Introduction to Organometallic Chemistry

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Lecture - 17
Oxidative Addition and Vaskas Complex mechanism

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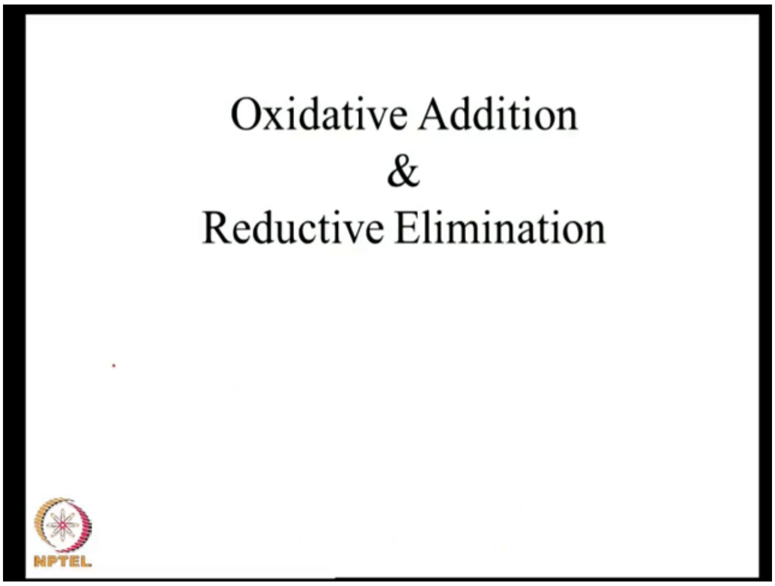

Oxidative Addition
&
Reductive Elimination

In this lecture, we will talk about a class of reactions which are called oxidative additions and reductive elimination, these to go hand-in-hand, because one is the reverse reaction of other. For the major part, we will talk about oxidative additions in these reactions in this lecture first, and then we will take a look at reductive eliminations.

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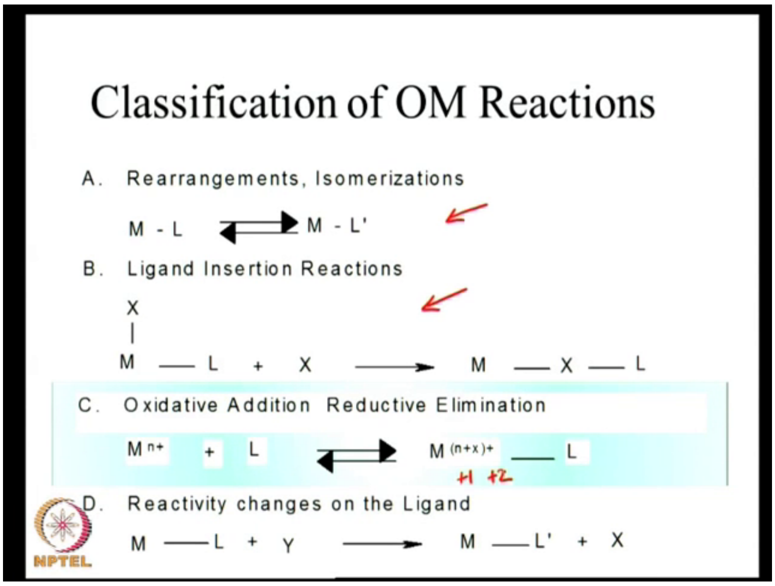

Classification of OM Reactions

A. Rearrangements, Isomerizations

$M - L \rightleftarrows M - L'$

B. Ligand Insertion Reactions

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

C. Oxidative Addition Reductive Elimination

$M^{n+} + L \rightleftarrows M^{(n+x)+} - L$

+1 +2

D. Reactivity changes on the Ligand

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

If you will recollect, we have classified the most of the organometallic reactions or most of the organometallic chemistry into 4 or 5 major classes of reactions. In this grouping, what we have done is we have taken the first 2 to be those reactions, where we do not have a change in the oxidation state of the metal atom.

So, the metal atom does not undergo any change in oxidation state in the case of A and in B. We do not have a change in the oxidation state of the metal, whereas in the class of reactions that we are going to discuss today, there is going to be a change in the oxidation state. It might either change by plus 1 or it could change by plus 2 units. In the reverse reaction correspondingly, you would have a reduction in the oxidation state of 1 or 2. So, these are reactions, which are very interesting and are unique to transition metal chemistry because it is only among the transition that you find variable oxidation state and the different oxidation state have relatively similar energies.

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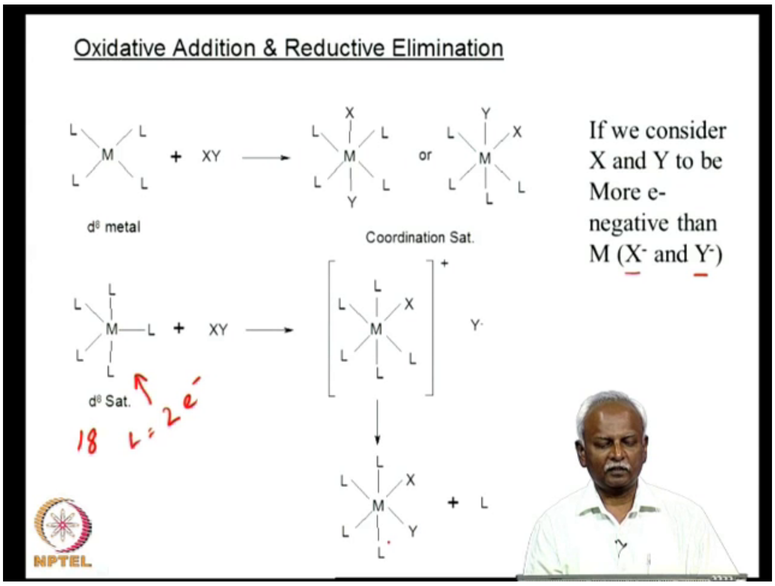

Oxidative Addition & Reductive Elimination

If we consider X and Y to be More e-negative than M (X^- and Y^-)

So, let us take a look at oxidative addition and the majority of the reactions that have been mechanistically studied. These are those reactions where you have d 8 metal complexes. Many of d 8 metal complexes have a square planar geometry. So, that is what we are going to take as an example. If you have X Y, the molecule the hetero nucleic, diatomic molecule X Y and if we add it to this d 8 metal complex, you can you can isolate a complex, which is octahedron ally coordinated. It is gotten the d 6 electron count.

Now, the question is what has happened to the oxidation state of the metal. If we consider the metal to be less electronic to the X or Y next, then it turns out that you would have to write X as X minus in this complex and Y as Y minus at least in the ionic method. It is easy to see that you now have 2 more negative ligands than what you started out with. You started out with 4 ligands. We do not know the character of those ligands, but you do not have a negatively charged species on the ligand.

Then, at the end of the reaction, you have 2 extra negatively charged species, which means the metal must have released 2 electrons to X and Y. So, that X became X minus and Y became Y minus. So, you end up with an oxidation state, which is plus 2 relative to your starting point. So, let us take a real life example. Now, you have d 8 coordinative saturated system. Then also you can have the same situation. You can add this X Y group, but if you start with a penta coordinated saturated co-ordiatively saturated metal complex, this is coordinatively saturated because you have if l is a 2 electron ligand. If l gives 2 electrons, then you have an 18 electron system right here.

So, when you add X Y or the new reacted with X Y, then you end up with a complex where you have the heterolytic splitting of X Y in such a fashion that you end up with L M L 5 X plus. Now, notice the oxidation state of M L 5 X plus is plus 2 units compared to what you started out with because X is considered as X minus. So, what you have is transfer of 2 electrons; 1 electron to Y to form Y minus 1 electron to X to from X minus. So, you have oxidation state change of 2.

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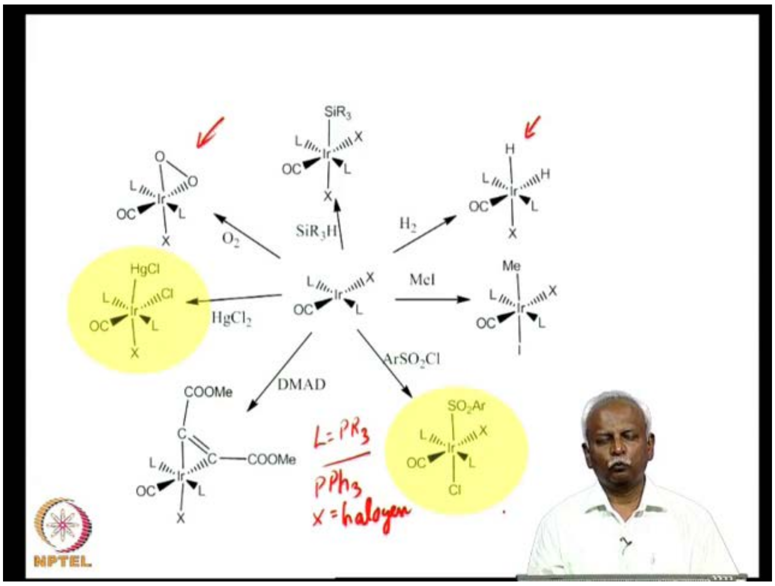

Now, let us take a look at some of the reactions that this complex has. It is actually a very popular complex. It was 1 of the first 1s that is discovered and very easy to understand and characterise L is phosphine or P R 3 group. L is P R 3 and very often, it is P P h 3. X is a halogen. X is a halogen, any halogen. Then you can have oxidative addition reactions that are plenty in the literature.

You have a species like h 2 adding to it. Then you have this complex here. You have oxygen adding to it. You have this complex here. So, you can see that 2 very different species, oxygen and hydrogen can add to this complex. This complex was discovered by vaska close to 1960s. So, it is called vaska’s complex. It is in fact a very popular system to study. Now, because you have a range of substrates it is convenient to classify them according to the type of reactions they undergo. The steps involved are not always the same. So, they have been classified into 3 groups. We will consider these groups one by one.

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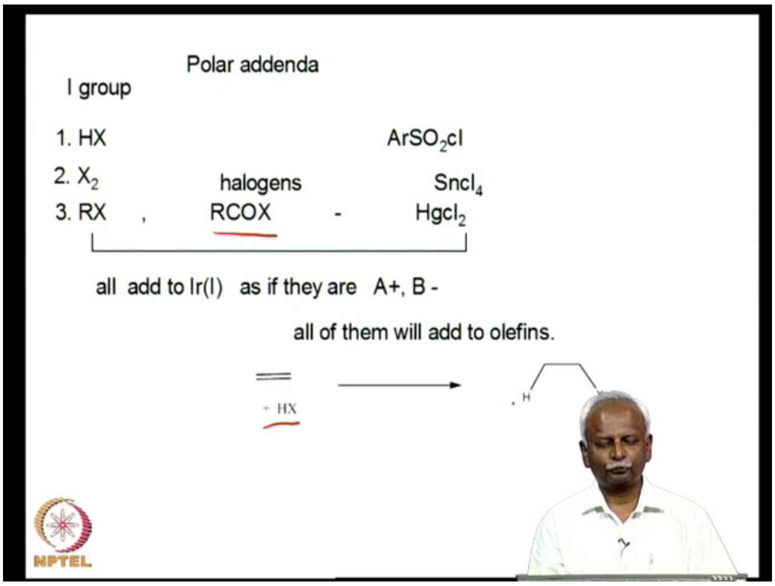

Polar addenda

I group

1. HX
2. X_2
3. RX , RCOX -

$ArSO_2cl$

halogens

$Sncl_4$

$Hgcl_2$

all add to Ir(I) as if they are A+, B -

all of them will add to olefins.

Now, if you take the first group, these are the molecules, which are polar. For example, H X that is hydrochloric acid H Cl, H Br, HI and so on. That belongs to 1 group and in the same group; you can also add X 2, which is just simple halogen molecule because they also behave in the same fashion. I will explain to you why that is the case. We can have very polar molecules, very highly polarised molecules like our Ar S O 2 Cl, which are clearly Ar S O 2 plus Cl minus. We can also have R C O X, which will polarise as R C O plus and X minus.

Now, if you will take all these molecules, although they look very dissimilar, they have one thing in common. That is a fact that if you take olefins, if you take an ordinary organic molecule olefins, add this H X 2 to it, any 1 of these molecules which we have listed above, all of them will add in this particular fashion. 1 part will add to 1 carbon and the other part will be attached to the other carbon. So, they will undergo simple addition reactions to olefins. So, if you take all these molecules, which undergo simple addition reactions to olefins, react them with vaska’s complex, they will undergo reaction. It will result in an oxidatively addition, which will undergo oxidative addition and form an oxidative addition product.

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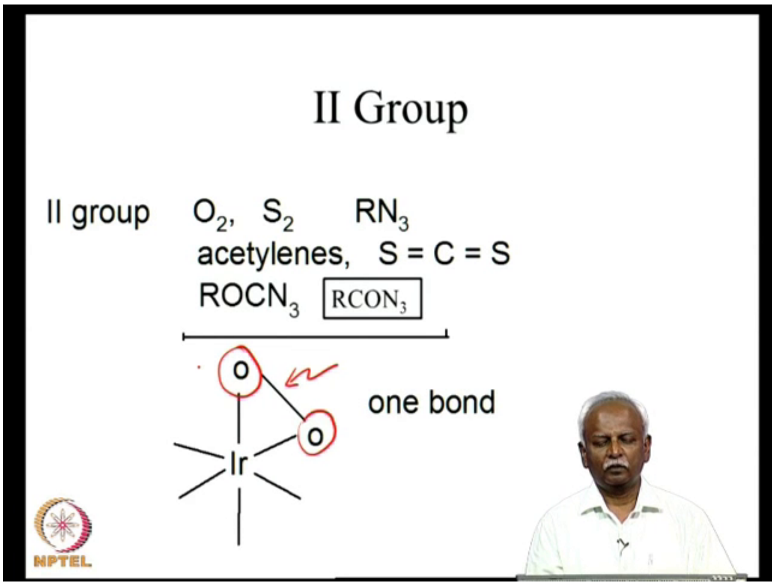

II Group

II group O_2, S_2 RN_3
acetylenes, S = C = S
$ROCN_3$ $\boxed{RCON_3}$

one bond

Let us take the second group. In the second group are the class of molecules. We have a unique feature that the 2 parts with, the molecule has got 2 parts, which are adding to the vaska’s complex and representative of all the molecules, which undergo oxidative addition. During the addition, 1 bond between the 2 parts of the molecules is retained. In other words, oxygen for example, has got a double bond between the 2 oxygen. So, double bond O and after the addition 1 bond, which is indicated here. 1 bond is in fact retrained.

So, although O double bond, O is the molecule you started out with, a single bond is retained at the end of the reaction. Now, what is the implication of this retention of the bond? That means that this molecule can add only in a cis fashion to the molecule to the metal complex. So, in other words, in the end of the reaction, the product you will always find 2 parts of the molecule, which are adding.

So, there is oxygen here and oxygen here. Both of them are in this cis position in the final complex. Secondly, you do not isolate intermediates during the course of this reaction. So, that separates class 1 from class 2. Secondly, you also find that class 2 is not necessarily polarised. They do not always add to olefins to form an addition compound within the organic reactions which we know.

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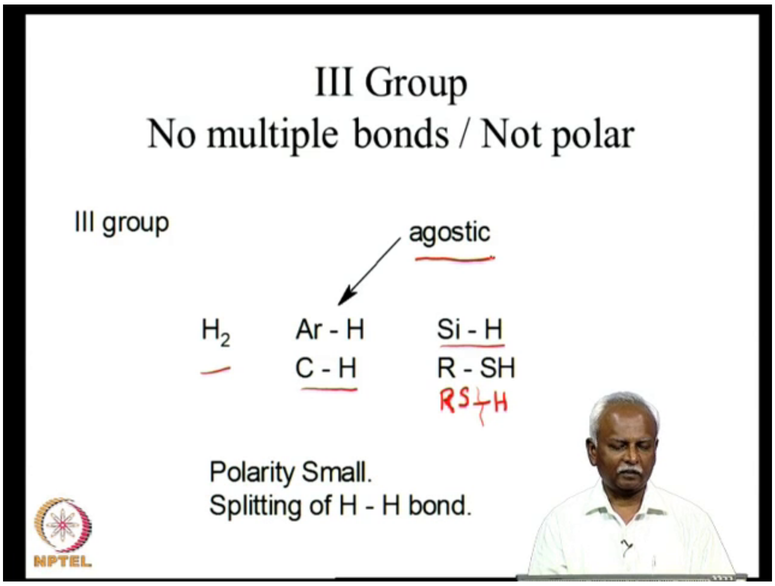

III Group
No multiple bonds / Not polar

III group

agostic

H_2 Ar - H   Si - H

C - H   R - SH

RS-H

Polarity Small.
Splitting of H - H bond.

So, let us proceed further with the third group. Here, you do have molecules, which are extremely covalent and non polar. They do not have any hint of polarity. Not only that, their electro negativity is almost similar to that of metal complexes. So, I have here listed several hydro compounds, hydrogen compounds di hydrogen itself as a first molecule, di hydrogen. We also have alkyl hydrogen.

So, those are non aromatic CH bonds. We also have aromatic CH bonds and we have Si H bonds. These are serine lanes. We also have RSH bonds. So, they should actually be written as RS dash H. So, the 2 parts being added are in fact, RS and H. So, these add on to the metal complex. So, the metal will now have RS and H added onto it. Now, many of these molecules are characteristic.

The characteristic feature of many of these molecules is as follows. They undergo an interaction with coordinatively unsaturated metal complexes in a weak fashion. This has been termed as an agnostic interaction. We will discuss this in greater detail later after we finished talking about oxidative additions, but nevertheless, the third group. What one needs to remember is the fact that they are not polar. They are non polar bonds, which are cleaved by the metal complex in order to form the oxidative leak added substrate substance.

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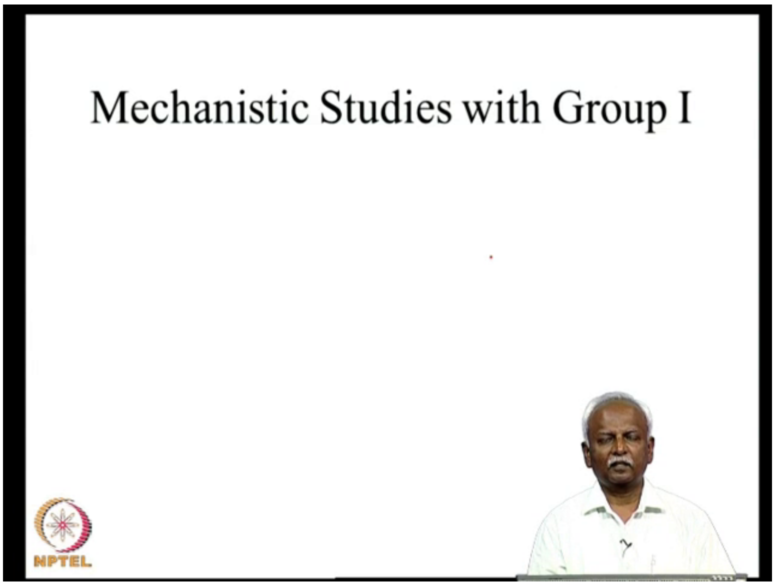

Mechanistic Studies with Group I

So, first let us take a look at the mechanistic studies with group 1 molecules. Group molecules, as I said can be very easily polarised into class.

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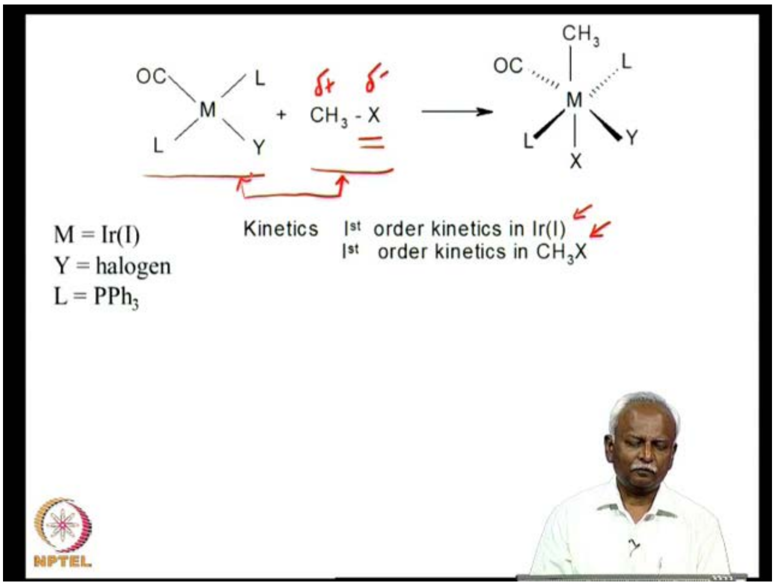

M = Ir(I)
Y = halogen
L = PPh_3

Kinetics Ist order kinetics in Ir(I)
Ist order kinetics in CH_3X

So, we have several great substrates, which behave like this. Typically, we can think about a molecule like methyl halide. Now, methyl halide is polarised as delta plus and delta minus. This is easy to see. As I told you halogen compounds are good, any good leaving group on the metal is good enough as X. X is in this particular example that we will be discussing, X is actually a halogen and the metal.

If metal is iridium and it is in the plus 1 oxidation state, it turns out to be similar to the vaska's complex when base 3. It is in fact vaska's complex. So, what are some features of these molecules? That we would like to consider that has been studied. The first thing that I would like to discuss is the kinetics. When you do kinetic study of this reaction methyl halide with vaska's complex, it turns out that first order in both iridium and first order in metal halide.

What that implicates is that during the course of this reaction, at least the rate determining step involves most probably a collision between these 2 molecules. These 2 molecules have to be collided in order for the reaction to happen. That is why, the concentration of both iridium 1 and the concentration of methyl halide makes a big difference in the rate of the reaction. So, that is the first thing that we note.

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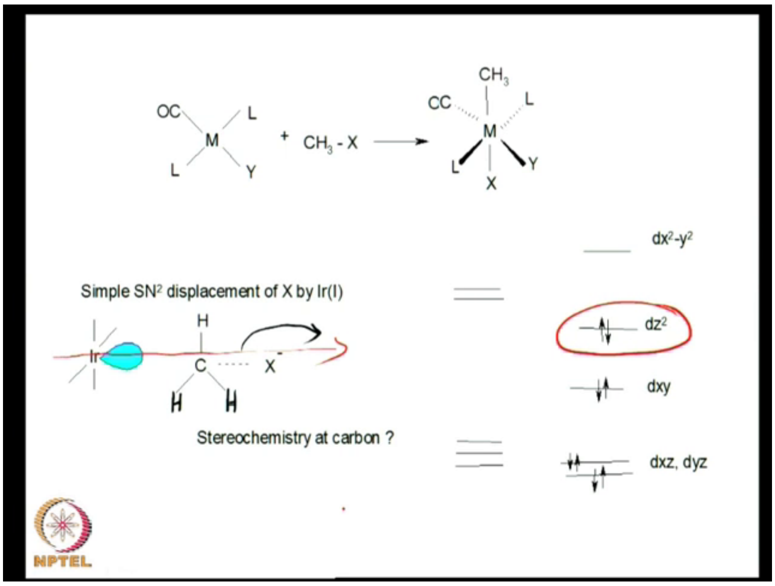

Simple SN² displacement of X by Ir(I)

Stereochemistry at carbon ?

The second thing that we note is that if this is in fact occurring through a collision of these 2 molecules, we can talk about the reaction as if it is a reaction of the iridium 1 as a nucleophile displacing the X group on the metal group, the X on the metal. Let me just complete this. So, if X on the metal group is in fact a halogen, this is leaving the methyl hallide as X minus. The iridium 1 is coming in and reacting with it. So, the methyl metal bond is being formed. That is what is pictured here. Now, we might be wondering how you can have a nucleophilic substitution by a metal complex.

If you look at the electronic structure of the iridium atom, which is there in iridium 1, you find that it is a square planar geometry. It is got 8 electrons in the d shell. So, if you remember this splitting diagram for when square planar complex is in fact, in such a fashion that the d x squared minus y squared is the highest lying orbital. The highest lying orbital among the d manifold and the highest occupied molecule orbital turns out to be the highest occupied molecule orbital turns out be the d z squared orbital has 2 electrons and that is the 1, which is the homo.

So, if you turn the square planar complex in such a way that you have the z axis in along here, then you can see that the d z squared will be pointed towards the methyl group. This will in fact result in a penta coordinated structure at the iridium. If you consider the X minus also, the t b p geometry at the methyl halide, X minus will be going away. You have a simple SN2 type reaction on the methyl halide. That is carried out by the nucleophilic addition of the iridium to the methyl group. X minus is the group. So, you can always ask what the stereochemistry carbon is; the question that we will come to late shown.

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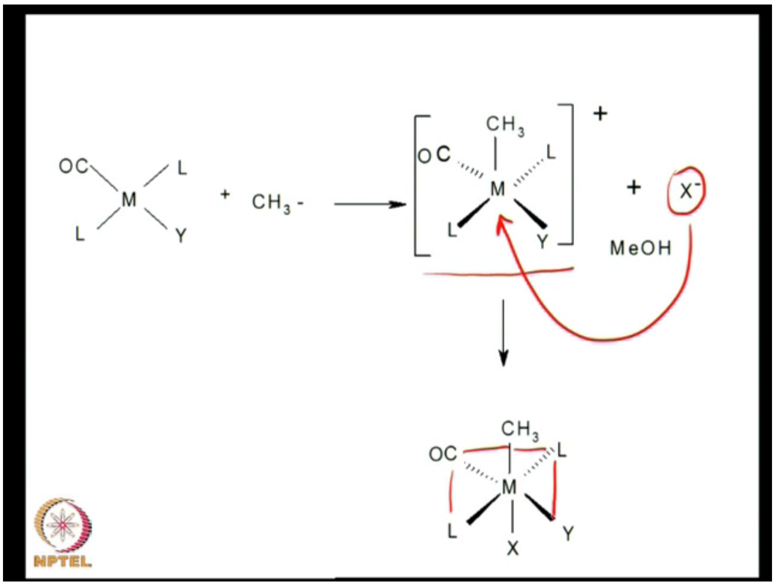

So, let us take a look at some of the features that support this type of reaction. First of all, it has been possible at least in some instances to find this penta coordinated intermediate that it is stable. It can be isolated, but in most instances, the X minus in the case of vaska’s complex, the X minus attacks the iridium atom again in the transposition to the methyl group. So, if it attacks here, you end up with the trans coordinated methyl halide. This is the vaska’s complex after oxidative addition. So, that is an octahedral complex.

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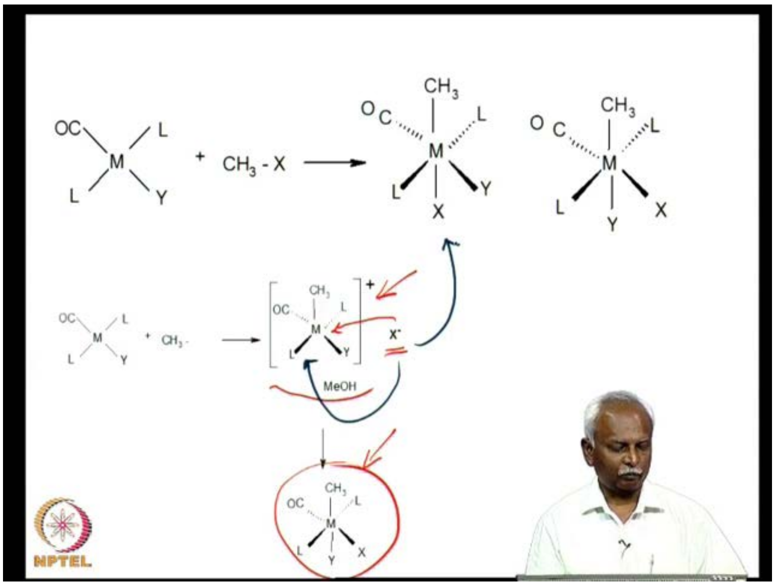

So, if you think about this reaction sometimes, it has been shown that you have a small isomerisation of the X and Y. Remember why is the species, which was attached is also halogen? Many times, it is a halogen and it is attached to the iridium atom. X is also a halogen. Sometimes, it is been possible to isolate an isomeric species. That gives you the indication that the intermediate must have been this penta coordinate pseudo square pyramidal geometry that was indicated earlier.

So, you have this as an intermediate. X minus can now come in and react with this penta coordinated complex, which I have indicated here. It results in the species, which is drawn below. Now, if it is thermodynamically more favourable to have X minus attack in this fashion, then you would have the formation of the product here. On the other hand, if X minus is thermodynamically more favourable to attack here, we will indicate this with different colour.

So, if X minus attacks here; we will have the product, which is listed here. So, depending on where the X minus attacks in the intermediate, you are able to isolate 2 different compounds. One where the X is in fact, trans to the methyl group. That is what is characteristic of these reactions in the first class. Sometimes, if it is most stable to have

X in the Y, in the transposition, then it has a small rearrangement. The attack takes place in a different place. You can have the isomeric product isolated.

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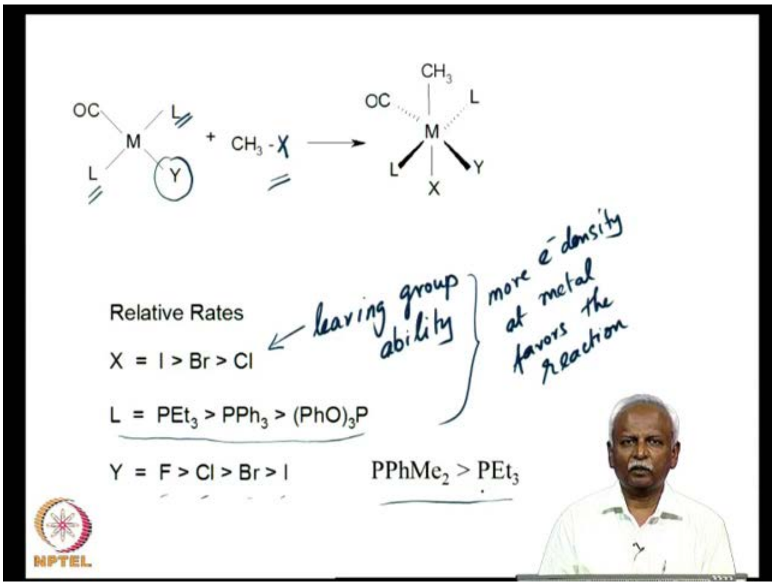

Relative Rates

X = I > Br > Cl

L = PEt_3 > PPh_3 > $(PhO)_3P$

Y = F > Cl > Br > I

$PPhMe_2$ > PEt_3

leaving group ability

more e⁻ density at metal favors the reaction

Now, what are the various factors, which support such a hypothesis? First of all, you had this bimolecular reaction between the methyl halide and iridium complex. Secondly, it was found that the X group, which is CH3X here CH3X the methyl halide, you have here undergoes reaction at different rates depending on the nature of X. So, if X is iodine, then the rate turns out to be fastest compared to bromine and chlorine, reacts the fastest. On the other hand, chlorine is the slowest. This is fitting the leaving group ability of X. So, this turns out to be correlating with leaving group ability.

So, the leaving group ability of X correlates with the rate of the reaction. Now, there is another indication that in fact, it is a nucleophilic attack by the iridium complex. How do we know this depending on the nature of 1 is a ligand which is attached to the iridium? If l is electron rich, then the reaction happens at a faster rate. So, here we are varied the second line. We are varied the nature of l and we can see that if it is tri ethyl phosphine. Ethyl groups donate more electron density to the phosphorus, which in turn donate more electron density to the iridium. So, iridium makes it much more suited to do this nucleophilic attack. So, there is more electron density at a metal.

These 2 factors suggest that more electron density at the metal is favourable favours the reaction. So, this is clearly supporting the fact that we have in fact, a nucleophilic attack where electron density of the metal does a nucleophilic attack on methyl group. The X leaves as X minus. So, there was one result, which was slightly difficult to understand. Based on this, what we have just seen here and that is the nature of Y if Y is a halogen.

If Y is electron rich, it should have promoted the reaction. On the other hand, it turns out that fluorine is much faster than chlorine than bromine and iodine. This is contradicting what we just said regarding the electron density of the metal. There was another slight difference if it was possible to show a PPhMe2 is much faster than PEt3. These 2 results can in fact be understood if we remember that the nucleophilic substitution at the methyl halide has 2 factors that will favour it. 1 is electron density of the metal. Another is the steric factor, which indicates that the incoming group has to be small in order to carry out the nucleophilic attack. If you have a very large group coming and attacking the metal, obviously that would lead to an unfavourable situation because the intermediate has to be a 5 coordinate intermediate at the carbon. That is very difficult considering the fact that carbon is a first row element.

It has got only 1 s and 2 s, 1s, 2 s and 2 p orbitals. So, you do not have too much space around the carbon in order to accommodate all this electron density. So, you would like to have a small group company, if you have larger groups than the rate turns out to be smaller. So, this is how it was understood. In fact, this is consistent with most of the data that we now have, which suggests that it is a nucleophilic attack. There are 2 components; 1 is an electronic component. Electronic component is indicating that if you have great electron density on a metal, you will do a faster nucleophilic substitution. The second factor is that the smaller the incoming group, the faster the reaction.

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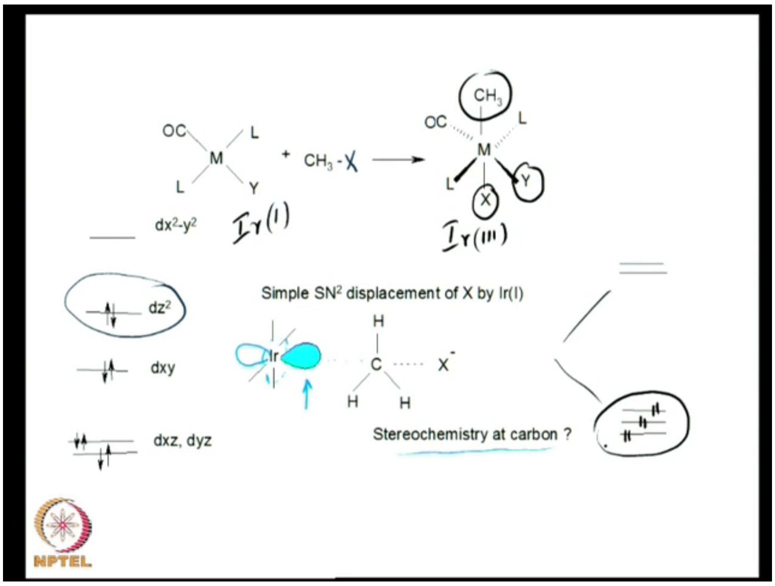

Simple SN^2 displacement of X by Ir(I)

Stereochemistry at carbon ?

So, here I have indicated to you the net result of this nucleophilic displacement, nucleophilic displacement of X by the iridium 1. You have X on the methyl group, which is being replaced by the iridium. So, what you end up with is this pair of electrons, which is almost like a 11 pair of electrons on the iridium. You do have a lobe on the other side. We can see this. We do have a lobe of on the other side. We have a Taurus here that is mostly the d z squared orbital.

That is how the d z squared orbital looks like. It is primarily this lobe, which we are concerned with because that is the part that is carrying out the attack on the methyl halide. In the transition state, you would have the famous umbrella inversion of the Walden inversion, where the X minus would be leaving and the iridium would be coming in. So, the stereochemistry of the carbon would be inverted at the end of the reaction. What you would have is a d 6 complex. We counted as a d 6 complex.

This is because we would have an iridium 3 species. Why are we calling it iridium 3 because you now have 3 anionic groups, we have 3 anionic groups. 1 is X, another is Y, another is a methyl methyl, because it is relatively more electron negative with respect to the carbon is more electron negative respect to the metal. We consider that also as a negative group. So, you end up with a 5 positive metal. As a result, the iridium 1 becomes iridium 3. This is iridium 1 here and this becomes iridium 3 here.

You would end up with 6 electrons of metal. These 6 electrons are now in our octahedral geometry. If you ignore the small symmetric petitions that will be caused by different ligands in an octahedral field, they will be split on this fashion. 6 electrons can be conveniently accommodated in the t 2 g set of orbital. You will have a stable situation0. So, that is why d 8 metal complexes undergo oxidative addition to form octahedral complexes, which become d 6 species and also 18 electrons in nature.

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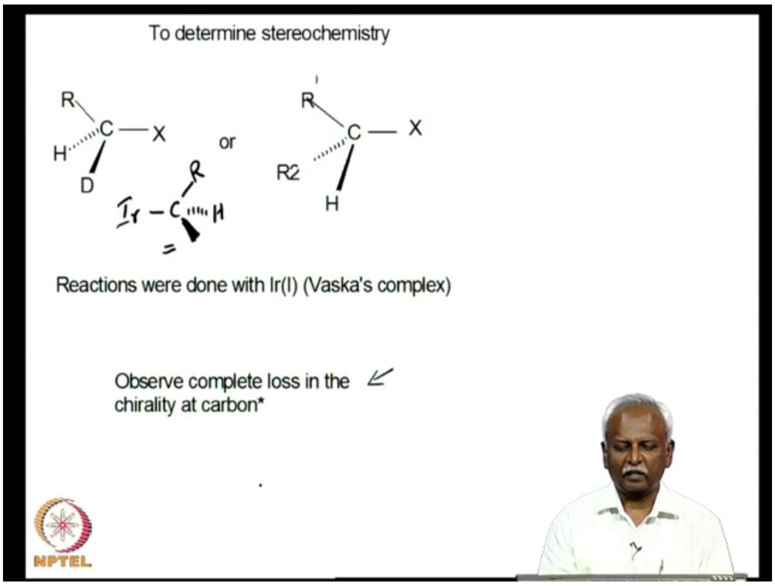

To determine stereochemistry

Reactions were done with Ir(I) (Vaska's complex)

Observe complete loss in the chirality at carbon*

So, let us move on now to determine the stereochemistry. A series of experiments were carried out. It is possible to have a single substituent on the methyl halide, which is undergoing substitution. So, if you make that R let us assume that that is alkyl group, then if X is a halogen, then you can have a Walden inversion at X. Let us say the vaska's complex undergoes the reaction with the species. You would end up with at the end of the reaction Walden inversion and the product should have been in this case in this instance. Let us write this out this group.

So, you would have this carbon undergoing Walden inversion for inversion stereochemistry. So, several reactions were done with vaska's complex. Surprisingly, they observed complete loss in the chirality of the carbon centre undergoing inversion, undergoing oxidative addition. So, this is a big surprise to organometallic chemistry community.

This was true whether one started out with a single substituent, which had a chiral centre generated with hydrogen and deuterium. If you have R and R1, R2, either way you ended up with laws of chirality at the carbon. So, one is left at a loss to explain how all the experiments, which were carried out earlier indicated an SN 2 type of substitution. Now, we are observing laws of chirality.

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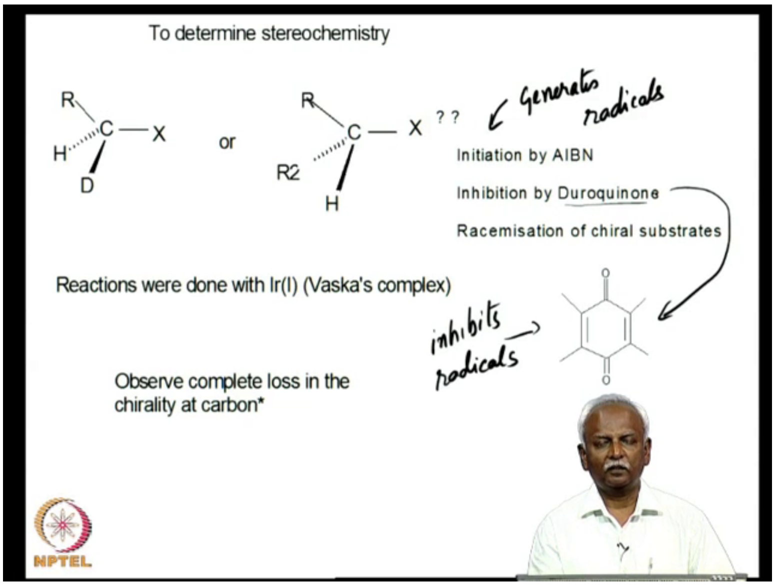

To determine stereochemistry

Initiation by AIBN

Inhibition by Duroquinone

Racemisation of chiral substrates

Reactions were done with Ir(I) (Vaska's complex)

Observe complete loss in the chirality at carbon*

So, the mystery was in fact solved when people started doing reactions very carefully by de oxygenation of the solutions, in which the reactions were carried out. Now, oxygen is paramagnetic and has the capacity to induce radical nature to a reaction. So, one has to deoxygenate the solution carefully. When one did that, this loss and chirality were sometimes not all, not completely observed.

So, people started doing reactions with aezo isobutyl nitrile or in the presence of duroquin1. Duroquin1 is a molecule that I have listed here. Now, aezo isobutyl nitrile generates radicals. This generates radicals. So, this inhibits radicals. So, it was shown that it is possible to promote this reaction in the presence of aezo isobutyl nitrile. It is possible to inhibit the reaction in the presence of duroquin1.

So, this clearly indicated that there was a radical nature to resolve reaction. That would easily explain why chiral substrates were racemes. So, this mystery regarding loss of chirality is that carbon was explained very simply by reactions, which were carried out in the absence of oxygen. Then by carrying out the reaction in the presence of radical promoters and radical inhibitors, it was possible to show that the nature of this reaction was in fact, affected by radical substrates as interim radical intermediates in the reaction. That also explained the chirality problem.

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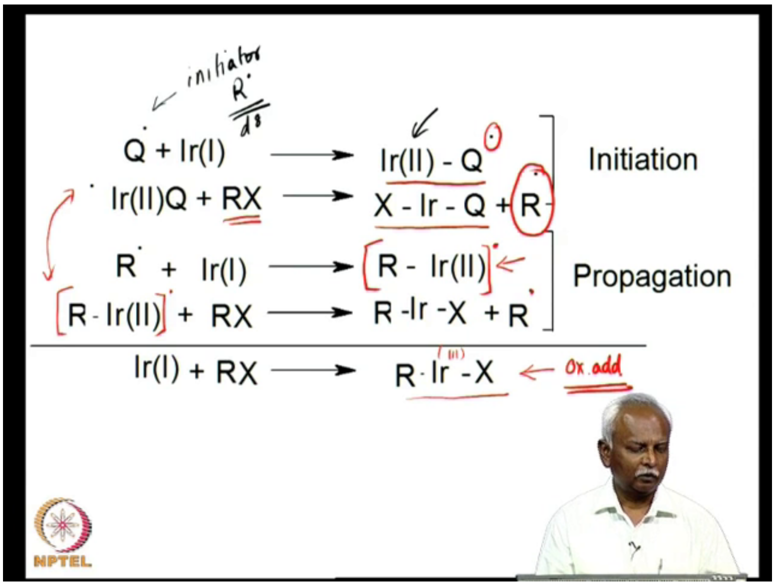

initiator $R^{\cdot}$ d^8

$\dot{Q} + Ir(I) \longrightarrow Ir(II)-Q^{\cdot}$

$Ir(II)Q + RX \longrightarrow X-Ir-Q + R^{\cdot}$

Initiation

$R^{\cdot} + Ir(I) \longrightarrow [R-Ir(II)]^{\cdot}$

$[R-Ir(II)]^{\cdot} + RX \longrightarrow R-Ir-X + R^{\cdot}$

Propagation

$Ir(I) + RX \longrightarrow R-\overset{(III)}{Ir}-X$ ← ox. add

So, let us take a look at what exactly is happening. Let us assume that there is a radically initiator in the reaction. So, if you have a radical initiator, then you could have the formation of iridium. To intermediate this, you should remember is only a catalytic initiator. So, Q dot is in fact an initiator. It could be any R dot for any radical species. If you use aezo isobutyl nitrile, the isobutyl radically would then be R dot. So, if R dot reacts with iridium 1, it generates a small amount of an iridium 2 species once again. This is because if you use an R dot, then we would consider I r, R as R minus I r plus. So, this would lead to an oxidation state change of plus 1 on the iridium. So, change in oxidation state of plus 1 takes place. So, that becomes iridium 2. Now, this iridium 2 is again, remember this is a d 8 species. So, if it becomes iridium 2. It will be a d 7 species. I will be an odd electron species. So, that is why we indicated by adding this dot. So, it is a radical.

So, this whole thing is a radical species. Now, if that reacts with RX, if that reacts with RX, remember RX is the group that is adding onto the iridium. So, this is purely the first step, is purely an initiation step where it led to the formation of iridium 2 radical. Iridium 2 radical reacts with RX, grabs X and forms I r Q X, which again is iridium 3 species and generates R dot. Now, this becomes our key intermediate. We need very little of the initiator that could be anything from oxygen to a radical species in the flask, which will lead to starting off of this reaction.

So, once you form R dot, then you can write a cycle, the catalytic cycle where you would react R dot with iridium 1 to generate the iridium 2 species are I r 2, which again would be the net species, would be a radical species. This is because you have reacted a radical R dot with even electron species. Now, this iridium 2 species, which has got a radical nature, will react with RX. This is identical to what we saw here. These 2 reactions are similar. These 2 reactions are similar. We just have RX reacting with this radical species to generate free radical again.

Now, because you have a radical intermediate, this whole reaction, what we will end up with is laws of chirality at the carbon, which is undergoing oxidative addition. Now, if you add up these 2 reactions, if you add up these 2 reactions, you see you can see with iridium 1 plus RX gives the iridium 3. I r is I r X, which is an oxidative league added product. So, this is the oxidative added product and that is what is isolated at the end of reaction.

So, you can see that radicals can induce this type of reaction. Whatever was studied with methyl was in fact coincide was fortuitous. This is because methyl is a substrate, which has got very little steric interactions. Iridium can do a nucleophilic substitution reaction on methyl halide very easily and carry out this nucleophilic attack. All the factors that we had looked at with methyl halide will point to the fact that you have SN2 type of reaction, but the moment you have any other alkyl group on the methyl, on the carbon undergoing substitution.

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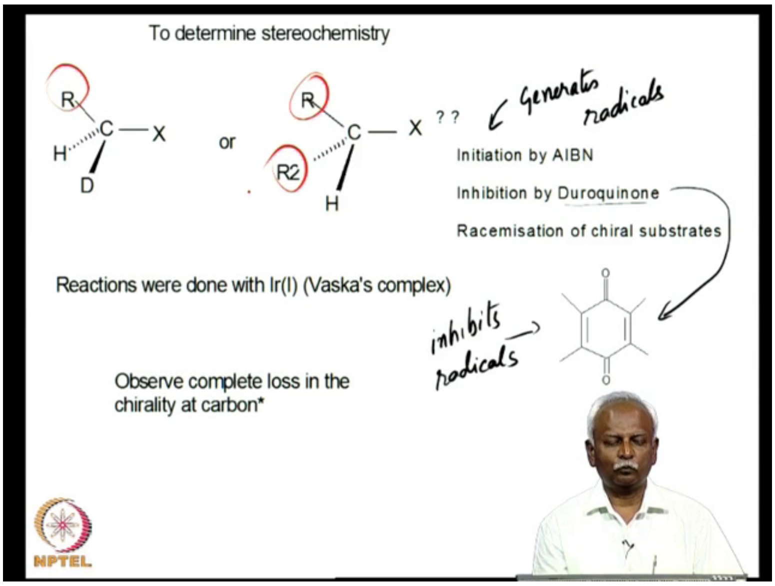

To determine stereochemistry

Generates radicals

Initiation by AIBN

Inhibition by Duroquinone

Racemisation of chiral substrates

Reactions were done with Ir(I) (Vaska's complex)

inhibits radicals

Observe complete loss in the chirality at carbon*

So, in other words, if you have R or 2 R groups, then the chances are that you will end up with the radical reaction and not SN2 type of reactivity. So, nevertheless, this has helped us to understand although we have this complication, it is helped us to understand how one can carry out nucleophilic substitution or an oxidative addition on a metal atom.

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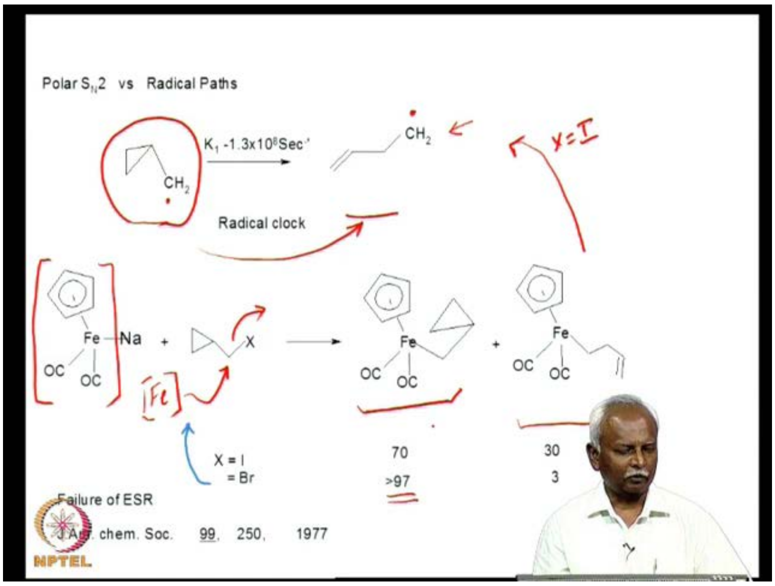

Polar S_N2 vs Radical Paths

Radical clock

Failure of ESR

J. Am. chem. Soc. 99, 250, 1977

Now, that were more reactions that were studied, which led to a beautiful understanding of how you can have radical intermediates in organometallic reactions. Let me tell you something fascinating about a molecule, which is called a radical clock. This radical clock is a cyclopropyl carbonyl radical. Now, if you have cyclopropyl carbonyl radical, it can bring open to generate the homo allylic radical. So, if this radical is formed in solution, ring opens at a very fast rate, which is known to be 1.3 into 10 power 8 second. That means every second, 10 power 8 molecules will convert from this ring opens state to this ring and acyclic form of this radical.

So, you can understand how fast this reaction happens. So, if it is involved in the radical is involved as an intermediate, one can easily detect the formation of products from this species. If the reaction in question happens at a faster rate than the ring opening of the cycle propyl carbonyl radical, then you would not have this ring opening reaction. So, let us take a look at what was a reaction that was carried out in order to understand this ring opening this radical nature of this reaction. So, the reaction in question is a cyclo penta dynyliron di carbonyl species.

This species as we are not discussed the cyclopentadynyl group itself we can just ignore it. Just let us do the electron counting. If you have Cp and Cp minus that means this is the aromatic Cp minus anion. Iron is iron plus, but nevertheless; there is a negative charge which is present on this whole species because sodium is a counter ion. So, the net charge on iron is actually 0. So, this is again a d 8 species. This d 8 species can react to a nucleophillic substitution. In fact, the iron if you write the iron in this fashion to indicate a Fe as Cp Cp 2, then this can indicate, this can carry out a nucleophilic substitution on this carbon and have a product, which is indicated here.

Now, this is a simple nucleophilic substitution that can happen in this reaction. That is what people expected, but if radicals are involved, if a radical intermediate is generated during the course of this reaction. As I have indicated here, if the cyclo propyl carbonyl radical is involved as an intermediate, then it can ring open to give you the homo allylic radical, which is again on the right hand side of the screen.

So, people carried out the reaction, this nuclear flick substitution reaction using the Cp Fe Co 2 minus anion. So, this anion was reacted with the cyclo propyl carbonyl halide. When X, the halide was iodide, they found that 70 percent of the reaction was in this channel. This means the ring unopened product was formed in 70 percent and the ring open product was formed in 30 percent.

That tells you that almost 30 percent of the reaction went through a radical pathway. So, radical reaction has happened and the ring opened very fast. So, that gave you the homo alylic product, which is indicative of the formation of this radical as an intermediate. On the other hand, if one used the bromo compound, surprisingly, the bromo compound resulted in greater than 97 percent of the nucleophilic substitution reaction product which is a simple nucleophillic substitution on the cyclo propyl carbonyl halide.

What we are pictured here has happened exactly. What we are pictured here has happened. This is with Br as a leaving group. We have only this channel with iodine as a leaving group. We have the radical channel. So, with iodine as the leaving group, we have X equals iodine and X equals Br gives you the ring unopened product. So, this is a beautiful chemistry, which illustrated the radicals are indeed involved. The surprising feature of this whole study was that e s r was not able to detect radicals in the reaction mixture. In spite of that, we were able to show because of the radical clock reaction favourable to show that radicals were indeed formed during the course of this reaction.

This brings me to the fact that absence of evidence is not evidence of absence. It is a very important principle that one needs to know in science in general and in reaction mechanism studies in particular. If you do not have particular evidence, it does not mean that it is not there. It is just that you are not been able to detect the radicals. In this case, e s r was not able to detect radicals; but a different technique, a chemical technique was able to show that radicals were involved.

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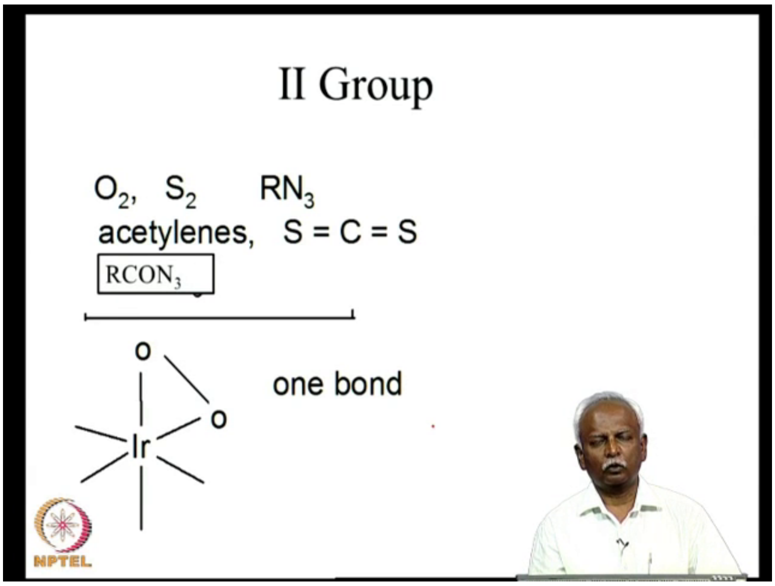

II Group

O_2, S_2 RN_3

acetylenes, S = C = S

RCON$_3$

one bond

So, now this brings me to the second group of reactions. The second group of reactions involves oxygen, sulphur or asides. When you react them with molecules like vaska's complex, they undergo a simple oxidative addition reaction. As I mentioned, 1 bond is retained always in the second class of molecules, which do oxidative addition.

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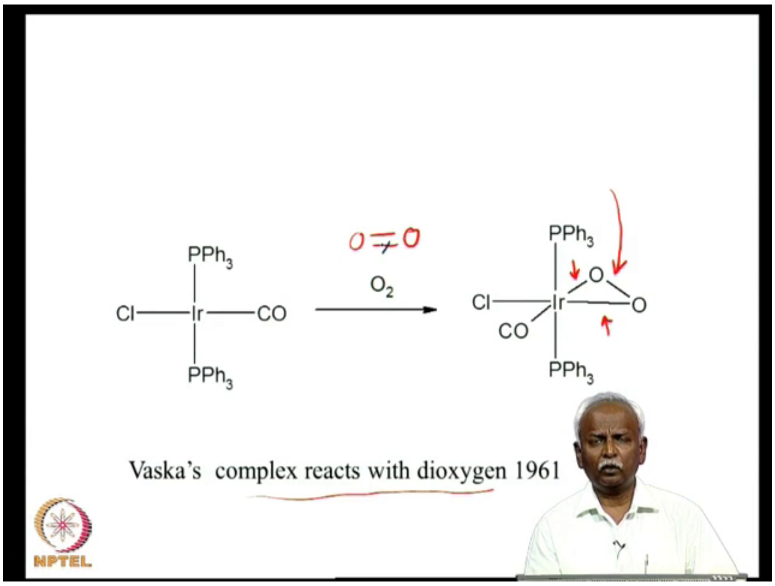

Vaska's complex reacts with dioxygen 1961

Now, vaska's complex itself was the first one which was studied. It was treated with di oxygen. Way back in 1961, that reaction was in fact studied by vaskas himself. What was shown was that the product has got a cis addition. The product is in fact, having 1 oxygen, 1 oxygen oxygen bond retained at the end of the reaction. If you recollect, it is important that we homolytically break 1 bond in all the oxidative additions. We homolytically break 1 bond and remove 2 electrons from the iridium, add it to the 2 adenda and found metal metaladdenda bonds.

So, in this particular case, it is iridium oxygen iridium oxygen bonds that are been formed. That leads to these are the 2 newborns that are formed the OO bond. First, you have double bond O and you have broken. So, we have broken this oxygen oxygen bond. So, the double bond has been converted into a single bond and the final product has got a bond which is intact between 2 oxygen.

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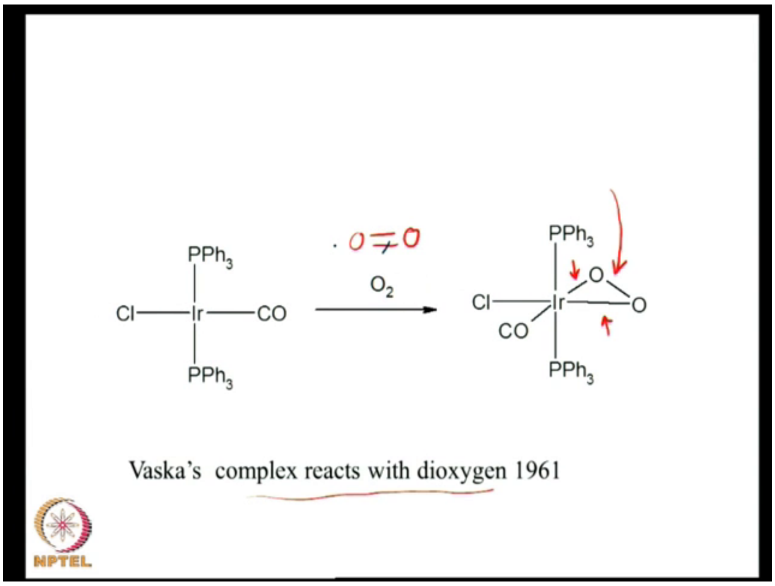

Vaska's complex reacts with dioxygen 1961

A similar situation happens with acetylenes. Here, you have a C triple bond C. The acetylene adds on to the iridium. You can see easily that the 2 carbons are attached to the iridium in a fashion. That indicates that you have these 2 newborns. If you assume that the oxidative addition involves carbon as carbon minus because it is more electronegative than iridium, then you end up with iridium 3 species. So, oxidation state is in fact a formal oxidation state. It is not the charge on the metal atom. It is something which one has to bear in mind when one is studying oxidative addition.

So, the characteristic feature of this oxidative addition in this case, is the fact that you have a change of plus2 in the metal atom in the oxidation state and the fact that it is retained in the c is position and the fact that it is such it is added in such a way that 1 bond is broken. If you start with a molecule, which has 3 bonds as in this case, you have 3 bonds, and then you end up with retention of 2 bonds. If you start with oxygen as in the previous case, we had 2 bonds and we ended up with retention of 1 bond.

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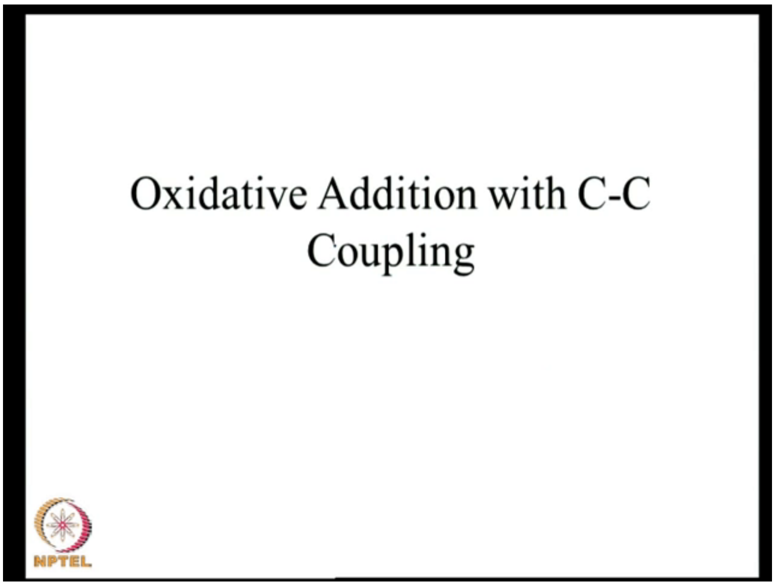

Oxidative Addition with C-C Coupling

So, let us proceed now with a slight variation in the oxidative addition reaction. Until now, we have been talking about oxidative addition with carbon with no change in the carbon centre. So, we will take a slight deviation and talk about oxidative additions, which involve a change in the organic substrate also.

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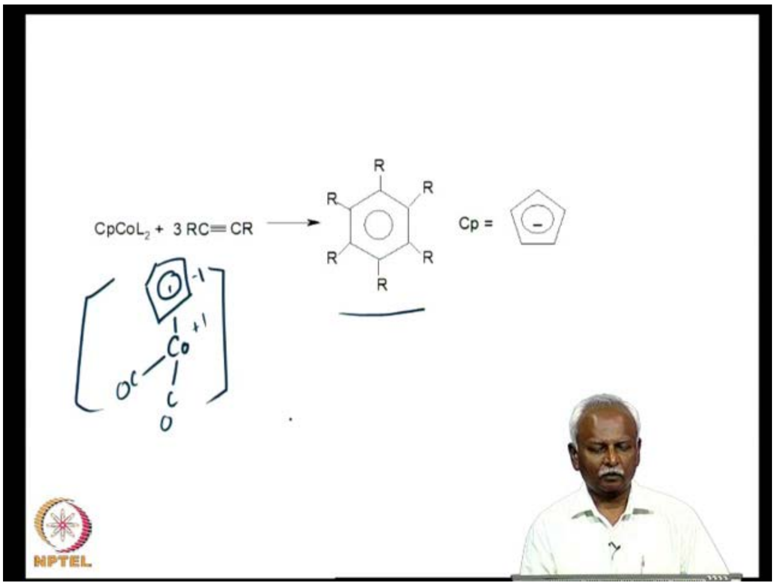

$CpCoL_2 + 3\,RC{\equiv}CR \longrightarrow$

Cp =

So, let us take a look at a molecule, which is very well studied. This is a cyclopentamidianyl cobalt complex. One can in fact draw this molecule in a different fashion. So, this is a cobalt centre bonded to all 5 carbon atoms and you have 2 neutral ligands. If you remember cobalt is in the plus1 oxidation state in this molecule because Cp is C p minus. This molecule is neutral. This is a neutral species. So, because this is a neutral species, this should be plus1 if this is minus1.

So, if you react this cobalt molecule with acetylenes, you have at the end of the reaction you have the formation of aromatic rings. What is interesting is that this reaction is of course, catalytic what I am describing. It can be done in this stoichiometric fashion. So, this turns out to be very interesting because it is a convenient way of generating an aromatic molecule starting with simple acetylenes.

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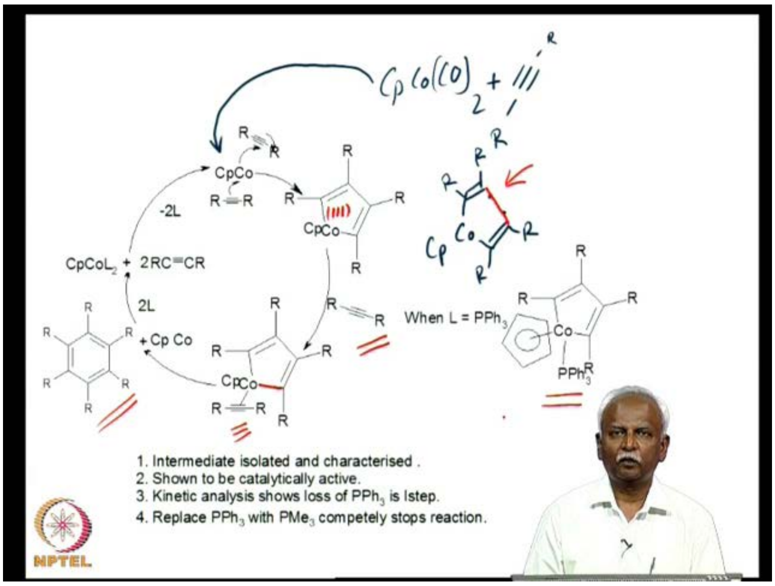

1. Intermediate isolated and characterised .
2. Shown to be catalytically active.
3. Kinetic analysis shows loss of PPh_3 is Istep.
4. Replace PPh_3 with PMe_3 competely stops reaction.

So, let us just take a look at this molecule, this particular reaction. First of all, you can have an oxidative reaction, in which you have 2 acetylene molecules reacting with this Cp C, which has lost the 2 ligands. So, you can replace the 2 carbon monoxide is that we had on the cobalt with 2 acetylenes. So, the reaction that we are talking about is Cp Co CO2 plus 2 acetylene molecules will lead to this intermediate. This intermediate can carry out an oxidative addition reaction. Remember, when you do an oxidative addition reaction, you break 1 of the bonds in the acetylene molecule and make 2 bonds to the cobalt. So, in this particular instance, if we broke 2 bonds on the acetylene 2 acetylene mol 2 different acetylene molecules, then you would end up with a species, which will formally look like this.

So, you can see that there are 2 unpaired electrons in the 2 acetylene molecules, which have oxidative added. Instead of taking 1 acetylene and carrying out an oxidative addition, you can take 2 a acetylene molecules and add 2 electrons to them in such a way that you form cobalt carbon bonds. Then you will end up with 2 electrons sitting on the 2 acetylene molecules, which can now form a bond very readily. Let us indicate this with a different colour, so that we remember that this bond is the newly formed carbon carbon bond. That is what is indicated here, which is now a cobalt 3 species.

This is the cobalt 3 species because we have Cp, Cp minus and 2 final groups attached to the cobalt atom. So, this species can now react with another third acetylene molecule, a third acetylene molecule. You can do this in 2 different ways. Remember, what we looked at when we talked about insertion reactions. This is an anionic group, which is this is an anionic group. This anionic group can now add onto the neutral acetylene molecule that we have here. So, you can have an insertion reaction. That will give you a 6 carbon chain, which is attached to the cobalt, which undergoes the reductive elimination and gives you the aromatic species.

It turns out that this reaction has been well studied. We will look at this in a little bit of detail. The main factors are that kinetic analysis showed that you need a loss of the ligand, which is attached to the cobalt before the reaction can happen. It was also shown by isolating some of these intermediates that you can have intermediates like this where you have oxidative addition on the cobalt. You have metalo cyclo pentadiene.

I am calling this metalo cyclo penta diene, because it is a cyclo pentadiene ring, in which there is a metal. So, this is the metalo cyclo penta diene, which has also been isolated and characterised. We can replace. If you replace PPh3 with PMe3, if you stop this reaction, you can stop this reaction by adding PMe3, then you can isolate and characterise an intermediate where you have this metalo cyclo penta diene on the cobalt.

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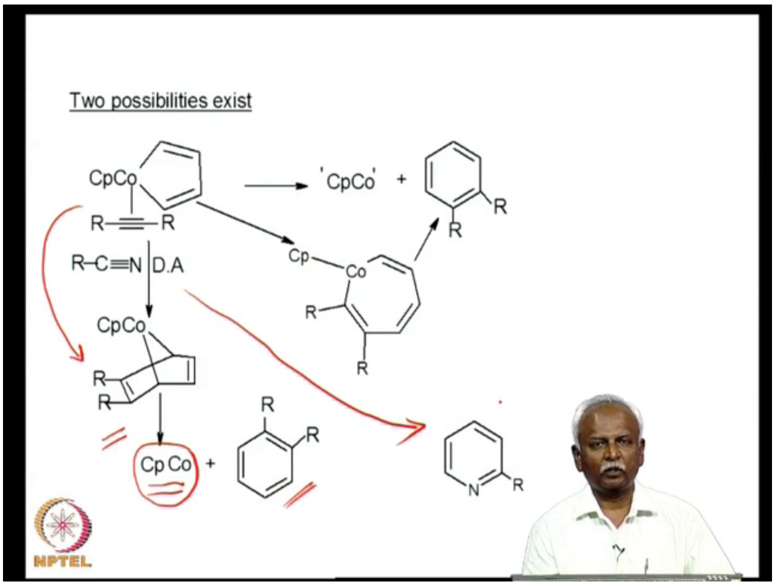

Two possibilities exist

So, the second step which involved the reaction of the metalo cycle penta diene with a third acetylene molecule was replaced with an acetonitrile or alkyl nitrile. Then it was shown that you can in fact, make pyridines. So, if you do the reaction with RC triple bond N, then you can form pyridines that I have indicated here. You can generate pyridines. If you treat it with R triple CN and if you have a simple RCR, then you can form acetylenes.

Now, this can happen as if it is the diels alder reaction. If you have a diels alder reaction, then between this metalo cycle penta diene and this alkyl, we form a diels alder reaction. This is a product that you end up with. That diels alder can now lose a molecular Cp Co, which is a catalytically active species. This is a catalytically active species, which can react with other acetylenes and go back to the catalytic cycle, but the product that you have got is the aromatic species.

Now, it turns out that if you have a mixture of acetylenes, you can have a variety of arene molecules generated. If you have nitriles present, you can have pyridines generated. It is convenient to make pyridines substituted readings using this method because it is often found that they first undergo oxidative addition and coupling happen with cobalt. Then the second step happens. That deals with nitriles or acetylene substituted acetylenes, so that you get aromatic compounds as I have indicated here or substituted pyridines as I have indicated here.

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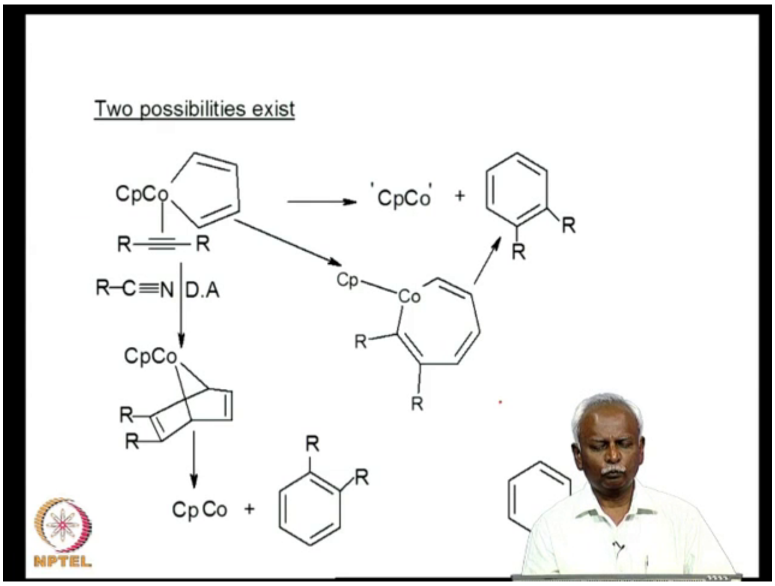
Two possibilities exist

Although there are two possibilities; these two possibilities can be distinguished.

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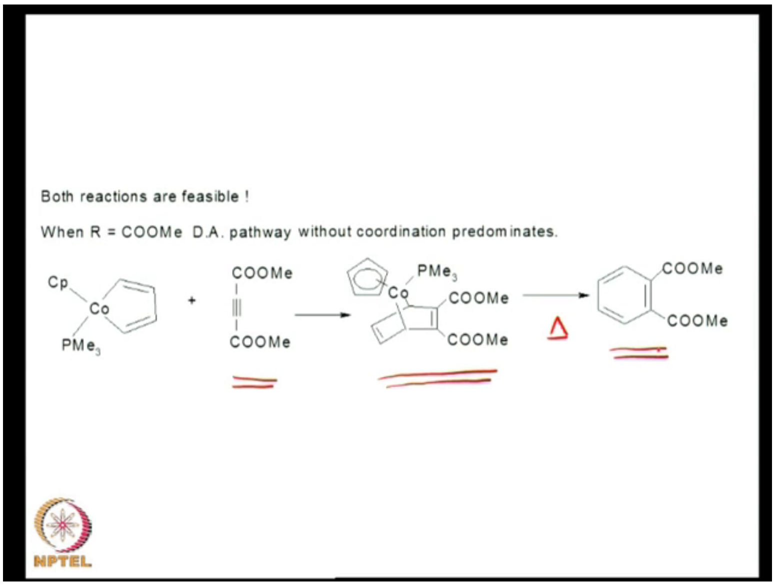
Both reactions are feasible !

When R = COOMe D.A. pathway without coordination predominates.

One can study this is by treating it with the molecule which will undergo diels alder reaction very readily. If you have di methyl acetylene di carboxylic, which is a very good dienophile, and then you can in fact, isolate an intermediate like this where you have PMe3 coordinated to the cobalt. The compound can be generated, which will on heating generate dimethylate. So, these are some reactions which have been carried out, where you have oxidative addition and the coupling reaction and an insertion reaction or it is a diels alder reaction.

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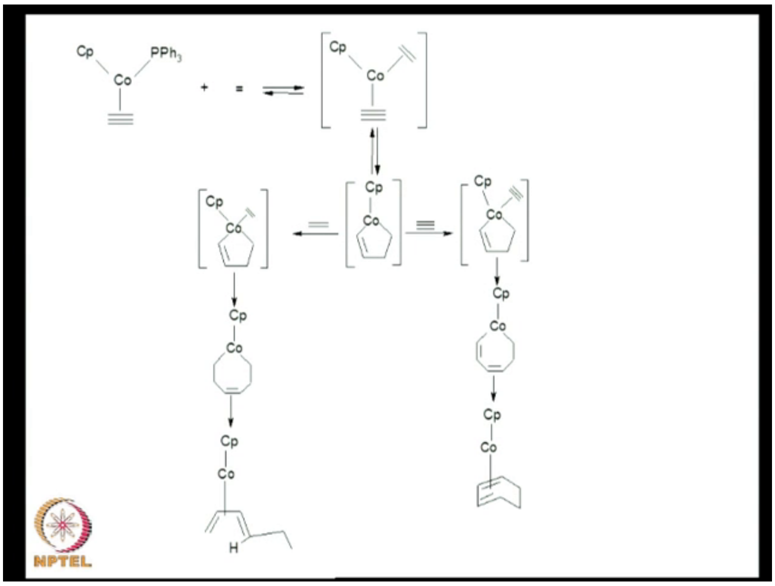

So, you have seen a variety of reactions, which are possible today. Let me conclude by going to the conclusion’s slide.

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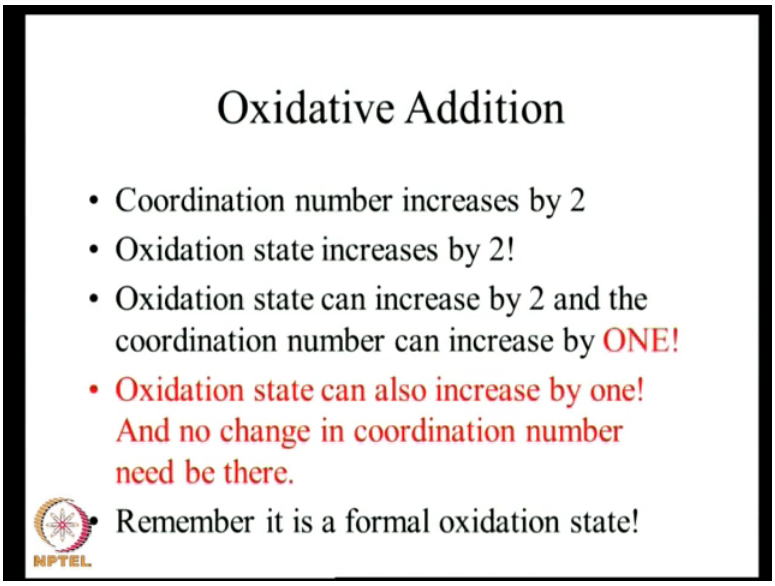

Oxidative Addition

- 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!

Usually, in all these reactions, the coordination number increases by 2. During oxidative addition, the coordination number increases by 2 and the oxidation state increases by 2 as well. It is possible that one can carry out of oxidation state; increase of 1 is also possible.

It is possible to increase oxidation state by 1 as well. We will look at some of these reactions where oxidation state can be changed by plus1 units in the following lectures. But, oxidation number and coordination number usually increase.

This is a reaction that is characterised by a change in the oxidation state of the metal. So, it is called characteristic of transition metals and is called an oxidative addition reaction. Invariably, you have a coordination number increase and that can also change by 1 or it can change by 2. Remember that it is a formal oxidation state change and it is not a real change in the charge on the show. With this, we conclude the first part of oxidative addition reactions. We will take up oxidative additions in future lectures as well.