Advanced Transition Metal Organometallic Chemistry
Prof. Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology - Bombay

Module - 10
Lecture - 48
C-Heteroatom Coupling: Hydrosilation

Welcome to this course on Advanced Transition Metal Organometallic Chemistry. As a part of our discussion on carbon-heteroatom coupling, we have been discussing various types of such reactions starting with carbon-boron coupling which we had seen in hydroboration. And then, we have seen C-N coupling in which we have looked into hydroamination as well as arene imination reactions.

And proceeding further along the line, we are going to take up another interesting reaction which is hydrosilylation reaction to be talking about. This hydrosilylation reaction is an addition reaction similar to that of hydroboration or hydroamination reaction that the addition of silicon hydrogen bonds to alkenes or alkynes.

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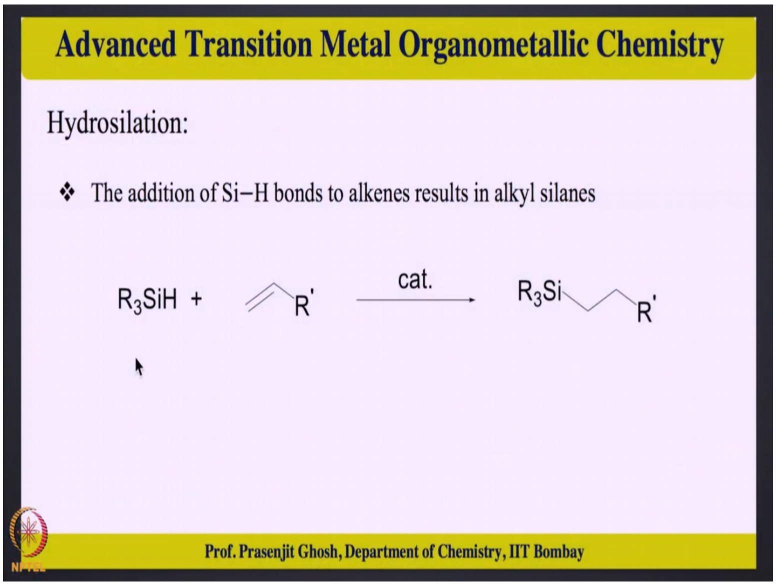

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Hydrosilation:

- The addition of Si–H bonds to alkenes results in alkyl silanes

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

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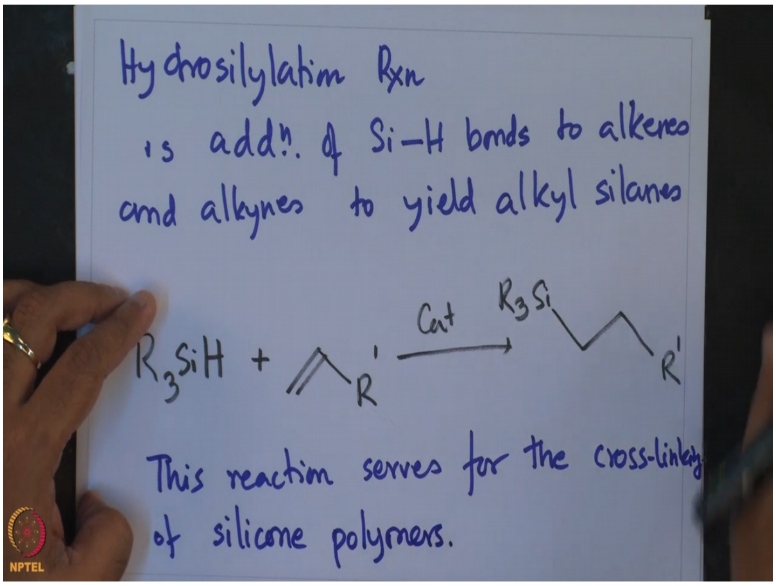

Hydrosilylation Rxn
is addn. of Si–H bonds to alkenes and alkynes to yield alkyl silanes

$R_3SiH + \text{alkene-}R' \xrightarrow{Cat} R_3Si\text{–CH}_2\text{CH}_2\text{–}R'$

This reaction serves for the cross-linki
of silicone polymers.

Reaction is addition of silicon hydride hydrogen bonds to alkenes and alkynes to yield alkyl silanes. Now, this is a very general method, a most trusted method for preparation of alkyl silanes. And this is exemplified by this reaction which is given over here. Trialkyl silane R 3 Si H + olefin in presence of a catalyst giving R dashed Si R 3. So, similar to the other addition reactions that we have been talking about, hydrosilylation also is a effective method to form carbon silicon bonds to by addition of Si H bonds to alkenes and alkynes.

And this also serves as a cross linking of silicone polymers. So, one interesting utility is that this reaction serves for the cross linking of silicone polymers. Now, this hydrosilylation can be done on other unsaturated bonds like, apart from carbon olefinic, it can also be, hydrosilylation can be performed on C-C, C-N, C-O, N-N, N-O and C triple N bond.

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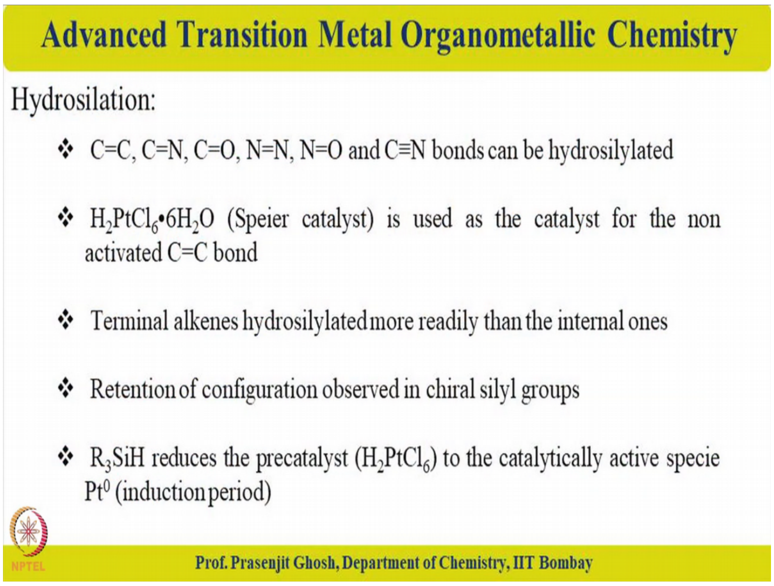

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Hydrosilation:

- C=C, C=N, C=O, N=N, N=O and C≡N bonds can be hydrosilylated
- $H_2PtCl_6 \cdot 6H_2O$ (Speier catalyst) is used as the catalyst for the non activated C=C bond
- Terminal alkenes hydrosilylated more readily than the internal ones
- Retention of configuration observed in chiral silyl groups
- R_3SiH reduces the precatalyst (H_2PtCl_6) to the catalytically active specie Pt^0 (induction period)

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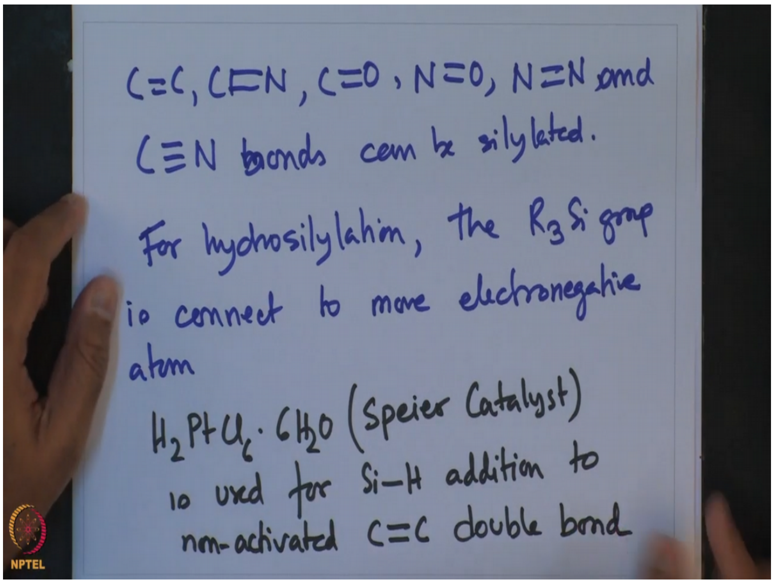

$C=C$, $C=N$, $C=O$, $N=O$, $N=N$ and $C\equiv N$ bonds can be silylated.

For hydrosilylation, the R_3Si group is connect to more electronegative atom

$H_2PtCl_6 \cdot 6H_2O$ (Speier Catalyst) is used for Si–H addition to non-activated $C=C$ double bond

So, this is kind of very interesting information that hydrosilylation can be done on C-C, C-N, C-O, C-O, N-O, N-N, C-N and C triple bond N, can be silylated. For hydrosilylation, the R 3 Si group is connected to more electronegative atom. So, in this case, for C-N the Si 3 R 3 Si would be on nitrogen; for C-O the R 3 Si would be on oxygen and hydrogen will be on carbon, is same over here. For N-O R 3 Si will be on nitrogen and C-N R 3 Si will be on nitrogen.

So, this is an interesting observation. And for there is a catalyst which is called a spicers catalyst which is the catalyst of choice for silicone hydrogen addition to non-activated double bond. And the complex is H 2 Pt Cl 6 dot 6 H 2 O. This is called speier catalyst. This is the catalyst, is used for Si H addition to non-activated C double bond C, double bond. And in terms, now in terms of the olefinic addition, there is another interest observation is that the terminal alkynes are silylated more readily than the internal olefins.

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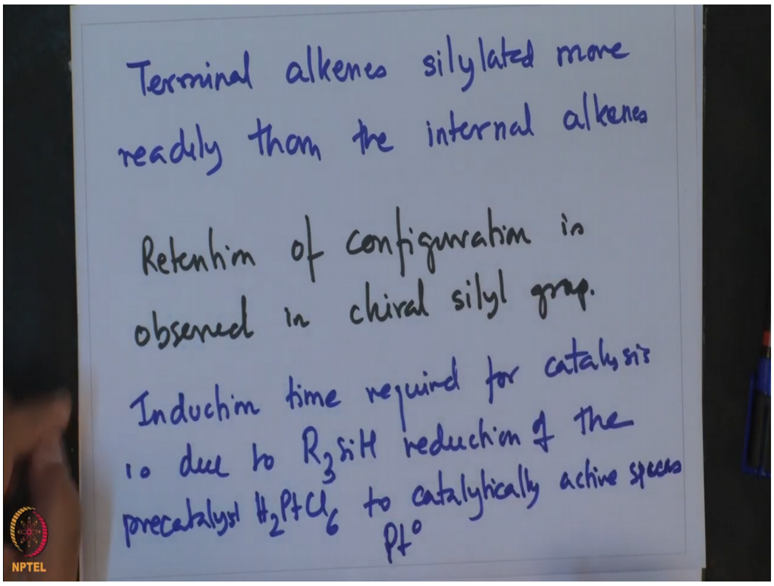

Terminal alkenes silylated more readily than the internal alkenes

Retention of configuration is observed in chiral silyl grp.

Induction time required for catalysis is due to R_3SiH reduction of the precatalyst H_2PtCl_6 to catalytically active species Pt^0

Terminal alkenes silylated more readily than the internal ones, alkenes. The another interesting thing is that, the retention of the chiral silyl group retain their configuration. So, retention of configuration is observed in chiral silyl group. So, that is a; of configuration is observed in chiral silyl group. And the catalytic active species is a palladium 0 species which is formed from the H 2 Pt Cl 6 upon reduction with R 3 Si H.

And there is a time required to do for this reaction to happen and which results in a long induction time. The induction time required for catalysis is due to R 3 Si H reduction of the precatalyst H 2 Pt Cl 6 to catalytically active species which is just Br platinum 0. So, this is an interesting observation that this hydrosilylation using speier catalyst H 2 Pt Cl 6 6 H 2 O does not really initiate right from the start.

So, there is a time in which the catalyst is formed from the precatalyst. And this the active species is platinum 0 and they are formed by the reaction of this platinum Pt Cl 6 H 2 by this reducing agent which is R 3 Si. So, in that strict sense, that since platinum 0 is carrying out this catalysis, this is not strictly a homogeneous catalyst catalysis that we have been discussing all the way. So, the catalytic cycle is given as follows.

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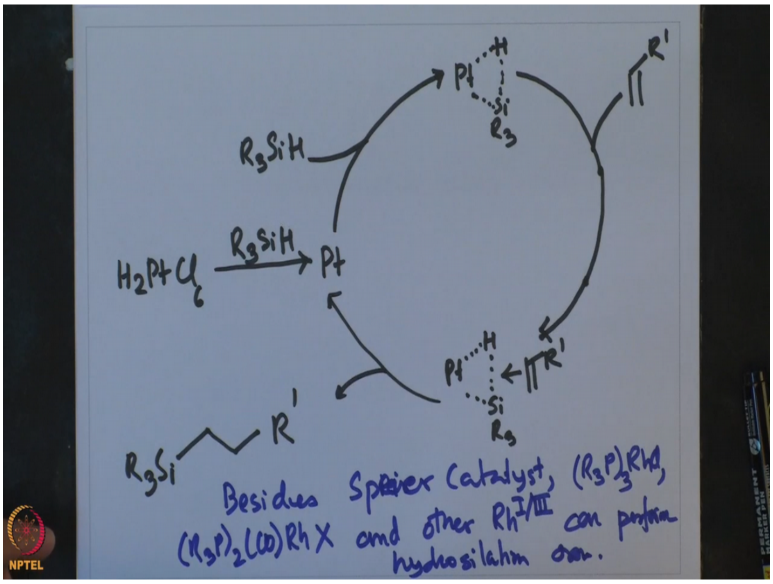

Besides Speier Catalyst, $(R_3P)_3RhCl$, $(R_3P)_2(CO)RhX$ and other $Rh^{I/III}$ can perform hydrosilation rxn.

H 2 Pt Cl 6 in presence of R 3 Si H giving platinum 0. And this platinum 0 then oxidatively add R 3 Si H to give this platinum based sigma complex of the type Si R 3 and then to this olefin R dashed attacks to give this olefin bound complex. Olefin attacks from the external side Si R 3, R dashed to give the corresponding product which is R dashed Si R 3 along with the regeneration of the platinum 0 species.

Now, this hydrosilylation reaction thus composes of 3 elementary steps. The first is the formation of the sigma complex. To that, second step involves the attack of the olefin to the sigma complex leading to the elimination of the product in the third step which is silylated alkane along with the generation of the platinum. Now, this, there are evidence of this formation of the eta 2 coordinated silyn complex.

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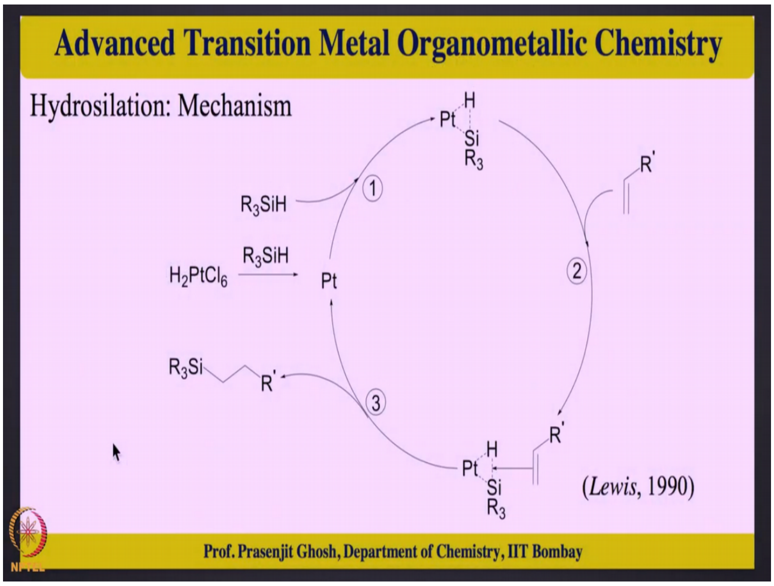

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Hydrosilation: Mechanism

(*Lewis*, 1990)

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So, this was the characterised by Kubas which gives credibility to this computed to this proposed catalystic cycle. So, apart from speier catalyst, the other catalyst which can perform hydrosilylation reactions are; besides speier catalyst R 3 P H 3 rhodium chloride. R 3 P whole 2 CO rhodium X and other rhodium I and III complexes can perform hydrosilylation reaction. Now, so this says that there are, one thing crucial about this hydrosilylation reaction in the platinum catalysed hydrosilylation reaction is the formation of this activated eta 2 silyn complex of platinum, which then undergoes this attack from the olefin.

The other interesting thing is, this addition of this platinum silyl hydrogen bond to the product. If one looks at the regio chemistry and it shows that this is a anti-markovnikov type addition where the hydrogen ends up on the most substituted carbon and the silicon ends up on the least substituted carbon. So, this is a platinum catalysed hydrosilylation reaction thus undergoes addition in a anti-markovnikov fashion as one may see.

So, we had seen this hydrosilylation reactions, how it proceed to give this silyl alkanes. And then, we are going to discuss in this context another interesting reaction which is dehydrogenative coupling. So, dehydrogenative coupling is another kind of reaction using silyl reagents that leads to the formation of silicon-silicon bonds result in organopolysilanes.

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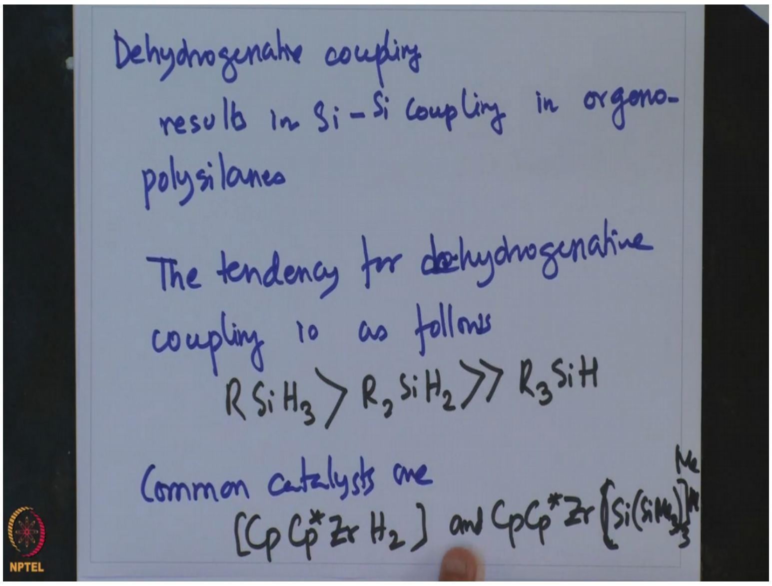

Dehydrogenative coupling result in Si – Si coupling in organo-polysilanes

The tendency for ~~de~~dehydrogenative coupling is as follows

$RSiH_3 > R_2SiH_2 >> R_3SiH$

Common catalysts are

$[CpCp^*ZrH_2]$ and $CpCp^*Zr\{Si(SiMe_3)_3\}Me$

So, dehydrogenative coupling results in silicon-silicon coupling in organopolysilane. The tendency to, towards degenerative dehydrogenative coupling is as follows. The tendency for dehydrogenative coupling is as follows. Which is, R Si H 3 R 2 Si H 2 > R 3 Si H. And the catalyst used in this cases are mixed CP type, very interesting catalyst. They are the catalyst used, common catalyst are mixed with the complexes, mixed with the metal hydride complexes like Cp Cp star zirconium H 2 and Cp Cp star zirconium Si Si Me 3 whole 3 Me. Okay.

So, these are a very common unusual type of complexes. One is Cp Cp star zirconium hydride dihydride. And the other is Cp Cp star zirconium Si Si Me 3 whole 3 Methyl. So, are used for dehydrogenative coupling. And we are going to take a look at the mechanism for this dehydrogenative coupling. And the active species of, for this complexes are metal hydride.

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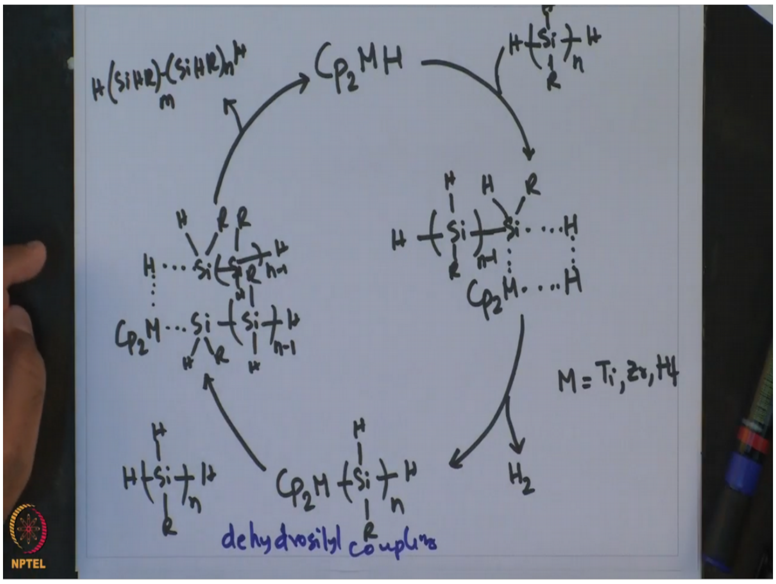

So, this is the Cp 2 M H where are the 2 cyclopentadienyl ligand. And then, the first reaction is the addition of the silyn H, Si, H, R, H. This silyn comes and adds and form a 4 membered sigma bond transition state. So, this is given as Cp 2 M, H, Si, H, R, H, then Si, H, R, H, whole n – 1. And these, since it is dehydrogenative coupling loses hydrogen this hydrogen H 2.

And the M over here is titanium, zirconium, hafnium to give this bis Cp Cp 2 M, Si, H, R, H, n silyn complex which again reacts with another molecule of H, Si, H, R, H, n in a similar sigma bond metathesis fashion to give this molecule Cp 2 M, Si, H, R, Si, R, H, H, n – 1, H, Si, H, R, Si, R, H, H, n – 1. Now, these will eliminate this couple product which is H Si H R m and Si which is Si H R n H along with this generation of the metal hydride bond.

So, this is a interesting reaction which initiates a condensation mechanism based on sigma bond metathesis and this is called dehydrosilyl coupling. So, this step is called dehydrosilyl.

So, dehydrogenative coupling results in the formation of the silicon-silicon bond. And by a mechanism which undergoes reactions in which, similar to that of the sigma bond metathesis.

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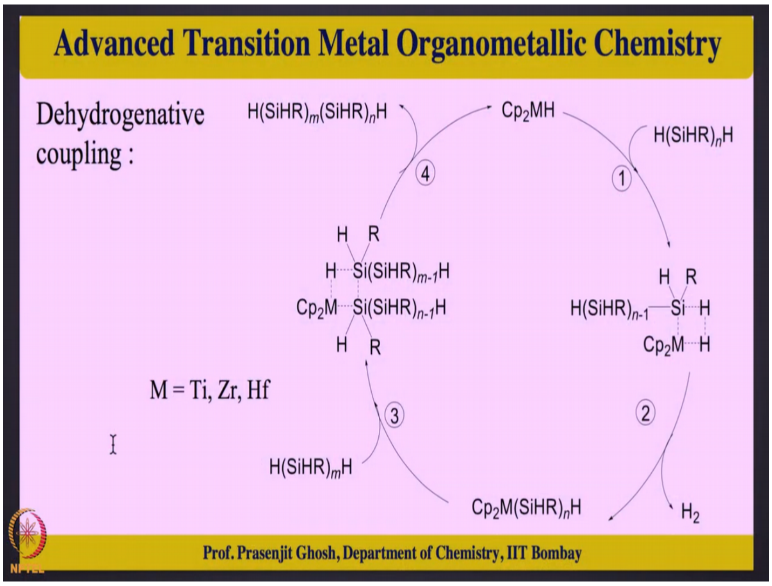

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Dehydrogenative coupling :

$M = Ti, Zr, Hf$

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

It also eliminates hydrogen gas as a part of this dehydrogenative coupling. So, with this I am going to conclude today's lecture. Today's lecture had been on hydrosilylation reaction. Has mostly been in continuation with our earlier discussions on various kinds of carbon-heteroatom bond forming reaction. And in that front, we had earlier on discussed C-N coupling, then C-B coupling in terms of hydroboration reaction.

And in this class, we have looked into this hydrosilylation reaction. To recapitulate what has been spoken up, spoken on today this hydrosilylation reaction is a very trusted method for producing alkyl silanes. And this is nothing but the addition of Si H bonds to alkenes and alkynes. Hydrosilylation reaction is also has a larger scope and utility as it can be extended to other carbon-heteroatom unsaturated bonds like C-O, C-N, N-N, C double bond N, C triple bond N.

All of these moieties can by hydrosilylated. And in such cates cases it has been found that R 3 Si trialkyl silyl moiety resides with the most electronegative atom. As far as the hydrocilylation of non-activated silanes, the platinum 4 catalyst called speier catalyst whose formula is H 2 Pt Cl 6 6 H 2 O is the catalyst of choice. And the mechanism sort of have been discussed in detail. And what it turns out that platinum 4 species in speier catalyst get reduced to platinum 0 in presence of trialkyl silane.

And then, this trialkyl silane reacts with this platinum 0 species active species to form a sigma complex of this silane and to which the olefin adds attacks and then results in the formation of the alkyl silane along with the regeneration of the platinum. This sigma complex has been structurally characterised by Kubas which sort of give evidence in favour of the proposed catalytic mechanism.

And there are other rhodium 1 and rhodium 3 complexes apart from the platinum 4 complex that we just discussed in the context of speier catalyst which can also carry out this hydrosilylation reaction. There are few things, the hydrosilylation reaction is preferred for terminal olefins, as well as opposed to internal olefins. And that, the chiral centre at the silicon undergo retention in configuration during this hydrosilylation reaction.

Going further, we have discussed another important reaction in this context. And this is about the dehydrogenative coupling. And the dehydrogenative coupling of this silyl reagent leads to the formation of silicone-silicon bond along with the regeneration of hydrogen gas. We have also looked into the mechanism of, for this dehydrogenative coupling. And we have seen that the mixed bis Cp complexes of titanium, zirconium and hafnium either dihydride or silyl methyl derivatives of this complexes are excellent catalyst for this dehydrogenative coupling.

As far as the active species for this dehydrogenative coupling are concerned, this is usually a bis Cp metal hydrogen. And then, it adds with silyl silane and in a 4 sigma metathesis fashion along with the regeneration of hydrogen gas to give a metal hydride silyl species which then again adds to a second molecule which sort of, in the same sigma metathesis fashion which sort of leads to the formation of the silane-silane bond silicon-silicon bond along with the generation of this metal hydride species.

So, this also is a 4 elementary step sequence and this is a interesting catalytic mechanism in which this silicon-silicon disilyn bonds are being formed. So, with this we come upon on to the end of this discussion on hydrosilylation reaction. We have seen that this is been an interesting reaction with lot of scope and the breadth and also lot of application of this reaction. And as a extension of that we have looked into dehydrogenative coupling where silicon-silicon bonds are formed in organopoly silanes.

So, with this I once again thank you for patiently being with me in this class and listening to this lecture. And we are going to take up another new dimension of organometallic catalysis, these are oxidation reactions particularly olefin oxidation in the next class. So, we have, with this hydrosilylation we have a sort of closed our discussion on a metal heteroatom bond forming reaction in general.

And then, move on to the metal organometallic complexes catalysed oxidation reaction. And to begin with, we are going to be looking at olefin oxidation reaction in the next class. Till then, goodbye and thank you.