Introduction to Organometallic Chemistry
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Lecture - 13
Alkynes eta two bonding

In this lecture, we will look at metal complexes that are formed by acetylenes.

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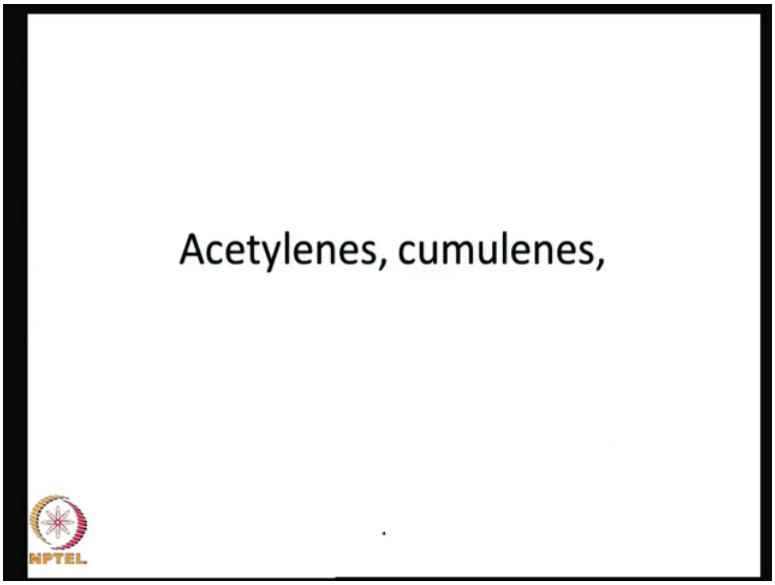

So, these are organometallic compounds that are formed with acetylenes and organometallic fragments.

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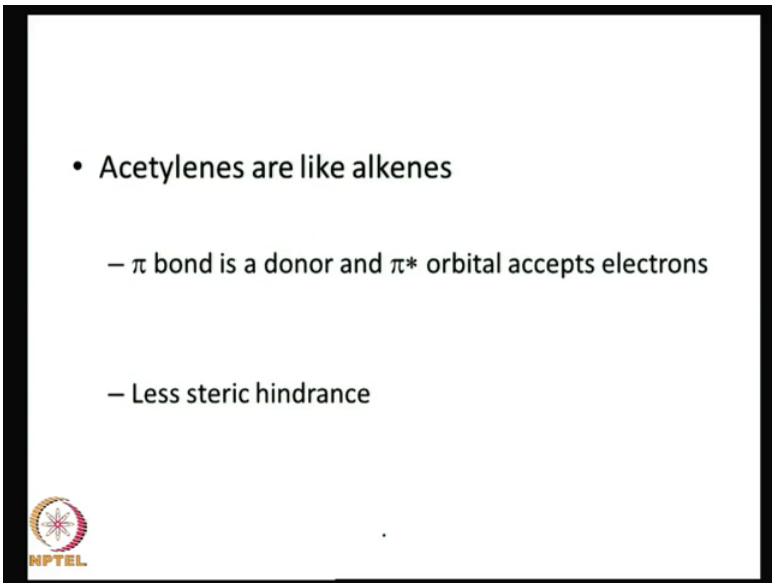

And to begin with let me say that acetylenes are very much like alkenes. There is a pi bond, rather there are 2 pi bonds and each pi bond would be associated with a pi star orbital or an anti bonding orbital. And the situation is very similar in the sense that the pi bond is able donate a pair of electrons to the metal complex. And just like the alkene which can accept a pair of electrons. The pi star orbital of an acetylene can also accept a pair of electrons.

Now, the difference between the alkene and the alkyne is that there is one less R group on the acetylene. And as a result one would expect lesser steric hindrance in the acetylene. So, let us take a look at the chemistry of acetylenes and metal complexes organometallic fragments.

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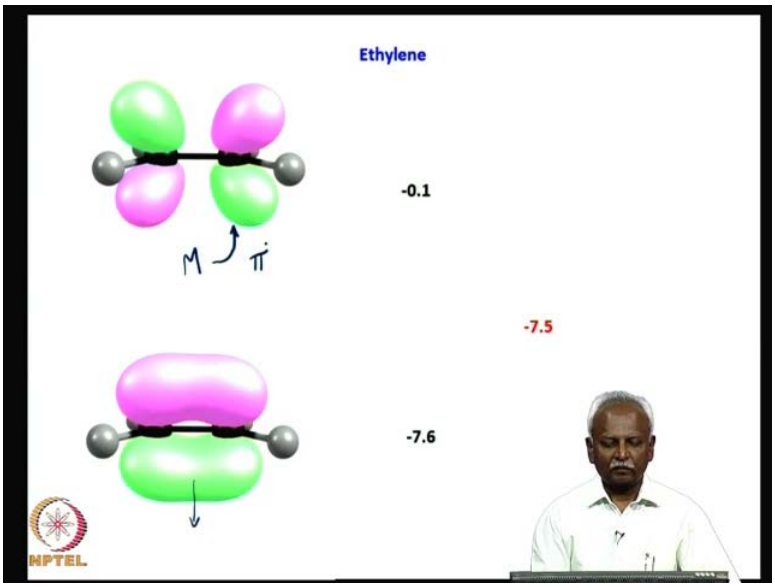

And to begin with, I would like to remind you the shape of the orbitals of ethylene. The pi and the pi star orbitals of ethylene are pictured here. The pi is on the lower part of the screen. And you can see that it consists of a single lobe on one side of the ethylene. And this pi cloud which is the bonding pair of pi electrons can be donated to the metal. So, it is from here that we have donation to the metal. And as we had mentioned earlier it is possible for a metal when it is bonded to the olefin to donate electron density into the pi star orbital of the olefin. As long as the symmetry is suitable it would be possible to form pi bond with the pi star orbital of the ethylene.

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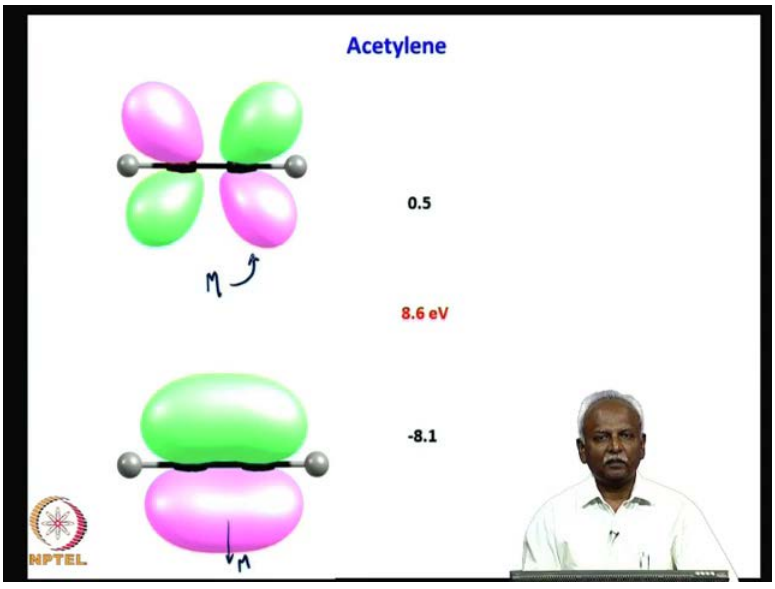

And you will notice that the acetylene has very similar orbitals. There are two of them. One of them is orthogonal or perpendicular to the other and the shape of these orbitals are extremely similar to what we saw for the ethylene. You have a pair of electrons which can be donated to the metal and a pair of electrons from the metal can be donated into the pi star orbital of the acetylene. So, you can see very clearly that there is similarity between the ethylene and acetylene in terms of the bonding interactions. Now, what we need to realize is that the energy of the homo is very important and is indicative of how easily it will donate a pair of electrons.

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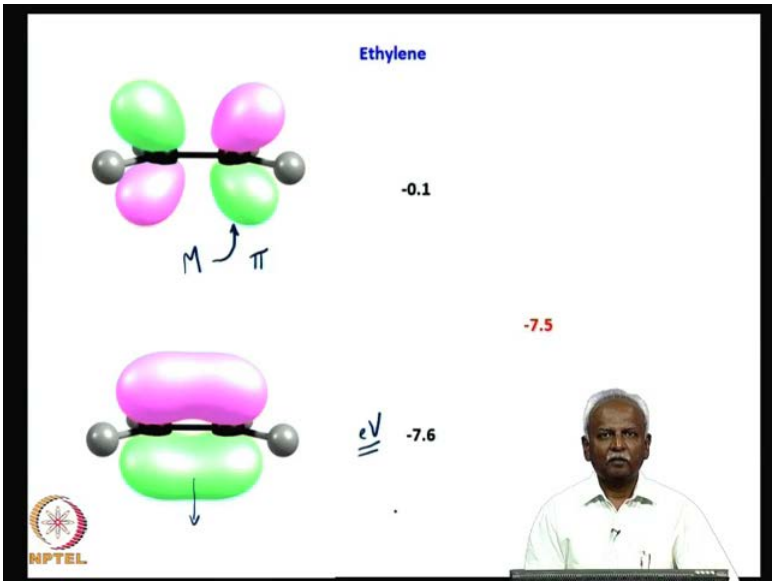

If you look at ethylene the energy was at minus 7.6 electron volts. So, these values are given in e V. And so you have a pair of electrons sitting at minus 7.6 electron volts in ethylene.

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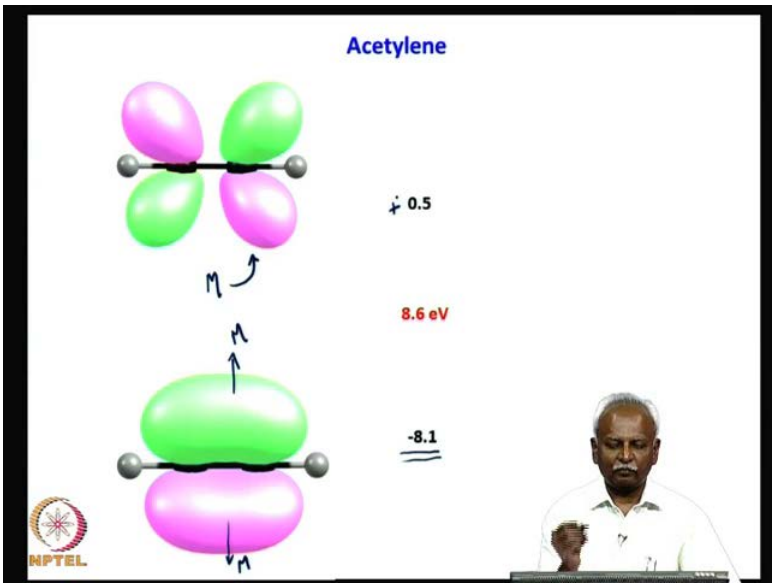

Whereas, in the case of acetylene this value has gone down to minus 8.1 electron volts. So, this indicates that because it is more tightly held by the acetylene these electrons will be less easily donated to the metal. So, donation to the metal would occur less readily in the case of acetylene, it is a poorer donor compared to ethylene. On the other hand let us take a look at the energy levels of the pi star orbitals. The pi star orbital of acetylene is at plus 0.5 e V.

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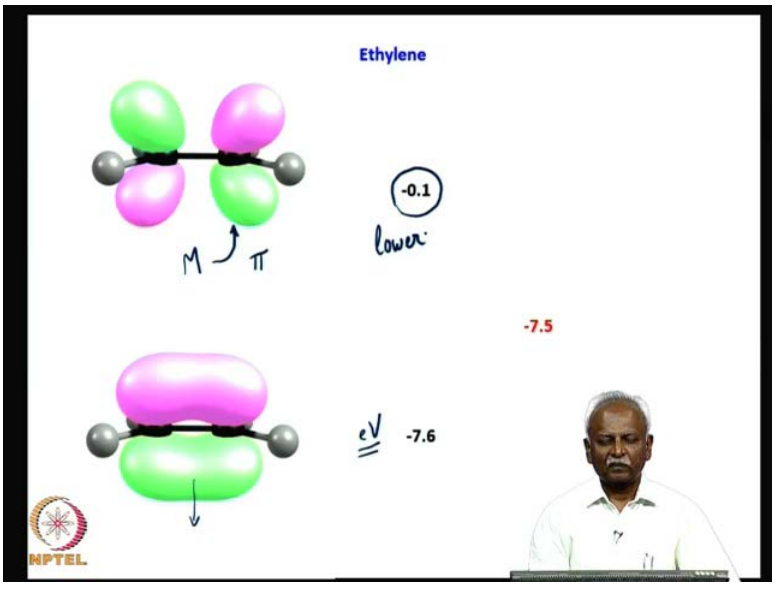

And in the case of ethylene it is at minus 0.1 e V. The fact that in the ethylene case this is at a lower energy level. This indicates very clearly that it would accept electron density more readily compared to the acetylene the acetylene because the energy level is higher you are going to have more difficulty in pushing the electrons to the higher energy level from the metal orbitals.

So, in a sense although ethylene and acetylene are extremely similar in terms of the bonding interactions, both the sigma bond formed by the metal with the acetylene and the pi bond formed between the metal and the acetylene are similar to what would you have with ethylene. The extents of interactions are likely to be weaker in case of acetylenes. With this preliminary introduction let us take a look at some of the compounds that can be made.

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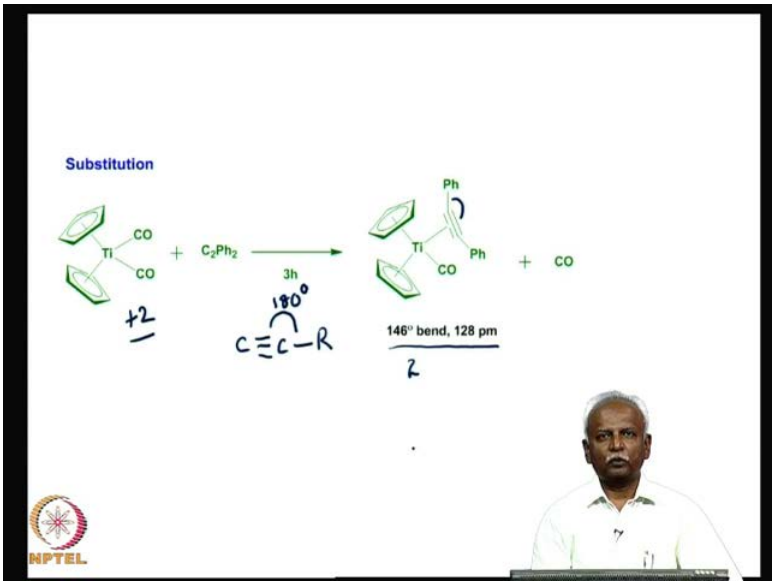

Here I have pictured a substitution reaction as I had indicated in the reactions with carbon monoxide it is easy to replace a carbon monoxide with a poorer pi acceptor ligand. This is because carbon monoxide that remains on the metal would like to enhance its pi accepting property and the extra electron density that is now on the metal is pumped into the pi star orbitals of carbon monoxide. And this synergistic interaction leads to a strong bond between the metal and the carbon monoxide, which in turn enhances the stability of the whole system.

So, it is possible to form a complex in which it is possible to have the acetylene which is biphenyl acetylene here complex to the titanium. You will notice that titanium is in the plus 2 oxidation state titanium is in this complex because cyclopentadienyl anion would withdraw electron density and would form a plus two complex preferentially. And in this plus 2 complex you have 2 electrons sitting on the titanium which are capable of back bonding with the carbon monoxide and with the acetylene.

What I have indicated here is 146 degrees bend is the bending of the alkyl group which is aryl group which is attached to the acetylene. In free acetylene you will remember that the bonding is such that you have an s p hybrid. And so the R group is at an angle of 180 degrees. When it binds to the metal what happens is that there is some reorganization of the hybridization. So, that you have a slight bending of the group which is attached to the alkyne.

And this bending happens away from the metal system. In other words it is the angle which is away from the metal which is lesser than 180 degrees. You will also have a slight weakening of the pi bonding between the two carbons. And as a result what you end up with is a elongated C triple bond C. So, this is a simple substitution reaction of a pi acceptor ligand with the acetylene.

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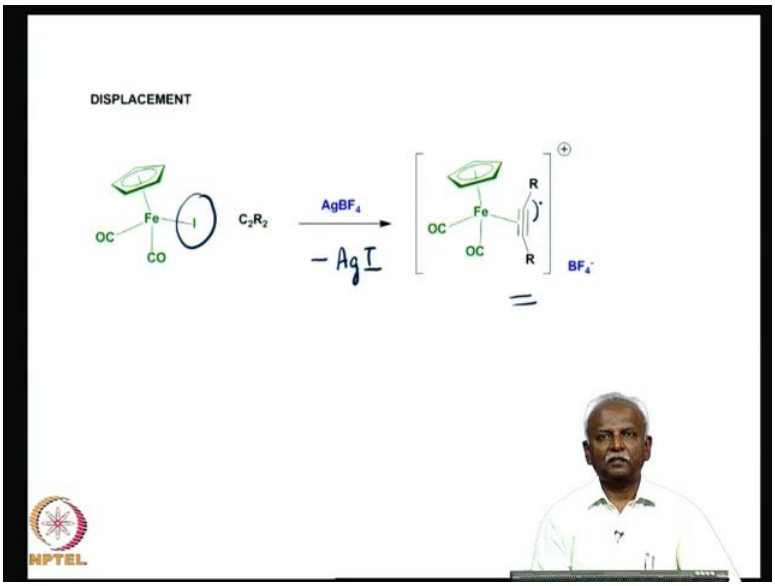

Let us move on now here is another example once again you can replace the iron iodo compound with C2R2 or any acetylene in the presence of species which will remove this

I minus. And so what you end up with is liberation or removal of Ag I, precipitation of Ag I and formation of an empty coordination site on the iron.

This empty coordination site is now filled with the acetylene. Once again depending on extent of back donation from the metal to the acetylene, you would have the bending of this R group away from the metal atom to the extent to which electron density is pumped into the pi star orbitals.

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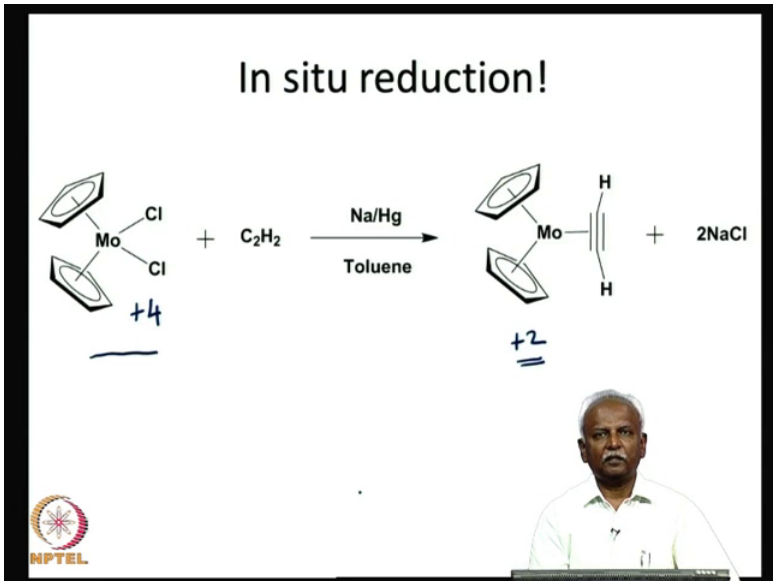

So, as I had mentioned the there is possibility for pi accepting behaviour for the acetylene because you have pi star orbitals. And this can be carried out only if the metal is in a lower oxidation state. So, very often it is necessary for high oxidation state metal to be reduced to a lower oxidation state. And in situ reduction is a convenient method and there are several reducing agents which are available to the organometallic chemist for bringing the oxidation state of the metal to the right value.

Here, we have reduced molybdenum which is in the plus 4 oxidation state. Molybdenum plus 4 is reduced to molybdenum plus 2. And this makes it a better pi donor and the acetylene is of course a pi acceptor. And you can do this reaction simply by reducing it with sodium amalgam and by bubbling acetylene through a solution of the molybdenum di chloride. And you can isolate the acetylene complex of the molybdenum plus 2 complex. Here of course, you would have pi accepting character for the acetylene and the acetylene hydrogens would be bent.

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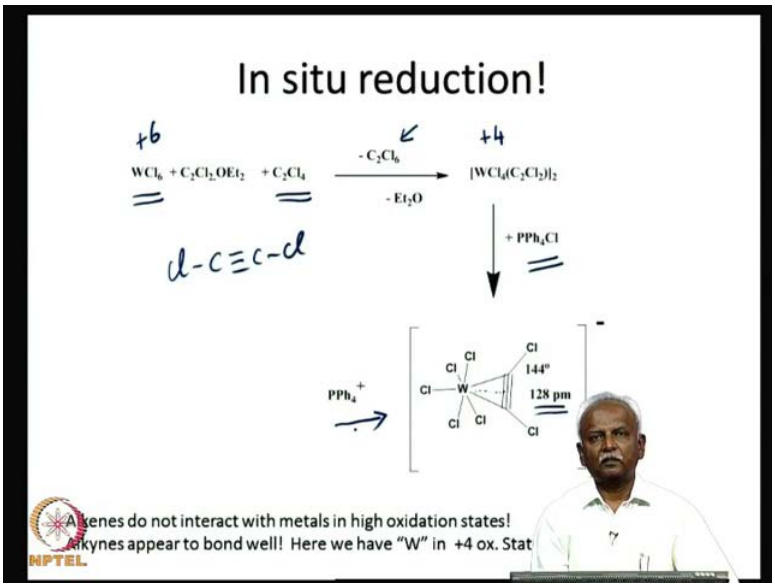

This example that I have pictured in this slide is a little more complicated but, nevertheless reminiscent of the fact that chemistry throws a lot of surprises and organometallic chemistry is no exception. You have the possibility for using tetrachloroethylene which is here tetrachloroethylene as a chloride acceptor. And so what happens is you end up reducing tungsten hexachloride that is W Cl 6 which is in the plus 6 oxidation state. You reduce it to the plus 4 oxidation state tungsten tetrachloride.

And you do that with an unusual reducing agent by this tetrachloroethylene. Tetrachloroethylene can be used as a reducing agent if it is capable of removing the chloride. And here it removes 2 chloride ions and that is eliminated as hexachloro ethane. So, hexachloroethane is eliminated in this process and tungsten 4 plus complex is formed. And because the reaction is carried out in the presence of C triple bond C Cl that is dichloroacetylene, you end up with a complex where dichloroacetylene is complex to tungsten.

And during the course of this reaction you have the formation of a octahedral complex, where the octahedron can be imagined to be formed with acetylene occupying one of the octahedral sides. And the chloride ion which is available for this complex is attached to the Trans position. So, here you have a bending which significantly larger about 40 degrees is bending away from the metal.

And you also have a bond lengthening which is significant and it becomes more towards the s p 2 hybrid in this particular instance. So, alkenes do not usually interact with metals in high oxidation states whereas, alkynes appear to bond. Well, here this is rather unusual situation where tungsten is in the plus 4 oxidation state and is still interacting with an alkyne.

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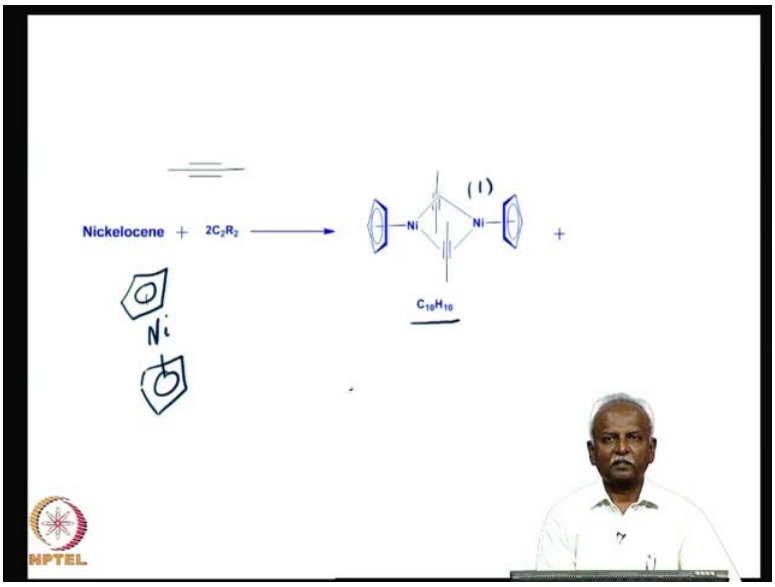

Now, there is one more unusual reaction that we will look at before we proceed with more discussion about the bonding and the type of interaction that is present between the metal and the alkyne. Here nickelocene which is basically the analogous compound of ferrocene. So, you have nickel bonded to two cyclopentadienyl anions. And as a result you would have a 20 electron complex. Remember nickel is D 10 and if you have 2 C P rings attached to the nickel.

You would end up with a total of 20 electrons around the metal. And this 20 electron system is unstable and it takes every opportunity to relieve itself of the excess electron density on the metal. And here in this case in this particular instance the presence of 2 acetylenes appear to carry out a unusual disproportionation reaction. This is a disproportionation reaction where the nickelocene has converted to a nickel 1 complex.

There is only one cyclopentadienyl ligand that is attached to the nickel now, and you have two acetylenes which are bridging the 2 metal atoms. Now, we will look at bridging acetylenes, but this gives you a simple example where acetylene can in fact act as a

bridge unlike ethylene which rarely acts as a bridge. There is probably only one example where ethylene acts as a bridge between two metal atoms whereas; acetylene very commonly bridges the two metal atoms. And we will take a look at why this is the case.

In during the process of this disproportionation nickel 2 plus has become nickel 1 plus. So, what is the species which has undergone oxidation. This must be the cyclopentadienyl anion which has got oxidised to cyclopentadienyl radical which has dimerised to give you C10 H10.

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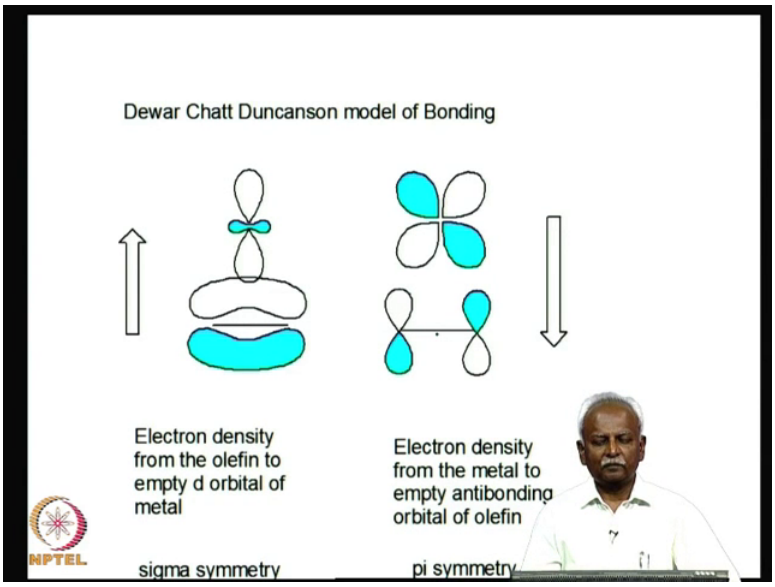

Let us take a look now at what exactly is happening in the case of ethylene and acetylene. This is a picture that we use to describe the dewar chatt duncanson model of bonding between ethylene and a metal complex. We noticed that there are two directions of electron flow and they turn out to be synergistic in nature more the electron density flowing into the metal the more it pumps back into the pi star orbitals.

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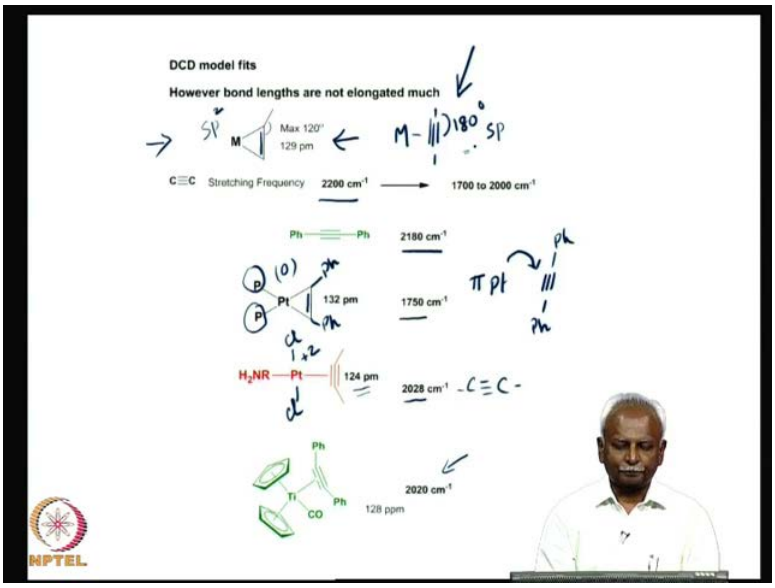

Now, the extreme instance of pumping in two electrons completely into the pi star orbitals would destroy the pi bond order. And the more it destroys one can think of the formation of a completely covalent bond between the metal and the carbon. And the hybridisation of the metal changing from an s p hybrid to an s p 2 hybrid. And so the description of the metal would be as a metallacylopropene. So, you would have the formation of a metallacylopropene.

Then the bending would be significant. So, here is the bond elongation indicated for a hypothetical complex. If you have a double bond here you start with acetylene. The extreme interaction is with a metal in a weak fashion and there is no bending between the 2 R groups. This turns out to be one eighty degrees and then the other extreme you have a bending, which is close to 120 degrees or this turns out to be like an s p 2 hybrid. Here so this is an s p 2 hybrid and this is s p hybrid on the carbon. So, this is usually understood in terms of the Dewar Duncanson Chatt model.

And it is also indicated by the stretching frequency changes. The stretching frequency of a C triple bond C typically lies in the region of 2200 centimetre minus 1. So, that means you have free acetylene you tend to have this strong carbon-carbon bond which in the case of diphenylacetylene is observed at 2180 centimetre minus 1. When you coordinate it to a metal which is in a low oxidation in the case that is pictured here this is platinum in platinum zero oxidation state. And there are two phosphines which are coordinated to

the metal atom. And the phosphines are poor pi acceptors and so there is excess electron density on the metal on the platinum. And so there is significant pi donation from the metal that is platinum onto the acetylene or diphenylacetylene.

So, what happens is this bond is significantly weakened and the complex looks more like a metallacylopropene. So, this complex is best described as a metallacylopropene and the bond distance between the 2 carbons has elongated to a significant extent and it is around 132 picometers. You will notice that the stretching frequency has also decreased very significantly almost 400 centimetres minus from 20, 180 centimetres minus 1 to 1750 centimetres minus 1. This is almost like what you would expect for a C double bond C, and that is what is pictured here in terms of the bending. And the rehybridization everything fits into a complete transfer of two electrons into the pi star orbitals of the acetylene breaking the carbon-carbon bond.

Now, here is another example this is also a platinum complex, but in this case platinum is in the plus 2 oxidation state there are 2 chlorines on the platinum. And the plus 2 oxidation state means that platinum would be reluctant to pump in electron density into the pi star orbitals. So, the bond elongation that you expect in this instance is much less it is hardly 124 picometers which means that it is not elongated significantly.

And you will notice that the stretching frequency has hardly decreased from 2180 centimetres minus 1 hardly 50 centimetre minus 1 decrease is there 50 centimetre minus 1 decrease is there in the stretching frequency of the C triple bond C. So, it is still remaining like a C triple bond C and the metal complex is best described using this description which I have given here. The carbon is an s p hybrid and it is a weak interaction between the metal and acetylene.

So, an intermediate complex is the one which we looked at earlier, where titanium is interacting with di- phenyl acetylene. And in this instance you will notice that it is about 160 centimetres minus 1 decrease in the stretching frequency is there. And you will also notice that the bond elongation is significantly larger than what you observed for the platinum 2 complex. This is now 128 picometers. So, what we notice is that just as an ethylene, it is possible to have a gradation in the amount of electron density that is pumped into the pi star orbital.

In the extreme case when you have significant electron density into the pi star orbitals. You would end up making it a complex that is a metallacyclopropene and that description is what is given here this is a metallacyclopropene. On the other hand if you do not have significant electron density into the pi star orbitals, you have just donation of electron density into the from the pi then the complex tends to behave as if it is a acetylene complex which is weakly interacting with the metal.

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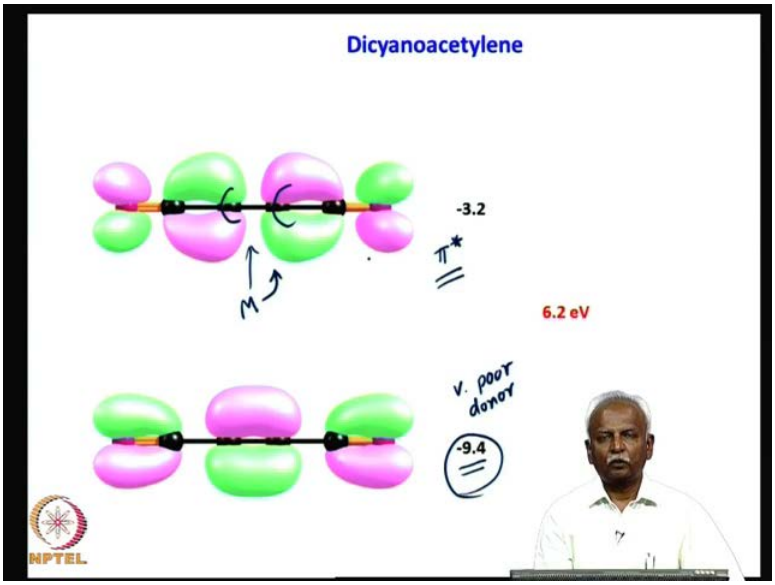

So, how can we increase or decrease the pi accepting character. It is easy to see that if you want to increase the pi accepting character, you should bring down the energy of the pi star orbital. If the pi star orbital is lower in energy it would be easy to pump in electron density from the metal into the pi star orbitals of the acetylene. So, here I have molecular orbitals of the pi and the pi star orbital of dicyanoacetylene. I have shown here that the energy value of dicyanoacetylene is now minus 9.4 electron volts. And so, what that does is that it makes dicyanoacetylene a very poor donor this is now a poor donor.

So, this is a poor donor because this energy level is way down at minus 9.4 electronvolts. On the other hand the pi star orbital is at minus 3.2 electronvolts. If you remember acetylene itself was at plus point one electronvolts. And so, the energy level of dicyanoacetylene is much lower this accepts electron density significantly more easily.

And this is because it is mixing with the acetylene group these are the 2 carbons which are sitting here this is the 2 carbons. And so the metal is interacting with the acetylene in

this fashion. So you can see that this because of delocalisation and the electron withdrawing nature of the cyano group, you have the formation of a pi star orbital which is at a significantly lower energy.

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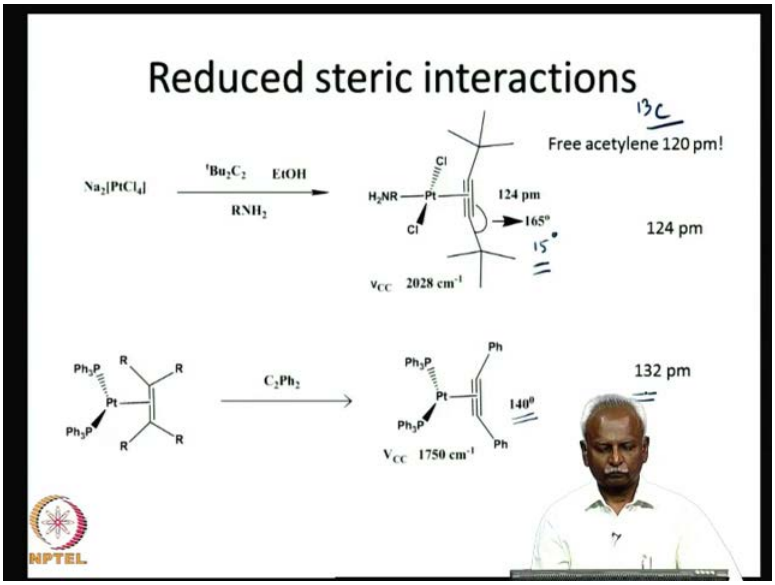

So, it is possible to modulate the donation and the pi accepting nature of the acetylene by changing the groups on the acetylene. If you have a very electron withdrawing group like a cyano or a carboxylate. Then, the pi accepting character would increase it is also possible to modulate the steric interactions of an acetylene. So, if you have a large group like a tertiary butyl group that is pictured here that would induce or make the complex weaker, a weaker ligand purely because it cannot approach the metal centre very easily.

So, here I have di tertiary butyl acetylene interacting with platinum 2. And you will notice that both the bond bending which is almost 15 degrees. Here I should say it is hardly 15 degrees here and the bond elongation which is hardly 0.04 angstroms or 4 picometers longer than what you find for the free acetylene. So, you can see that there is very little interaction.

On the other hand this can be compared with platinum zero complex which I talked to you earlier where you have a bond bending angle of 140 degrees. It is also possible where there is an indication of these changes where electron density around the carbon is changing from carbon 13 NMR spectra. So, these are 13 CNMR spectra of the acetylenes and their complexes. And you can see that these also vary in a systematic fashion

depending on what complex you have. If you have a weak complex you have very little change and if you have a strong complex where you have a significant electron densities coming from the metal you have a large change for the chemical shift.

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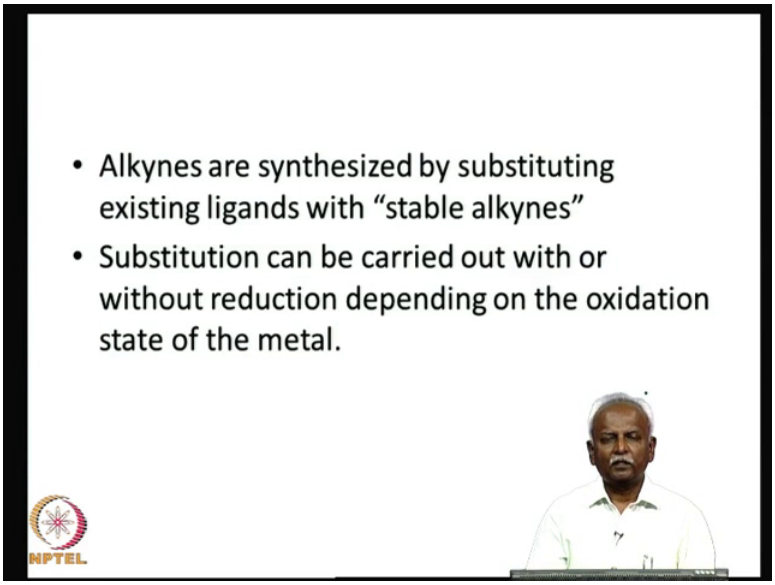

So, alkynes can be sub-synthesised by substituting existing ligand they can be pi acceptors or pi donors. We had 2 instances where halides were replaced by acetylenes. Tt is also possible to replace carbon monoxide with acetylenes. And so if you a stable alkyne then it is possible to make the complex very readily by a simple substitution reaction.

And we also notice that substitutions can be carried out with or without reduction. And depending on the oxidation state of the metal if you have a high oxidation state it is often preferential preferred that you reduce it to a lower oxidation state using a suitable reducing agent.

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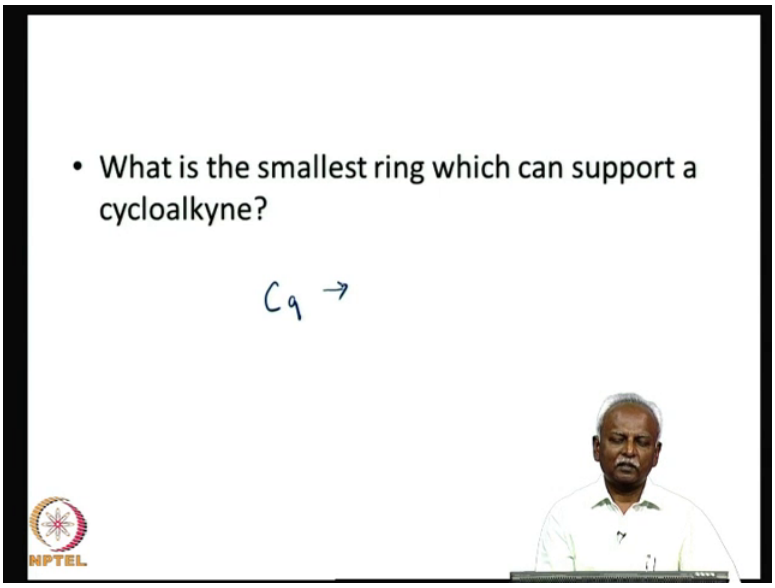

Now, let us take a look at some unusual complexes that are formed with acetylenes. And before we proceed further I should ask you a question about what is the smallest ring that can support a cycloalkyne. A cycloalkyne in a ring system so a C 9 ring system is probably the one where it can support the alkyne very comfortably. In all other instances it is difficult, it becomes a strained ring system and would invariably undergo some reactions with the alkyne very readily. So, it is possible to form a stable cycloalkyne only if it is C 9 or larger.

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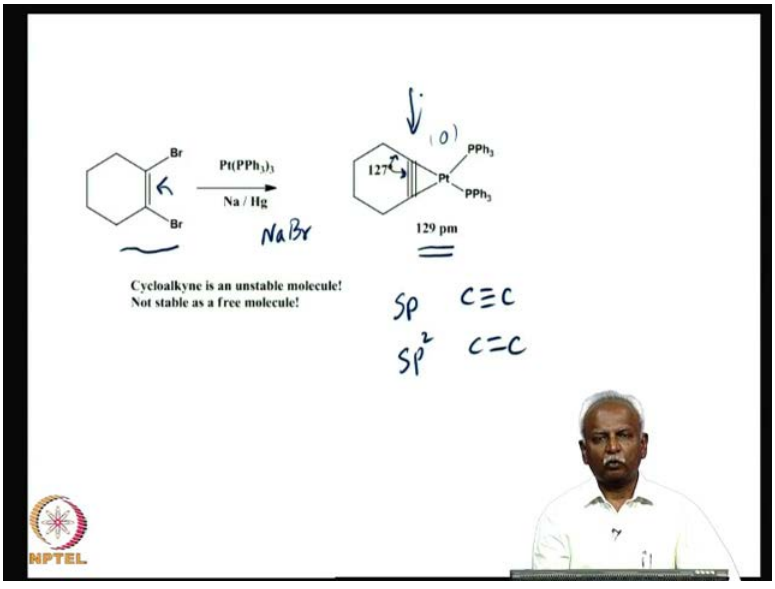

On the other hand we notice that even with a cyclo hexene system this can be converted into a hexyne complex. Now, what we are doing here is that we are generating a triple bond C triple bond C inside a small ring. And in this instance it is a 6 membered ring where we are forming the C triple bond C. So, this distance of 129 picometers is smaller than what you would expect for a double bond which is here the starting compound. And it is longer than what you would expect for a triple bond.

And this angle of 127 degrees which is there in the ring is larger than what you would expect for a carbon double bond carbon system. So, this is an unusual system where we have reduced the organic moiety eliminated 2 bromine atoms as NaBr of course. And this results in the formation of C triple bond C. And this C triple bond C is now bonded to platinum zero molecule and this stabilises the cycloalkyne. So, the free cycloalkyne is not a stable entity it cannot be synthesised in the Free State, but once it is complex it becomes more stable.

To understand this little better you can recollect what we talked about in terms of pumping in electron density into the pi star orbital to the extent that the hybridization changes from s p in a C triple bond C to an s p 2 in carbon-carbon double bonded system. So, you have a situation where it is in between the carbon-carbon double bond and the carbon-carbon triple bond. And this enables one to make a very unstable molecule in the coordination sphere of the metal. This is not unusual for organometallic chemistry and there are several instances where unstable molecules are stabilised.

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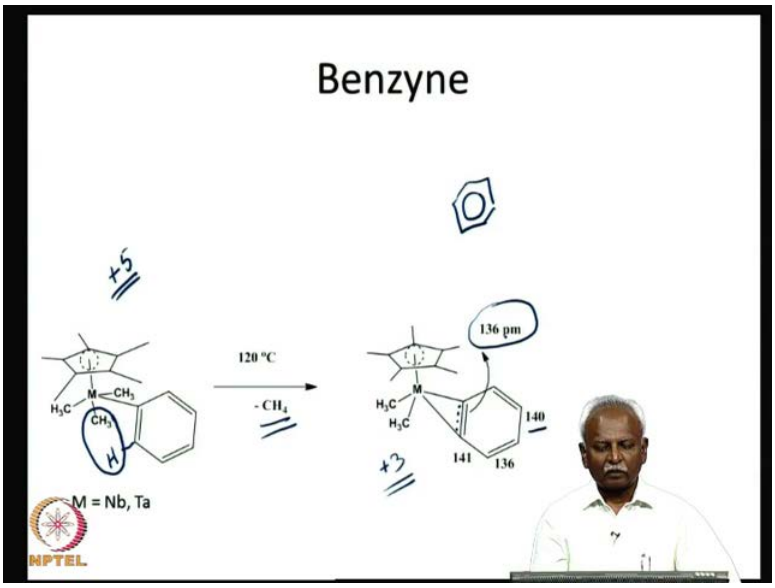

Now, one can also generate this by eliminating a few molecules from higher oxidation state metal. If you have a niobium or a tantalum complex which is in the plus five oxidation state, you can eliminate a molecule of methane. So, hydrogen which is here on the benzene ring is eliminated along with a methyl group on the metal. And so what you have is elimination of CH 4, and during this process you will notice that there is a triple bond that is formed between these two carbons.

And this triple bond is coordinated now to the metal. You will also notice that the bond distance is significantly longer than what you would expect for a triple bond it has been elongated significantly. The metal is now in the plus 3 oxidation state formal oxidation state of plus 3. So, it has two electrons which can be pumped into the pi star orbitals of the benzene. And so you will also realize that this complex has got single bonds and double bonds in an alternating fashion.

You no longer have the resonance structure of free benzene where you can simply draw a circle to indicate the fact that double bonds and single bonds are alternating. And they changing very rapidly and you have full fledged resonance structure. Here you have fixed double bonds and single bonds you have 140 picometers for the bonds between the double bonds and close to 136 picometers for the double bonded system. And what should have been a triple bond or at least what seem to be a triple bond you will notice that it is 136 picometers as well.

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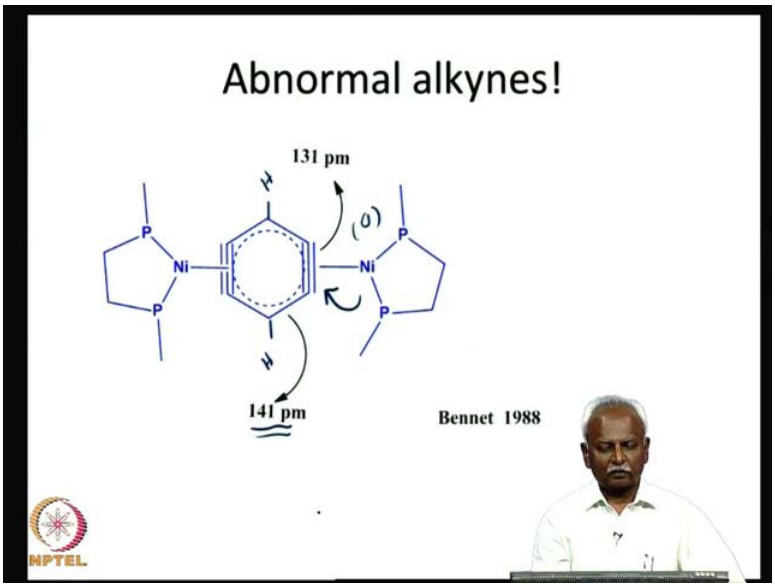

So, I have now a couple of systems which I would like to show you in a 3 dimensional fashion because these complexes are indeed extremely unusual. Here is dibenzyne and you have 2 hydrogens which are attached to these 2 carbons. And the nickel is coordinated to 2 triple bonds. Nickel is in the zero oxidation state here it has 2 phosphorous ligand, which are coordinated to it.

And as a result what you have is an extremely electron rich nickel centre and this pumps in enough electron density to reduce the C triple bond C nature of this dibenzyne to a C double bond C. It was also noticed that the carbon-carbon bond is elongated significantly to 141 picometers. So, this is almost like a single bond between the carbon and this becomes more or less like the double bond.

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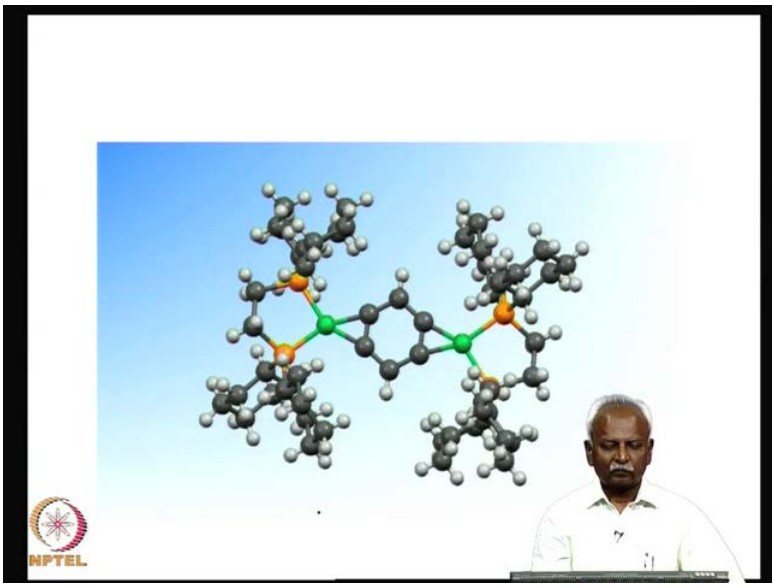

So, let us take a look at some of the structures now. Here is the structure of benzyne with the nickel complex that I have showed you. You will notice that there are 2 hydrogens which are on the central 6 membered ring. These are the 2 hydrogen atoms that I am talking about. So, here is the hydrogen atom here on the ring 6 membered ring and the triple bond is between two carbons and that is coordinated to a nickel zero system.

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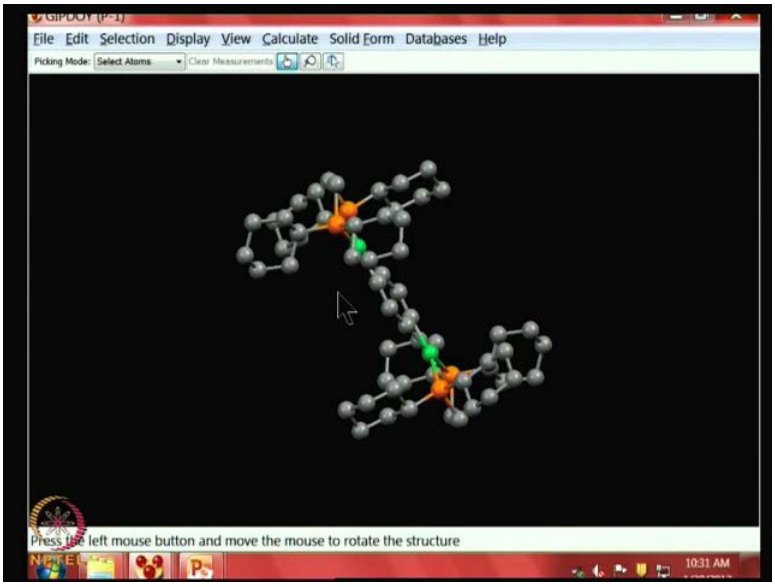

In order to appreciate the complex more fully I will show you the possibility of looking at it in a three dimensional fashion. And here is a complex which is you can look at this

complex in a three dimensional fashion where I am rotating it. So, that you can see the planar nature of the benzene ring all the carbon atoms are eclipsed. You have the two phosphorous atoms on the nickel which is a bis cyclohexyl phosphine or ethane.

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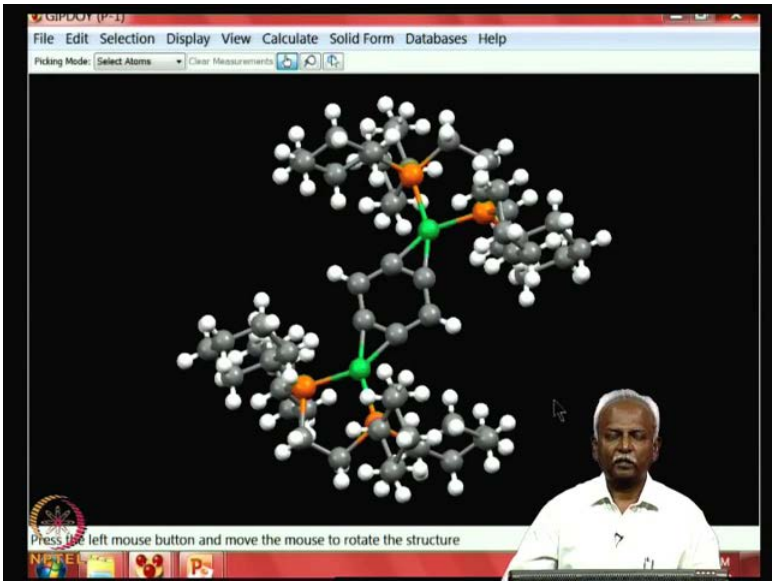

Now, I will show you another structure where here is the structure where I have indicated the same structure, but now with hydrogens. In the previous structure which I showed you there were no hydrogens. And you can see that the hydrogens are perfectly planar in plane with the benzene ring, just as you would expect for simple benzene. The only difference is that now in the plane of the benzene ring there are two nickel atoms, and you can see them now completely eclipsed when I turn it like this.

You can see that the benzene ring is in the same plane where the nickel atom is present. So, this is an amazing complex where you have a carbon-carbon triple bond between the two carbons which I have highlighted here. And the 2 carbon are coordinated to a nickel atom in such a way that you would have a bis alkyne complex in a six membered ring. So, this unusual system is possible only because of the organometallic nature.

You have electron density being pumped into the pi star orbital to such an extent that you have now a 3 membered ring which I have indicated here this 3 membered ring is a metalla cyclopropene. Let us go back to the presentation where we looked at this complex acetylenes.

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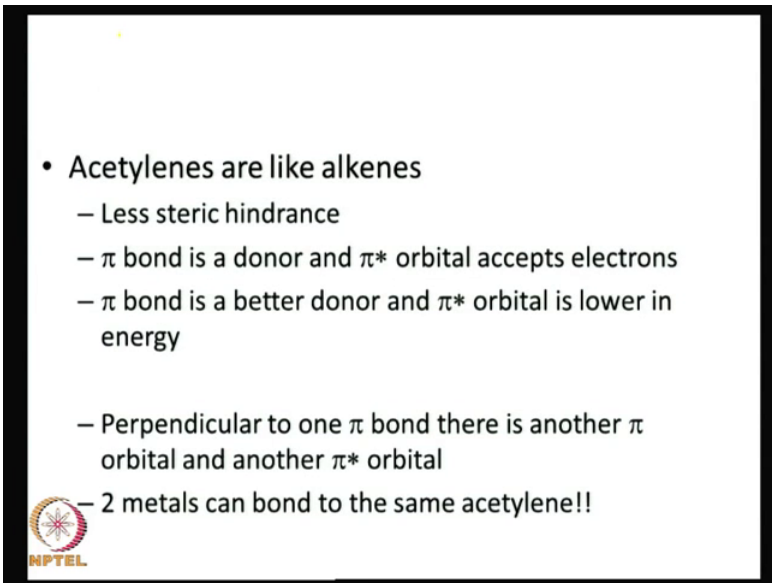

So, clearly acetylenes are like alkenes, they have less steric hindrance you have the pi bond which is a donor a pi star orbital which accepts electrons. And if you want the pi bond to be a better donor it has to be at a higher energy level. And in the case of simple acetylene itself we noticed it is at a lower energy level. And so acetylene is actually a poorer donor compared to ethylene.

Now, we also notice that perpendicular to one pi bond there is another pi orbital on the acetylene. And this allows for the possibility of forming acetylene which is bridging to metal centres. And let us takes a look at the bonding interactions in these cases and the type of complexes that are formed.

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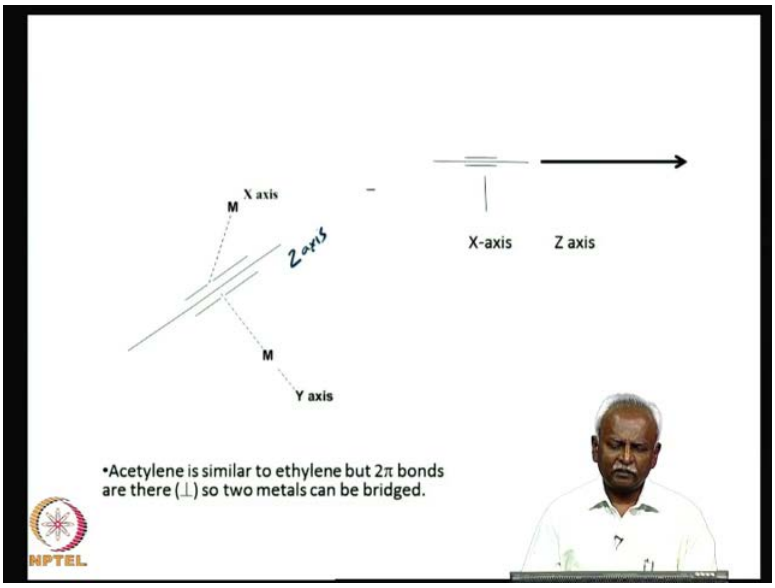

So, first let us try to understand how you have two orbitals which are perpendicular to one another and how this allows for an interaction like this. It is very easy to understand simple interaction of acetylene with a metal centre. And I told you that this is exactly the same way an ethylene molecule interacts with a metal centre. Now, perpendicular to one pi bond there is another pi bond. So, if you draw the axis as X and the Cartesian coordinates with the centre midpoint of the acetylene.

As the origin you would have the X and the Y axis which I have indicated here. And you can put 2 metal centres to interact with the 2 pi bonds. The carbon-carbon bond access itself would be the Z axis. So, this would be the z axis. And you have two perpendicular pi bonds along the x and the y axis. And these two pi bonds would interact with two different metals and that is the way a simple bridging complex can be made.

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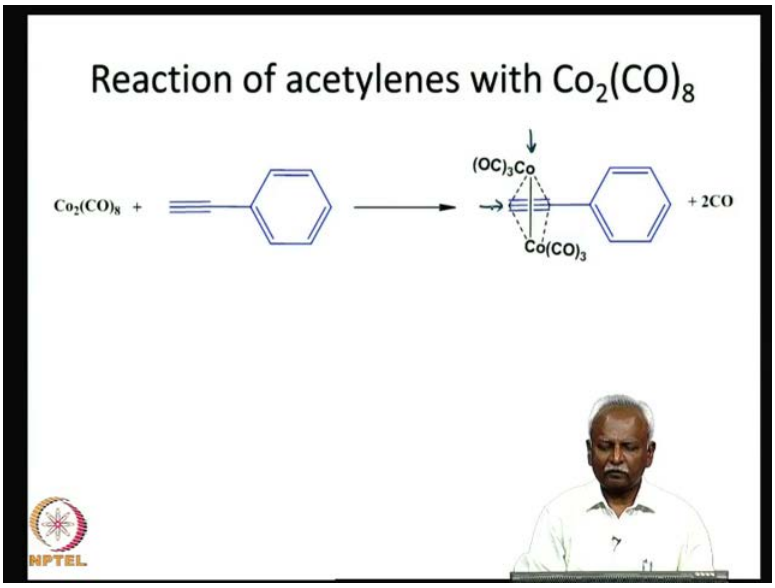

So, let us take a look at some of the complexes that can be formed a very common and very useful reagent is dicobalt octacarbonyl. When you treated with any acetylene molecule any alkyne molecule I should say, then you end up with a di nuclear complex where there is a cobalt-cobalt bond which is holding this tetra nuclear system together.

And the acetylene is in fact perpendicular to this cobalt-cobalt vector. So, these two bonds are now perpendicular to each other. And as a result you form a nice complex between the di cobalt unit and the acetylene molecule. Now, one cobalt is interacting with one of the pi bonds and the other cobalt is interacting with the second cobalt.

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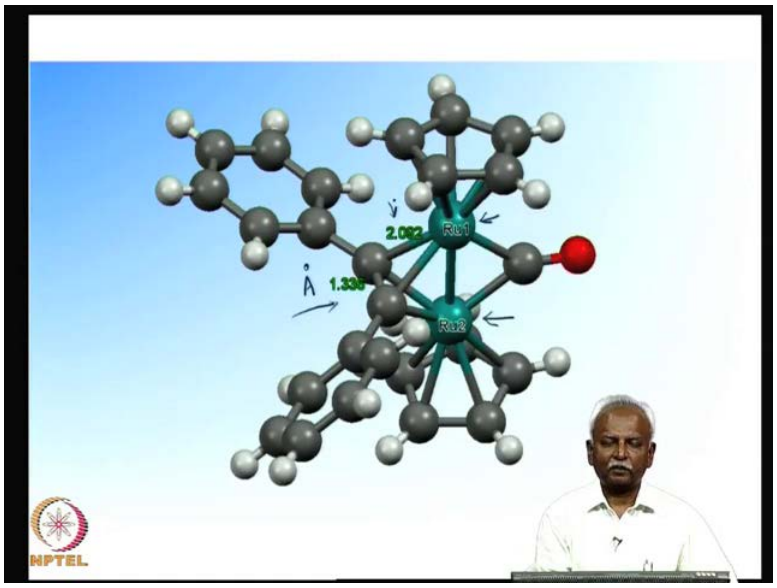

So, we will look at couple of molecules where in fact it is possible to see them. But, before I do so let me show you that the molecule is easily understood as a tetrahedron where two corners of the tetrahedron are occupied by metal centres. Here I have an example of a ruthenium complex which has formed a similar system. You have the 2 ruthenium centres which are shown here as blue bright blue ruthenium centres. And these ruthenium centres are interacting with the acetylene molecule.

This is again diphenyl acetylene. The acetylene carbons are pictured here they are separated by a distance of 1.336 angstroms. So these units these distances are now marked in angstroms this would be 133.6 picometers. And the metal carbon bond is a typical metal carbon single bond distance and that is around 2.092 Angstroms. And there is a hint of a double bond character between the metal and the carbon because it is slightly shorter than what you would expect for a pure single bond. So, here is the situation and you can see that one metal is interacting with acetylene in a perpendicular fashion to the other metal which is interacting to the other acetylene pi bond.

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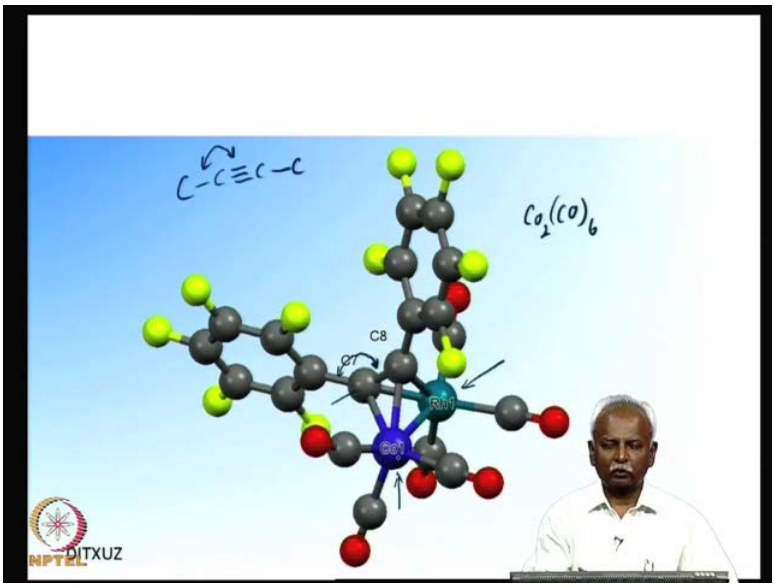

Let us take a look at another complex now. Here we have a penta fluro substituted acetylene molecule. The two hydrogens on acetylenes are substituted by a C6F5 unit. So, that makes it extremely electron withdrawing. What is another interesting fact about this molecule is that one of them is cobalt and the other one is a rhodium centre. So, here is a rhodium centre and here is cobalt both of them come from the same group.

And so you can still form a molecule which is very similar to what is formed with CO 2 CO 6. And you have the bending of the acetylene molecule. So you can see that this bond is significantly bent. It is no longer in a linear fashion, if it is simple acetylene but, you can see that it is significantly bent in this complex. And you can see that the two metal atoms are interacting with two different pi bonds on the acetylene moiety. And this if this is the Z axis you can see that the X the p orbital on the X axis is interacting with cobalt and the Y orbital is interacting with a rhodium atom.

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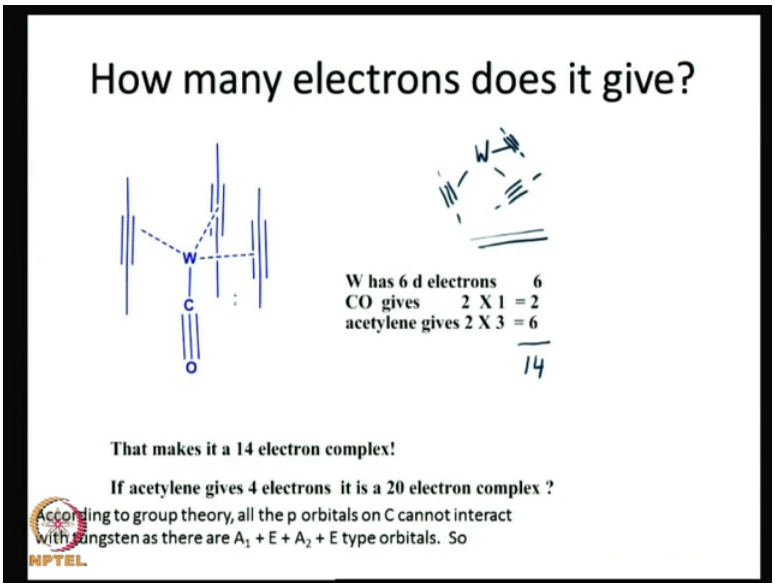

Let us take a look at some complexes where more than one acetylene is bonded to the metal atom. And look at the type of interaction that can form between the acetylene and the metal centre. So, here I have a tungsten zero complex and the tungsten zero has got 6 electron. So, you have carbon monoxide which will give you 2 electrons and we have 3 acetylene molecules. And the 3 acetylene molecules if they give 3 electrons each then it turns out to be a 14 electron complex. This adds up to fourteen electrons. And so this is way below what you would expect for a stable organometallic complex. And yet this molecule is quite stable and it has been isolated and characterised using X ray crystallography.

So, there was a debate as to whether this molecule is in fact giving more than two electrons form each acetylene. And before we go to a debate on the electron count I would like to show you the 3 dimensional structure of the molecule which is significantly different from what is pictured in many of the textbooks because the textbooks picture the tungsten as interacting with 3 acetylenes in this fashion. And this gives the impressions that the plane in which the 3 acetylenes are interacting with the tungsten are in a basal plane.

And whereas, in the 3 dimensional structures you can see that the midpoint of the acetylene the plane containing the midpoint of the acetylenes is the plane where almost the plane on which the tungsten atom is present. If it is interacting with the 3 acetylenes

in a fashion like this, then the number of electrons could be more than two, and we will come to a discussion about. First let us take a look at the structures of these complexes. So, here I am going to show you the structure of the complex with three acetylenes are coordinated.

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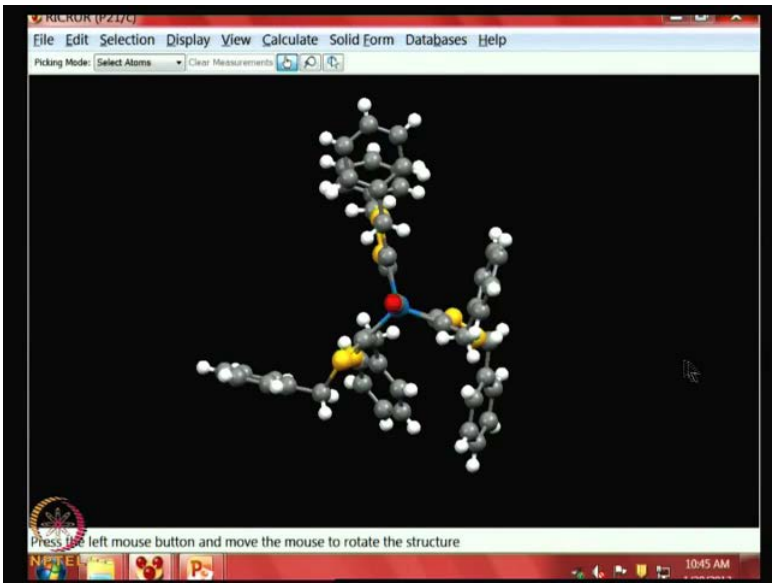

This is a three-dimensional representation of the complex, and you will notice that tungsten is in the centre of this molecule the tungsten is pictured with the blue coloured atom. And it is interacting with three acetylenes in such a way that it is almost in the midpoint of the plane which is formed by the 3 acetylene groups. And if you align that in such a way that you are looking at it through the carbon monoxide oxygen, this is the oxygen atom which is pictured in red colour here.

Then you will notice that the 3 acetylenes are eclipsed which means that it is only 1 pi bond from the acetylene molecule which is interacting with the central metal atom here. So, only two electrons are donated to the metal atom and it is not more than 2 as which is indicated in several textbooks. So, let us take a look at the electron counting in these molecules. I will go back to the picture where we had a electron counting being done. If acetylene gives 4 electrons then it would be it would end up as a 20 electron. And that is not the case because of the way in which it is oriented.

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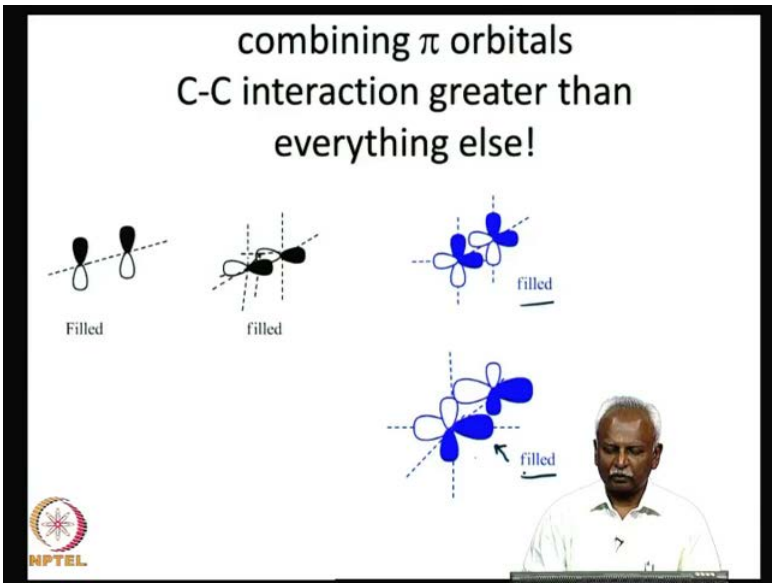

This discussion came about because you have the possibility of giving 4 electrons from acetylene. How is this possible? You will remember that there are two filled orbitals on the acetylene. And these two filled orbitals are orthogonal to each other and one can combine the two filled orbitals. If you bring in the metal centre in such a way that you can interact the metal with the 2 pi orbitals at the same time.

In between the two pi orbitals then you can see that you can form a sigma bond as in this case or you can also form a pi type of interaction between the metal and the filled orbital on the acetylene. So, this is one filled orbital one combination of the filled orbitals on the acetylene. And this is a second filled orbital combination on the acetylene.

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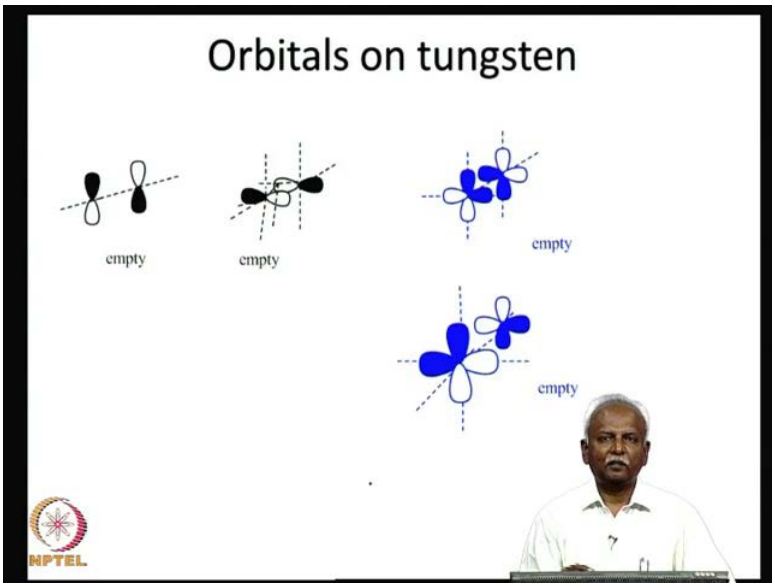

So, if you look at the empty orbitals in the same way you can form two different types of orbitals on the acetylene. And these two types of acetylene orbitals can interact with two different orbitals on the metal atom. And as a result you can have a total of 4 electrons being donated to the metal atom. But as you noticed the orientation of the acetylene is in such a fashion that it can interact with only one pi bond on the acetylene molecule.

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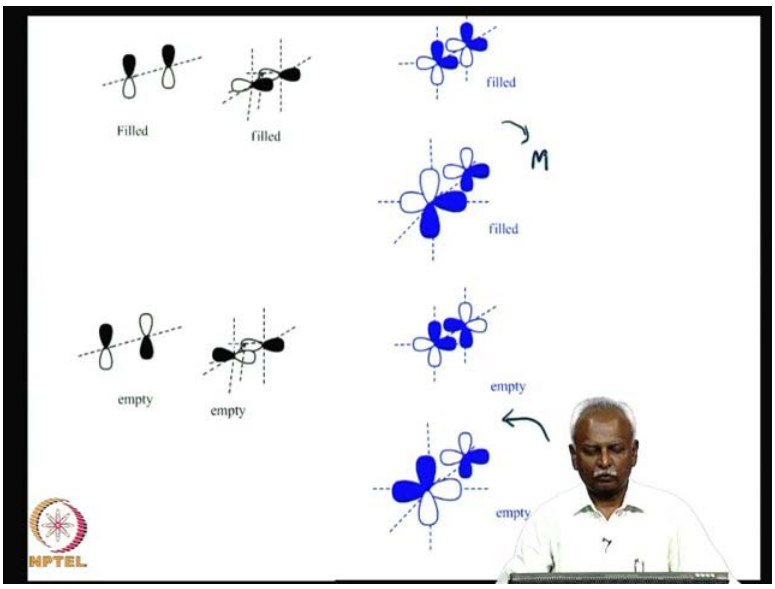

So, if you look at the full set of four pi orbitals on acetylene the two filled and the two empty ones. You can notice that the metal has both sigma and pi type of orbitals which

can be filled and which can donate electron density from the filled metal orbitals onto the empty orbitals. And it can also accept electron density onto the metal from the filled orbitals on the acetylene. So, acetylene can in fact as a 4 electron donor, but in the tungsten complex that we just looked at it is acting only as a 2 electron donor

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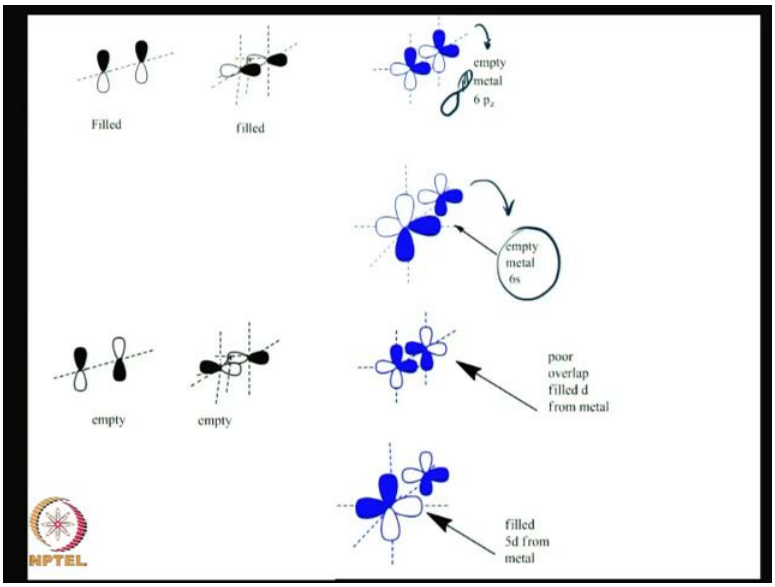

So, the orbitals which are suitable for such an interaction are indicated here. So, if you have a metal atom coming in between the 2 pi orbitals in such a fashion you can have accepting tendency for metal 6 S. So, electron density can be pumped from the acetylene onto the 6 S in the sigma fashion. And the metal can accept electron density into the P or P Z orbital which is appropriately oriented to accept electron density from the you can picture it like this. You can accept empty metal orbital will accept electron density from the acetylene onto the P Z orbital. So, you can have d orbitals in fact pumping in electron density into the empty orbitals on the acetylene pi star

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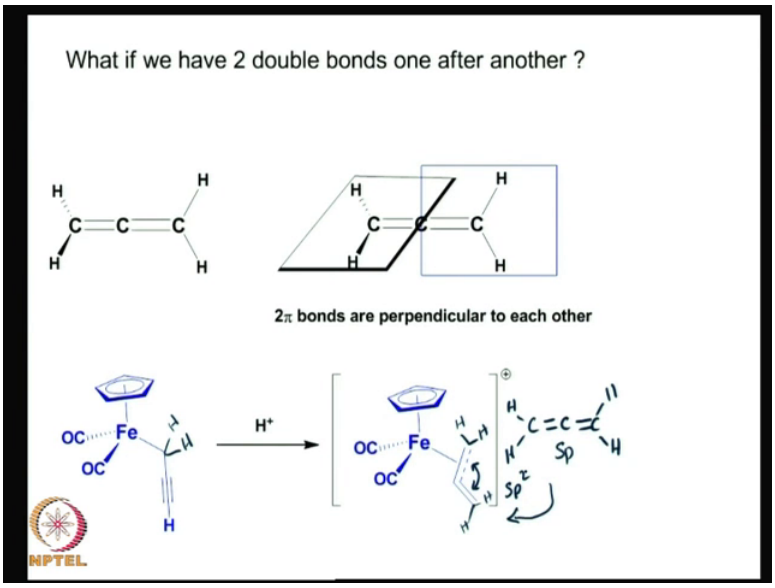

So, you can see that there are a variety of possibilities when you have multiple double bonds. Now, multiple double bonds can also be present on 2 different atoms on adjacent atoms. In other words these are cumulenes and cumulenes are easily made. And they can be stabilised in the coordination sphere of a metal atom or a metal complex. Here I have pictured for you a unique example of a propargyl complex which is a C H2 sigma bonded complex to iron.

And if you add an acid to this it forms a propargyl complex is transferred to a cumulene complex or an alkyne. So, here is a complex where you have two carbons which are a cumulene. This is an allene complex to the metal and you will notice that there is a significant bending of the two carbons so it is no longer a s p hybrid here it was a s p hybrid to start with it has become more like an s p two hybrid. So, you have very similar bonding situations between the allene and the metal centre.

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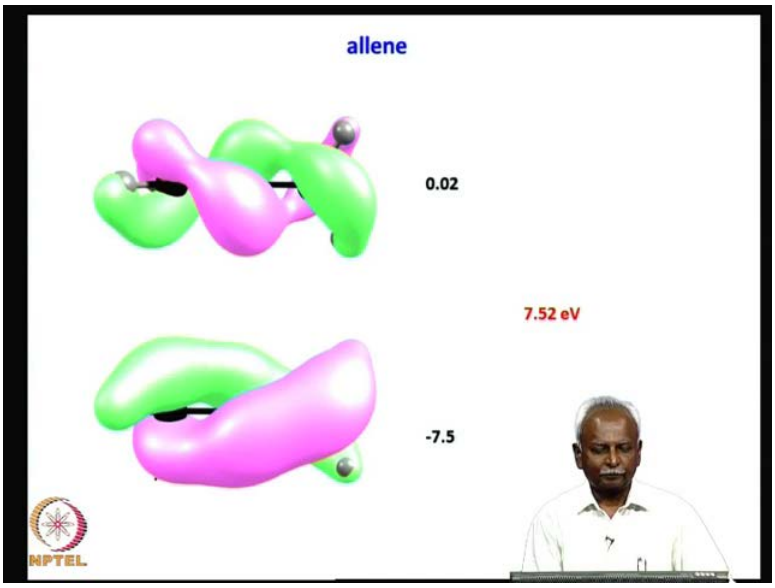

The molecular orbitals of the allene are extremely complicated but, nevertheless there are two pi bonds which are perpendicular to each other. And it is interesting to note that in the lowest energy the pi bond that is donating electron density to the metal centre. You can in fact have a smooth flow of electron density from one end of the carbon allene system to the other end. And as a result the metal can traverse from one end of them allene to the other end very readily.

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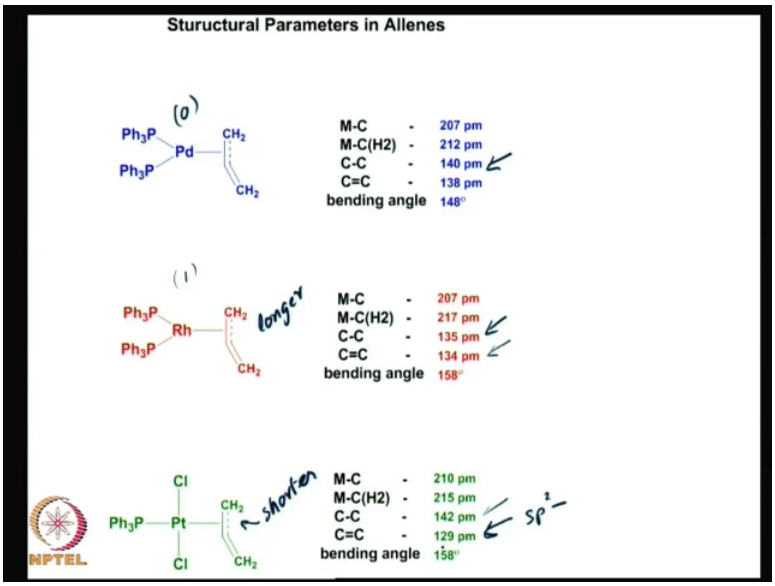

So, here are a few complexes of allene with metal centres. And you will notice that in fact you have the same type of bonding interactions which are significant. If you have a platinum two complex then the bond distance that is available between the 2 carbons. So, here is the platinum 2 complex. Here is the distance 142 picometers whereas, if I have a rhodium 1 interacting with the 2 carbon centres, the rhodium one is lengthened into a significant extent.

Here it is 135 picometers you compare that with 129 picometers which is there on the platinum 2 plus complex. So, this bond is shorter. This is shorter because of the oxidation state this is a longer distance. And this is readily understood on the basis of back bonding between the metal and the carbon-carbon bond. So, the carbon-carbon bond that is not interacting with the metal as almost the same type of bond length that is about that is indicated as C double bond C. And the C double bond C is usually just a single it is not interacting with the metal. And so it is s p 2 hybrid which is interacting with another s p 2 hybrid. So, this is a typical double bonded distance that you have 129 picometers.

So, you can notice that a palladium zero complex has extensive back bonding. And the back bonding results in a very long bond between the two carbon atoms. So, this bond length from zero to a rhodium 1 complex this is a rhodium one complex elongates to a lesser extent 135 picometers. And then it becomes even shorter because of reduced pi accepting nature. So, this concludes our discussion about complexes where you have double bonds interacting with metal centres and the Dewar Duncanson and Chatt model is probably the best way to understand the interactions in these systems.