Introduction to Organometallic Chemistry

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Lecture - 18
Reductive Elimination

Oxidative addition and reductive elimination are two key reactions in organometallic chemistry, especially when it comes to transition metal organometallic chemistry. This plays a very important role. So, it is important that we spent some time understanding it and figuring out.

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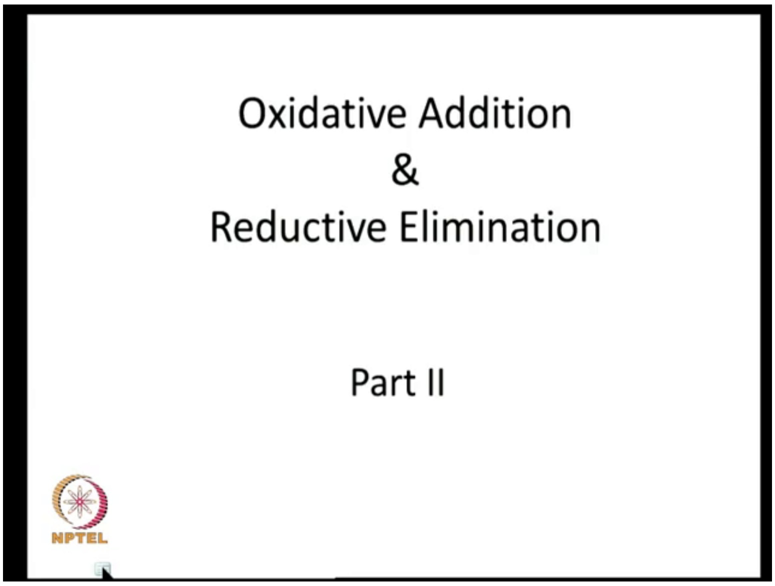

Oxidative Addition
&
Reductive Elimination

Part II

What are the conditions under which oxidative addition occurs and how we can have reductive elimination in a catalytic cycle. So, this is the second part of the description of oxidative addition and reductive elimination.

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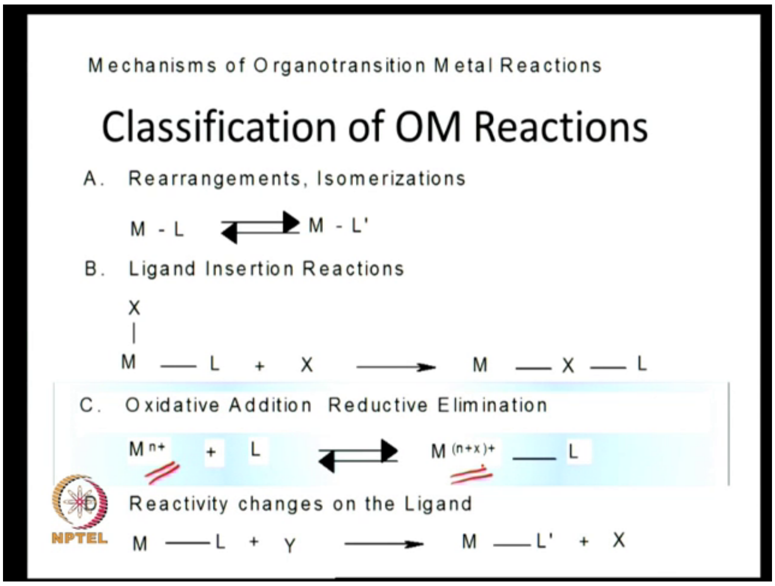

Mechanisms of Organotransition Metal Reactions

Classification of OM Reactions

A. Rearrangements, Isomerizations

$$M - L \rightleftharpoons M - L'$$

B. Ligand Insertion Reactions

$$\overset{X}{\overset{|}{M}} — L + X \longrightarrow M — X — L$$

C. Oxidative Addition Reductive Elimination

$$M^{n+} + L \rightleftharpoons M^{(n+x)+} — L$$

Reactivity changes on the Ligand

$$M — L + Y \longrightarrow M — L' + X$$

So, we continue where we left off in the previous. So, the important thing to remember is that, in the oxidative addition we have a change in the oxidation state of the metal and invariably you also have the formation of a new metal ligand bound. And that results in an expansion of the coordination sphere of the metal. So, the name addition and the fact that you have a change in the increase in the oxidation number, the formal oxidation number of metal results in the oxidation part.

So, this reaction as I just mentioned can be a reversible reaction and so you can have both oxidative addition and reductive elimination in the catalytic cycle. And the thermodynamics of this process turns out to be extremely important. It is facile in the case of transition metal chemistry but, not in the case of main group chemistry, where only oxidative addition happens. So, let us take a look at what else is special, the fact that we have written M as n plus in the oxidative addition reaction. On the left side we have written as n plus, and on the right side after the reaction we have changed it to n plus x, plus x turns out to be a variable. Sometimes it is 1, very often it is 2.

So, that is not a crucial aspect. The ligand can accept one electron or it can accept two electron or in some cases as we shall see in the first part of the stock, it can accept one electron from two different ligands. And so, a new compound can result in the process. So, let us take a look at some of the possibilities in oxidative addition.

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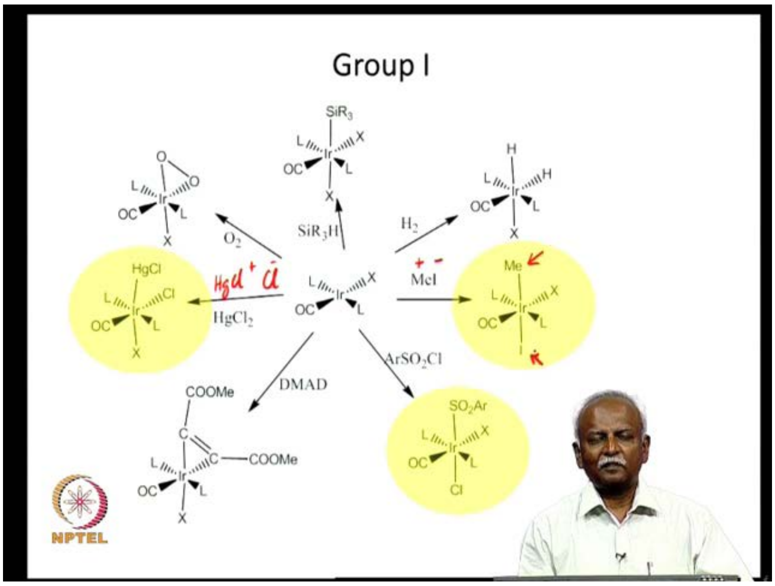

Group I

So, we also classify the type of oxidative additions based on the agenda that you have Vaskas complexes, is a typical complex and it undergoes a variety of oxidative addition. And we classify them into three groups, the first group was the group that could be polarised into plus and minus parts. And so, if you have methyl iodide we could mark it as M e plus and I minus. If you have Hg Cl 2 then we can write this as Hg Cl plus and Cl minus.

So, you have an agenda that the molecule can be split into a positively charged in a negatively charged species. Then it is convenient to have oxidative addition in the transposition of the Vaskas complex, and so you end up with the three molecules which are marked in yellow in this projection. So, you have M e and I added in the transpositions of the Vaskas complex. So, this is the first group which is highly polarised and it will add in a trans fashion, and then we talked about a second group of molecules where multiple bonds are there in the part, that is adding onto the metal that is being oxidised.

So, one example would be oxygen. And so, during the oxidation O 2 which has got a double bond between the two oxygens, adds onto Vaskas complex. And as a result it forms two new bonds to iridium and at the same time the bond between the two oxygen atoms changes from a double bond to a single bond. This change a double bond to a single bond, requires that the two atoms that are added onto the iridium are now sist related to one another..

So, at the end of the reaction in group 2 class of oxidative editions, in the group 2 you end up with sist additions, and we have two examples here which are again marked in yellow. These molecules are characterised by two key features, one of them is the fact that there is a multiple bond between the two atoms which are adding across the metal and the second is the fact that they are not highly polarised. So either dimethyl acetate dicarboxylate or oxygen are not highly polarised. Thus plus and minus species at the end of the reaction you have, the bond retain and so you have a sist addition.

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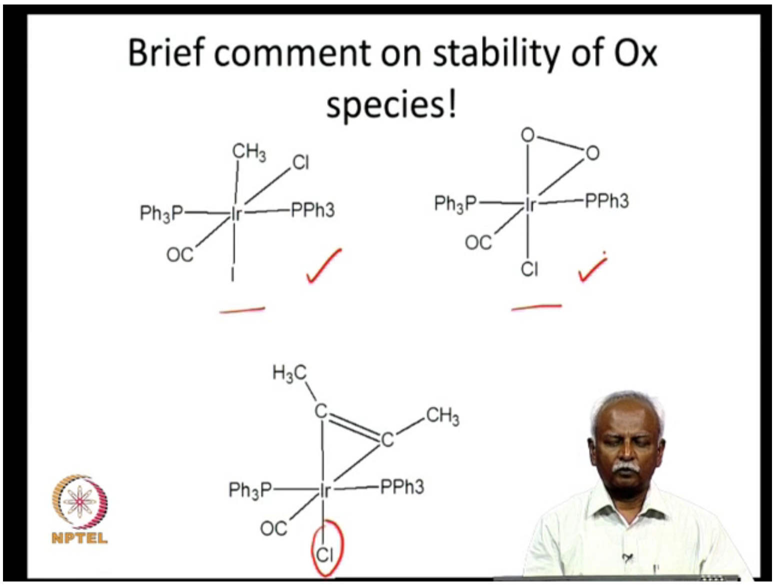

Brief comment on stability of Ox species!

So, a brief comment on the oxidating, on the brief comment, on the stability of the oxidised species is in order when you have Vaskas complex, you have iridium in the oxidation state 1 at the end of the reaction. When you added methyl iodide for example, you end up with an oxidation state of 3.

So, if you have more electro negative elements attached to the iridium then the plus 3 oxidation state is more stable. In both cases that I have listed here on the screen, you have iridium attached to iodine and chlorine or iridium attached to two oxygen atoms and chlorine. Either way you tend to have a stable species, because these electron withdrawing groups will stabilize the higher oxidation state, electron withdrawing groups at the same time have got pi electrons which are pi donor atoms. And so, this stabilize the higher oxidation state. So, the oxidation or the oxidative addition proceeds from left to right in a very exothermic fashion.

On the other hand, there are species were the group that is adding on is not so electron negative. And so, we have this example here of dimethyl acetlyne which is oxidatively added. And at the end of the reaction we will notice that iridium is in a formal oxidation state of plus 3, but, nevertheless you will notice that the only electron withdrawing group that is there on atom on the iridium atom is the chlorine bond, chlorine atom or a chlorine ligand.

So, as a result of this particular factor the reaction proceeds from left to right rather reluctantly, and the oxidised species is not as stable as in the case of Vaskas complex undergoing oxidation with electro negative species. So, this is apparently a disadvantage for oxidative addition but, nevertheless it allows for many catalytic cycles to take place. And that is what we are going to take a look at this in this lecture.

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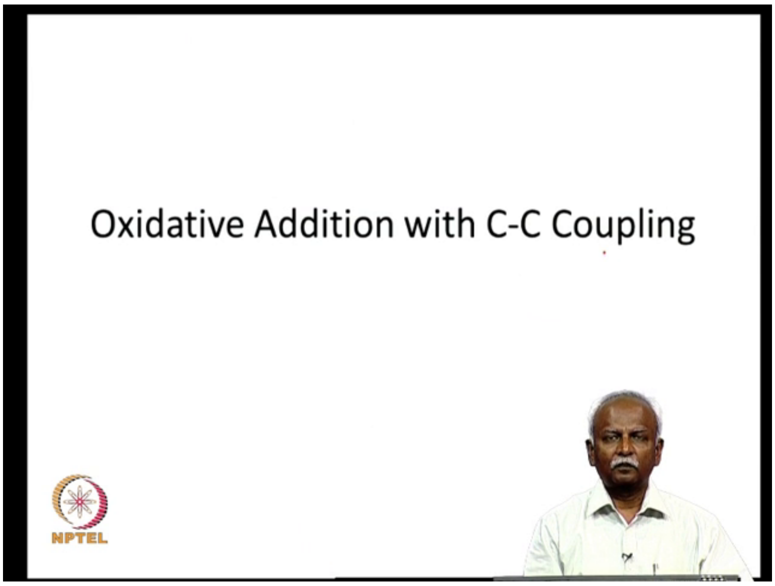

Oxidative Addition with C-C Coupling

So, oxidative addition with carbon carbon coupling is a special case.

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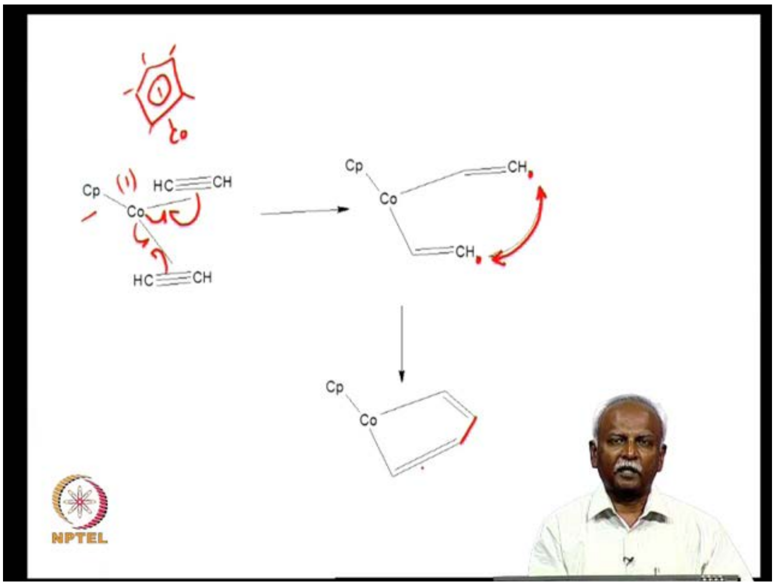

Where you have the oxidation taking place with concomitant formation of a carbon carbon bond. Let us take a look at exactly how this happens. Imagine a cobalt 1, this is a cobalt 1 atom which is coordinated to Cp ring. A Cp ring is very simply a cyclo-penta-diagonal ring, a cycle pentane diagonal which is coordinated to the cobalt 1.

So, this is your Cp coordinated to cobalt, and this particular bond p is now interacting with two acetylene molecules. Now, when you have oxidative addition in such a fashion that these triple bonds become double bonds and the bond between cobalt and oxygen is formed. A bond between cobalt and oxygen is formed. So, exactly what is happening is you have cobalt giving one electron and so we indicated with a half arrow, and it gives one electron to the acetylene, and acetylene gives one electron and so forms a covalent bond.

This covalent bond now results in the formation of a radical species which will have two electrons sitting on the two carbon atoms. Here, the covalent bond is been formed between cobalt and carbon and the radical species, di radical species is formed. A di radical species between these two C H units as indicated by this arrow. If a covalent bond is formed between these two C H bonds then what you end up with is the formation of a metalo-cyclo-pentadiene bond, that is formed is marked in red here.

So, metalo-cyclo-pentadiene can be formed by oxidative addition. This is indicated by these two half arrow on the cobalt coming out and forming a covalent bond with an acetylene, resulting in a vinyl radical. The two final radicals form a metalo-cyclo-pentadiene.

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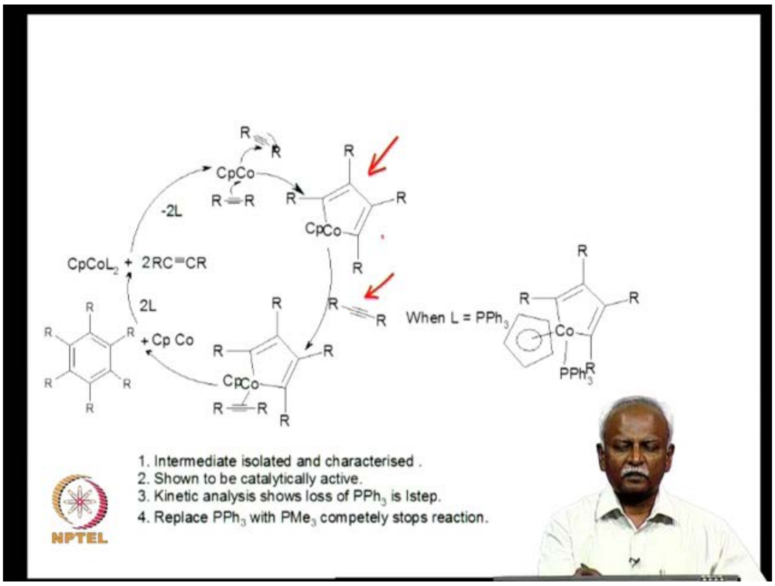

1. Intermediate isolated and characterised .
2. Shown to be catalytically active.
3. Kinetic analysis shows loss of PPh$_3$ is Istep.
4. Replace PPh$_3$ with PMe$_3$ competely stops reaction.

So, now this metalo-cyclo-pentadiene is involved in a variety of reactions which resulted in a cluster of catalytic cycles with cobalt as a key player and acetylenes as the initial reactants. Now, after the formation of the metalo-cyclo-pentadiene here, and this fast reaction results in the formation of a species, which can interact with a third molecule of acetylene. Now, let us come back to the slide, but first let us take a look at what are the ways in which these two species can in fact react.

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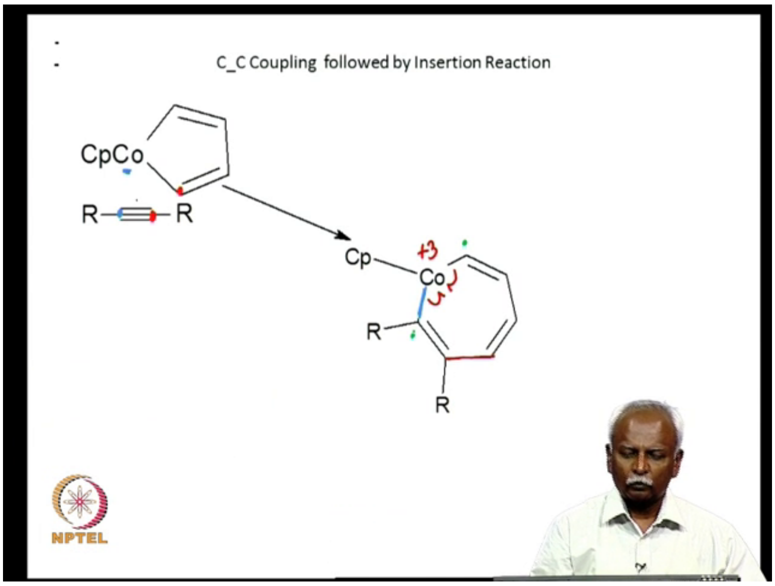

C_C Coupling followed by Insertion Reaction

Let us say you have a carbon carbon coupling followed, that is what we said is a formation of the metalo-di-cyclic-pentadiene followed by an insertion reaction, remember? Insertion is a simple addition of an anionic species from the metal interacting with the neutral species on the metal. So, here the neutral species turns out to be acetylene. So, acetylene is a neutral ligand which is attached to the cobalt and the anionic species or the negatively charged ligand is the one which we have marked in red.

So, if this bond migrates to the neutral species and the neutral species in turn forms are bond to the cobalt. Exactly what is going to happen is that we are going to have a reaction such that two new bonds are formed, one between the vinylic carbon which is here. Vinylic carbon which is here, and the acetylinic carbon which is here. Both of them are marked in red.

And if you mark the other acetylinic carbon and the cobalt centre, if a new bond is formed here, that will lead to the formation of this blue bond here. So, let us mark the two colours that we have the two new bonds in the two colours. So, the red coloured carbon atoms are joined together to form this new bond, and the blue bond is formed between the cobalt and acetylinic carbon.

In the next step, we can infact do the opposite of oxidative addition. In other words if we remove the cobalt carbon bonds in such a way that they get back the cobalt, gets back its two electrons in this particular unit. In this molecule cobalt is in the plus 3 oxidation state. So, if we remove half an electron from here, and half an electron from here, than cobalt will become plus 1 again and then these two vinylic carbons will be left. So, let us just mark the vinylic carbons. So, they will be left with one electron each, and so in the subsequent step you will be able to form.

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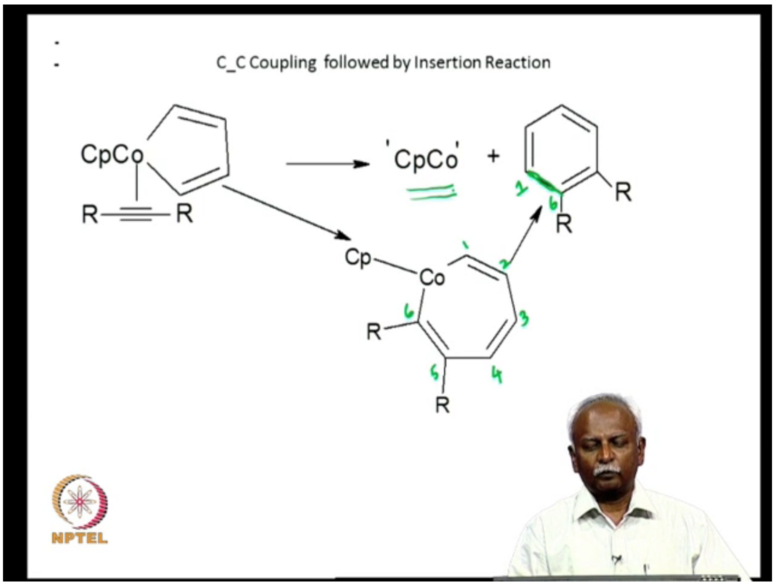

C_C Coupling followed by Insertion Reaction

In the subsequent step you will be able to form a carbon carbon bond, and that carbon carbon bond results in the formation of an acetylene. So, basically you have 1, 2 ,3, 4, 5 and 6 carbon atoms attached to the cobalt, and if atom numbers 1 and 6 combine together, if 1 and 6 combined together. So, that is exactly these two carbon atoms, 6 here and 1 here. Then you will end up with both formation of this new bond between 6 and 1 and that results in the formation of a benzene ring. And the stability of the aromatic benzene ring results in a very fast reaction to form the six membered ring and regeneration of the cobalt 1 species with a cyclopenta diagonal group.

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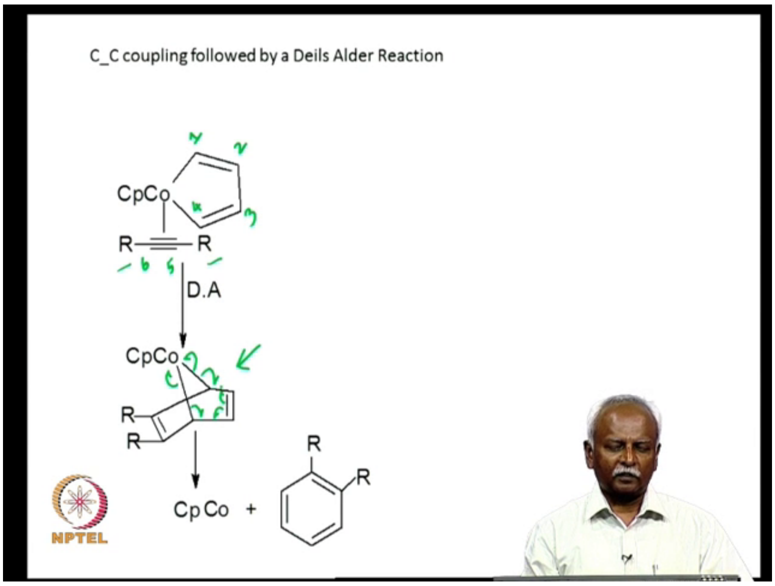

C_C coupling followed by a Deils Alder Reaction

The same reaction could be described as a de-solder reaction, and when you have very electron withdrawing groups when R is very electron withdrawing, then you end up with de-soldered type of reaction. And in this case also it is important to understand the four carbon atoms which formed the diene. These are the four carbon atoms which formed the diene and these are the two carbon atoms from the acetylene which form the dienophile..

So, the diene and the dienophile react together such that a new bond is formed between atom numbers 4 and 5 and atom numbers 1 and 6, so that results in a bicyclic intermediate which is pictured. Here is bicyclic intermediate can again do a cyclo reversion reaction or a reductive elimination. And so, in this particular instance you have to transfer half a electron, one electron from here and one electron from here, resulting in the formation of two new pi bonds.

The formation of the stable aromatic ring, such that you end up with a, so you end up with a very nice aromatic system at the end of the reaction. So, these are two ways by which you can have the formation of an aromatic ring using the methlo-cyclo-pentadiene which was generated from cobalt 1 and two acetylenes.

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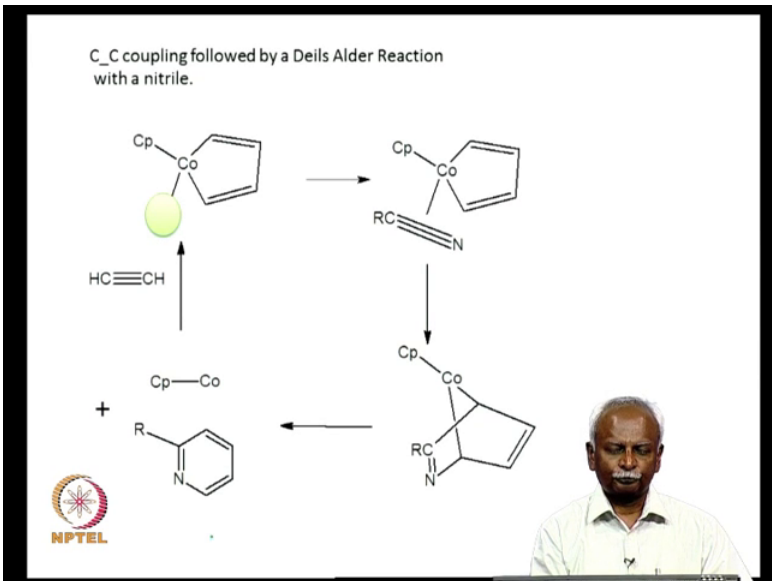

C_C coupling followed by a Deils Alder Reaction with a nitrile.

So, the same reaction could have happened with an acetylene, it could also happened with a nitriles. So, if you want to use an nitrile then you could carry out the reaction in such a way that you end up with a pyridy. So, instead of acetylene, if you use a nitrile then the same reaction could undergo de-solder type of reaction and result in the formation of a substituted pyridy.

This was exploited by several workers, notably by K P C old hart who use this reaction to synthesise a variety of interesting molecules. Now, the first step which involved the formation of a metalo-cyclo-pentadiene was a very fast reaction, and in fact that is the reason why you can in fact do this cyclo cyclic ring formation reaction with two acetylenes and one aceto-nitrile or one nitrile molecule. So, you can vary the molecule in such a way that the two steps can be distinguished. The very first formation of the metalo-cyclo-pentadiene and the subsequent de-solder addition can be distinguished. They appear to be two separate catalytic cycles.

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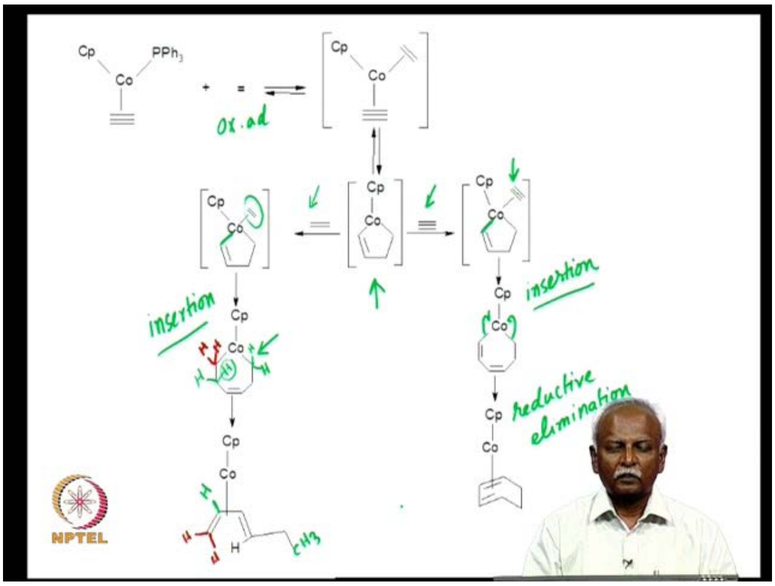

So, let us now take a look at a slightly different reaction. In this case instead of adding two acetylenes to the cobalt, we slow down the reaction by adding a molecule of di-phenyl-phosphine. The rate at which the two acetylenes combine together is now slow down, because the dissociation of the tri-phenyl-phosphine is a rate limiting step. So, by adding acetylene with a alkene we end up with a metalo-cyclo-pentene.

So, this is the metalo-cyclo-pentene, earlier we had a metalo-cyclo-pentadiene. So, in this metalo-cyclo-pentene we can have a choice of adding the ethylene. In this case we can either have an ethylene adding which is what is pictured here. All we can have an acetylene which is pictured here, and then you can form two different types of molecules.

Let us first take the reaction cycle which is pictured on the left. So, if an ethylene molecule is added, we end up with if the molecule, thus an insertion reaction. So, this is an example of an insertion reaction and the insertion is carried out by this vinylic group forming. A bond to the neutral molecule which is the ethylene molecule which is pictured here.

So, the ethylene is a neutral molecule and the vinyl group is anionic group, which migrates to the ethylene molecule and as a result the ring expands just as we described in the previous set of slides. We have explained how this insertion can increase in a ring expansion reaction, the ring expansion leads to the formation of the seven membered ring, a metalo-cyclo-heptene. So, here you have one double bond which is in the third position with respect to the cobalt, and this particular molecule can now have an option of doing a reductive elimination. Either directly to give you a metalo, sorry this intermediate now has the ability to do a cyclo reversion reaction such that it forms a cyclohexane.

On the other hand, if you realise that there are two hydrogens on this carbon. The two hydrogens on this carbon and one of them is very close to this alkyle group which is attached to the cobalt. So, if you have this C H 2 group abstracting one hydrogen from this carbon centre, you can end up with a C H 3 unit such that you now have the formation of a butadiene, which is substituted in the one position..

So, you now have a butadiene which is coordinated to the cobalt, but, again you had a reaction in such a fashion that cobalt is undergone a reductive elimination. And the vinyl group, the alkyl group the C H 2 unit is obstructed a hydrogen so that it forms a C H 3 and the C H 2, which we will mark with a different colour so that it is easy to follow. So, this C H 2 group is what we have here, this is the C H 2 group and the C H which we had marked in green is right here. So, the C H 2 which was on the right side has become a C H 3 and that is what is pictured here. And the vinyl group is generated by the abstraction reaction that was on the ring.

Now, we have another possibility, you can also do an addition of acetylene to this metalo-cyclo-pentene. If you do an acetylene addition then you can end up with a cyclohexane diene generated from this ring system, and to do that one has to do the migration of this vinyl group onto acetylene. So, this is a vinyl group that is attached to the cobalt which will migrate to the acetylene, which is the neutral molecule. So, this is again an example of an insertion reaction.

So, in this type of reaction you first have an oxidative addition, you have an oxidative addition, oxidative addition followed by an insertion reaction. And then a subsequently you have the reductive elimination. So, you now have the reductive elimination, and to understand the reductive elimination you can think of the cobalt taking back one electron from this. From this bond in such a fashion that cobalt 3 becomes cobalt 1 again and you have the formation of a cyclohexane diene at the end of reaction.

So, this helps us to understand how the carbon-carbon bond formation coupled with oxidative addition can result in the formation of a cyclic metalo cyclo pentene or metalo-cyclo-pentadiene and these groups can subsequently add on a variety of molecules. Variety of neutral molecules through an insertion reaction, and if you have very electron withdrawing groups they can also undergo a de-solder type of reaction subsequently.

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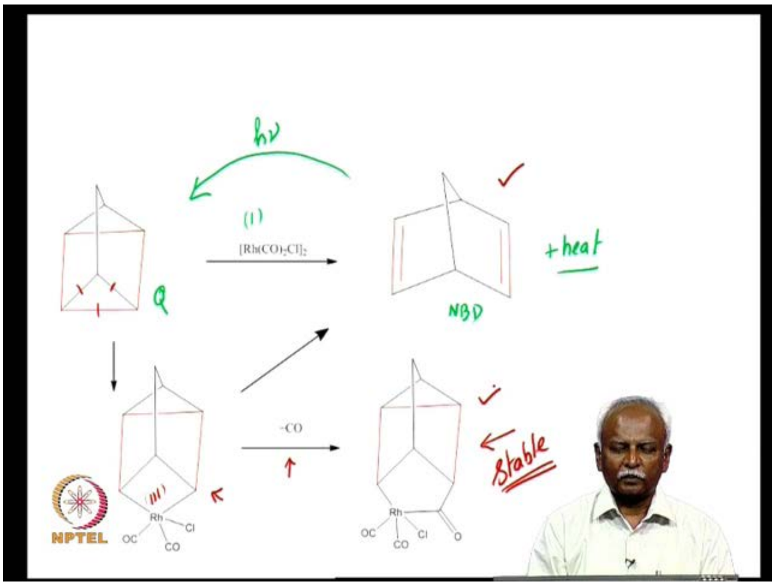

So, during the course of studies with quarterly cyclene it was noticed the quarterly cyclene is a molecule which will reopen to give nobornadiene. So, this is nobornadiene and this is quadra cyclone. Now, it is interesting that norbornadiene could be converted to quadracyclene by photolysis, and because this is a energy rich molecule, quadracyclene is an energy rich molecule.

It was taught that if one can store energy from by absorbing sunlight, converting nobornadiene to quadracyclene then it would be possible to harvest sunlight using this particular reaction, because a forward reaction of converting quadracyclane to nobornadiene was exothermic. So, here if one could generate heat and so you could harvest light energy and converted to some chemical energy.

Now, it turns out that the reaction which leads to conversion of quadracyclene to nobornadiene has to catalysed. If this not happen at room temperature without any catalyst and that is because this is an orbital control reaction, and the cyclo reversion turns out be difficult rhodium 1 complexes. So, this is an example of a rhodium 1 complex was a good catalyst for this process. And initially it was taught that this was reaction which was a case of orbital control reaction were the symmetry rules were circumvented by addition of rhodium orbitals into the equation.

So, this theory however was proven to be wrong by Jack Halprin, who showed that in the presence of carbon monoxide and new compound could be isolated. So, what was really happening was that restrained cyclopropane ring which can be marked here. This strange cyclopropane ring which will mark with a single line. So, this cycle propane ring could re-open and you could have an oxidative addition of rhodium so that the rhodium 3 species can be formed.

Now, this rhodium 3 species turned out to be capable of doing a cyclo reversion reaction in such a fashion that nobornodiene can be generated. On the other hand, if you have carbon monoxide in the reaction medium, here we have added carbon monoxide. Then you could have an insertion reaction of carbon monoxide in such a way that a new product could be isolated.

So, because this product was stable, this is stable and could be isolated, the intermediacy of rhodium 3 compound was sufficiently explained, both the formation of nobornadiene and the formation of this insertion product. So, this was a theory which was short lived, it was thought that orbital symmetry control with metal atoms is useful for converting quadra cyclic nobornadiene. On the other hand, what was really happening was an oxidative addition and a cyclo reversion reaction leading to the ring opening.

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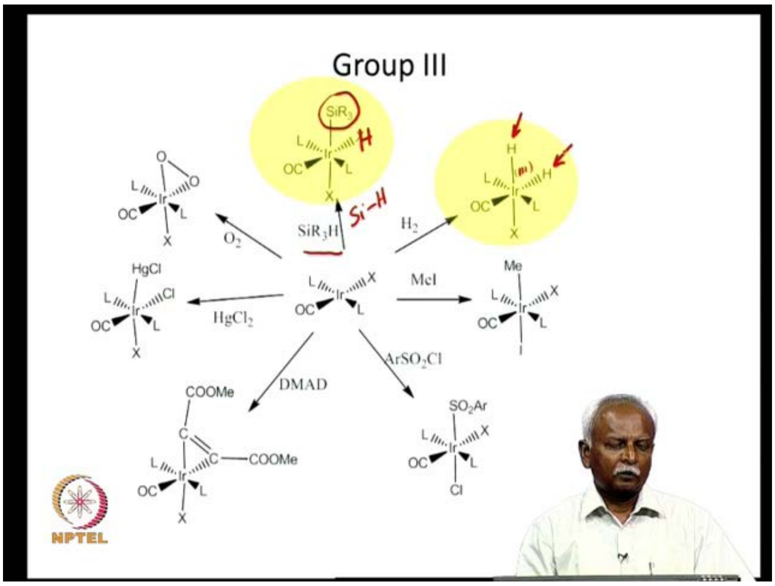

Group III

Now, we come to the third group of molecules which can undergo cyclo, we come to the third group of molecules where you have oxidative addition of a set of molecules which are not polarised. But at the same time many of them are found to be adding in a sist fashion, these molecules because they are not very ionic in nature. They do not ionise plus and minus nor they multiple bonded but, nevertheless after addition reaction, they very often found in the sist geometry.

There are two examples which are listed with Vaskas complex here and both cases, you have an iridium. The complex formaly a iridium 3 complex being formed as a result of oxidative addition of an S i H bond here, the S i H bond has been broken and you have the addition of 6 here. This should been H and an S i R 3 group. So, on the other hand you have a hydrogen molecule that also undergoes a oxidative addition. And iridium now has a formal oxidation state of iridium 3 and the two groups which are added on are formed in the sist position. So, group three type of molecules also add in a sist position, they are not polar and they are not multiple bond.

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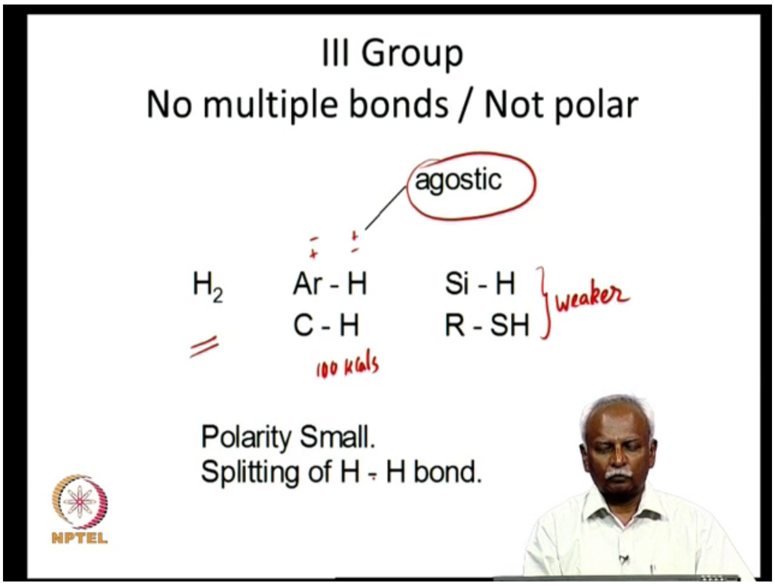

III Group
No multiple bonds / Not polar

agostic

H_2 Ar - H Si - H
C - H R - SH weaker

100 kcals

Polarity Small.
Splitting of H - H bond.

So, these molecules are strange because many of them undergo they have a common feature and that is a fact that they have very little ionisation of this group as plus and minus. They do not ionise like this, nor they ionised as minus and plus but, still they are able to undergo weak interaction with the metal in what is called an augustic way.

This augustic interaction is something which will have to deal with later, but suffice to say at this point that all these molecules are sometimes found to have weak interactions with the metal. And in spite of that weak interaction they are able to break a very strong bond, the metal is able to break a very strong bond between the carbon and hydrogen which is worth about 100 kilo calories per mole..

Similarly, H 2 which is also called a strong bond or S i H, and S H are off course weaker bonds. These are weaker but, nevertheless the interaction of the metal with these bond is able to break the bond and form two new bonds, one with the metal and hydrogen and the other is with the carbon silicon or an other hydrogen atoms. Let us take a look at how exactly these reactions turn out.

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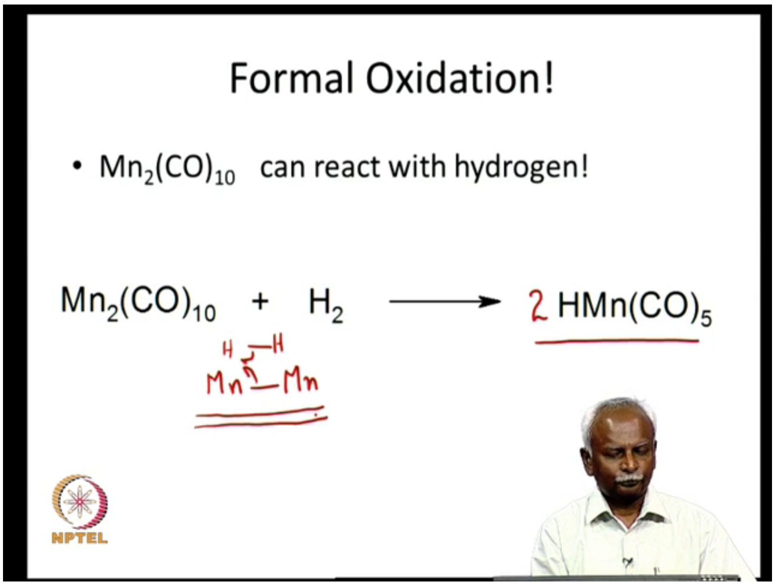

Formal Oxidation!

- $Mn_2(CO)_{10}$ can react with hydrogen!

$$Mn_2(CO)_{10} + H_2 \longrightarrow 2\ HMn(CO)_5$$

The first thing that we need to notice is that this reaction is in fact a formal oxidation, it is not indicated or the charge on the metal atom. Now, M n 2 C O 10 that is di manganese deca-carbonyl can in fact react directly with hydrogen under pressure. So, if you treat M n 2 C O 10 with H 2 then you get two molecules of H M n C O 5. And this can be understood as a very simple breaking of the manganese manganese bond.

So, in M n 2 C O 10 you have manganese manganese bond and you have in the other reactant the H H bond. And so, if you now break this in such a way that if formed a new bond between the manganese and hydrogen, then you end up with H M n C O 5 because hydrogen is slightly more election negative than manganese.

It is written as a hydride complex, but as we have mentioned in the lecture metal hydrides, H M n C O 5 will actually behave like a weak acid. It is in fact possible to ionise it as H plus and M n 0 5 minus. So, this should be regarded as a formal oxidation reaction, not a real removal of electron, but nevertheless we can write the whole reaction to indicate to the transfer of a electron from manganese onto the M n H bond.

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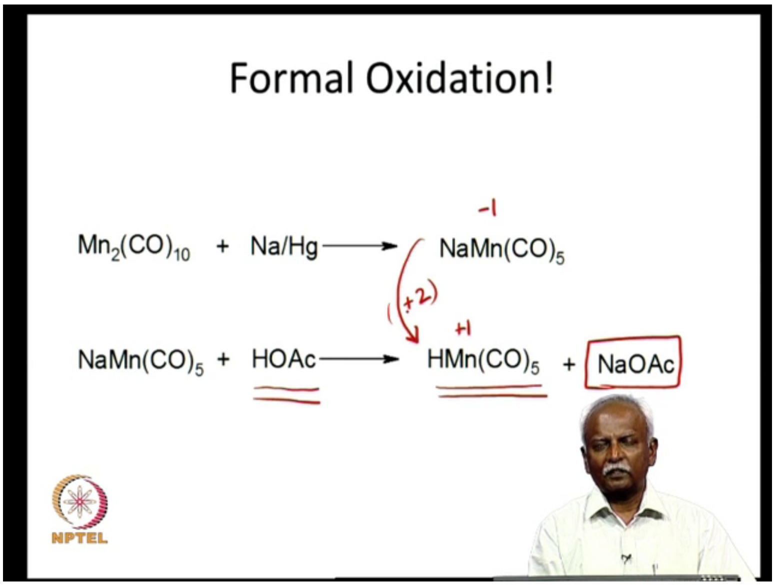

Formal Oxidation!

$$Mn_2(CO)_{10} + Na/Hg \longrightarrow \overset{-1}{NaMn(CO)_5}$$

(+2)

$$NaMn(CO)_5 + \underline{\underline{HOAc}} \longrightarrow \underline{\underline{\overset{+1}{HMn(CO)_5}}} + \boxed{NaOAc}$$

Now, the situation is even more amazing when we consider the reaction between M n 2 C O 10 and sodium, which results in the formation of M n C O five minus. M n C O 5 minus has got an oxidation state of minus 1. So, this is N a plus and M N C O 5 minus, M n has minus 1 oxidation state, that negative charge is in fact nicely stabilised by the carbon mono oxides which are surrounding the manganese.

So, this stable molecule now reacts with a proton and that proton is coming from acetic acid. And so, the proton is transferred to manganese and H M n C O 5 results this same H M n C O 5 which we encountered in the reaction with hydrogen. And in the course of this reaction sodium acetate of course be extruded. Now, H M n C O 5 again has got a formal oxidation state of plus 1, and so you have changed the oxidation state in this process by 2 units.

So, it looks as if there are two electrons which have been removed from manganese. So, this is a interesting case of a oxidative addition reaction which has in fact not changed in reality the number of electrons of the manganese, but never the less formally we have to call it an oxidative addition.

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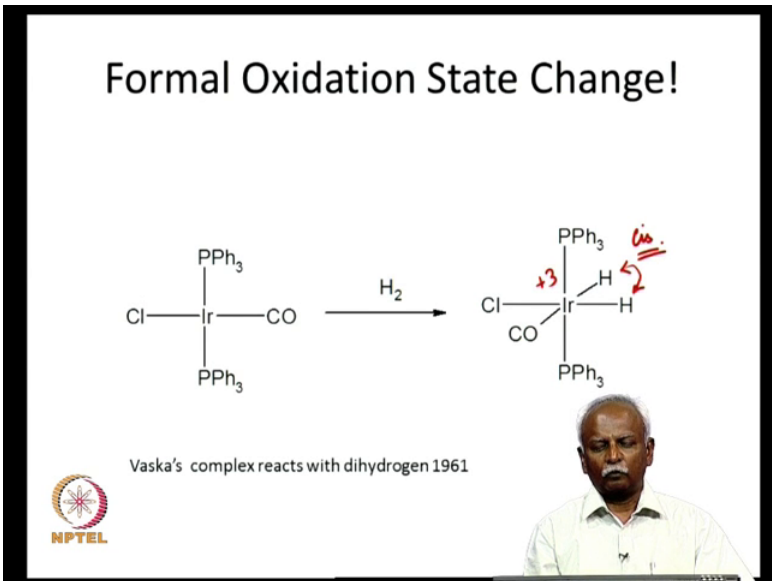

Formal Oxidation State Change!

Vaska's complex reacts with dihydrogen 1961

Now, vaskas complex was in fact the first complex where many oxidative additions were studied. So, this is another example where direct addition of hydrogen can be carried out with vaskas complex, and interestingly you can add hydrogen under pressure and you can form a compound in which two hydrogen atom are added to iridium, and again the formal oxidation status plus 3. So, notice that two hydrogens are present in a sist position. So, this sist position is characteristic of group 3 and so this is sist addition of two groups. So, this is discovered as early as 1961 and subsequently a variety of reactions have been studied where oxidative addition has been observed.

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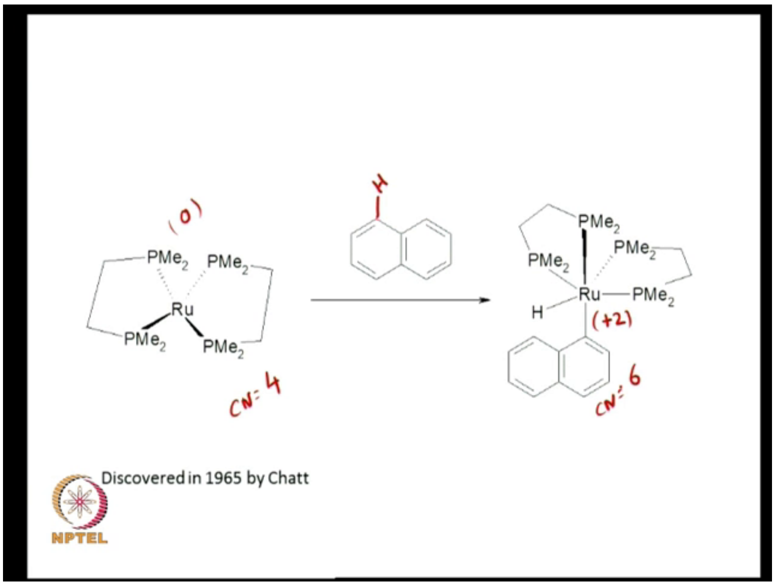

Discovered in 1965 by Chatt

Now, the more interesting and challenging reactions are those in which you have oxidative addition of very non polar bonds. In this particular instance I have shown you a C H bonds O, you can see that this is a C H bond that is being oxidative added in such a fashion that ruthenium now goes from 0 oxidation state. This is 0 oxidation state to plus 2 oxidation state, but notice once again in the final compound the coordination number has changed from 4 to 6.

The coordination number has changed from coordination number 4 to coordination number 6, and oxidation state has increased by plus 2 units and two non polar groups have been added to the ruthenium. In this particular case, hydrogen and naphthyl group. Now, exactly how the ruthenium is able to carry out this type of addition reaction is in fact the key feature which separates transition metal chemistry from main group chemistry.

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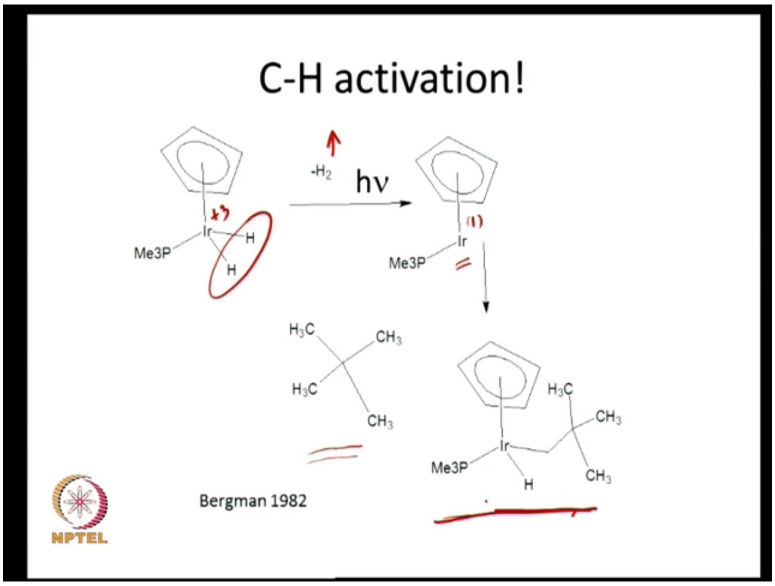

C-H activation!

Bergman 1982

Here is another example which was again a very interesting example because here we are going to take not a aromatic ring hydrogen, but an alkyl hydrogen. The challenge in carrying out alkyl group hydrogen atom activation is quite remarkable. Here, we have taken a iridium complex which again has got cyclo penta diagonal mohite, and this cyclo penta diagonal mohite now stabilises the iridium bond. If you use iridium 3 in this particular instance, this is still iridium 3.

If you exite it with light, it extrudes a molecule of hydrogen and results in the formation of an iridium 1 species, that iridium 1 species because you do not have the hydrogen any longer in solution. H 2 is liberated from the reaction mixtures. So, you have a vacant co ordination sphere on the iridium, and the electron who are iridium grabs a C H bond on the tetra methyl methane and this resulting in the formation of alkyl iridium 1 species and iridium H bond.

Notice in these cases a strong C H bond is replaced by the iridium H bond and iridium carbon bond. Many of these reactions can be carried out with 4 b and 5 b elements, but they are not favourable or not in the reaction is not possible with 3 b elements. Because there as on why 3 d elements do not work out well is because the 3 d metal carbon bond is much weaker than the 3 d than the 4 d metal carbon bond or the 4 d metal hydrogen bond. The 4 d and 5 d elements form very strong hydrogen bonds to hydrogen and bonds to carbon.

So, this reaction was discovered only in 1992 by Bergman which spear headed a lot of effort on C H activation. C H activation is important because you can now use that to functionalise what comes out of the petroleum feed stocks, and what cannot be used for as a fuel can now be functionalised and useful in making useful chemicals.

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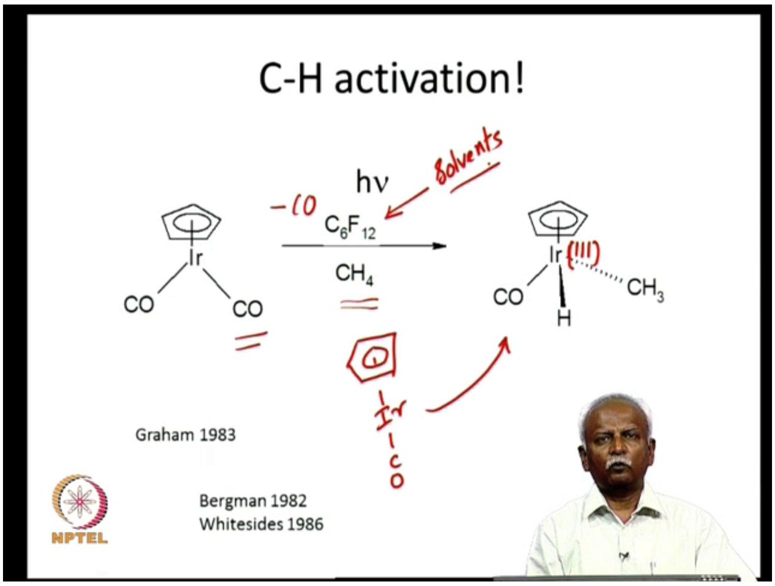

C-H activation!

Graham 1983

Bergman 1982
Whitesides 1986

Here is another example which is discovered very close to the discovery of Bergman that was done by Graham in 1983. And here a iridium 1 complex was again photolised and during the photolysis carbon monoxide was liberated. C O was liberated minus C O and because of vacant C O ordination sight on rhodium upon iridium and the presence of methane. You can have oxidative addition of a C H bond to their iridium 1 species resulting in the formation of a methyl iridium hydride, which is formally the irridium is not plus 3 species reason plus the oxidation state.

So, you have several cases where you can have oxidative addition of bonds which are not polarised and bonds which are quite strong. They are broken up by the metal because you have a vacant co ordination sight and in this particular instance the intermediate would be as follows. This is the iridium 1 carbonyl complex, now it is highly coordinative unsaturated and so it will take any molecule that it can react, that is why you have to use C 6 F 12 as a solvent. Or the solvents where you have a C H bond would become too reactive and they would react with the iridium 1 centre.

So, you have to use a non reactive solvent which is per fluorinated sight a hexane, cyclohexane. So, as sequential a discovery of the Graham and Bergman, several people several more people studied the C H activation reaction purely, because C H activation turns out to be a key reaction if one has to use petroleum feed stocks more effectively.

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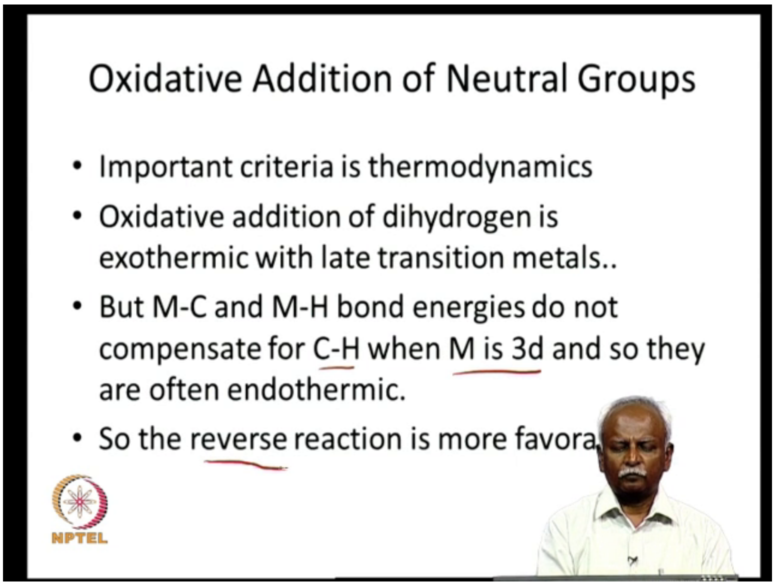

Oxidative Addition of Neutral Groups

- Important criteria is thermodynamics
- Oxidative addition of dihydrogen is exothermic with late transition metals..
- But M-C and M-H bond energies do not compensate for C-H when M is 3d and so they are often endothermic.
- So the reverse reaction is more favora

So, what you are seeing in this class of reactions is that C H activation or neutral bonds like aromatic C H bonds or a S i H bond can be activated and made to form an S i M H bonds or M C M H bonds. During the course of this reaction the oxidative state of the metal changes by plus 2 units. The important criteria whether this reaction will work or not work or will proceed from right to left or not is dependent on the fact that you have strong 4 d and 5 d metal hydrogen bonds and strong metal carbon bonds.

If the metal is 3 d, if the metal is a 3 d element then the metal carbon and metal hydrogen bond energies are not sufficient to compensate for the bond that is broken which is a C H or an S i H bond. So, very often they turn out to be an endothermic reaction, and it is only possible to push it to one side by the addition of a third molecule, which might in fact compensate for this loss and energy or the C H bond.

So, 4 d and 5 d transition elements undergo oxidative addition with the third class of molecules more readily than 3 d elements, and if indeed there are examples where you have C H activation or H H bond breakage and formation 2 M H bonds. Then with 3 d elements there reverse reaction is a favoured reaction. So, the reverse reaction happens much more readily and you have reductive elimination.

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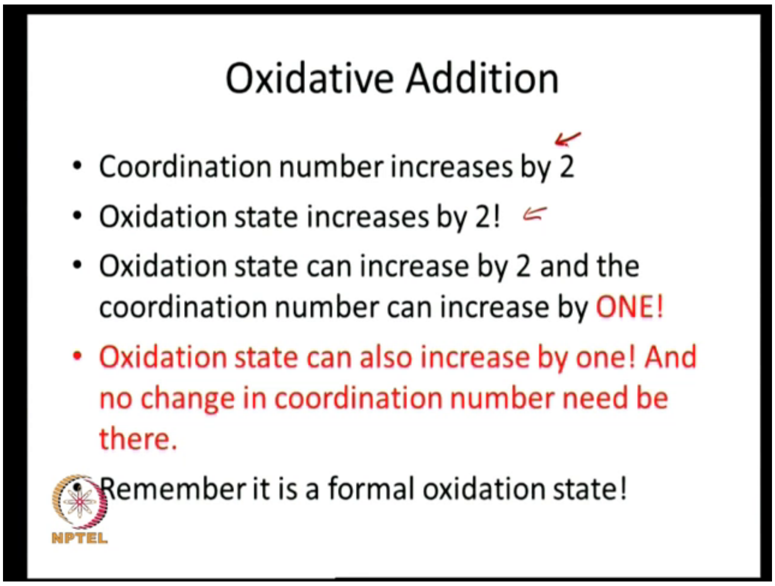

Oxidative Addition

- Coordination number increases by 2
- Oxidation state increases by 2!
- Oxidation state can increase by 2 and the coordination number can increase by ONE!
- Oxidation state can also increase by one! And no change in coordination number need be there.

Remember it is a formal oxidation state!

Now, coordination number increases by 2 during oxidative addition and by the same count you can have reductive elimination. But reductive elimination will be accompanied by a reduction in the coordination sphere number, and in the oxidation states or reductive elimination will lead to the opposite behaviour. That is they will lead to decrease in the oxidation state and decrease in the coordination number.

So, it is also possible to have oxidation state changes where the oxidation number of the metal increases by 1 and manganese is one example, where you have manganese 0 going to manganese plus 1 in the case of manganese hydride. And it is also possible in other cases as in the case of lithium, for example you can have oxidation state of 1 and we have a oxidation oxidative addition reactions. So, you can have a coordination number increase that is also 1 2 oxidation number can also change by 1 or 2, remember that it is a formal oxidation state that is going on during because of this reaction it is not a real oxidative addition.

So, with this we conclude discussion on the nature of oxidative additions and reductive elimination. It is during the course of this talk we have seen how some reductive eliminations can happen, especially when you have the third class of molecules or in the second class of molecules. Where we can form carbon-carbon bonds and readily eliminate neutral groups so that catalytic cycles can be accompanied.