Advanced Transition Metal Organometallic Chemistry

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Module - 12
Lecture - 56
Organometallic Catalysis Reactions: Hydrogenation of Alkenes

Welcome to this course on Advanced Transition Metal Organometallic Chemistry. Today we are going to take up a very impactful reaction which is the hydrogenation of alkenes and which represents one of the finest demonstrations of the utility of organometallic complexes in homogeneous catalysis. Now, if one looks at hydrogenation of olefins; hydrogenation of olefin is sort of complementary to oxidation of olefins.

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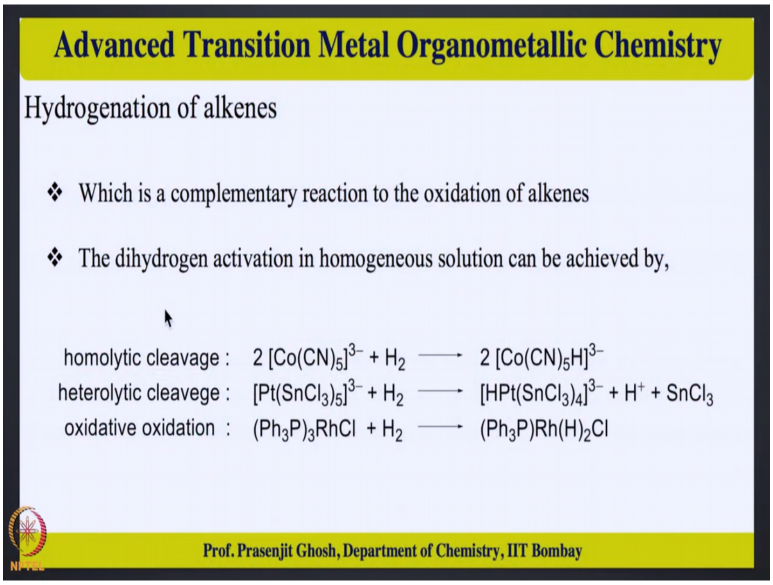

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Hydrogenation of alkenes

- Which is a complementary reaction to the oxidation of alkenes
- The dihydrogen activation in homogeneous solution can be achieved by,

homolytic cleavage : $2\,[Co(CN)_5]^{3-} + H_2 \longrightarrow 2\,[Co(CN)_5H]^{3-}$
heterolytic cleavege : $[Pt(SnCl_3)_5]^{3-} + H_2 \longrightarrow [HPt(SnCl_3)_4]^{3-} + H^+ + SnCl_3$
oxidative oxidation : $(Ph_3P)_3RhCl + H_2 \longrightarrow (Ph_3P)Rh(H)_2Cl$

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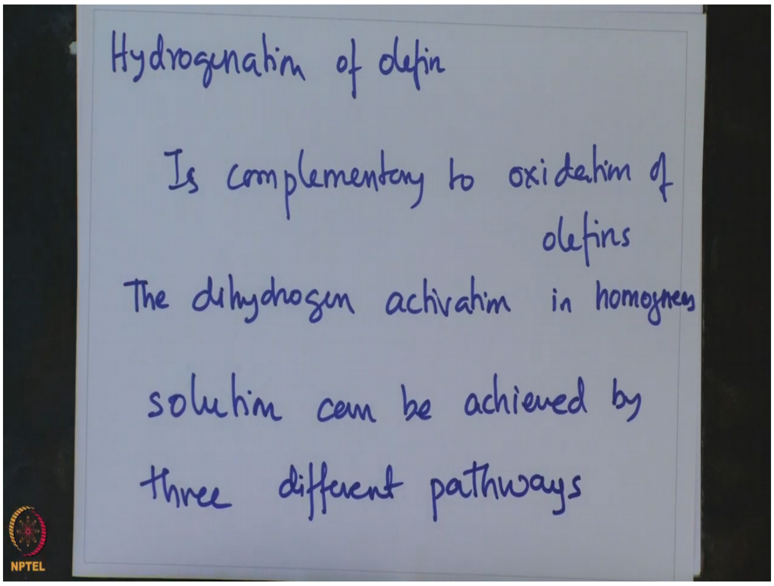

Hydrogenation of olefin

Is complementary to oxidation of olefins

The dihydrogen activation in homogeneous solution can be achieved by three different pathways

Is complementary to oxidation of olefins. And what we had seen is that oxidation of olefins is in fact very well extensively studied, particularly from the industrial perspective. Oxidation of olefins; we have discussed lot of a large-scale utility. For example, Wacker reactions where ethylene was oxidised to acetaldehyde or this epoxidation reactions where olefins were oxidised to epoxides which are useful intermediate to ethylene glycols.

So, oxidation of olefins is in fact a very important reaction to perform from a industry perspective in large-scale processes. And we had seen several industrial processes like Wacker oxidation which is known for more than hundred years or so. Or this Halcon/ARCO oxirane process of epoxidation where propene is converted to propylene oxide, that too in huge amounts by this chemistry which represents oxidations of olefins.

So, as we had seen that oxidations of ethylene is quite important and there are several industrial processes which are important with respect to this olefin oxidation chemistry is concerned. On the contrary, this, when we look at the complementary reactions which is reductions of olefin which is represented by this reaction which is hydrogenation of olefin. Hydrogenation of olefin is nothing but reduction of olefin.

That also is equally important from industrial point of view. Because lot of chemistry is designed against the olefin hydrogenation reaction. Also complementary towards this olefin, hydrogenation reaction is this olefin oxidation reactions which to with which we are comparing this reaction in back and forth. So, I would like to note that olefin oxidation reaction is thus an attempt to convert olefin to other oxygenated useful chemicals, chemical intermediates which can which are of relevant importance to various synthesis of various organic targets.

So, with that now, we are going to focus today's lecture on hydrogenations of alkenes and we know as has been mentioned that hydrogenation of alkene is just a complimentary reaction to that of oxidation of olefins. Now, in the hydrogenation of alkenes, the primary step of interest of course is the dihydrogen activation. And how does dihydrogen gets activated by transition metal complexes in homogeneous solution.

And one needs to look at ways and means in which the dihydrogen can be activated in solution. And this actually can be done in 3 different ways. So, we are going to look at it in bit more details. Dihydrogen activation in homogeneous solution can be achieved by 3 different pathways. And we are going to discuss this in bit more details. This 3 different pathway involves a homolytic cleavage of hydrogen, heterolytic cleavage of hydrogen and oxydative oxidation using hydrogen. So, 3 different pathways are homolytic cleavage;

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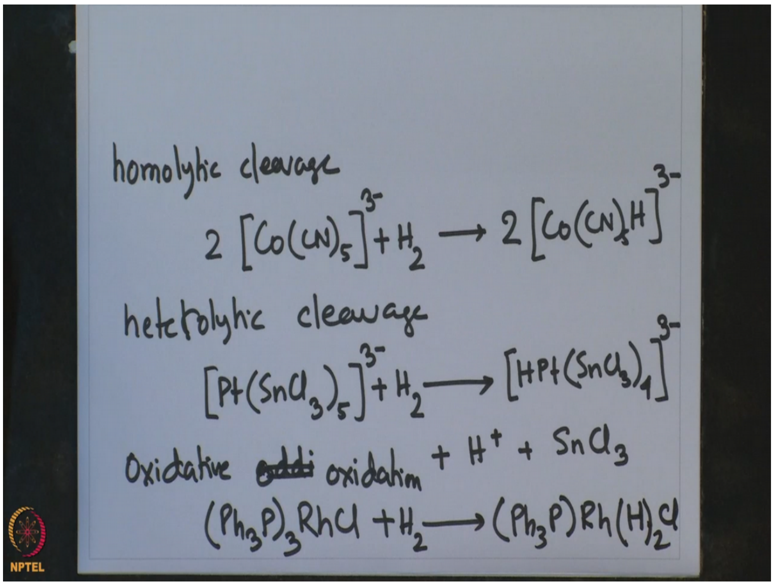

homolytic cleavage

$$2\,[Co(CN)_5]^{3-} + H_2 \longrightarrow 2\,[Co(CN)_5H]^{3-}$$

heterolytic cleavage

$$[Pt(SnCl_3)_5]^{3-} + H_2 \longrightarrow [HPt(SnCl_3)_4]^{3-} + H^+ + SnCl_3$$

Oxidative ~~oxdi~~ oxidation

$$(Ph_3P)_3RhCl + H_2 \longrightarrow (Ph_3P)Rh(H)_2Cl$$

And that is represented by 2, this equation 2 Co CN 5 3 –, + H 2 giving 2 Co CN 5 H 3 –. So, this is a homolytic cleavage which means that dihydrogen is splitting into 2 hydrogen atoms. The next comes heterolytic cleavage. Heterolytic cleavage of hydrogen means that dihydrogen is cleaved as H + and H –. So, it is cleaved as proton and hydride. And an example of heterolytic cleavage is platinum Sn Cl 3 whole 5 3 –, + H 2 giving H Pt Sn Cl 3 whole 4 3 –, + H +, + Sn Cl 3.

And next come oxidative addition. And where oxidative addition is just oxidative addition of hydrogen to a metal centre. This is like any other oxidative addition reaction. Oxidation; and this is given by the reaction Ph PPh 3 whole thrice rhodium chloride + H 2 giving Ph 3 P rhodium H 2 Cl. So, this is 3 different this is a way of cleaving hydrogens. So, what we saw that there are actually 3 processes that are prevalent by which hydrogen can be activated.

Now, one of the first hydrogenation catalyst is this Wilkinson catalyst. The good thing about Wilkinson's catalyst is that it can carry out hydrogenation of olefins under very mild condition.

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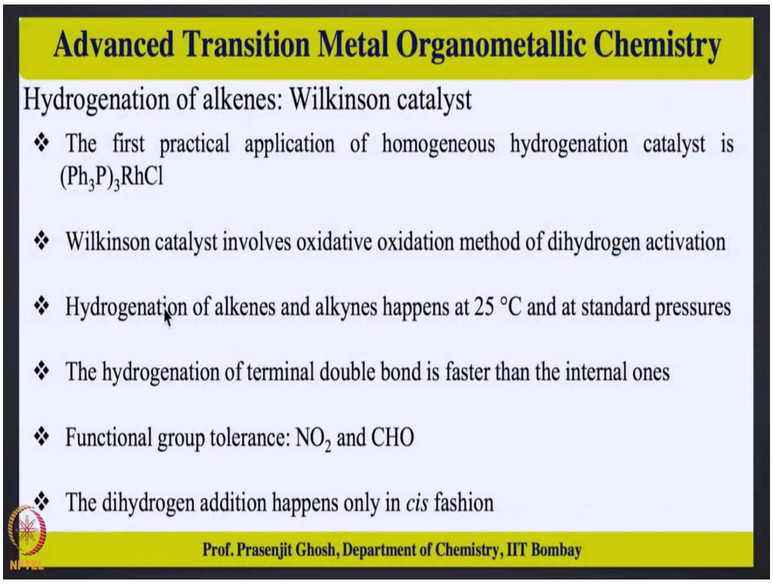

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Hydrogenation of alkenes: Wilkinson catalyst

- The first practical application of homogeneous hydrogenation catalyst is $(Ph_3P)_3RhCl$
- Wilkinson catalyst involves oxidative oxidation method of dihydrogen activation
- Hydrogenation of alkenes and alkynes happens at 25 °C and at standard pressures
- The hydrogenation of terminal double bond is faster than the internal ones
- Functional group tolerance: NO_2 and CHO
- The dihydrogen addition happens only in *cis* fashion

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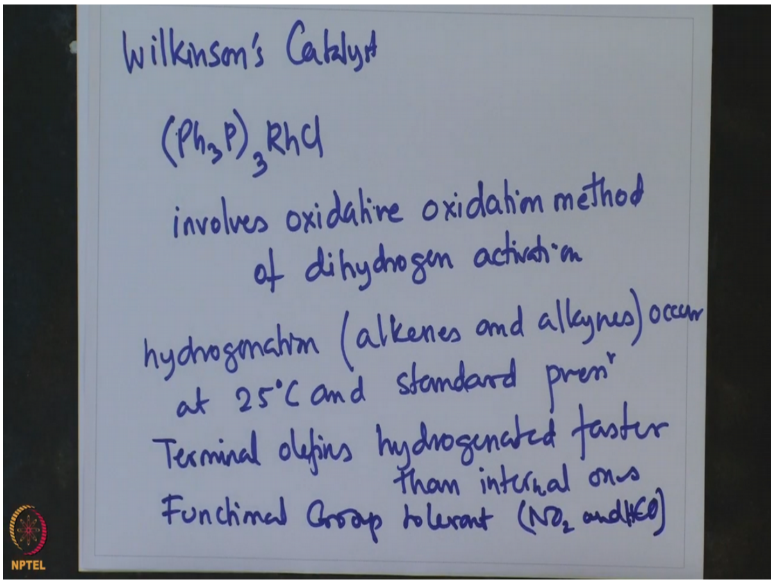

Wilkinson's Catalyst

$(Ph_3P)_3RhCl$

involves oxidative oxidation method of dihydrogen activation

hydrogenation (alkenes and alkynes) occur at 25°C and standard presr

Terminal olefins hydrogenated faster than internal ones

Functional Group tolerant (NO_2 and HCO)

So, catalyst which is of the formula Ph 3 P whole 3 rhodium chloride and it involves the way it functions it involves oxidative oxidation method of dihydrogen activation and hydrogenations of alkene and alkynes occurs at 25 degree centigrade under standard pressures, hydrogenation of alkenes and alkynes occur at 25 degree centigrade and standard pressure.

So, what does that mean is that, this is a highly active catalyst which can not only activate dihydrogen, but also add across this unsaturated substrates like alkene and olefin at a very mild condition of 25 degree centigrade that is the room temperature and standard pressure. And the catalyst also carries out terminal double bond faster than internal ones. Terminal olefins hydrogenated faster than internal ones.

This also is a functional group tolerant; groups like NO 2 and C CHO. So, function group tolerant. And this cis addition the dihydrogen addition happens in cis fashion. So, cis fashion. So, these are few attributes of this homogeneous catalyst which is this Wilkinson's catalyst. Wilkinson's catalyst is the rhodium 1 triphenylphosphine rhodium chloride, tris triphenylphosphine rhodium chloride.

It involves oxygen activation by oxidative addition method. This oxidative addition occurs in a cis fashion. The hydrogenation conditions are really mild at 25 degree centigrade and standard pressure. So, that gives a very good efficiency for this catalyst. Hydrogenations of terminal double bond occur faster than hydrogenation of internal olefins catalyst is functional group tolerant.

And dihydrogen addition occurs in a cis fashion. So, these are a key attributes of this Wilkinson's catalyst which is nothing but alkene and olefin hydrogenation catalyst. And then, we are going to look at the mechanistic pathway following which this Wilkinson's catalyst function.

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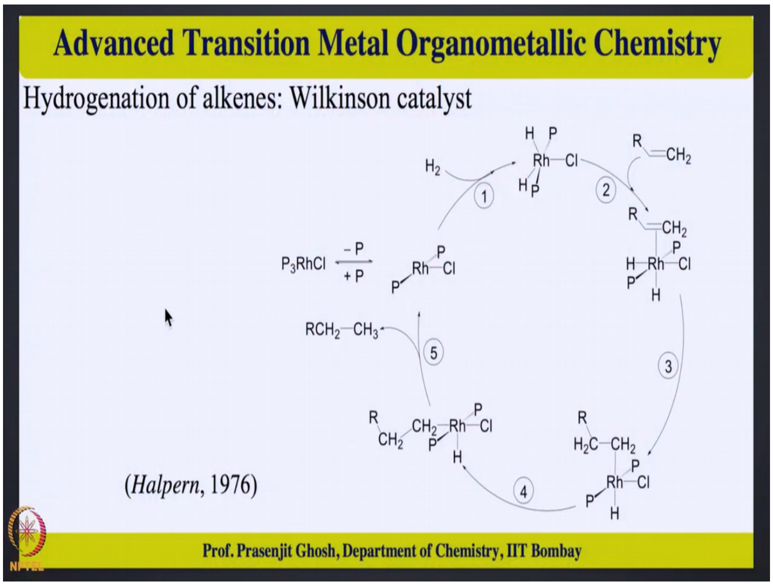

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Hydrogenation of alkenes: Wilkinson catalyst

(*Halpern*, 1976)

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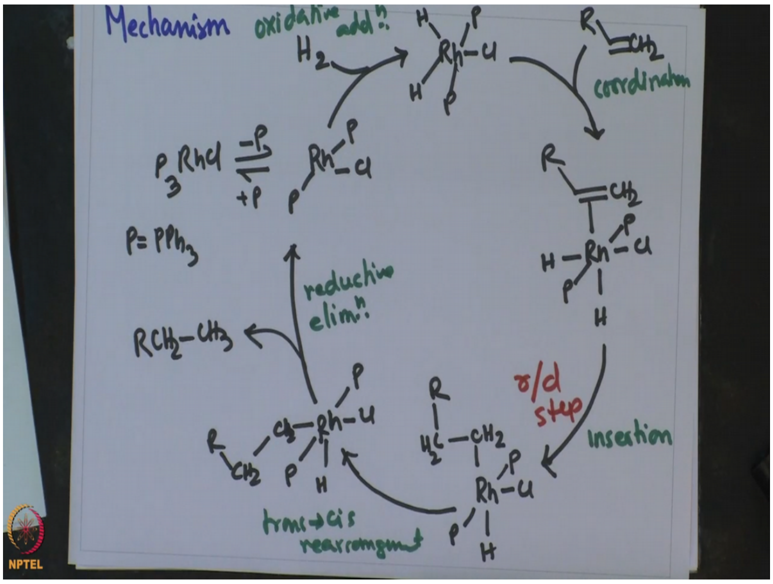

So, the catalysis starts from R 3 P 3 Rh Cl. P = triphenylphosphine that loses a phosphine to give rhodium P, P, chloride. So, this adds dihydrogen. So, this is the oxidative addition to give rhodium chloride P, phosphene, phosphene, H, H. So, this step is the oxidative addition step. And subsequent to that, the oxidative addition is the olefin coordination R CH 2 giving R, rhodium, P, P, Cl, H, H.

So, this is nothing but the olefin activation step or can be said as coordination step. Subsequent to this coordination the migration of the olefin to this rhodium hydride bond, leading to the formation of rhodium alkyl reagents are formed. So, this olefin migrates into one of the 2 rhodium hydride bond to give this rhodium alkyl moiety. So, this is, this step is the migratory insertion or called the insertion step subsequent to the formation of rhodium alkyl.

The next step involves this rearrangement of this cis and trans geometrical isomers where this rhodium hydride phosphine compound rearranges to P CH 2 CH 2 R. So, this is a, can be thought of as a geometrical rearrangement cis-trans rearrangement. And this step is called the cis-trans rearrangement step. Cis rearrangement step, to finally the reductive elimination step where this alkyl and hydrogen reductively eliminates to give the hydrogenated alkane R CH 2 CH 3 along with the formation of the starting initiating precursor which is P rhodium P 2 CL.

So, this is the reductive elimination step. Now, of these step, this third step is the rate determining step which is the insertion of the olefin into the rhodium hydride bond. So, this is the rate determining step which has been proposed based on computational study, that this migration of coordinated olefin to a rhodium hydride bond is most likely be the rate determining step of this catalytic cycle.

So, what one sees that, this Wilkinson's catalyst is a good hydrogenation catalyst which can function at a room temperature and standard pressure. And not also it does hydrogenation of terminal olefin faster than the internal olefin. And the mechanism consists of 4 elementary step. The first one being oxidative addition, followed by coordination, then insertion, then 5 steps. The catalytic cycle consists of 5 elementary step.

First one is oxidative addition, coordination, insertion, cis-trans rearrangement and reductive elimination. Of the different step, the third step which involves migratory insertion of the coordinated olefin on a rhodium hydride bond is supposedly the rate determining step of this reaction. Now, 1 important attribute of this Wilkinson's catalyst that it can carry out hydrogenation of terminal as well as internal olefin. However, the internal olefins and is hydrogenated at a slower rate.

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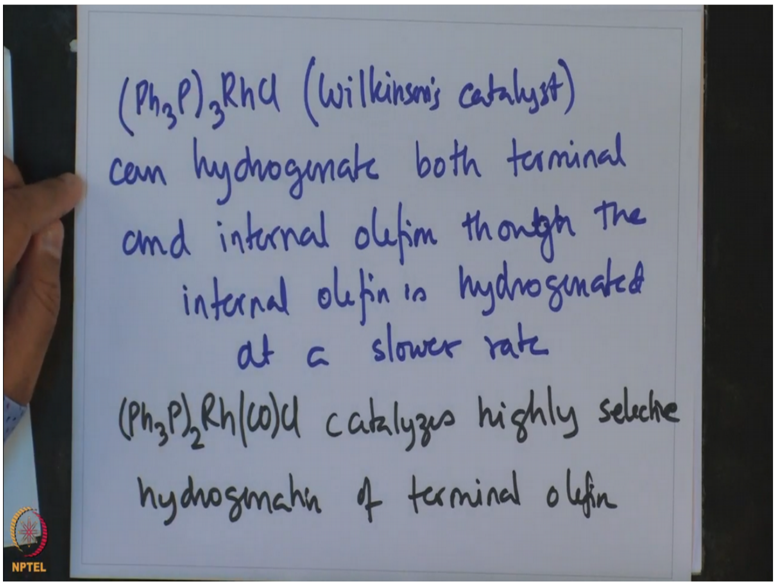

$(Ph_3P)_3RhCl$ (Wilkinson's catalyst)
can hydrogenate both terminal
and internal olefin though the
internal olefin is hydrogenated
at a slower rate

$(Ph_3P)_2Rh(CO)Cl$ catalyzes highly selective
hydrogenation of terminal olefin

Ph 3 P whole 3 rhodium chloride which is Wilkinson's catalyst can hydrogenate both terminal and internal olefins though the internal olefin is hydrogenated at a slower rate. However, this another catalyst which has 2 P Ph 3 rhodium carbonyl chloride catalyses highly selective hydrogenation of terminal olefin.

So, this is an interesting observation that if one modifies the catalyst from Wilkinson's catalyst that has triphenylphosphine and 1 chloride attached to rhodium which can hydrogenate both internal as well as a terminal olefinic bonds to bis triphenylphosphine rhodium carbonyl chloride which catalyses highly selective hydrogenations of only termination olefin.

Though Wilkinson catalyst is extremely good catalyst with high efficiency, one of the drawbacks of Wilkinson's catalyst is a its selectivity. And that can be achieved if one modifies the catalyst update to 2 triphenylphosphine rhodium carbonyl chloride which can selectively do hydrogenation of terminal alkynes.

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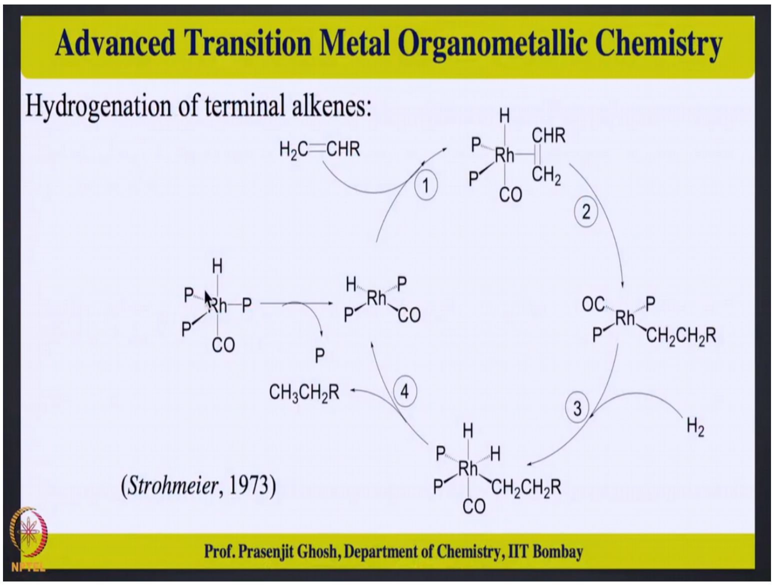

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Hydrogenation of terminal alkenes:

(*Strohmeier*, 1973)

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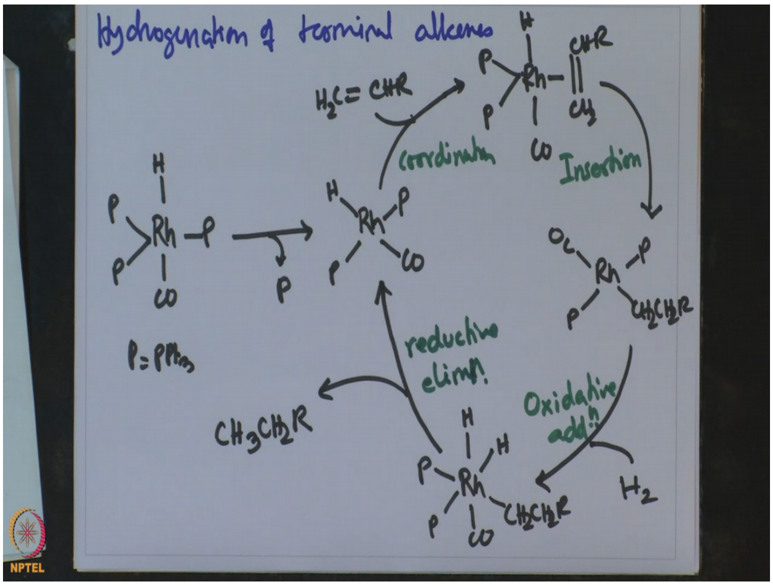

And this is explained by this catalytic cycle rhodium, P, H, CO, P, P. P = PPh 3 loses 1 triphenylphosphine to give this rhodium square planar complex P, P, CO, hydrogen. So, the first is that the terminal olefin coordinates to this square planar complex to give a 5 membered P, P, rhodium, CH 2, CHR, H, CO. So, this is a coordination step followed by this insertion of the coordinated olefin to the rhodium hydride bond giving rhodium P, P, CH 2, CH 2 R and CO.

So, this step is the insertion step followed by hydrogen addition which is an oxidative addition. This addition occurs in a cis fashion as has been mentioned for the Wilkinson's catalyst and proceeds in the same way. So, we have this oxidatively added cis dihydride moiety attached to hydro rhodium CH 2 CH 2 R, CO and then 2 phosphine in cis orientation.

And that, reductively eliminates to give the desired product CH 3 CH 2 R and giving back the initial starting active species which is bis phosphine rhodium hydrochloride.

So, what we see that this selective hydrogenation of terminal kind can be carried out with this catalyst of rhodium bis phosphine carbon monoxide hydride. And that it can hydrogenate terminal alkenes in 4 elementary step. The first one involves coordination of the olefin, the second one involves insertion of the coordinated olefin to the rhodium hydride bond. Then subsequently, oxidative addition of a dihydrogen molecule, followed by reductive elimination to give the desired reduced product.

So, with this, I would like to conclude today's discussion on hydrogenations of alkenes. As mentioned in the beginning of the class, hydrogenation of alkenes is an, yet another big discovery which is practiced in the industrial scale. And hydrogenation of alkene is nothing but the complementary of alkene oxidation reactions which 2 are also equally important from industries point of view.

We have looked at the types of hydrogenation reactions, hydrogen activation pathways. And what we had seen that the hydrogen activation pathways proceeds in 3 ways. First is the homolytic cleavage, second is heterolytic cleavage of dihydrogen and lastly it occurs by oxidative addition. And then, we have looked into 1 important example of hydrogenation of olefin reaction, particularly using Wilkinson's catalyst which can carry out hydrogenations of terminal, as well as internal olefins and alkynes at mild conditions and normal pressure.

And then, though the internal olefins are hydrogenated at a lower speed; and then, we looked into this catalyst which is a bis triphenylphosphine rhodium carbonyl hydride which can carry out this hydrogenation of selectively terminal olefins in the similar catalytic pathway. So, with this, I would like to conclude today’s discussion on hydrogenation of olefins. We are going to talk more about hydrogenation of alkenes for chiral, achiral as well as chiral system when we meet next.

I sincerely thank you once again for patiently listening to me in this lecture. And I look forward to being with you in the next lecture when we complete the remaining part of hydrogenations of olefin reactions. Thank you.