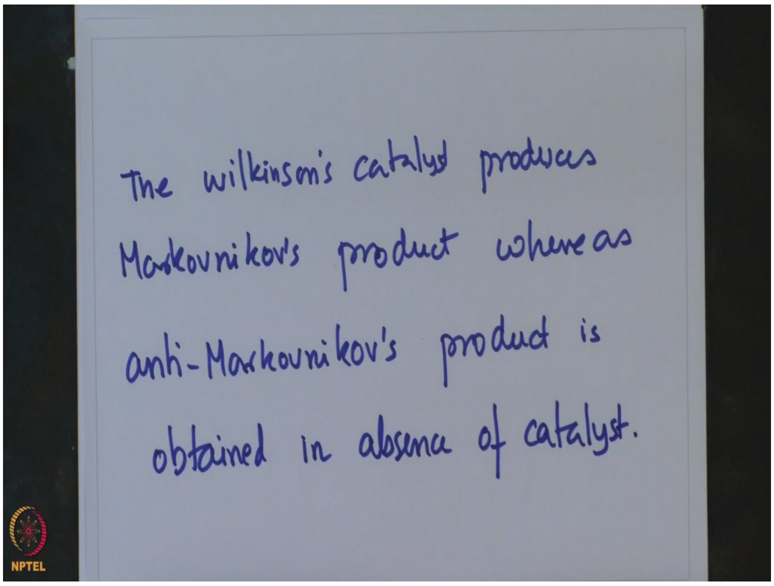

The wilkinson's catalyst produces Markovnikov's product whereas anti-Markovnikov's product is obtained in absence of catalyst.

So, this is kind of interesting that the Wilkinson's catalyst produces Markovnikov product, whereas anti-Markovnikov product is obtained in absence of catalyst. So, the hydroboration reaction has also been extended for asymmetric for organic synthesis in enantiomeric fashion. And we are going to take a look at one such example in which this, the reaction is done in an highly enantioselective fashion. So, this is examples of asymmetric hydroboration reaction.

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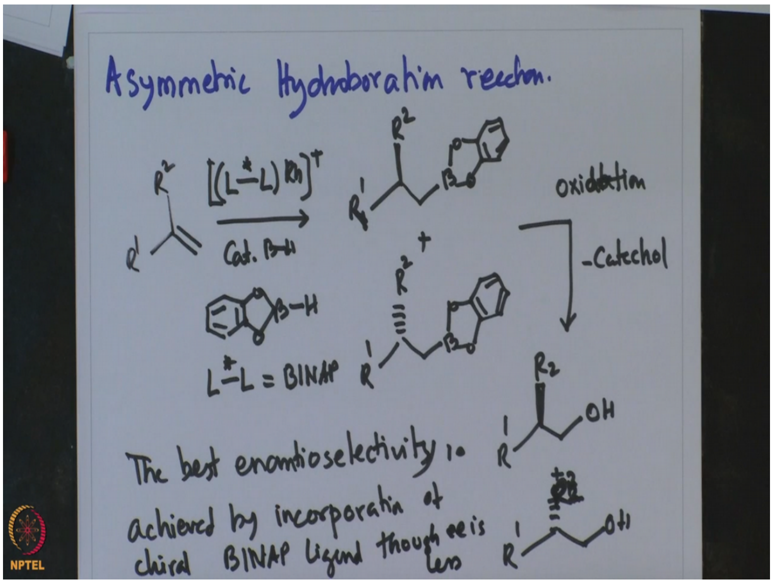

Asymmetric Hydroboration reaction.

L*L = BINAP

The best enantioselectivity is achieved by incorporation of chiral BINAP ligand though ee is less

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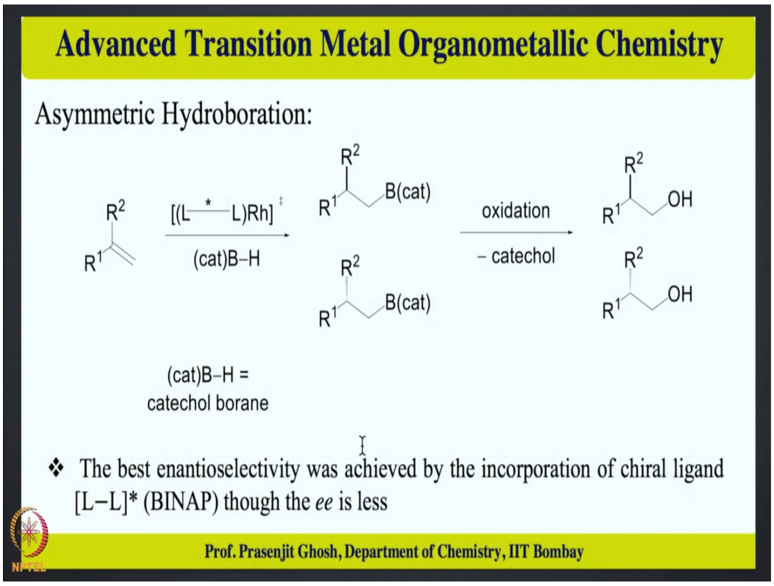

Advanced Transition Metal Organometallic Chemistry

Asymmetric Hydroboration:

(cat)B–H =
catechol borane

- The best enantioselectivity was achieved by the incorporation of chiral ligand [L–L]* (BINAP) though the *ee* is less

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And the beautiful example is given by R 2, R 1, presence of this chiral catalyst L, L, star, rhodium, cation and catecholborane which is; and L, L, star is BINAP giving the following 2 compound R 1, R 2, B and the opposite enantiomer R 1, B which upon oxidation gives catechol and the corresponding alcohol R 2, R 1, OH + R 1, R 2, OH. So, the even though you know the best in enantioselectivity is achieved using this BINAP ligand.

The best enantioselectivity is achieved by incorporation of chiral BINAP ligand though ee is less. So, what one see is this hydroboration reaction can also be extended to carry out addition of B H to olefin in a asymmetric fashion. And the best enantioselectivity though have been achieved with BINAP ligand, however the ee in this still remains less and needs to be optimised further. So, here is a another interesting addition reaction that we had spoken about.

And this is this hydroboration reaction. 2 things which comes in our mind that chemoselectivity of the hydroboration reaction can be altered when by using a catalyst when it is uncatalysed it was reducing the ketone whereas you know substrate containing the ketone and the olefinic bond and when catalysed with Wilkinson's catalyst it was reducing the olefin. Further more, there is a sharp distinction between this hydroboration reaction of olefin when catalysed as opposed to when uncatalysed.

It when catalysed, this hydroboration reaction in olefin proceeds by a Markovnikov addition. Whereas when uncatalysed, this hydroboration reaction of olefin proceeds in an anti-Markovnikov fashion. We have also observed that these hydroboration reaction can also be used to carry out olefin reduction in an asymmetric fashion. However, the enantiomeric excesses obtained for this reaction is still in its infancy and needs further improvement, though the best enantioselectivity has been achieved using this chiral BINAP ligand.

Now, as far as the catalytic cycle of hydroboration reaction is concerned, we have seen that this hydroboration reaction consists of 4 elementary steps. The first one obviously is the oxidative addition, followed by olefin coordination subsequently (()) (22:32) olefin insertion. And then finally, reductive elimination. Now, these hydroboration mechanism is quite similar to the nickel catalysed hydrocyanation reaction we had discussed earlier.

There also it had a similar kind of catalytic cycle. However, this hydroboration reaction is startlingly different from various other kind of C-C bond forming reaction like palladium mediated cross coupling reaction which also had 4 elementary steps. But the 2 were same and 2 were different. The 2 steps that were same were oxidative addition, reductive elimination and the steps which are different were transmetallation and cis-trans isomerization in terms of the palladium mediated cross coupling reaction.

So, with this, we would like to conclude in today's topic of hydroboration. And with this, we have looked into various kinds of carbon-heteroatom bond forming reaction. The ones that we have looked so far are 2 methods for C-N bond forming reaction and 1 method for C-B bond forming reaction. And we are going to move on to another interesting topic which is C-Si bond forming reaction in the form of hydrosilylation reaction in the subsequent topic.

Now, with, we have as far as the C-C or C-N or C-B bond forming reaction, we have seen that these bond forming reactions are of 2 approaches or 2; 1 is simply this metathesis reaction and the other where other is just the addition reaction to the olefin or alkyne unsaturated compound. So, hydroboration reaction falls into that category whereas the other C-C cross coupling reactions falls into the category of the metathesis type.

Now, as far as utility is concerned we had seen that hydroboration reaction indeed has a lot of examples in terms of uncatalysed reactions which is a routine organoboron hydride reagent used for various forms of reductions of carbonyl moieties or olefins and so on and so forth. And they can also be used using metal catalyst fashion for carrying out the reduction. And in this particular example today, we have seen how Wilkinson's catalyst was used for reducing the olefinic bond using boron catechyl hydride reagent.

So, with this, I would conclude today's discussion on hydroboration reaction in general. We had seen how this reaction can be controlled chemoselectively. We have also seen the mechanism of this reaction and particularly we have observed how this reaction differ from the sense of the traditional C-C bond forming reaction and how does it resemble quite similar to that of the hydrocyanation reaction that we had earlier discussed.

We have also looked at the kind of addition that one observes. And what we had noted that in terms of hydroboration of olefin, the Wilkinson’s catalyst mediated hydroboration reaction allows the reaction to proceed in a Markovnikov fashion in which sodium hydride moiety attacks the olefin from the less ended side. Whereas the uncatalysed hydroboration of olefin proceeds in a anti-Markovnikov fashion.

And this is similar to what people learn in their first year freshmen organic chemistry course, that hydroboration reaction proceeds in anti-Markovnikov fashion. So, we see the chemoselectivity, the type of addition can be controlled and made different by using different catalyst. And that is where the power catalysis comes into play. So, with this I am going to conclude today’s lecture and we are going to be taking up another such carbon-heteroatom bond forming reaction.

And this one is going to be another utility oriented hydro reaction which is hydrosilylation reaction in the next class when we meet. I sincerely thank you for patiently being with me and listening to this lecture today and I look forward to being with you in the next lecture when we take up this topic of hydrosilylation reaction in more detail. Till then, goodbye and thank you.