Advanced Transition Metal Chemistry
Prof. M.S Balakrishna
Indian Institute of Technology, Bombay

Lecture - 43
Oxidative Addition and Reductive Elimination Reactions

Hello everyone. Once again, I welcome you all to MSB lecture series on transition metal chemistry. I started discussion on oxidative addition and reductive elimination reactions and in my previous lecture I showed a scheme in which I considered many substrate molecules which can undergo oxidative addition or which perform oxidative addition on a metal and let me continue from where I had stopped.

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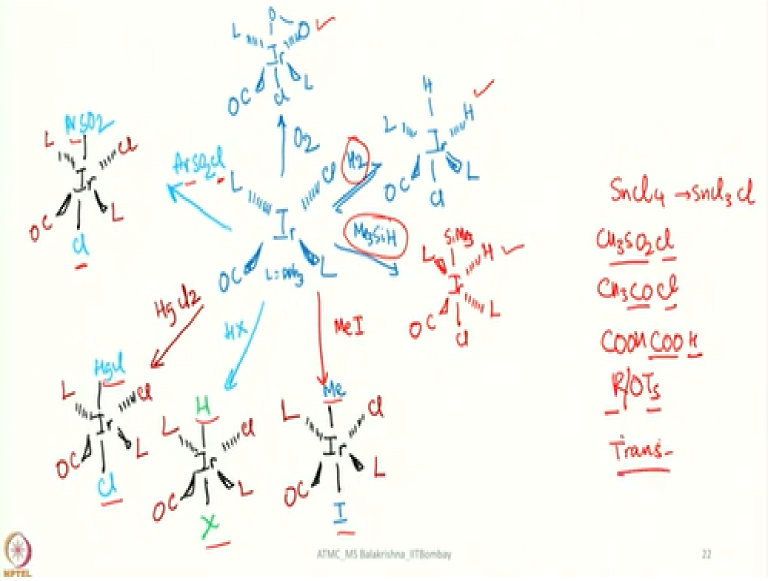

So, this is the scheme yesterday I wrote. You can see the difference between few substrates and their addition on to the metal centre. For example, if you see hydrogen, hydrogen is added sideways, that is in a cis manner, and then if you look into oxygen that is also added in a cis fashion. So, that means oxygen or hydrogen when they are added first, they go and sit something like this, and then they split into two anionic ligands.

And then if you just look into Me$_3$Silane, it also follows the same sequence and then these three, but look into other reactions here. So, just to differentiate the chlorine or chloride ligand that is coming from the substrate molecule and also one that is already present I have given different colours. Let us look into this one here. If you see, this one is coming here, and this one is coming here.

That means they are added trans positions on iridium moiety and then if you look into mercury chloride again same thing it is added here and here. And then if you look into typical addition of hydrogen halide they are going to opposite ends and same thing is true in case of methyl iodide that means why that is happening like that. It is not just with these substrates if you consider substrates such as $SnCl_4$ this can also add like $SnCl_3$ and Cl.

And then if you consider CH_3SO_2Cl this also adds this one, this one separately transpositions on iridium here. If CH_3COCl these two fragments will be added after this bond is broken, C—Cl bond is broken. And if you take even this one, so this will be added like that or if we consider this one, this splits and this is added and this is added separately and then trans addition will be there.

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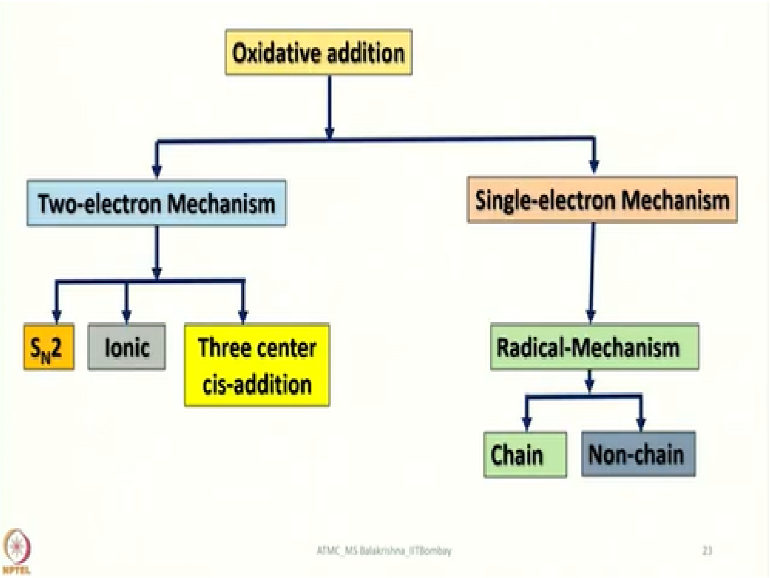

Oxidative addition

Two-electron Mechanism

Single-electron Mechanism

S_N2

Ionic

Three center cis-addition

Radical-Mechanism

Chain

Non-chain

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23

So, with this now let us try to understand the different methods or mechanism through which one can perform oxidative addition reactions. I have shown here oxidative addition mechanism can be broadly split into two categories. One is two electron mechanism, another one is single electron mechanism. Within two electron mechanism you can notice three different type of oxidative addition reactions one is S_N^2, one is ionic, one is three centred cis addition.

Of course, the moment the terms you see here you can correlate this one with we saw few substrate molecules in the previous scheme. The substrate molecules which are added onto the metal in a three centred cis concerted manner is called three centred addition. In case of single electron mechanism, we can come across radical mechanism and also radical mechanism can be further split into chain and non-chain mechanisms.

So, now let us try to understand these mechanisms one at a time. To begin with let us focus our attention on three bond concerted cis addition. Whatever the mechanism I have written here has to do something with the class of substrate molecules we are choosing. You recall, I made a statement that all substrate molecules can be divided into three classes one is non-electrophilic and the second one is non-electrophilic intact and the third one is electrophilic.

So, whatever the substrate molecules you are thinking that they can do or perform oxidative addition on a metal will fall into one of these categories. So, now with this information let us look into the mechanism of addition through three centred concerted addition in which the two anionic ligands will go to cis positions on the metal centre. So, now that means the oxidative addition reactions can be classified into broadly three types.

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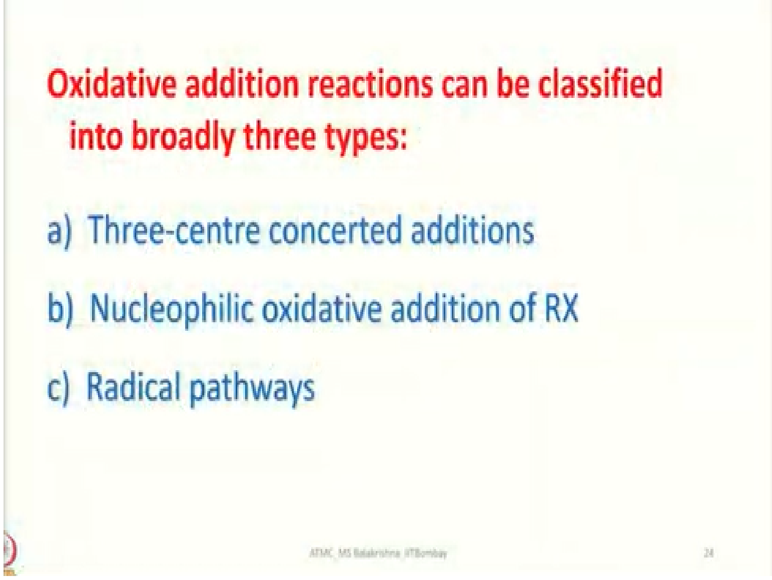

Oxidative addition reactions can be classified into broadly three types:

a) Three-centre concerted additions

b) Nucleophilic oxidative addition of RX

c) Radical pathways

One is three centred concerted additions, nucleophilic oxidative addition of RX that means polar molecules, and radical pathways. So, that means when we perform oxidative addition substrates molecules while adding follow one of these pathways. So, let us consider three centre concerted addition.

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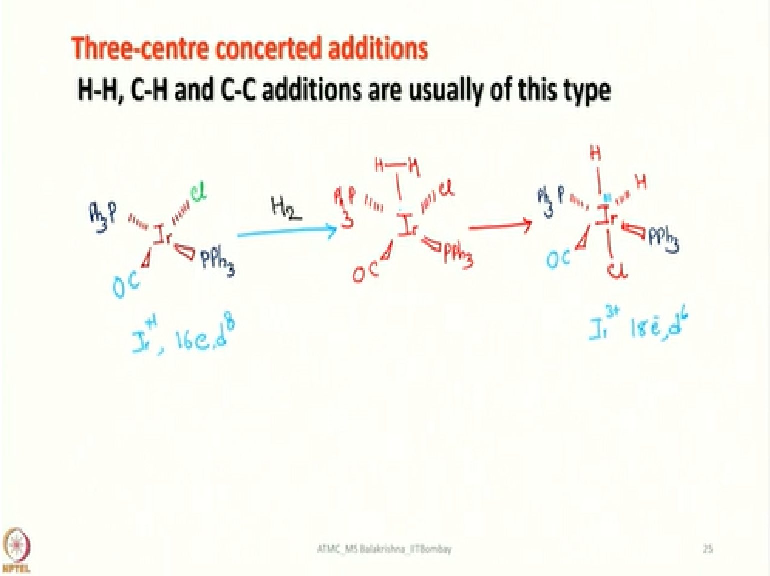

Three-centre concerted additions

H-H, C-H and C-C additions are usually of this type

Here whether you consider H-H bond, whether you consider C-H bond or C-C bond all these additions are taking place in this type of mechanism. They have very similar one also I wrote many other including BH, SiH etcetera. Let me write a typical three centre concerted addition again considering Vaska's compound and simplest molecule H_2 because it is very vital in organic reactions. So, we start here iridium is in plus one state and this is a 16 electron species and start with is a d^8 species.

Now iridium is in plus 3 and if you count electrons, it is 18 electron species, and it is a d^6 system. So, that means this is what exactly happens here. H_2 before it is getting ready for oxidative addition, it has to be pre-coordinated to the metal centre in this fashion and then it abstract two electrons from iridium to generate two hydride anions and they will be added, so here oxidative addition is complete.

If you see here, this intermediate this one, we have d^8 system. we have still iridium is in plus one state and then this is an 18 electron species here, this is fine. Now let us look into two aspects, one is electronic aspect and another one is thermodynamic aspect. So, how thermodynamics can explain formation of this two iridium hydride bonds by breaking one H-H bond.

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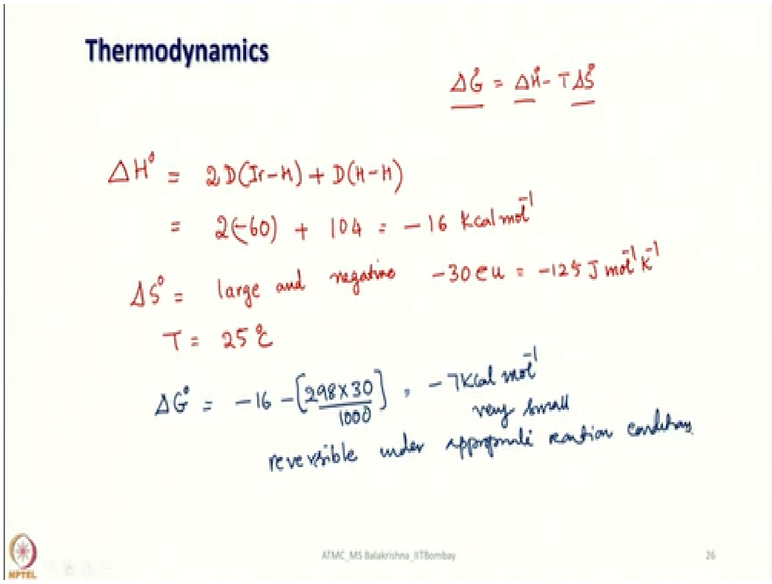

Thermodynamics

$$\underline{\Delta G^{\circ}} = \underline{\Delta H^{\circ}} - T\underline{\Delta S^{\circ}}$$

$$\Delta H^{\circ} = 2D(\text{Ir}-\text{H}) + D(\text{H}-\text{H})$$

$$= 2(-60) + 104 = -16 \text{ kcal mol}^{-1}$$

$\Delta S^{\circ} =$ large and negative -30 eu $= -125$ J mol^{-1} K^{-1}

$T = 25$ °C

$$\Delta G^{\circ} = -16 - \left[\frac{298 \times 30}{1000}\right] = -7 \text{ kcal mol}^{-1}$$

very small

reversible under appropriate reaction conditions

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26

So, here you should remember one equation that you are all familiar with. So, now we have to find out these entities from this oxidative addition reaction to calculate the value of free energy. So, in this reaction first let us look into ΔH^{o}. So, to in order to calculate this one what we have to see is: one H-H bond is broken and we have formed two new iridium to hydrogen bonds.

Formation of 2 iridium to hydrogen bonds and then breaking of one H-H bond we should consider here. For this one if you put the values that are available this is -16 k mol^{-1}. So, now we have to calculate ΔS, of course if you look into that reaction ΔS is large and negative because H_2 is disappearing and, in that place, we are getting a solid, ΔS this is very large and negative.

So, this is -30 entropy units or this is equivalent to minus 125 J mol^{-1}K^{-1}. Of course temperature is 25 ^{o}C. Now if we incorporate this to calculate ΔS G what we get is -7 kcal mole^{-1}. So, what does it indicate? If you look into ΔG, it is very small that means if the ΔG value is anywhere between ± 10 to 15 kilo calories, with appropriate reaction condition one can think of reversing that reaction.

That means the way we add H_2 through oxidative addition we can get rid of H_2 through reductive elimination. That means reaction may be made reversible under appropriate condition. So, that means by using an appropriate reaction condition we should be able to reverse this reaction. Once if we get an idea that we can reverse the reaction, then the catalytic application automatically comes into the picture that means here this reaction can be used.

whether we are bringing back the same H_2, we are taking the H_2 source to bring back the complex that was underwent oxidative addition, that is a different thing. Always one can do that, what one can get from these thermodynamics calculations is this reaction can be reversible. Now let us look into the kinetics involved in this one.

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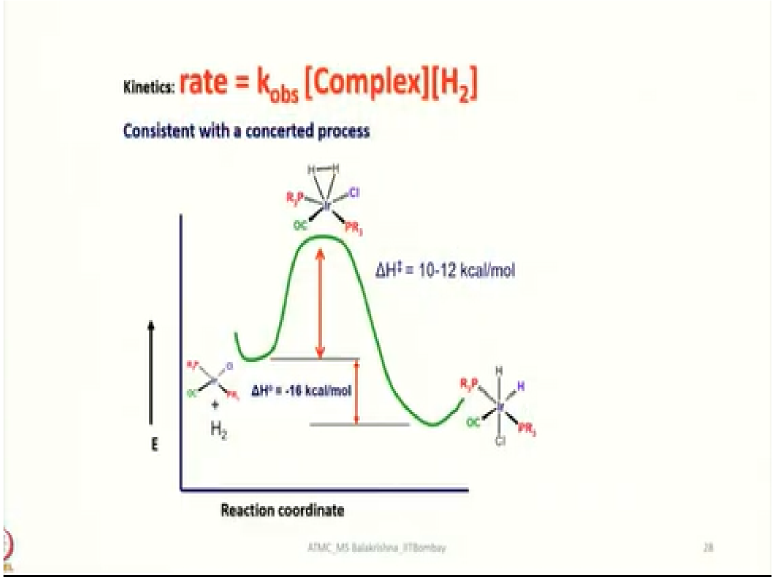

Kinetics: rate = k_{obs} [Complex][H_2]

Consistent with a concerted process

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Of course, here the rate depends on the concentration of complex as well as H_2 substrate molecule here. This rate constant is consistent with a concerted process. You can see here this is the reaction coordinates I have shown in this one to start with, where we have iridium(I) complex and then of H_2 is added. It forms a transient species where it is still a neutral ligand binding through these two electrons, between two H atoms, and then enthalpy is for this one is about 10 to 12 kcal mol^{-1}.

Once hydrogen addition is completed, we get this iridium 3 complex here this is quite stable and the difference is about -16 k mol^{-1}. So, in this one overall reaction, ΔG is about minus 7 kilo calories per mole. So, these thermodynamic aspects tell us about the reaction and whether it is exothermic or endothermic and if the ΔG of that particular reaction or conversion is well within 10 to 16 kilo calories per mole it can be made reversible.

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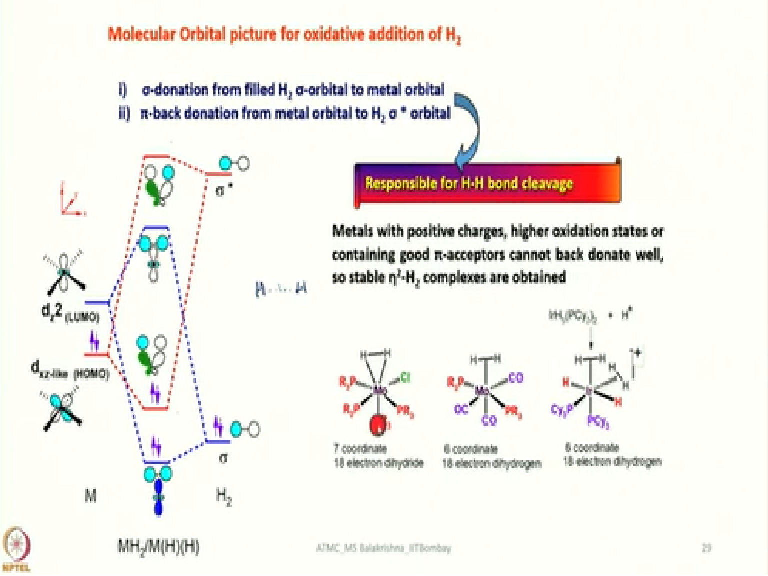

Molecular Orbital picture for oxidative addition of H_2

i) σ-donation from filled H_2 σ-orbital to metal orbital
ii) π-back donation from metal orbital to H_2 σ* orbital

Responsible for H-H bond cleavage

Metals with positive charges, higher oxidation states or containing good π-acceptors cannot back donate well, so stable η^2-H_2 complexes are obtained

7 coordinate
18 electron dihydride

6 coordinate
18 electron dihydrogen

6 coordinate
18 electron dihydrogen

Now let us look into how for example I had mentioned earlier take a olefin and add hydrogen and high pressure in a closed reactor and then heat it for several hours. But still hydrogenation do not proceed completely and probably you can get 5 to 10% of olefin converting into hydrocarbon. Whereas the same reaction one can do it in presence of a metal compound such as Vaskas compound.

In some cases, you can achieve 100% hydrogenation at lesser temperature under less hydrogen pressure with ease. So, that means something conventionally it is not possible, how that can be done using metal complex, that means we have to look into this thermodynamic aspect as well as electronic aspects and also the bonding and how metal initiates breaking of H-H bond which is not easy. I will show you molecular orbital picture here.

This already I showed you when I was talking about the classification of ligands by donor atoms under hydrogen ligands. So, here this H_2 molecule having two electrons between two H-H and then that interacts with appropriate metal here so say d^8 system. In this case what happen, these two electrons represents the sigma bond between metal to hydrogen. H_2 molecule addition depends whether we retain this as a neutral ligand or how quickly or how slowly, this is split into two anions to form two metal hydride bond, can be seen here in this case.

Once a pair of electrons are donated through sigma bond what happens? H-H bond would be weakened. So, H—H bond something like this is there it starts elongated after coordination. Because now the electrons are not really residing between these two to hold H atoms together, instead what happens electrons are moving towards the metal through sigma donation, it is elongated.

Now because of back donation σ* is pulling electrons from one of the orbitals here it is say d_{xy}, you can take d_{xy}, d_{yz} or d_{xz}. This is the HOMO for metal highest occupied molecular orbital. And now this is shared between sigma star by generating pi bonding and antibonding orbitals. So, now basically what happens we are taking out a pair of electrons between two hydrogen atoms through sigma bonding.

Not only that, the same time we are also adding electrons to the sigma star anti-bonding orbital. So, that means these two kinds of bonding affects H-H and eventually H-H bond is broken very nicely. So, this you cannot imagine when we are simply taking in a conventional reaction and olefin and H_2. The moment H_2 comes near the metal, what happens?

Electrons between two H atoms are pulled and the electrons from metal is added to sigma star. Two kind of loss suffered by H_2 results in the breakage of H—H bond completely and thus oxidative addition would be completed. So, that means sigma donation from filled H_2 to sigma metal orbital and then by back donation from metal orbitals to H_2 σ* orbital, this eventually results in H-H bond cleavage.

The next question is, is it possible to still use H_2 as a neutral ligand and by preventing its oxidative addition. Yes, it is possible, then we have to consider following aspects. Metal with positive charge and metal should be in higher oxidation state or containing good π-acceptor ligands. So, that means when the metal is positively charged and metal has higher positive charge, it is a reluctant pi donor.

And again, metal is in higher access state it has electron deficiency as a result it is a reluctant pi donor. And also, if we have very strong pi acceptor ligands already present on the metal like carbon monoxide they take larger share of metal π-electrons towards it. So, that less number of electrons are left for back donation to sigma star of hydrogen. So, that means in that case what happens metal cannot do back donation well to sigma star of hydrogen.

So, stable η^2 H_2 complexes can be generated. So, that means yes, you can either stabilize H_2 as a neutral molecule binding to metal centre or you can split that one to generate two anions for completing oxidative addition reaction. I will show you a few examples here you can see in these cases here. You can see H-H bond is about to break here, whereas here H-H bond is retained and H_2 is coordinated in η^2 fashion.

Whereas in this case, we have both terminal hydrides as well as molecular hydrogen binding. So, that means as I mentioned here it is seven coordinate and 18 electron complex. So, here these phosphines are not very good by acceptors compared to carbon monoxide as a result what happens and pi-acceptor ability of hydrogen is more or less comparable to those of tertiary phosphines.

As a result, what happens? It also fights for a larger electron share in the back bonding. As a result what happens, more electrons come here and then H-H bond cleaves. Whereas in this case we have better pi acceptor ligands, here carbon monoxide which will take lion's share and leaves very little or no electron density for the donation from metal to H_2 σ^* as a result, what happened this H_2 is retained.

So, that means, we have to choose what we are looking for, whether we want to break H-H to add oxidatively to generate two hydrides or we want to retain as a neutral that is in our hand, we have to choose right kind of ancillary ligands with sigma donor and pi acceptor properties and also suitable oxidation state on metal. So, that we can always tilt equilibrium either way.

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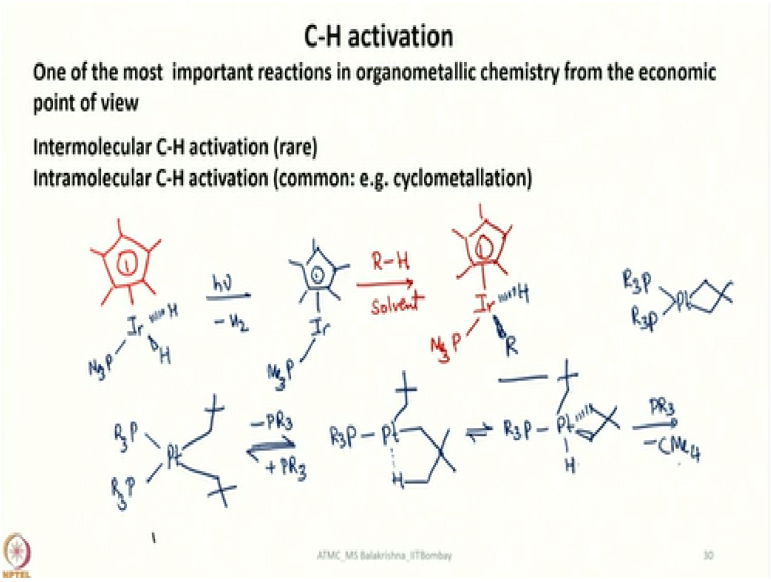

C-H activation

One of the most important reactions in organometallic chemistry from the economic point of view

Intermolecular C-H activation (rare)
Intramolecular C-H activation (common: e.g. cyclometallation)

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So, now let us look into C-H activation. This is one of the most important reactions in organometallic chemistry from the economic point of view. And of course, here when we try to do C-H activation, we can come across two type of activation one is inter molecular C-H activation, it is very rare, and other one is intra molecular C-H activation, very common. Cyclometallation happens here. And also, this intra molecular C-H activation is responsible in many reactions.

Let me show you one such C-H activation. So, if I want to perform C-H activation here, what I should do is first I have to vacate some coordination sites on the metal. For that, one best way would be to shine UV light that means you do photo chemical reaction. Under this condition H_2 is eliminated to generate this transient species. Now you can see reaction, this species is ready for oxidative addition.

Now we bring an appropriate molecule having C-H bond in appropriate solvent. This is a typical C-H activation reaction here, this is intra molecular C-H activation and then one can also think of intra molecular C-H activation that can only happen in some cases where we are using special type of molecules or there is some way, we can generate that kind of intermediates. So, let me show that one. Let us consider a platinum complex, we have these two groups.

Before we perform any further reaction one of the tertiary phosphine should go and this will be in equilibrium situation. This is very similar to β-hydrogen elimination. Tertiary phosphine is in solution, now what happens this Me_3CH_2 is there this will abstract this one. So, this CMe_4 will come out and we end up with, this is one example for intra molecular C-H activation.

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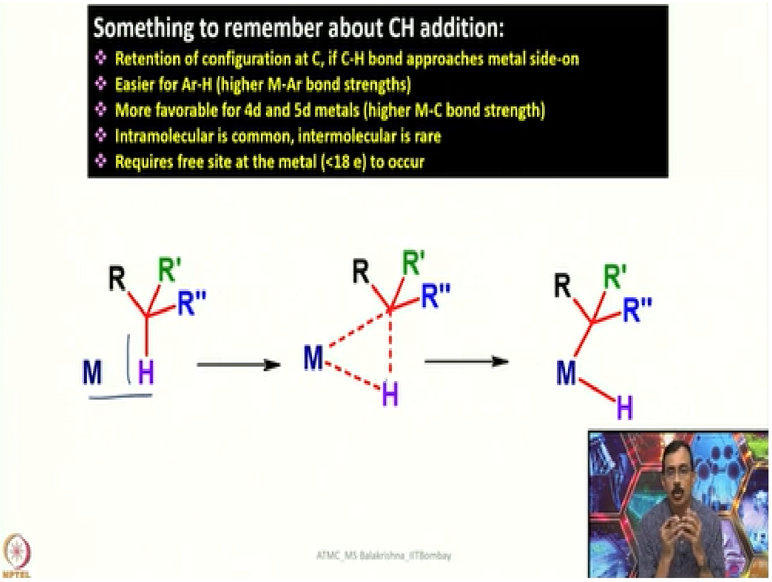

Something to remember about CH addition:

- Retention of configuration at C, if C-H bond approaches metal side-on
- Easier for Ar-H (higher M-Ar bond strengths)
- More favorable for 4d and 5d metals (higher M-C bond strength)
- Intramolecular is common, intermolecular is rare
- Requires free site at the metal (<18 e) to occur

So, now we should look into some aspects here. Whenever we perform CH addition retention of configuration takes place at C if C-H bond approaches metal side on. Always in a three bond concentrated addition, the substrate approaches in a side-on position something like this, that is shown here. So, in this case, it forms a three membered intermediate that is the reason we call it as three centred concerted addition.

And then what happens it breaks here and oxidative addition is completed. So, in this case easier for all especially for aryl groups, because usually with 3d, 4d, 5d, metal-aryl bond strength increases and also compared to alkyl, aryl bonds are more stable because of reinforcement of metal to carbon bond due to the delocalized electrons present on carbon more favourable for 4d and 5d metals because, they have higher metal to carbon bond strength. Intramolecular is common, intermolecular is rare requires free sight at the metal to occur.

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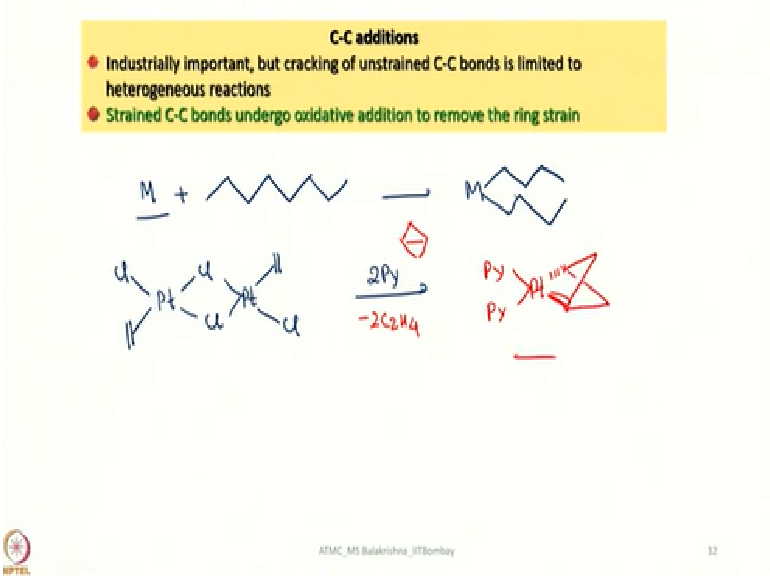

C-C additions

- Industrially important, but cracking of unstrained C-C bonds is limited to heterogeneous reactions
- Strained C-C bonds undergo oxidative addition to remove the ring strain

Now let us look into C-C additions. Industrially important reactions and of course the cracking of unstrained carbon-carbon bonds is still limited to hydrogenous reactions. And no matter how much we talk about homogeneous catalysis in the present scenario the contribution towards total catalysis from homogeneous catalysis is only about 16%, the 85% of the catalytic reactions are heterogeneous in nature.

Whenever we talk about petrochemical industries are doing olefin cracking to generate a whole bunch of organic molecules, extensively heterogeneous catalysis is used. Only sometimes C-C addition is possible especially when we have very strained molecules where C-C bond is very strained because of very congested three or four membered rings are there in it. Strained C-C bonds undergo readily oxidative addition to remove the ring strain.

One such example let us consider here. So, what I am telling is, cracking means CH activation. So, it is not easy to do this kind of reaction using homogeneous catalysts and even if you do it probably the yields are so low and if you master this one there is very good scope in industries to perform this kind of reactions at lower temperature especially with cheaper metals.

If we can do something with iron cobalt or nickel, yes, we are making fortune. Then I was telling you about strained ringm let me give an example of how strained rings can break C-C bond and that can be added on to the metal. I am considering here well-known complex. I am sure you are all familiar with this compound. Take this metal complex in presence of at least two equivalents of pyridine and then this molecule here.

This is an example for strained ring adding on to the metal through oxidative addition. So, let me discuss more related to this topic in my next lecture until then have an excellent time reading. Thank you for your kind attention, see you in my next lecture.