Introduction to Organometallic Chemistry

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Lecture - 22

Metal-allyls complex-synthesis, bonding

In this lecture, we will discuss a very important class of molecules called metal allyl complexes.

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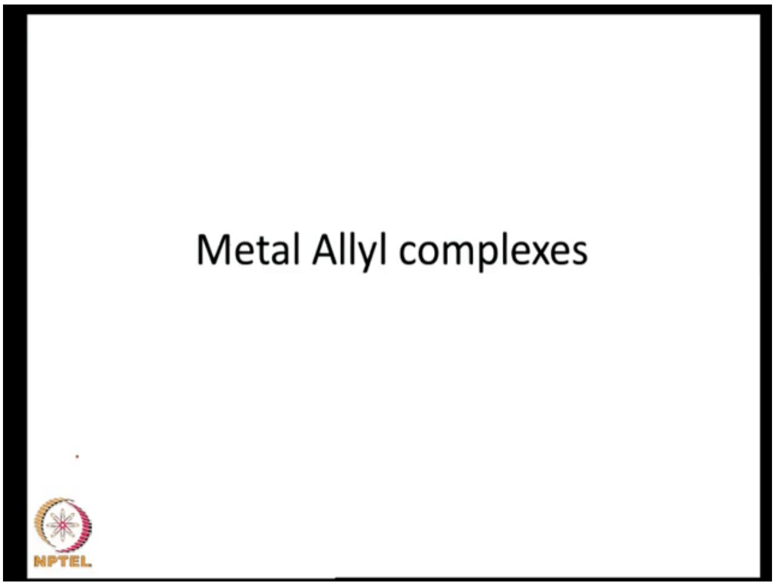

Metal Allyl complexes

These metal allyl complexes are indeed very complex because they adopt a variety of interesting structures. They undergo variety of interesting reactions as well.

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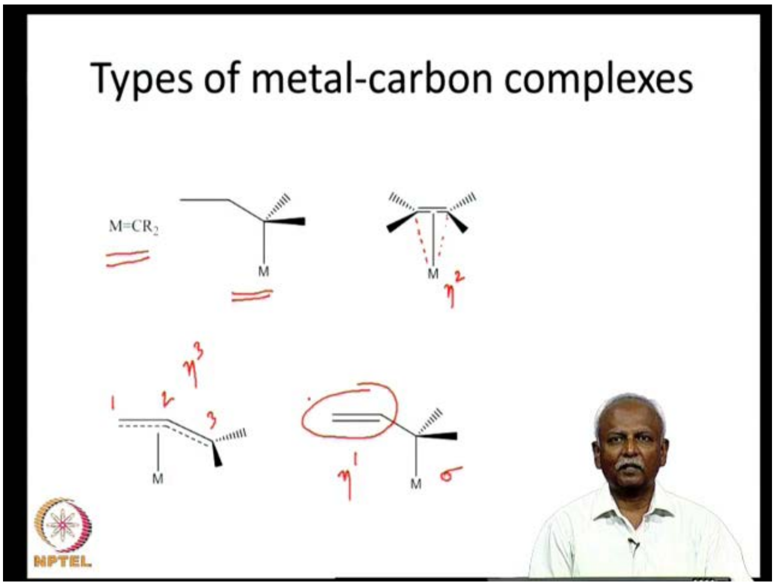

Types of metal-carbon complexes

So, before we plunge into metal allyl complexes, let us just get the context, in which we are talking about them. We started by looking at molecules where we had a formal metal carbon double bond. These are molecules like carbines and also metal carbonyls where you do have a metal carbon double bond, which can be written valence bond formulism use a double bind to indicate the type of interaction between the metal and the ligand.

The important thing is that there is only 1 carbon attached to the metal. Following that, we also discussed metal alkyl complexes. These are complexes where there is a metal carbon sigma bond and there is no formal pie bond between the carbon and the metal. So, these are typified by the example that I have given you here. Any alkyl compound, metal alkyl compound represents a case where you have only a sigma bond between the organic ligand and the metal.

We also talked about metal olefin complexes where 2 carbons are interacting equally with the metal atom. Although we do not indicate these interactions specifically, you can see that these are molecules in which 2 carbons are bonded to the metal. So, we write them as hapticity is 2 and indicated with eta 2. So, this eta 2 symbol indicates that 2 carbon atoms of the ligand are interacting with the metal atom.

Today, we are going to talk about metal allyl complexes, which are interesting because they have 2 forms which are predominantly found in the literature. 1 form, in which 3 carbon atoms of the allyl moiety are interacting with a metal and in almost a equidistant the metal is almost equidistant all 3 carbon atoms. So, in other words, carbon atom 1 2 and 3 are interacting equally with the metal. So, hapticity is 3. So, we indicated with eta 3; notation eta with a super script 3 to indicate that 3 carbon atoms are interacts with the metal simultaneously.

The same molecule can also interact with the metal through only 1 carbon atom. When it does so, we have a eta 1allyl species. This is also an allyl compound, but this is a eta 1 allyl where there is only a sigma bond between the metal and the carbon moiety. The double bond, which is present on the carbon species, is not interacting with the metal. We shall see specific examples of these molecules as we go through this lecture.

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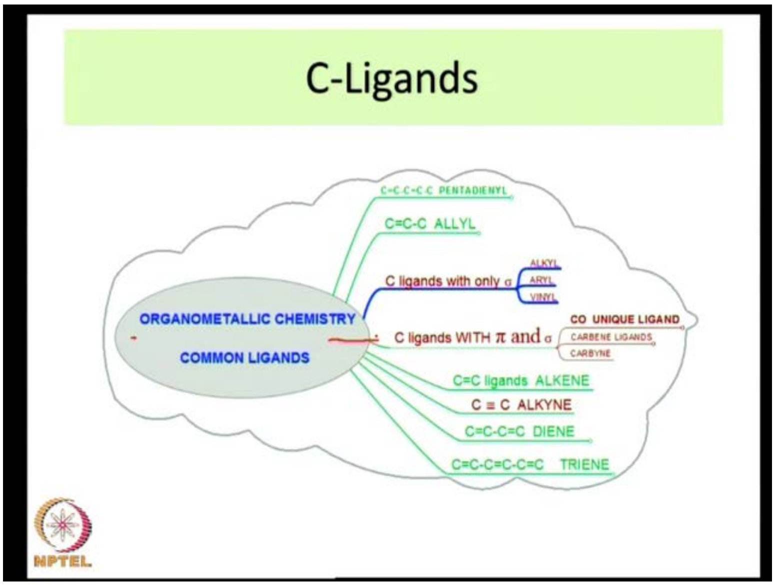

C-Ligands

ORGANOMETALLIC CHEMISTRY

COMMON LIGANDS

C=C-C=C-C PENTADIENYL

C=C-C ALLYL

C ligands with only σ

ALKYL

ARYL

VINYL

C ligands WITH π and σ

CO UNIQUE LIGAND

CARBENE LIGANDS

CARBYNE

C=C ligands ALKENE

$C\equiv C$ ALKYNE

C=C-C=C DIENE

C=C-C=C-C=C TRIENE

So in the context of the ligand space that we are examining an organometallic chemistry, you will notice that these sigma molecules are all listed above the central line where carbon monoxide is falling. So, if you can need this central line and all molecules, which have only a sigma bond and or a sigma and a pie bond are indicated above this line. All those which are interacting with the metal with only a pie fashion are indicated below this line. So, these are the type of ligands, where you have a sigma bond as well as a pie bond in the molecule. So, today we will be discussing the allyl complexes in all organometallic chemistry.

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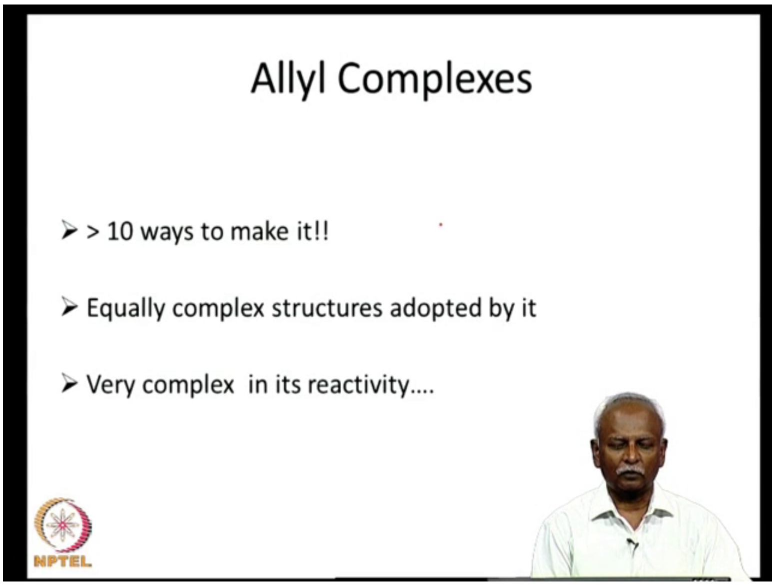

Allyl Complexes

- > 10 ways to make it!!
- Equally complex structures adopted by it
- Very complex in its reactivity….

As I mentioned earlier, allyl complexes are in fact very complicated because of the way in which they interact with the metal. There are a variety of ways to make them. Today, we will concentrate on the ways by which we can make these allyl complexes. Later on, we will talk about the reactivity of these metal complexes. So, today we will try to cover the ways by which we can make his allyl complexes and the type of structures they adopt in solution and in the solid-state.

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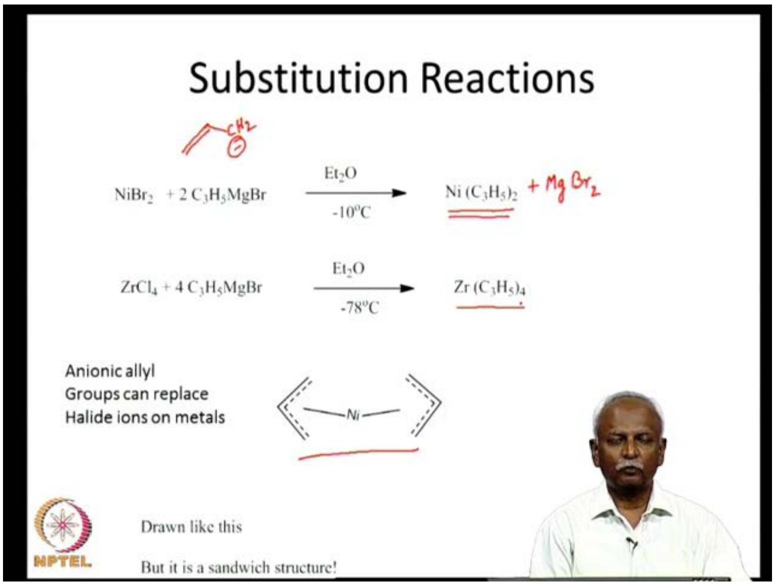

Substitution Reactions

$$NiBr_2 + 2\,C_3H_5MgBr \xrightarrow[-10^oC]{Et_2O} \underline{\underline{Ni\,(C_3H_5)_2}} + MgBr_2$$

$$ZrCl_4 + 4\,C_3H_5MgBr \xrightarrow[-78^oC]{Et_2O} \underline{Zr\,(C_3H_5)_4}$$

Anionic allyl
Groups can replace
Halide ions on metals

Drawn like this

But it is a sandwich structure!

First, let us talk about the simple substitution reaction in these reactions. 2 examples are given here in this slide. If you treat a metal halide with an allyl magnesium bromide, which is a simple Grignard reagent allyl bromide with magnesium turnings will give you magnesium bromide. This allyl magnesium bromide is predominantly C3H5 minus. In other words, you can think of it as it fits C H 2 C H C H 2 minus.

The allyl anion is what we are talking about is a predominant species. That is formed when you have an allyl magnesium bromide although it may not be in an isolated form. That is the net species, which reacts with the nickel bromide. So, it displaces a B r minus. So, what you end up getting in this reaction is MgBr2. As at the end of this reaction, magnesium bromide would precipitate out and of this allyl complex of nickel is formed. Now, the complex that is formed can be written in this fashion. The anionic allyl groups are indicated here as being coordinated to the nickel atom in a sandwich fashion although we draw it in a flat 2 dimensional representation like this. The molecule is in fact like a sandwich.

We will talk about this in a few minutes. The same reaction can be done with a variety of metal halides. This allows you to prepare homoleptic metal allyl complexes. Homoleptic; again let me repeat the molecules, in which there is only 1 type of a ligand. So, in this particular case, you have only allyl ligands and zirconium because the oxidation status plus 4 you have 4 allyl molecules, which are attached to the zirconium. Nickel is divalent. So, we have 2 allyl groups on the nickel. The nickel group in the periodic table nickel palladium platinum form very interesting allyl molecules allyl complexes.

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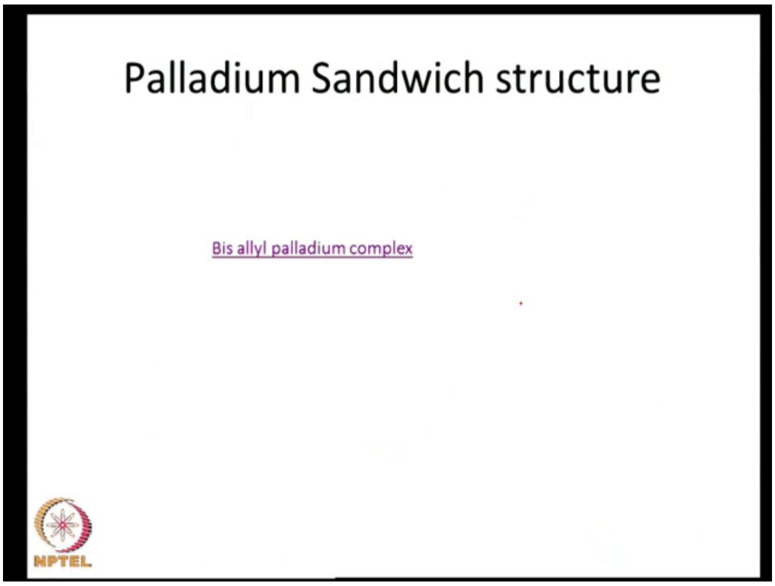

Palladium Sandwich structure

Bis allyl palladium complex

I will show you a structure of a allyl palladium complex to start with, so that you can appreciate the type of interaction that is there between the metal and the allyl moiety.

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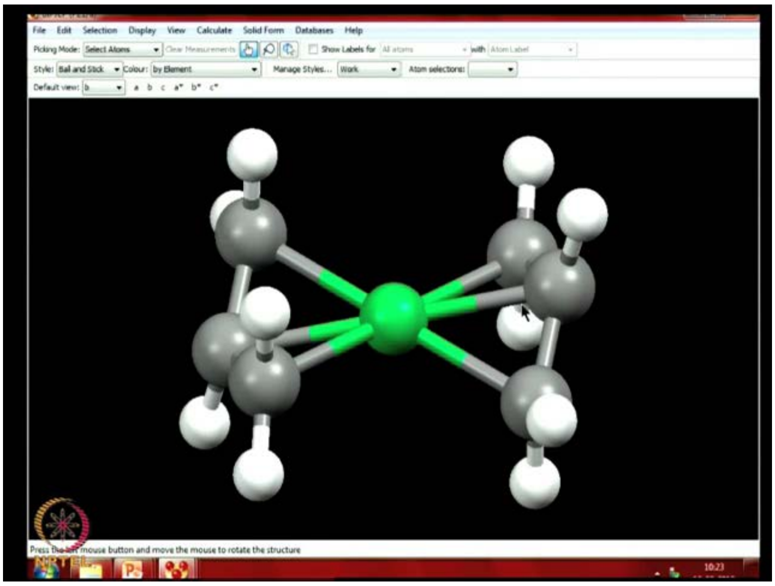

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So, this is the complex in which we have a metal atom, which is sandwiched between the 2 allyl groups. You notice that the allyls are staggered. In other words, when one case the central atom has got hydrogen pointing upward and in the other case, the central atom has got hydrogen pointed downwards, which I am indicating with an arrow.

So, here is 1hydrogen pointing upward. That is the central carbon atom. We can label all the atoms. You can see that the 3 carbon atoms are equally bonded to the nickel, which is present here. So, this is a case where you have the 3 carbon atoms almost equally bonded to the central nickel. You will be able to see these distances in a moment will measure them. This is 2.020 to the terminal carbon. 2.026 is the distance between the terminal carbons. The central carbon is at a distance of 2 angstroms.

So, you can see that they are almost the same distance the central carbon atom in the terminal carbon atom. You can see that the 2 allyl groups are in fact, in a sandwich like fashion between the central metal atoms here. So, you can appreciate this 3 dimensional structure and the way in which the allyl group is interacting with the metal. You will also notice that the allyl group is almost planar.

If I align it in such away with its almost planar, all the hydrogen atoms and the carbon atoms are in a approximate plane and between these 2 pains, the metal atom is centrally located. The carbon atom that is in the centre is slightly elevated slightly or away from the metal atom or so it appears, but you can see from the distance that it is in fact, almost equally placed from the metal as the terminal carbon atoms. So, these are some very interesting molecules that are formed by the metal allyl species.

You can have with zirconium. You will have 4 other allyl groups. It will be a arranged in a tetrahedral fashion. The only difference is that because it is a tetrahedron, here are more steric crowding, but nevertheless zirconium being a large metal; is able to accommodate all 4 allyl groups around it. So, let us just get back to the presentation here. Let us move on.

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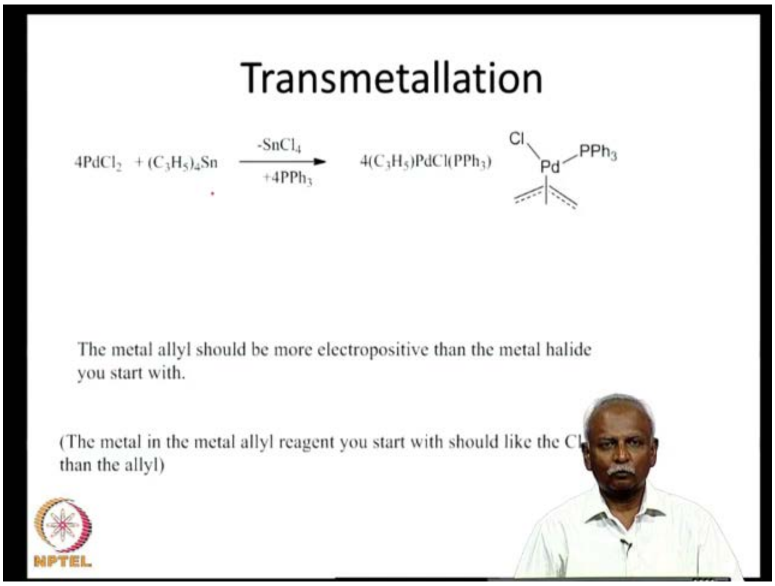

Transmetallation

$4PdCl_2 + (C_3H_5)_4Sn \xrightarrow[+4PPh_3]{-SnCl_4} 4(C_3H_5)PdCl(PPh_3)$

The metal allyl should be more electropositive than the metal halide you start with.

(The metal in the metal allyl reagent you start with should like the Cl than the allyl)

If you instead of doing a simple substitution reaction, we can also do a transmetallation reaction. I distinguish the substitution reaction from the transmetallation reaction purely because in the transmetallation reaction, I have an allyl tin group, which is a main group allyl complex. It is sigma bonded where the allyl group is sigma bonded to the tin.

This allyl group is not heavily polarised as allowing minus and tin plus. It can react with the palladium chloride in such a way that you can transfer 1 allyl group to the palladium. When you do that and you react it with 4 molecules of a triphenyl phosphine, you end up with a very interesting complex where you have palladium coordinated to allyl group and a triphenyl phosphine moiety and the chloride.

This molecule has been studied extensively because it reacts with nucleophiles. It allows you to carry out a nucleophilic substitution on what is apparently an allyl group, which is originally allyl, almost like an allyl minus. In spite of that, it can undergo reactions with nucleophiles. So, the metal allyls usually should be. If you wanted the transmetallation reaction, the metal allyl should be little more electro positive than the metal to which you want to transfer it to.

And similarly, the metal to which you want to transfer to a palladium if it is a palladium chloride than the chloride group is transferred to the group, which is transferring the allyl group. So, that should like the chlorine better. So, in this case, that is the tin. So, this turns out to be an exchange of 2 groups. That is why we call it as a transmetallation.

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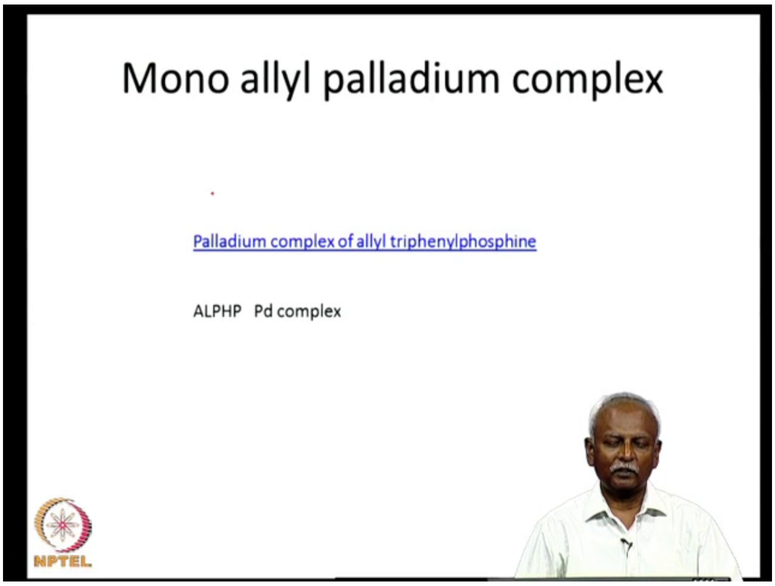

Mono allyl palladium complex

Palladium complex of allyl triphenylphosphine

ALPHP Pd complex

Now, we will just take a look at the palladium allyl triphenyl phosphine complex because that is also system where you have 3 allyl groups pointed towards the metal atom.

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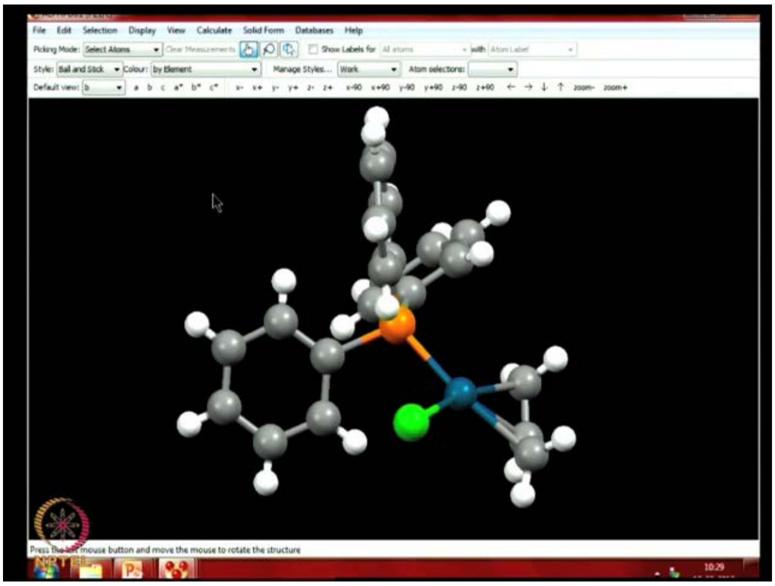

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Here is the molecule which has got a triphenyl phosphine. So, the phosphorus atom is shown in bright orange here. The phosphorus atom is bright orange. The metal itself is present just as in the other case in the nickel case. It is present in almost equidistant from the 3 carbon atoms, which are interacting with it and allyl group is almost planar.

There is a small deviation of the hydrogen from the plane in which the 4 CH 2 CH 2 units are present. So, the central hydrogen is moving away from this plane away from the metal atom. This turns out to be a unique 4 allyl complexes 1 of the hydrogen atoms. So, the central hydrogen atom moves away from this plane, not very much, maybe by a few degrees, but nevertheless, it moves away. So, the bond distance between the carbons and the palladium and the orbitals are oriented in the right way to have maximum interaction.

We will talk about this interaction little later, but you can see that this is a molecule in which there are 3 carbon atoms. The 3 carbon atoms are indicated herein are grey. The 3 carbon atoms are interacting equally with a palladium and the chlorine atom is coordinated to the palladium as well.

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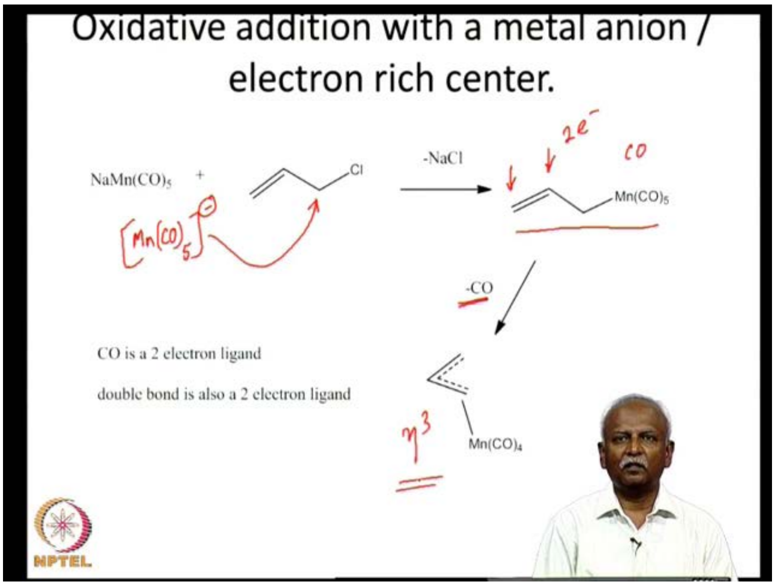

Oxidative addition with a metal anion / electron rich center.

CO is a 2 electron ligand

double bond is also a 2 electron ligand

So, let us get back to our presentation. Now, if you want to prepare an allyl moiety apart from transmetallation and apart from the substitution reaction that we talked about, also carry out that is called an oxidative addition reaction. These are reactions, which are talked about little earlier. If you have a metal halide of metal, a metal anion and an alkyl halide, the metal and anion can carry out a nucleophilic substitution reaction on the chloride.

In principle, this is MnCO5 minus. So, we can talk about it as MnCO5 minus and sodium plus. This MnCO5 minus makes a nucleophilic substitution reaction a Sn2 reaction basically. It forms an intermediate, which is a sigma allyl complex. So, in this sigma complex, which you have indicated here, we have a carbon metal sigma bond and this double bond which is present in the allyl moiety. These 2 carbons are not interacting with the metal.

We will see a crystal structure of 1 of these molecules shortly, but once this sigma allyl complex is formed, you will notice that these 2 carbon atoms, this double bond can give 2 electrons to the metal. On the metal, you have carbon monoxide units. So, this carbon dioxide is also a 2 electron donor. So, one can do a substitution reaction whether carbon monoxide is replaced with this double bond in an internal attack.

So, that is exactly what happens. We have loss of carbon monoxide and the formation of an allyl manganese complex. This manganese complex has 3 carbon atoms bonded to the metal just as we have shown in the earlier crystal structures. So, in a initial step, you do form a sigma allyl complex, but the sigma allyl complex is fleeting in nature. It is not stable. It will quickly rearrange to give you the eta 3 molecule or the tri hepto allyl species, which we are able to isolate finally.

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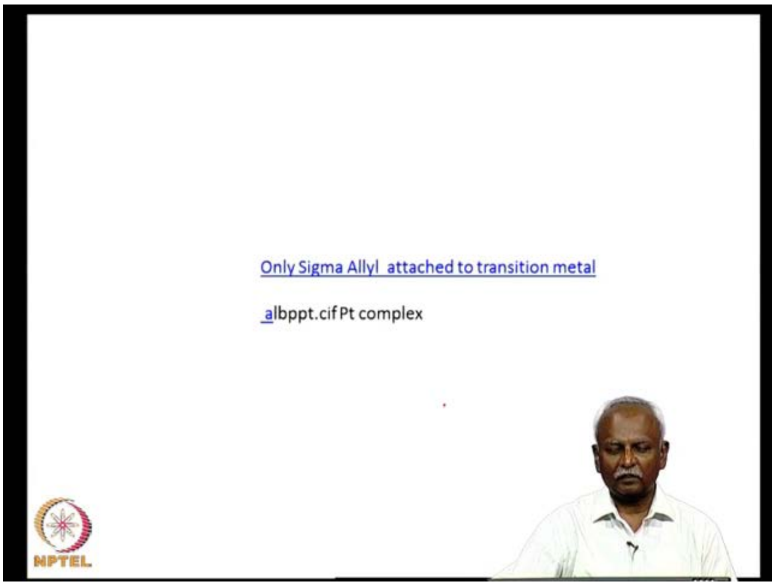

Only Sigma Allyl attached to transition metal

albppt.cif Pt complex

Now, it is possible to have only the sigma allyl attached to the transition metal in some complexes.

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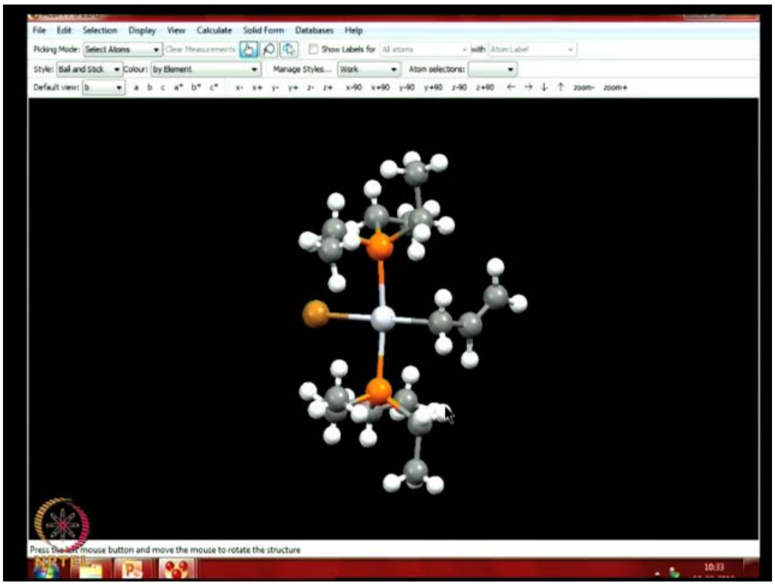

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If you want to see a structure of this, I will now show you a structure of this molecule where you have only a sigma allyl species, which is attached. Here is a platinum complex, not the manganese complex that we talked about earlier. Here is a platinum complex, which has got only the carbon atom, the terminal carbon atom attached to the metal.

So, here we will take a look at the distances, which are present. This is platinum, which is attached to the terminal carbon. If you measure this distance, let us measure this distance again between the platinum and the carbon is 2.086 angstroms. So, this is the carbon which is attached to the metal, whereas in the same way, if you measure the distance between the terminal carbon atom, let me show this to you in this orientation. So, you can see the 2 distances very easily. Here is the distance between the carbon atom, which is attached to the platinum and that is 2.086 angstroms. The carbon atom, which is further away, which I have marked in yellow, is at the distance of 3.874 angstroms.

In other words, the double bond these 2 carbon atoms, which I have indicated for you in yellow. Now, this carbon atom and the second carbon atom are not really interacting with the platinum. So, this is a clear example of a sigma allyl complex, where only the terminal carbon atom is interacting with the metal. The 2 carbons, which have the double bond, are not interacting with the metal at all.

So, the carbon carbon double bond is clearly indicated by short 1.3 angstrom distance between the 2 atoms. The 2 atoms, which are bonded through a sigma bond, are close to 1.5 angstroms or 1.485 angstroms. So, it is very clear that only isolated double bond is present. The carbon metal distance is close in 1 case to 2.086 and the other case, it is 3.8 angstroms. So, it is a very clear indication that it is a sigma allyl complex.

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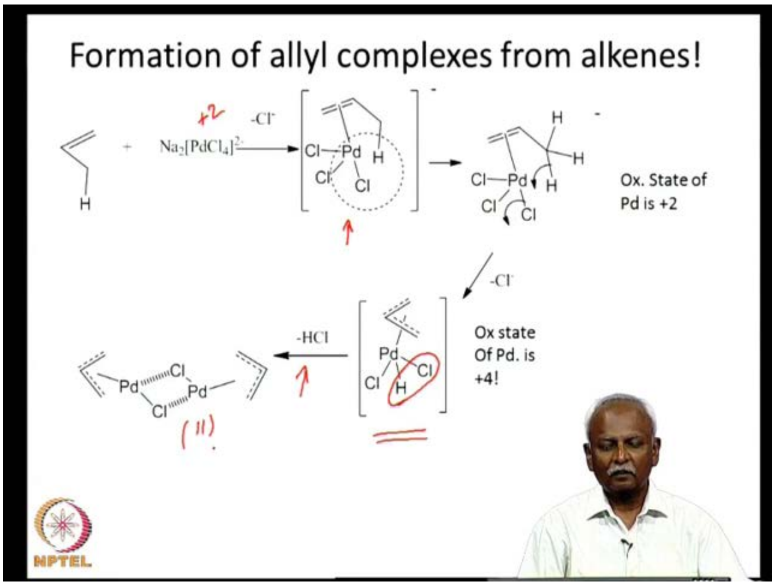

Formation of allyl complexes from alkenes!

So, it is interesting that you can have a variety of different coordination modes between the allyl group and the metal atom. We have seen 3 instances. 1 in which it is like a sandwich, 1 in which it is pie bonded and attached to other ligands as well and the third example where it is only sigma bonded to the metal atom.

So, because all these 3 forms of the allyl complex are equally accessible, we have very complicated chemistries, which can result from the interaction of these 3 reforms. Let us proceed further with a synthesis of metal allyl complexes from alkenes this time. These are some very interesting reactions that happen when you treat an alkene compound, alkene organic alkene, which has got allylic hydrogen, which can be abstracted by the metal.

In this case, it is a palladium 2 complex palladium PdCl4 2 minus, which is interacting with the allyl group. It first forms an olefin complex. This complex is indicated here. Here is the olefin complex. Only the double bond is interacting with the metal, but because you have a hydrogen, which is adjacent to the metal, you can have what is called abstraction of a hydrogen.

That abstraction of a hydrogen can result in a formal oxidative addition resulting in this palladium complex, which is formally in a plus 4 oxidation state. Now, the oxidation state of plus 4 is not common with palladium, but nevertheless, it has been observed. So, it is possible that this reaction goes through an oxidative addition. Then, it can rapidly eliminate the molecular hydrogen chloride. That is exactly what is represented here.

The isolated complex is a palladium chloride dimer because allyl group is a negatively charged species. You can see this molecule that palladium has retained the plus 2 oxidation states reverted back to the plus 2 oxidation state we started with palladium plus 2. Then, we found olefin complex. In the olefin complex, we had an oxidative addition, abstraction of the palladium.

That results in a species, which is palladium in the plus 4 oxidation state. You are having 2 chlorides, 1 hydride and 1 allyl species. So, this species rapidly loses its rear and is thus a reductive elimination. It forms the palladium 2 complex which you have indicated here. So, this is 1 way in which we can understand the formation of an allyl complex from alkene.

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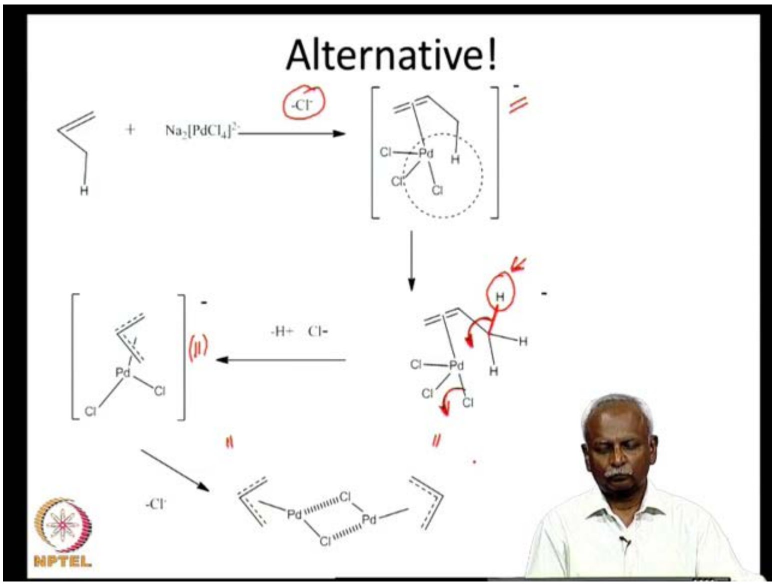

Alternative!

Let us talk about an alternative way, in which we can understand this reaction. Here, I have formed the double bond. You have an olefin complex, which is formed between the palladium and the alkene. After it forms the palladium olefin complex, the hydrogen which is present on the allylic position, this position it can be removed from the molecule as H plus.

In other words, the pair of electrons, which are held between the hydrogen and the carbon, are donated to the palladium. That is indicated here. The chloride leaves from the coordination sphere of the metal. You should remember that palladium first had 2 extra chlorides. It was PdCl4 2 minus. In the initial coordination of the alkene, we lost 1 chloride. That is what is indicated here. So, we have a mono negative species to start with. If you lose an H plus and simultaneously lose a Cl minus, this hydrogen goes off as H plus. This hydrogen goes off as H plus. This chloride goes off as Cl minus. We will be still left with a negatively charged species.

Notice that we have not increased the oxidation state of the palladium during the course of this reaction. As a result, what we have ended up with is a palladium 2 species in this case. Here also, palladium is in the plus 2 oxidation state. So, you have an allyl group 2 chlorides and the net negative charge. As a result, this molecule can now use a Cl minus and form the dimeric species, which I have shown in the previous case also.

So, in order to form this beautiful palladium allyl dimer palladium chloro dimer, you need, you can do it in 2 different ways. You can understand it in 2 different ways. 1 case is where you do not need to an oxidative addition and a reductive elimination. In the other case, you do end up with an oxidative addition and the palladium 4 complex, which rapidly eliminate Cl because topologically, you cannot distinguish the 2 processes. It is not possible to figure out exactly how the reaction is happening, but nevertheless, the final product formed is the same.

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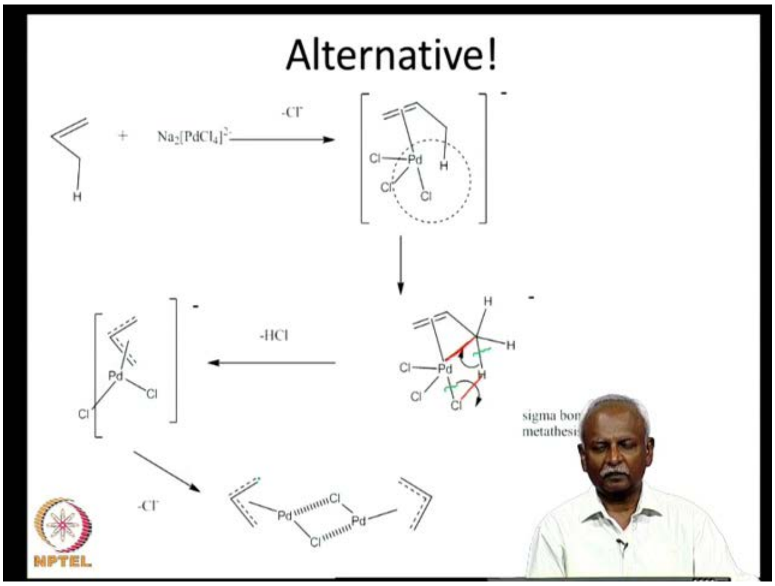

Alternative!

So, let us look at this the alternative. Another alternative way of understanding this is to think of it as a sigma bond metathesis. Now, after forming the palladium olefin complex, one can think of this H as revealing as H Cl. So, you have a sigma bond metathesis palladium forms a new bond between the carbon and the metal and a new bond between hydrogen and chlorine. The old bond that was present, the old bond which is present between the carbon and hydrogen palladium and chlorine are broken.

So, in the sigma bond metathesis, 2 sigma bonds are broken, 2 new sigma bonds are formed and hydrogen hydrochloric acid is eliminated. You have formed the complex. So, whether you think of it as sigma bond metathesis or you think of it as a loss of the proton and a chloride, either way you would end up with no oxidation state change in the palladium and the formation of a palladium allyl chloro complex. So, these are 2 different ways of understanding the reaction without an oxidative addition.

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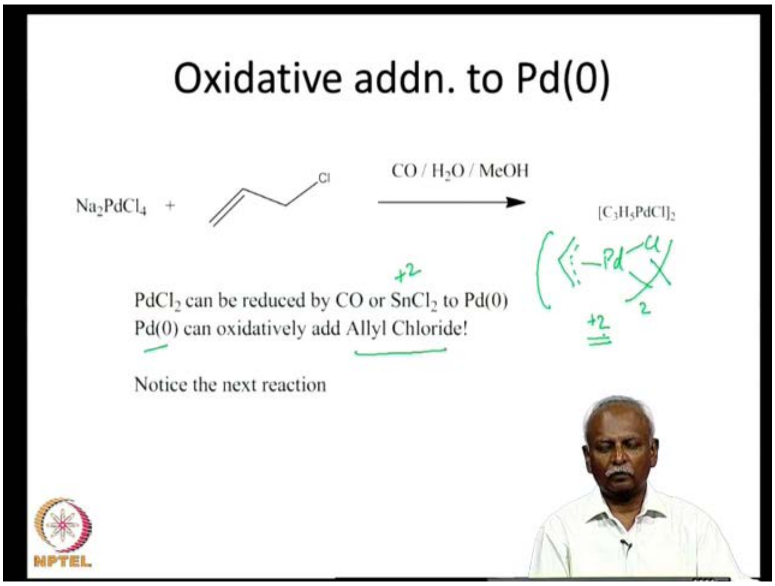

Oxidative addn. to Pd(0)

$PdCl_2$ can be reduced by CO or $SnCl_2$ to Pd(0)
Pd(0) can oxidatively add Allyl Chloride!

Notice the next reaction

Now, oxidative addition to palladium definitely happens in situation where you reduce the palladium 2. Here, again we start with any 2 PdCl4. Palladium is in the plus 4 oxidation plus 2 oxidation state need 2 PdCl4. You reduce it with carbon monoxide, carbon monoxide or SnCl2 or tin chloride.

Tin in plus 2 oxidation state can reduce palladium to palladium 0. Tin will get oxidised to palladium 4. Tin will get oxidised to tin 4 and will become SnCl4. Palladium will get reduced to palladium 0. Now, palladium 0 can oxidative add allyl chloride. So, this is a simple reaction, which will also lead to the chloro palladium allyl complex, which we can represent like this.

So, this is the dimeric species that we are talking about the same complex, which we have been showing in the last 3 slides. So, you will notice that here palladium 0 has changed to palladium plus 2. So, this is an oxidative addition to palladium 0. It is promoted either by an initial reduction of the palladium 2 to palladium 0 with carbon monoxide or with tin. Both of them are known to course this reaction to proceed forward.

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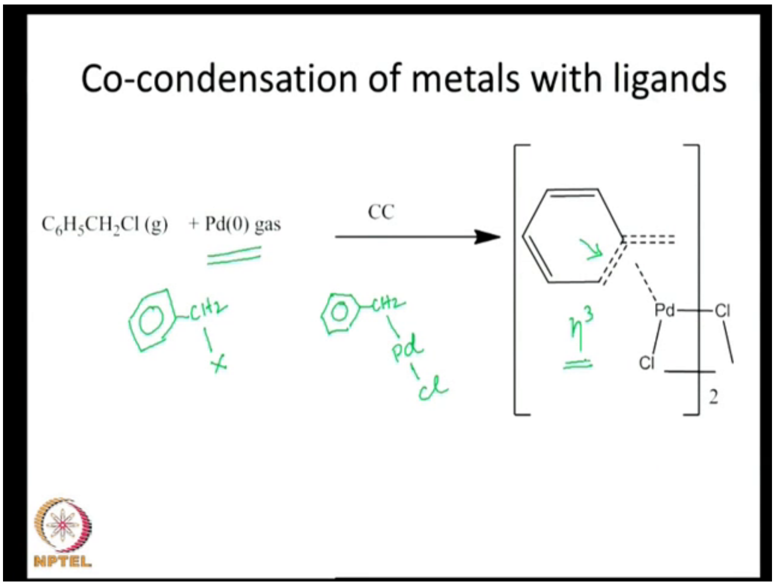

Co-condensation of metals with ligands

$C_6H_5CH_2Cl$ (g) + Pd(0) gas $\xrightarrow{CC}$

Now, it is always possible to use palladium metal or any metal in a 0 oxidation state when you do a co condensation reaction with a ligand. Then, you can make the allyl complexes. In the case of the co condensation reactions, the advantage is the metal is present in a very highly reactive state.

This case, we are using palladium as an example. When you have a benzyl chloride, so here, you have the benzyl chloride. You have a very reactive, very reactive metal atom. You can undergo an oxidative addition. This is in fact, a molecule which would have formed only a sigma complex because you have an aromatic molecule. You have an aromatic molecule. You have the possibility for oxidative adding it to the halogen.

So, this is what you would expect, but surprisingly, the double bond, which is present on the benzene ring, just this double bond also interacts with the metal. So, you have an allyl complex with the benzene ring participating in the reaction and partly it will lose the aromaticity. Surprisingly, there are many metals, which can do this. So, benzyl halides can oxidatively add to the metal atom. On oxidative addition, 1 of the double bonds interacts with the metal atom is to form an allyl compound, in which it is a eta 3 molecule. The hapticity is 3. It is looking just like other allyl complexes.

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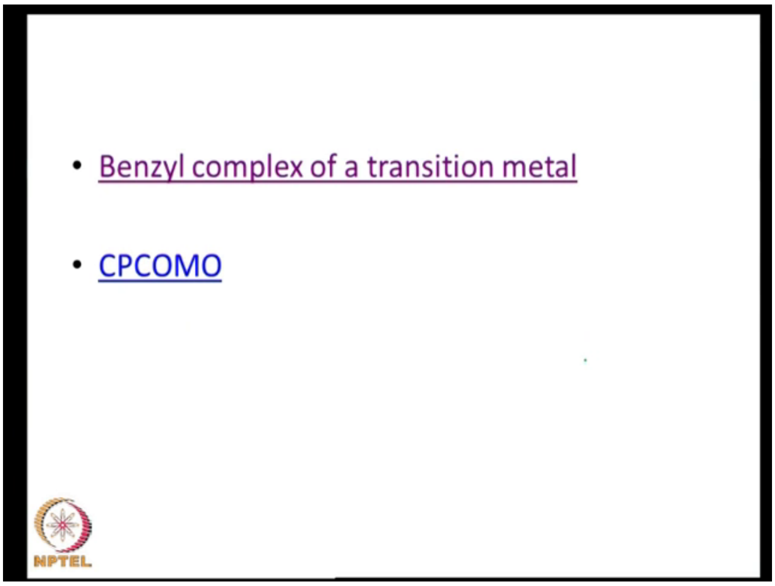

- Benzyl complex of a transition metal
- CPCOMO

Let us take a look at this molecule because this is in fact, a very strange compound. You can have the benzyl interacting with a metal atom.

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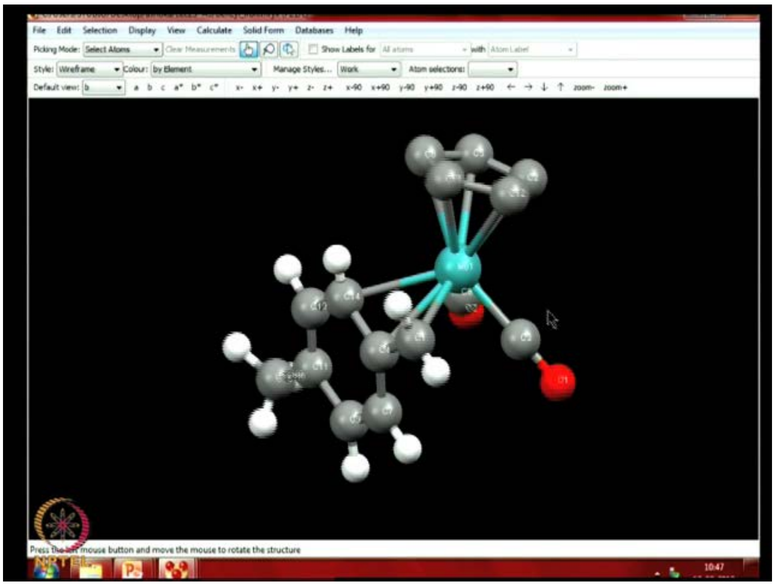

Press the left mouse button and move the mouse to rotate the structure

So, we will take a look at the benzyl case. So, here is an example, which has been taken from molybdenum compound. We will not worry about the remaining ligands on the molybdenum, but you can see that there is a very nice aromatic ring, which is present. This aromatic ring is interacting in such a fashion with the molybdenum such that 3 of the carbon atoms this C 1, C 4, C 14, all of them are interacting with the molybdenum in an equal fashion. So, if you want to measure the distance, you can see that this carbon is at a distance of 2.2 angstroms. The first carbon the benzyl carbon is at a distance of 2.2 angstroms. I have indicated it here. The central carbon, which is C 4, is only at a distance of 2.3 angstroms.

So, 2 carbon atoms are interacting almost an equidistant fashion from the molybdenum atom. The third atom is at a distance of 2.48 angstroms. So, although it is slightly away, you can see that all 3 carbon atoms are interacting with the molybdenum. It looks like a allyl complex. In fact, from the electron count, you can see that this double bond, it is in fact, interacting with the molybdenum atom.

To show that there is bond alternation, you can look at the carbon carbon bond distance of the bond, which is opposite this. That is clearly 1.42 angstroms. It is much longer compared to the other 2 double bond. So, there is some bond fixation or the localisation is completely destroyed. 2 bonds are short, 1.328 angstroms.1 bonds is very long.

So, this really looks like a complex, in which the allyl moiety is interacting. 1 or the other double bonds has decided to interact with the metal in such a way that the aromaticity of this benzene ring is destroyed. So, the gain that is, therefore this molecule in going from this aromatic system to this non aromatic system. It is because it can satisfy the molybdenum requirement for 2 extra electrons. Those 2 extra electrons are coming from the pie bond, which is present here. So, it is interesting that you can have this alternative way of interacting with a metal even. If you have a aromatic system part of the aromatic system, it can interact with the with the metal and form a pie allyl complex.

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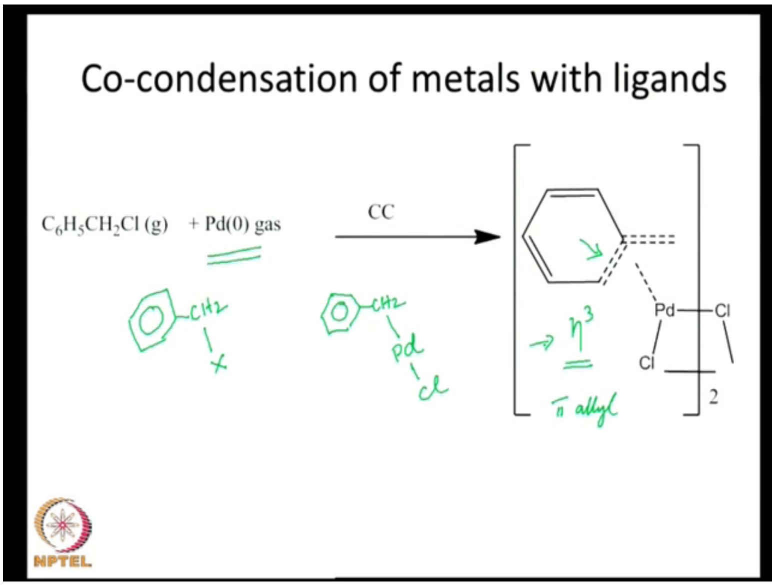

Co-condensation of metals with ligands

$C_6H_5CH_2Cl$ (g) + Pd(0) gas $\xrightarrow{CC}$

So, these are called pie allyl complexes or tri hepto species or eta 3 complexes. All 3 nomenclatures are used in the book.

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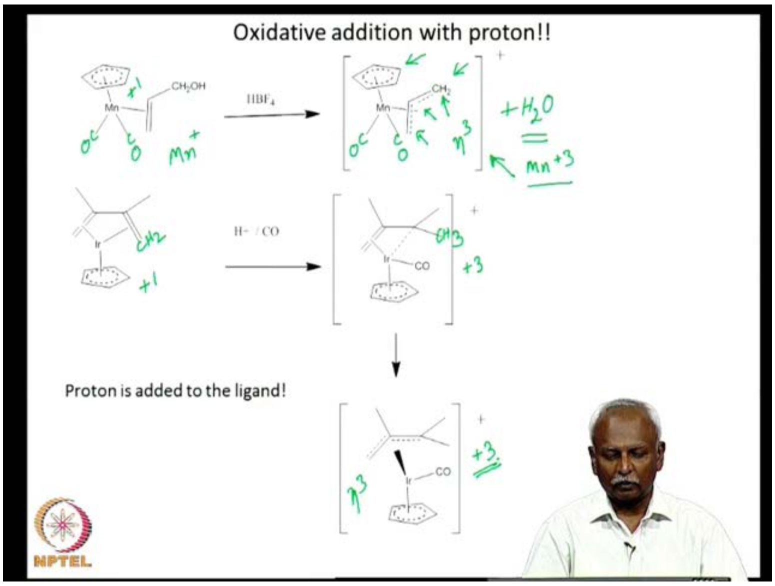

Oxidative addition with proton!!

Proton is added to the ligand!

Let us move on. Let us take a look at another way of making allyl complexes. In this case, what I have shown you is a system, in which there is a formal oxidative addition oxidation state change. These are molecules, in which there is manganese in plus 1; manganese is present in a plus 1 oxidation state. There 2 carbon monoxide units. So, what happens is there is an olefin complex. This olefin complex, there is an allyl COH.

This OH group can be protonated with a strong acid like HpF4 beforehand. If it protonates, it and loses a molecular water. After protonation, if it loses molecular water, then formally this allyl moiety will become an allylic cation.

Now, all 3 carbon atoms of this allyl group, all 3 carbon atoms, which will indicate with green arrows, all the 3 carbon atoms can now interact with the metal atom with the manganese in an eta 3 fashion. So, because this is eta 3 interaction and formally, we talk about allyl as allyl minus, the carbon is always considered as more electro negative than the metal you end up with an oxidative addition reaction.

This is because manganese is in the plus 1 oxidation state in this molecule after protonation and loss of water molecule. You will end up with the cationic species. This cationic species has got 2 negatively charged molecules or ligands 1 is c p minus and the other is the allyl minus. So, as a result, what you end up with is manganese in plus 3 oxidation state. So, here manganese is in the plus 3 oxidation state. You started with manganese plus 1. So, you uniformly carried out an oxidative addition reaction. A similar situation happens when you protonate a diene complex.

Here is an iridium complex, which is a butadiene unit. It is coordinated to the iridium. Here also, iridium is in the plus 1 oxidation state. After the reaction, after protonation, iridium goes to plus 3 oxidation state. Now, in order to show this reaction, exactly how it is reacting, I have indicated this double bond. This is CH 2 unit. Here, this CH 2 unit, if it is protonated, it will become a methyl group.

That is methyl group. It is now indicated. Initially, it was indicated in green CH 2. Now, this becomes a CH 3 group. Once it becomes a CH 3 group, you will notice that this carbon can equally interact with the iridium. All 3 carbon atoms, the 2 carbon atoms that are part of the diene and 1 carbon atom that is part of the in the all 3 of them can interact with iridium. Now, you have the possibility of an allyl complex. So, here also, it is an eta 3 allyl complex and iridium because you have protonated it. You will need to add a class charged this molecule. If you count the number of an anionic groups present iridium, the already 2 anionic groups has a plus 1 charge. So, iridium is in the plus 3 oxidation state.

So, these are cases where you can do an oxidative addition with a proton, oxidative addition with a proton resulting in a change, a formal change in the oxidation state of the metal and a formation of an allyl molecule. So, in both cases, you get iridium. So, iridium 3 and manganese 3 species and both cases you have hepta 3 coordination.

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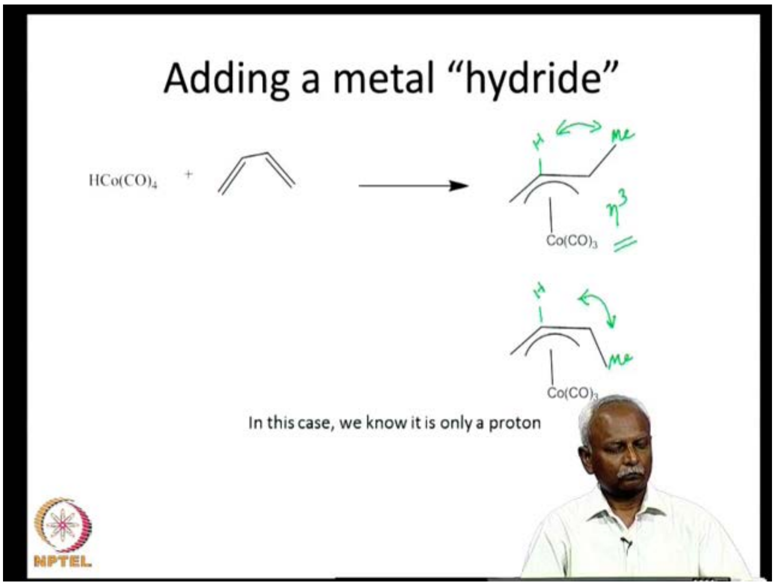

Adding a metal “hydride”

In this case, we know it is only a proton

Now, there is another anomalous reaction, which we should talk about. That is the formal edition of HCoCO4. That is a formal addition of a metal hydride. A classic example is its CoCO4. We have discussed this earlier. Hydrates are anomalous because many times they will react as if they are protons. The hydrogen reacts as if they are protons. So, HCoCO4 is a strong acid. In fact, if this metal hydride formal metal hydride is added to diene, it ends up the in forming an eta 3 allyl complex. It ends up in forming eta 3 allyl complex.

Here, I have a cobalt example. You will notice that when you add the hydrogen, the hydrogen can be added to the diene to the diene, so that it forms this allyl complex. The methyl group can be either oriented away from the central hydrogen. So, if you talk about the central hydrogen as unique hydrogen, the methyl group can be added in such a way that it is pointed in the same direction.

So, this methyl group is same with respect to the central hydrogen. It can be a time to the central hydrogen. So, this results in the formation of 2 different molecules, either s n or anti molecule.

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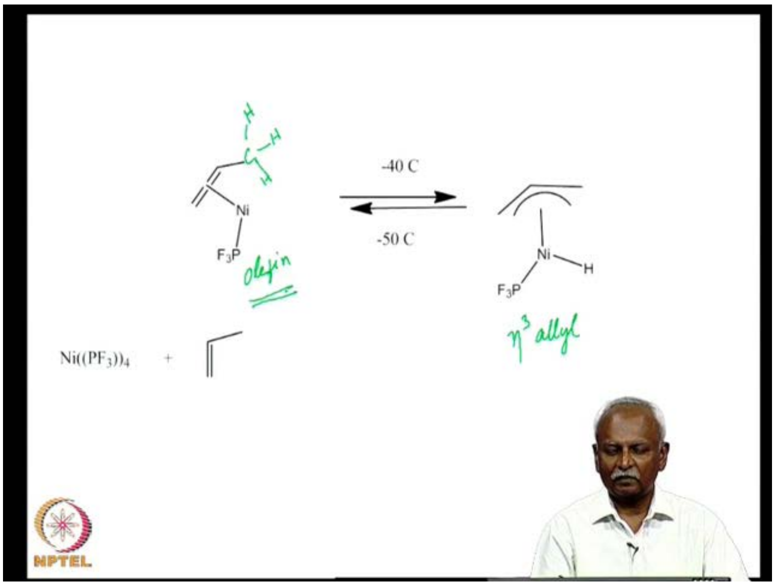

One last example is where you have a hydrogen transfer, which results in the formation of allyl molecule. Here, you have a methyl group and 1 of these hydrogen can be transferred to the nickel such that you from an allyl molecule. This molecule is, in fact, a dynamic system. At temperatures above 40 degrees, you have the formation of a eta 3 allyl complex. If you cool the molecule, if you cool the reaction system, then you end up with a olefin complex. So, this tells you how the energy required for transferring the hydrogen from the alkene moiety from the allylic position of the alkene to the metal is very small. So, you are able to transfer the hydrogen very easily and form a eta 3allyl molecule.

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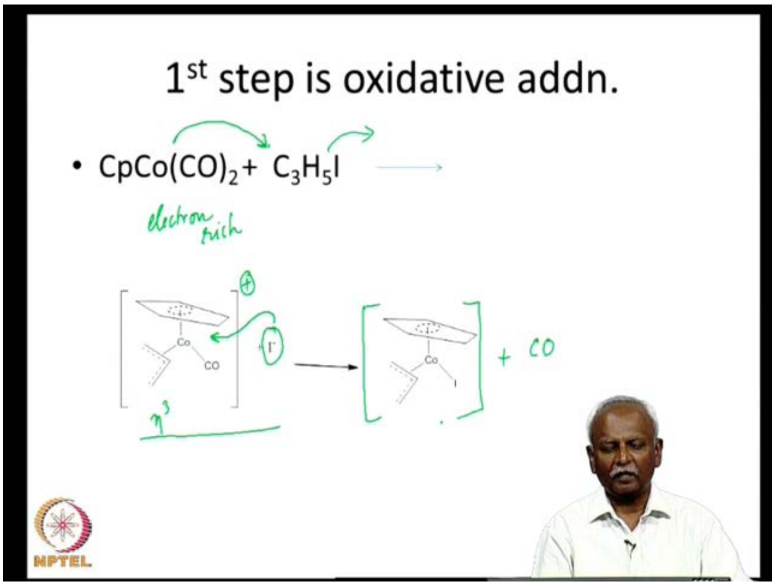

1st step is oxidative addn.

- $CpCo(CO)_2 + C_3H_5I \longrightarrow$

electron rich

So, here is yet another example, which is formally an oxidative addition. In this particular case, there is no negative charge, but still, CpCoCO2 is the electron rich species. This is an electron rich species. This electron rich species does a nucleophilic attack on this allyl. As a result, the iodide goes out. It forms a species, forms of intermediate, in which you have eta 3 allyl coordinated to the cobalt. Iodide is a counter ion, but during the course of this reaction, iodide attacks the cobalt. Again, this iodide moiety attacks the cobalt again and displaces the carbon monoxide. So, you end up with a cobalt neutral compound. This is a positively charged species.

Now, you have a completely neutral molecule, in which cobalt is in the plus 3 oxidation state. Here also, it is an oxidative addition but nevertheless earlier, we looked at a manganese compound, which is negatively charged. It underwent or it attacked an allyl halide, displaced the chloride. Here, we have a neutral molecule, which is carrying out nucleophilic attack on an allyl halide, which is an allyl iodide species.

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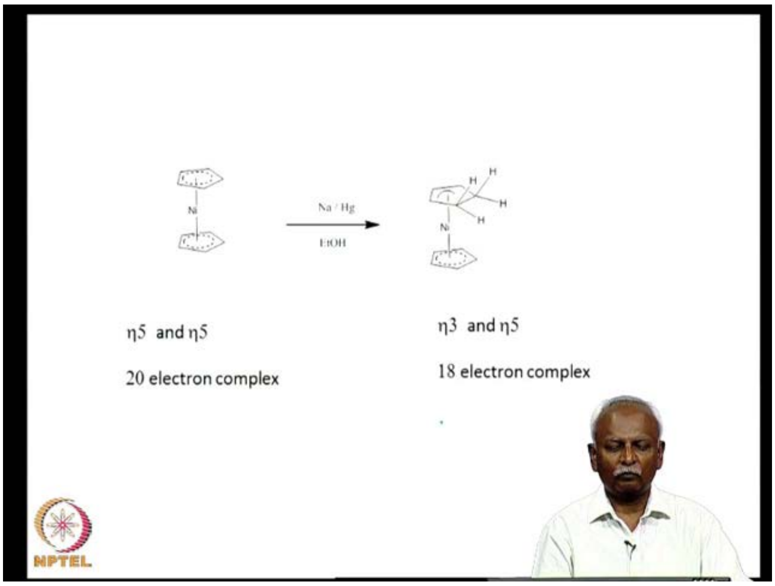

η5 and η5

20 electron complex

η3 and η5

18 electron complex

So, a variety of reactions have been shown. These are examples, which we will talk about later where allyl molecule is formed from larger ring systems. So, we will skip this.

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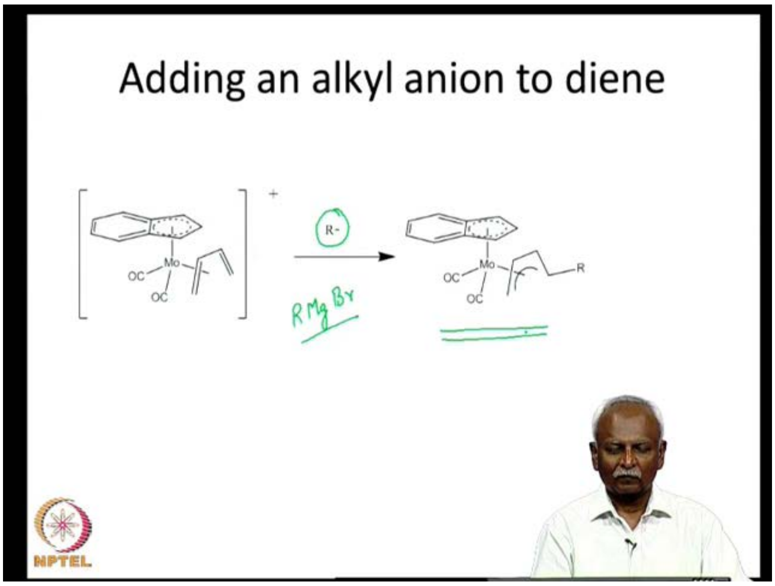
Adding an alkyl anion to diene

Here is a species where you again have a diene. Instead of adding a hydride, instead of adding H plus or H minus, we are adding a R minus. This R minus can be R Mg Br. This R Mg Br essentially does a nucleophilic attack on the double bond here. It results in the formation of an allyl molecule. So, there are a variety of ways, probably more than 10 ways we have considered, in which we can form an allyl molecule.

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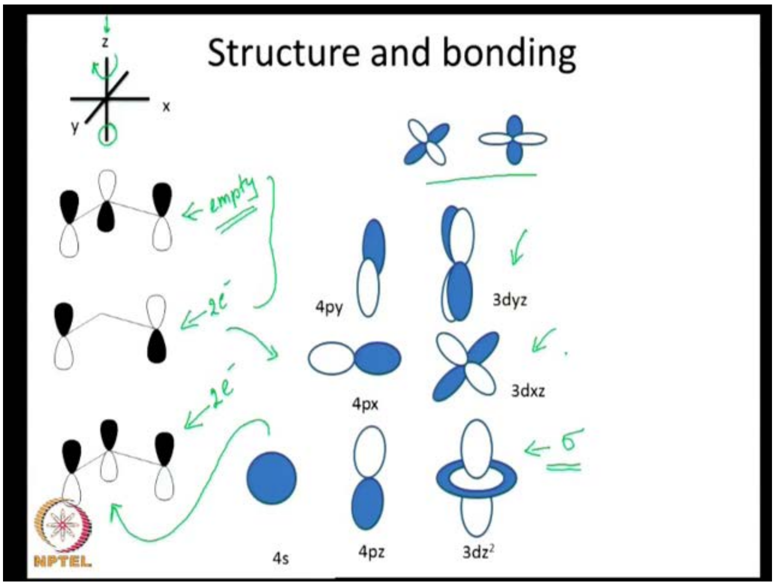

Structure and bonding

Now, what we have to look at is the structure and bonding in these molecules. I have drawn out the allyl system, which is a 3 carbon system, in which there are 3 pie bonds. There are 3 p orbitals, which are not utilized in bonding. So, if you look at this particular system, you will notice that the 3 p orbitals can combine together to form 3 molecular pie molecular orbitals out of which, this is the lowest energy orbital, in which all 3 of these lobes have the same sign. Now, the best way to illustrate this is to show, is to overlap these molecules, overlap these orbitals.

Here, on my on the right side of the screen, you have the metal orbitals. On the right side of the screen, you have the metal orbitals. On the left side, you have the allyl group and the allyl orbitals. The best way to understand which orbitals would overlap with the metal orbitals overlap with the pie orbitals of the allyl group; one has to just move these groups of these groups to the right position. See if they will form an overlap of positive overlap. You will notice that the 4 s orbital can form a nice overlap with new if the allyl group is present.

Let us say in the x y plane, so if the allyl group is present in the x y plane, if the metal is present in the z-axis at this position, if the metal is present in the minus z axis and along the z axis, but in the minus part of the z-axis, then you can see very clearly that the s, 4 s, 4 p z and the 3 d z 3 d z square orbital, all of them are capable of interacting with the lowest energy pie molecular orbital.

So, the lowest energy pie molecular orbital will have 2 electrons, which will have 2 electrons. These 2 electrons can interact or can be donated to the 4 s, which will be empty the 4 p z and the 3 d squared if it is empty as well. So, you can realise that if you are talking about an allyl anion, as we formally talk about, there are 2 electrons in this orbital also.

So, these 2 electrons can be in fact, interacted with or these 2 orbitals on the metal, the 4 p x and the 3 d x z, both of them can interact with the second pie molecular orbital which will also have 2 electrons if it is an allyl anion. So, the 2 donor orbitals on the organic system, the 2 pie molecular orbitals of the organic system can donate electron density to the metal orbitals, which are indicated here.

Now, comes the highest energy molecular orbital, which is the third pie. This is invariably empty. So, whether you talk about an allyl anion or an allyl cation, the last highest occupied molecular orbital is always empty. That orbital can interact with the 4 p y orbital. The 4 p y orbital can interact and the 3 d xyz orbital can also interact; the 3 d y z orbital is 1 in which the 2 lobes are pointed are going in and out of the plane of screen. So, you can see some the second lobe is almost hidden by the front lobe.

So, these 2 orbitals can interact nicely with the empty orbital. Now, because you can have electron density on the 3 d y z, the 3 d y z can in fact, donate electron density back into the empty orbitals of the pie. This will lead to stabilisation of the pie system through back donation of electron density.

Now, it is also possible that we talk about the allyl group as an allyl cation. In which case the 3 d x z can also donate electron density back into the allyl group? So, there can be a lot of give and take. The electron count, the metal electron count on the metal is important. The electron count on the allyl group is also important.

You will remember that we generated the allyl group starting with an allyl alcohol by protonation and elimination of water. In that case, it is very obvious that we are talking about an allyl cation, which is donated to the metal. In that case, we can say confidently say that the 2 orbitals both orbitals will be empty, but formally, we always talk about it as if it is an allyl anion.

So, the back donation from the metal to the allyl pie star orbitals must be happening only from the 3 d y z. Now, the 2 d x squared minus y squared and the d x y orbitals do not have suitable combinations with the allyl orbitals. They are not interacting with the metal. They are not interacting the allyl group, but all other groups, all other the s p and the 3 d orbitals are capable of interacting with the allyl moiety.

You will also realise that these 3 orbitals interact with the allyl group in a sigma fashion. These 3 groups interact in sigma fashion. So, the allyl moiety can freely rotate about the z axis. So, if you think about the allyl moiety as sitting in the x y plane, then the metal can rotate along the z axis can spin about its axis freely. This is because the sigma there is a strong sigma bond, which is formed between the allyl group and 3 orbitals on the metal.

However, there are 2 orbitals, which are interacting in a pie fashion. That are the orbitals, which are marked as 3 d x z and the 4 p x. These 2 orbitals if you rotate the allyl group with respect to the metal atom along the around the z axis, so around this axis, if we rotate it, if you rotate the metal atom, then what will happen? What will happen is that we will lose the second p the pie orbital interacting with the 4 p x and the 3 d x z.

So, these 2 orbitals will stop interacting or rather overlap, go to 0. The interaction energy will become 0. So, the extent to which these 2 interactions pie interactions are important determines how much you can rotate the allyl group with respect to the metal atom just like we discussed in the olefin case.

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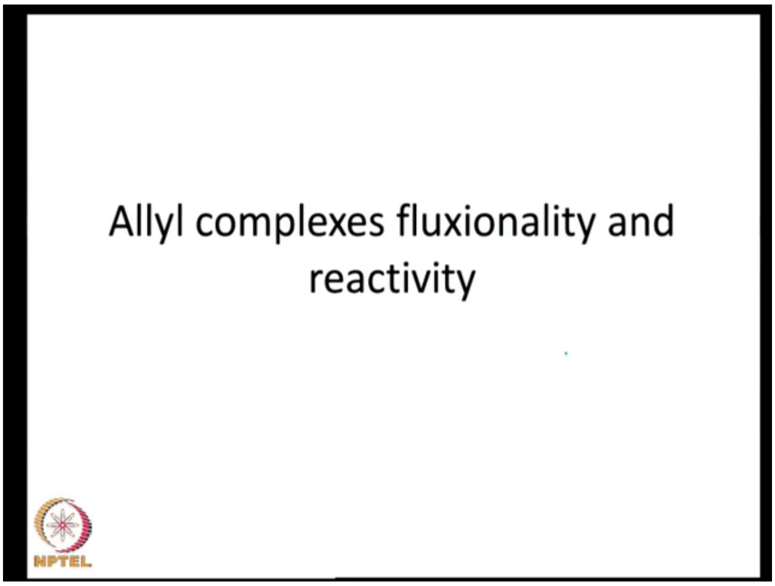

Allyl complexes fluxionality and reactivity

Now, having discussed the structure of the allyl molecules, we must talk about the fluxionality and the reactivity. Let us take look at the functionality of allyl complexes. We will discuss this in 2 dimensions to show this figure.

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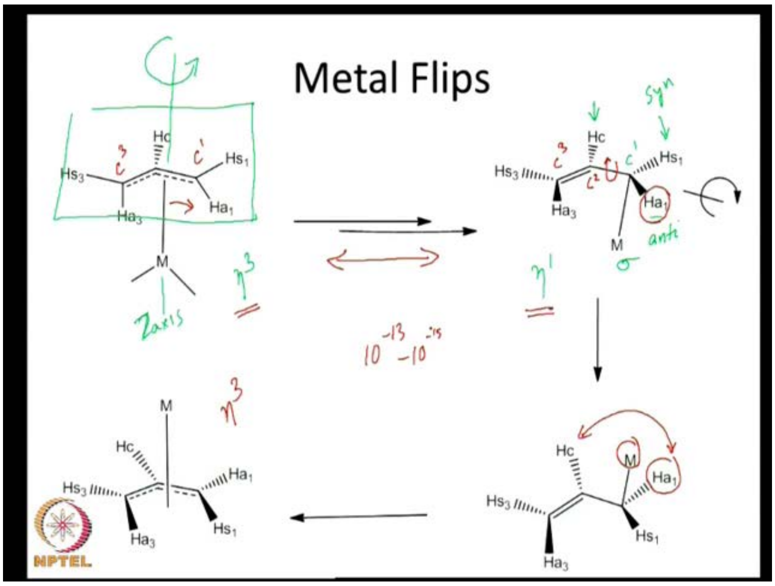

Metal Flips

We will try to illustrate it with a small video clip when we look at how this allyl group can relate. So, here is a metal, which is shown interacting in pie fashion and the plane in which the allyl group is present. This is the x y plane that we are talking about. This is a z axis. So, this is the z axis that we are talking about. So, when you rotate the metal atom with respect to this plane, when you rotate the metal with respect to this along this axis, we can keep the sigma interactions intact, but pie interactions will fail.

Now, it is possible for the metal by a slight movement towards one direction. So, it can move towards a high carbon atom 1. The carbon atom 1 is the one which is bearing Ha 1, Hs 1. The a indicates the fact that it is anti to the central hydrogen. The central hydrogen is marked as Hc. Ha indicates that it is anti to the central hydrogen. s indicates that it is synced to central hydrogen. So, this is anti and this is central, central hydrogen. So, these 2 hydrogen atoms will come closer to the metal, if the carbon 1 is interacting with a metal in the sigma fashion. So, this is a pie allyl eta 3 system and this is the eta 1 system.

So, we can go from an eta 3 to an eta 1 system failure rapidly by simple movement of the metal along this axis. So, that let us just mark this out. So, if the metal moves in this direction, then it can go from the eta 3 to the eta 1 fashion. This can go back and forth very rapidly. This eta 3 to eta 1 migration can happen very rapidly. It can go either to C 1 or it can go to C 3.

So, we let us mark this as C 3. So, either you can go to C 3 or it can go to C 1. Both of them are equivalent. As a result, you can see how the molecule can go from a sigma complex to a pie complex and can go to this alternatively. In addition what happens is, if the metal rotates around this bond, then from the minus z axis, it can move to the plus z plain.

If this happens, then the allyl group is intact in the same position allyl group is present in the x y plane. Then the metal is moved from the minus z position to the plus z position. So, the metal can come back to the central position. So, it will become a eta 3 system, but the metal is in the plus z position. So, this type of a metal flip can result in a new complex.

You will notice that because we have maintained the sigma bond, what was originally Ha 1 has now become, has now come to a different position. It has come; it has formally become synced to the central hydrogen. So, the position of the sin and the anti-hydrogen has got interchanged. As a result of this, flipping takes place of the metal from 1 side of the allyl group to the other side.

So, this is called the metal flip. In the following lecture, we will talk about how the allyl group can flip. So, there are 2 things that we are talking about. One is a fact that the metal can go from an eta 3geometry to eta 1geometry. That also leads to a fluxional behaviour. It will rapidly interconvert the 2 carbon, C 1 and C 3. There is another fluxional behaviour. That is rotation of the metal or rotation about this carbon bond, carbon C 1 C 2 bond about the C 1 C 2 bond. If you have a flip, then the metal goes from the plus z to the minus z or the minus z to the plus z.

As a result, you have interchanging of 2 hydrogen atoms. The 2 hydrogen to which the metal was attached will now get interchanged. What was anti will become sin and what was sin will become anti with respect to the central hydrogen. So, you have a fairly interesting fluxional behaviour. This is because these are rotations that can happen in the time scale of 10 power minus 13 to 15 seconds.