**Advanced Transition Metal Organometallic Chemistry**

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**Module - 12**
**Lecture - 57**
**Organometallic Catalysis Reactions: Asymmetric Hydrogenation of Alkenes**

Welcome to this course on Advanced Transition Metal Organometallic Chemistry. We had been discussing hydrogenation of alkenes. This is one of the key reactions of organometallic catalysis. Now, hydrogenations of olefin are sort of complementary to oxidation of olefins. And with regard to oxidation of olefins we had seen that 2 important industrial processes exist. One is that about conversion of ethylene to acetaldehyde, the other is on epoxidation reaction converting propylene to propylene oxide.

And the complementary feature is conversion of ethylene to alkanes by hydrogenation reaction. So, hydrogenation reaction is a feature which is complementary to that of ethylene oxidation reaction. Now, in our last lecture, with respect to alkene hydrogenation, we had gotten introduced to catalyst which is Wilkinson's catalyst which is renowned for its ability to hydrogenate alkenes, alkynes under mild conditions and standard pressure.

What is unique about this Wilkinson's catalyst, is the fact that it can hydrogenate both internal as well as terminal alkynes under very mild conditions. Now, on looking into the catalytic cycle for Wilkinson's catalyst, what is important is to see that, this Wilkinson's catalyst first activates dihydrogen because of, by the way of oxidative addition. The oxidative addition takes place in a cis fashion.

And then, the olefin gets activated by coordination to the catalyst. And finally, the insertion of the coordinated olefin onto the rhodium hydride bond is supposedly the rate determining step in this hydrogen alkene hydrogenation reactions as carried out by Wilkinson's catalyst. Another thing which makes Wilkinson's catalyst so popular is its functional group tolerance. And that it is tolerant to various functional group present in the substrate.

And does not come way in affecting its catalysis yield. Now, we have also in the last class discussed about an improved catalyst which is sort of a modified versions of Wilkinson's

catalyst which instead of containing 3 triphenylphosphine ligand contains 2 triphenylphosphine rhodium carbonyl hydride as the active catalyst. And the speciality about this catalyst is that it can only hydrogenate terminal olefin and does not really attack the internal olefins.

So, there is a order of selectivity associated with this catalyst which is a modified versions of Wilkinson's catalyst. Now, we had also looked into the catalytic cycle of this particular catalyst. And what we had seen that the cycle sort of initially starts with a coordination of olefin followed by the insertion of the olefin into the rhodium hydride bond and subsequently the oxidative addition of dihydrogen.

And finally, the cycle closing with reductive elimination giving rise to the product. Now, in this context on olefin hydrogenation; be talking today about another catalyst which is of the formula L 2 R H Sol 2 which is, which was reported by Schrock and Osborn.

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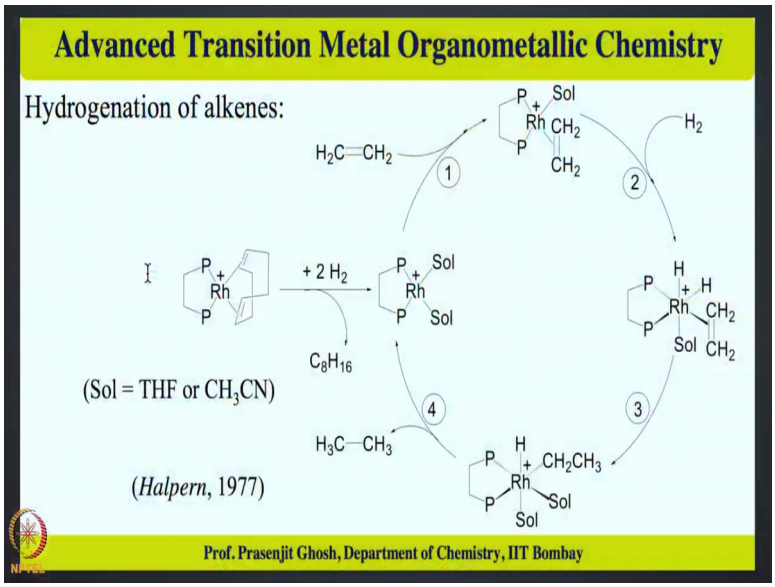


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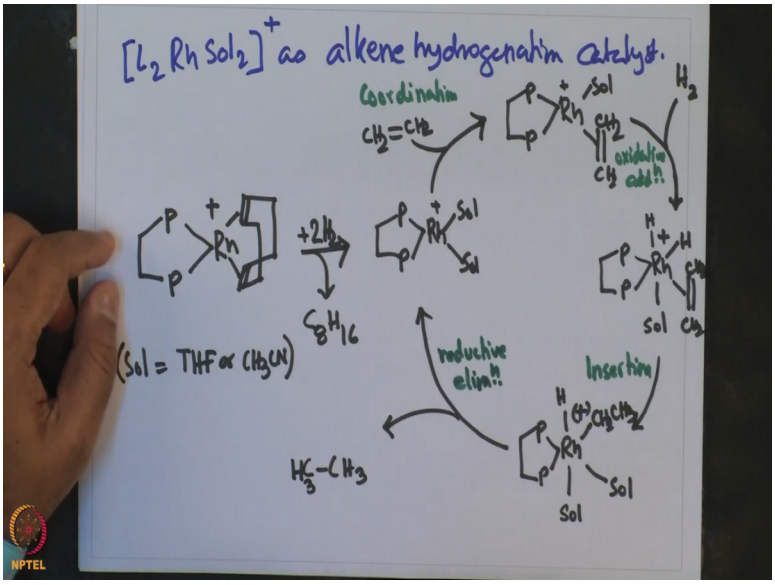


L 2 rhodium Sol 2 + as alkene hydrogenation catalyst. Now, the catalytic cycle is given as P. These are chelating phosphine ligands bound to rhodium. This, so, this in presence of 2 hydrogen actually hydrogenates this diolefin to give cyclooctane which is C 8 H 16. So, actually the hydrogenation occurs. And then, the cycleooctane does not coordinate with rhodium; so, leaving solvents to go and bind to the rhodium.

So, Sol is some coordinating solvents like THF or CH 3 CN. This giving phosphene rhodium + Sol. So, this is a bis solvated chelating phosphene bound rhodium +. So, that then binds to ethylene alkene. And this step is thus called a coordination step giving rhodium + solvent. Now, after the activation of olefin, by coordination to rhodium occurs, then the oxidative addition of hydrogen take place.

This is the oxidative addition step to give this compound chelating phosphene, rhodium, hydride, hydride, CH 2, CH 2, solvent. And there is a cationic charge, followed by the insertion; insertion of the olefin in the rhodium hydride complex. This insertion of this olefin in the rhodium hydride bond takes place giving to rise to the rhodium ethyl moiety as is shown over here; rhodium hydride, solvent, solvent, CH 2 CH 3 +.

And that this step is called the insertion step followed by the reductive elimination with of ethyl with this hydrogen giving ethane and giving back the catalyst. And the catalyst is regenerated. So, the last step is a deductive elimination step where this rhodium precatalyst disolvated rhodium yielding phosphine rhodium 1 active catalyst is regenerated. So, this is a useful catalyst which was reported by Schrock and Osborn.

And it has a different structure, particularly if one compares the structure of this with respect to the Wilkinson's catalyst. However, this is important motive anyway in being able to carry out the hydrogenations of alkene. Now, with these 3 catalyst that we had discussed about in alkene hydrogenation reaction, particularly the Wilkinson's catalyst that can hydrogenate both alkene and alkyne at ambient condition.

And also can hydrogenate both the internal and terminal alkenes. And its improved variant which can only hydrogenate the terminal alkene. And lastly, we have also spoken about this disolvated cationic rhodium chelating phosphine precatalyst which was reported by Schrock and Osborn which also effectively carry out hydrogenations of alkenes. Now, having said this we move on to look at the scope of this reaction in asymmetric catalysis.

And that also is a big and important domain in hydrogenation reaction. And there are a significantly a lot of work has been performed to develop this area of asymmetric hydrogenation of alkenes.

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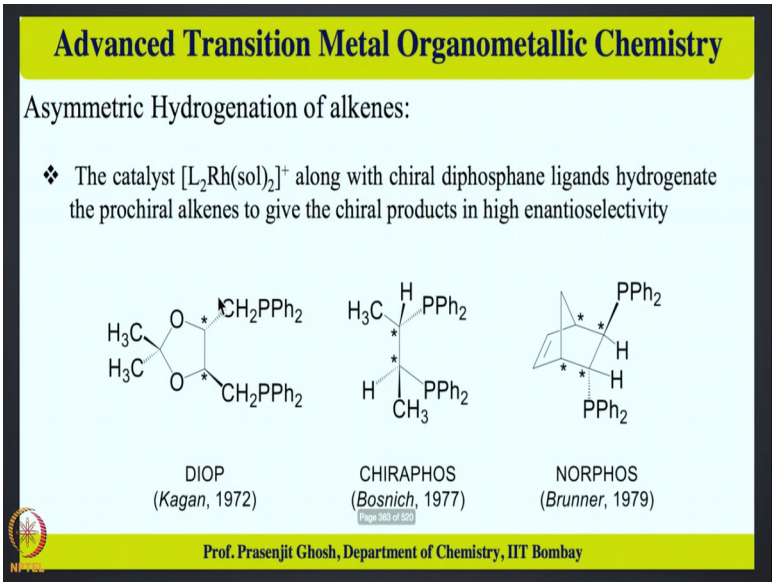


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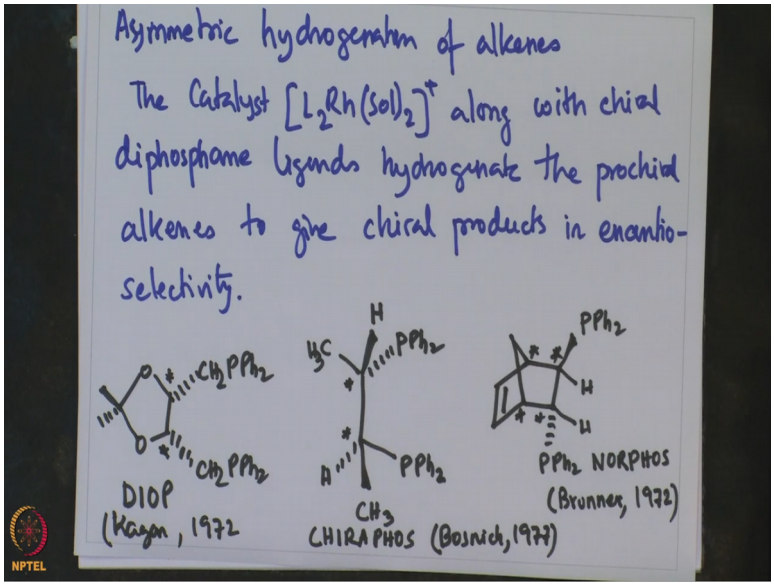


Now, one of the important feature of asymmetric hydrogenation of alkenes is for L 2 rhodium dissolvent twice cationic compounds if some chiral ligands are put in place. Then, they can hydrogenate prochiral alkene to give chiral products in high enantioselectivity. So, the catalyst L 2 rhodium Sol 2 + along with chiral diphosphane ligands hydrogenate the prochiral alkenes to give chiral products in high enantioselectivity.

And there are wide variety and different types of these diphosphine ligands. And some examples are given over here. CH 2 P Ph 2 CH 2 P Ph 2 and this dimethyl; this is called DIOP. And this was reported by Kagan, 1972. Another important ligand is CHIRAPHOS which is H PPh 2 methyl H CH 3 PPh 2. And this is CHIRAPHOS. And this was reported by Bosnick, 1977. And NORPHOS, this is a interesting ligand PPh 2 PPh 2; and it has 4 chiral centres as is shown over here.

DIOP has 2 chiral centres and CHIRAPHOS has 2 chiral centres. And this is called NORPHOS and reported by Brunner, 1979. So, what one sees that in these L 2 rhodium disolvated + type of complexes, if one puts chiral diphosphine ligand of the types DIOP or CHIRAPHOS or NORPHOS, then this is the catalyst can hydrogenate prochiral alkenes to give chiral products in high enantioselectivity. So, now look at this, the one that which is reported by Noyori or popularly known as the Noyori catalyst. And this is developed in and around BINAP.

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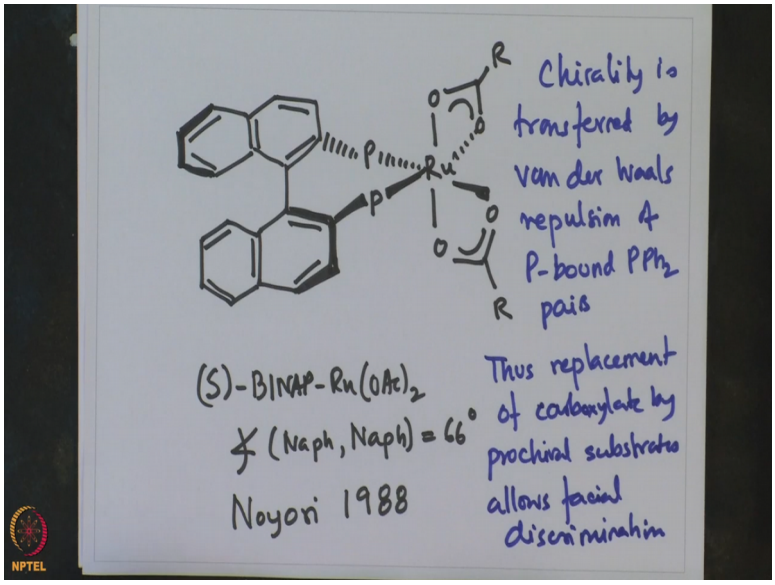


And the catalyst is given as; and this is S BINAP ruthenium diacetate. So, this page of the BINAP ring is coming up and this side of this BINAP ring is pointing towards us. And this particular configuration is known as the S configuration. P, P, bound to ruthenium and ruthenium is bound to acetate R, O, O, R. And so, this naphthalene-naphthalene angle, Naph, Naph is about 66 degrees.

And this is reported by Noyori or the famous Noyori catalyst in 1988. Now, one interesting thing about this that chirality is transferred by van der Waals repulsion of P bound P Ph 2 pair. Chirality is transferred by van der Waals repulsion of phosphorus bound P Ph 2 moiety pairs. And replacement of this acetate by prochiral substrate allows facial differentiation. Thus, replacement of carboxylate by prochiral substrate allows facial discrimination.

And this is what leads to the origin of enantioselectivity. So, this is a interesting attribute of this particular catalyst where this L is a BINAP ruthenium diacetate ligand where the naphthalene, naphthalene the angle is about 66 degree and the chirality is transferred by van der Waals repulsion of the phosphoron bound PPh 2 pair. And this replace, and the replace which transfer the chirality onto ruthenium.

And replacement of these carboxylates by prochiral substrates allows for facial discrimination which eventually leads to higher chirality transfer. And this is illustrated in this beautiful example in which this rhodium catalyst can lead to the chirality transfer.

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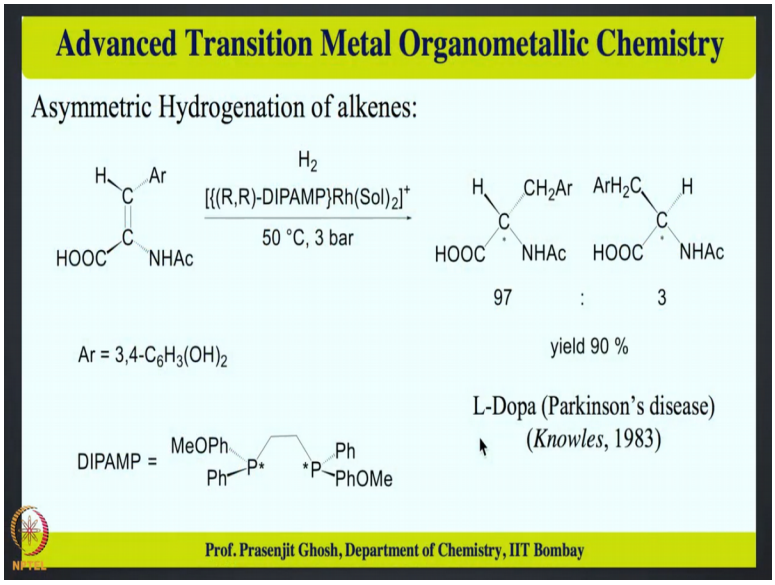


So, as far as the Noyori's catalyst is concerned, the Noyori's catalyst is suitable for asymmetric catalysis. And that we will illustrate giving a example.

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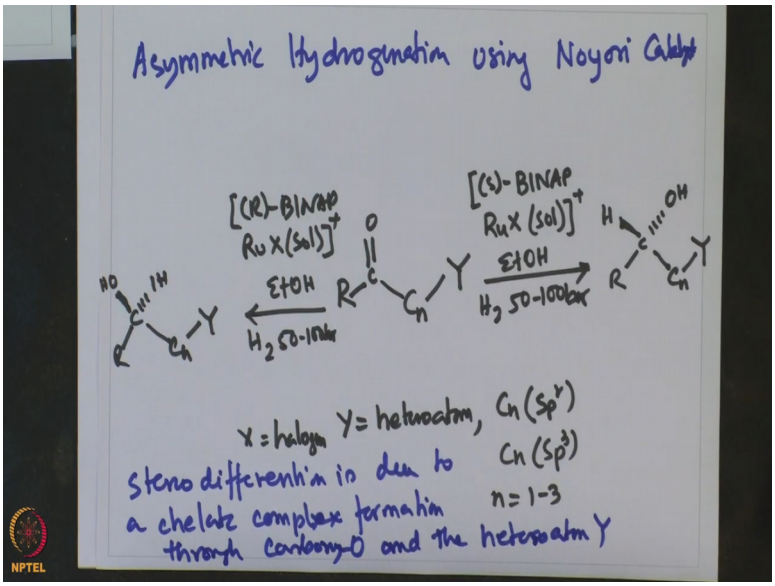


So, asymmetric hydrogenation using Noyori catalyst. So, if and this is illustrated as R, C, O, C n, Y = heteroatom. C n can be Sp 2 or C n can be Sp 3 carbon centres, n can be 1 to 3. So, that when treated with S BINAP ruthenium X solvent + ethanol. Hydrogen 50 to 100 bar; X = halogen. Then one gets R, C, hydrogen, OH, C n, Y. On the other hand, if the same substrate which is a prochiral substrate is treated with R BINAP Ru X solvent in ethanol in hydrogen pressure 50 to 100 bar.

Then one gets OH, H, R, C n, Y. And this stereo induction where S catalyst gives a 1 enantiomeric pure product, where R catalyst gives the other enantiomeric pure product. And

this stereo differentiation is attributed to formation of a chelate complex. Stereo differentiation of substrate is due to a chelate complex formation through carbonyl, oxygen and the heteroatom Y.

So, this heteroatom Y is a very much required which is respect to the binding to the ruthenium, both Y and oxygen binds. And that sort of helps in the chirality transfer. So, this is a beautiful example where the role of this heteroatom adjust into the carbonyl group getting hydrogenated is appreciated. So, with this, I would like to draw today's conclusions on our discussion on hydrogenation of alkenes.

To conclude, let me just summarise what we had been talking about in this hydrogenation reaction. To begin with, we have looked into a new kind of hydrogenation catalyst which is L 2 rhodium disolvated cationic complex. These are also useful for hydrogenation purpose is under obtained by from diolefin counterpart by using hydrogen. Then, we moved on. And then, subsequently we looked at this Noyori catalyst where this is Noyori catalyst is sort of a improved version of this Schrock and Osborn catalyst that we had just discussed.

And then, Noyori catalyst consists of this chiral BINAP ligand bound to ruthenium and rhuthenium in terms it bound to 2 carboxylate groups. And we had seen that this hydrogenation asymetric hydrogenation can be performed selectively using substrates like R CO C n Y. C n can be SP 2 SP 3 centre, n can be 1 2 3. Y is a heteroatom and X is a halide. And it turns out that S, 1 form of the ligand, S form of the BINAP ligand complex gives one tenth of enantiomer and the R form gives the other.

And the primary reason for such a differentiation is due to the formation of a chelating complex of the substrate to the catalyst where oxygen binds to the rhodium centre along with the heteroatom Y which allows the stereo differentiation. So, with this, we come to an end on, end of today's lecture on alkene hydrogenation reaction. And we are going to take up some more discussion on alkene hydrogenation in our next class.

I sincerely thank you for your patient hearing of this class and we look forward to take up this hydrogenation of alkene in bit more detail in the next class followed by hydroformylation reaction that we would be discussing. So, till then goodbye and thank you.