Diene and polyene complexes

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Lecture - 16

Introduction to Organometallic chemistry

Diene and polyene metal complexes are a natural extension after discussing olefin complexes.

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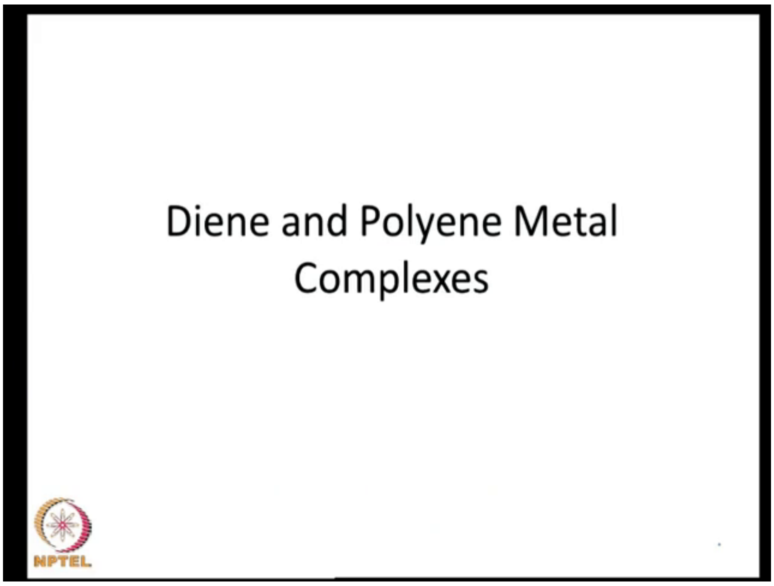

Diene and Polyene Metal Complexes

So, in this lecture, what we will do is to look at some of the diene complexes that are readily available and also look at the structure and bonding in these systems.

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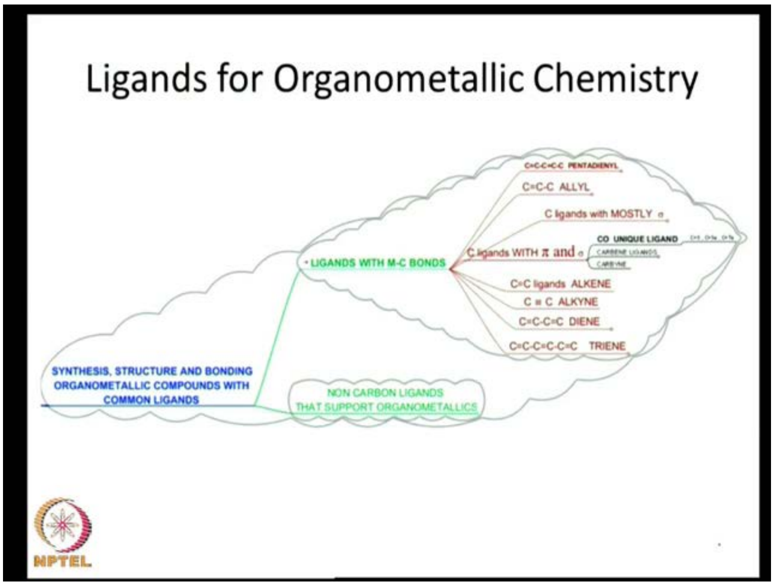

Ligands for Organometallic Chemistry

If you look at the ligand space that is available for organometallic chemistry, you will notice that they can be roughly divided into 2 halves, especially ones which are having a metal carbon bond. So, these are the ligands, which are available when you have a metal carbon bond. This is indicated by this large cloud compounds that support organometallic chemistry and support metal carbon bonds. Here, you do not have, do not generate a metal carbon bond. Inherently, such as phosphines and nitrocylls are formed are another class. These are indicated by this smaller cloud.

So, if you take the ligand space, which has only metal carbon bonds, you can divide them into 2 groups. One group is a one, which has got an even number of carbon atoms bond to the metal. These are alkenes, alkynes dienes and trienes. So, it is this group that we are talking about. In the second group, we can talk about a series of ligands where we have an odd number of carbon atoms bonded to the metal.

These are listed on the top. In between, there is a unique carbon monoxide ligand and some substitute for carbon monoxide and also some components where you have only this sigma bond. Those are the alkyls. This is indicated by metal alkyls vinyls and etcetera. So, today we will talk about the chemistry of metal poly olefins dienes mostly.

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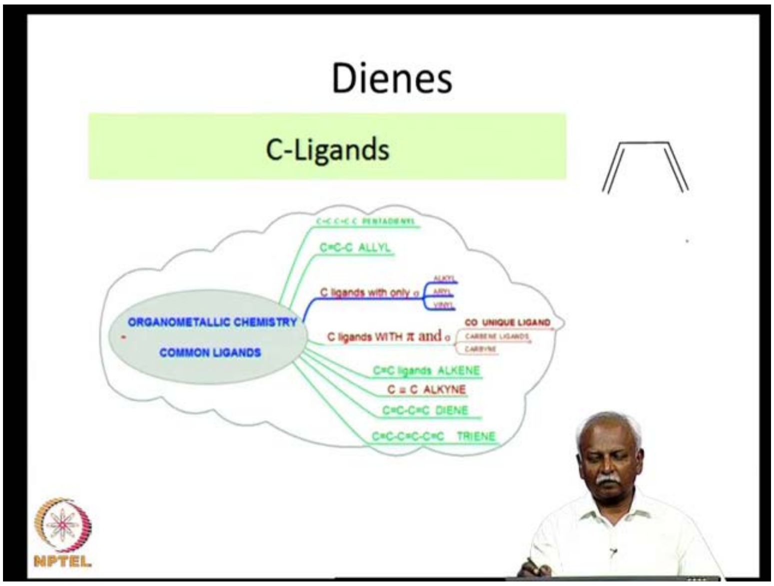

Dienes

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 ≡ C ALKYNE

C=C-C=C DIENE

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

If you look at dienes, these are just examples of compounds where you have 2 double bonds strung together. It is quite common in organometallic chemistry.

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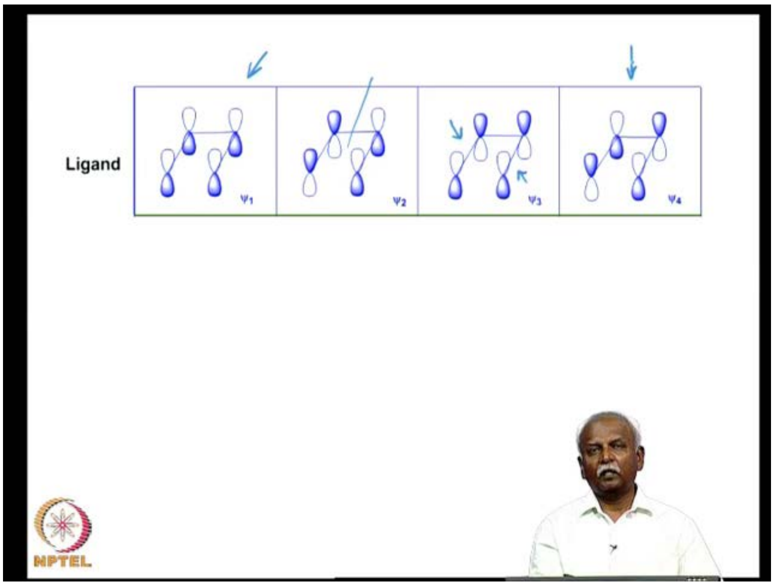

Ligand

If you look at the molecular orbits of pi system that is there in diene, you will notice that the most stable or the lowest energy pi bonding orbital is the one which is labeled as psi 1. It has the phase of all 4 p orbitals the same. So, you have no node in the pi orbital manifold.

Secondly, you have a system where you have a single node. It is denoted here as psi 2. Then, the third molecular orbital has got 2 nodes. These 2 nodes are indicated here. The orbital which has got 3 nodes that is the highest energy orbital, would be molecular orbital, would be vacant. So, let us take a look at the metal orbitals that are available for interaction with a simple polyene system, the diene system which is shown here.

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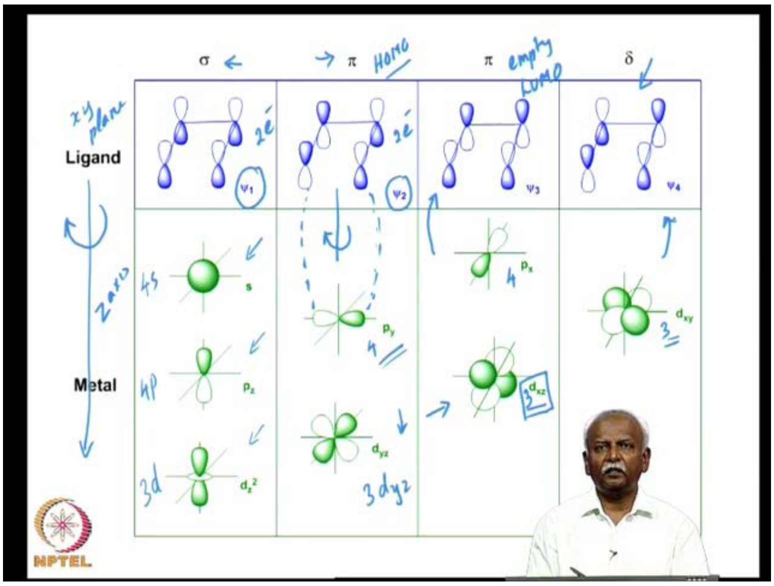

The metal orbitals can be conveniently drawn in this particular fashion. If you take a 3 d element, then you have the 4 s orbital which is available. So, this is the 4 s orbital, which is available. Then, you have the 3 p, the 4 p orbitals, which are available. Then, you have 4 p orbitals, which are available. These are 4 p x, 4 p y and 4 p z orbitals. They are higher in energy. Then, the corresponding d orbitals are the 3 d orbitals, which are drawn here.

You will notice that we have drawn the d z square xy xz and y yz. We have not drawn the d x square minus y z orbitals that is there. Of course, you can note it down as d x square minus y z orbital. It is something, which does not have a proper overlap with the butadiene orbital. We will see that in a minute. So, let us take a look at how these orbitals can be matched up. Interestingly, if you draw in this particular fashion, you will realize that they are exactly in the same order in which they match the butadiene orbitals. So, here are the butadiene orbitals.

The 4 s orbitals and the 4 p z, 4 s, 4 p z and the 3 d z squared all have the right combination to overlap with the totally symmetric combinations of p orbitals, which form the lowest pi bonding orbitals. So, that is the psi 1. That will be filled with 2 electrons. So, you have 2 electrons here. So, for butadiene, you have 2 totals of 4 pi electrons. So, you have 2 electrons here also. This combination of s p and d z squared has to be empty in order to interact favorably with the filled psi 1 orbital.

So, this is the filled orbital. This has to be metal orbital has to be an empty one in order to form a fir rule combination. So, invariably it is going to be the 4 s and the 4 p, which are most suitable if you have a late transition metal. If you have an early transition metal of course, where the 3 d minus 4 is also relatively empty, then you can utilize the 3 d orbitals, 3 d z squared for interacting with this one. Notice what happens when you move on to the next higher line orbital. This is your homo orbital. The highest occupied pi molecular orbital on the butadiene has got 1 node.

So, you need to choose an appropriate atomic orbital on the metal atom. So, this has to be either the 4 p y. If you orient the butadiene in such a way in this fashion, then you will have to choose the 4 p y and 4 d or the 3 d, 3 d y z in order to interact with this filled side too. So, the filled side 2 can interact with 3 d y z or 4 p y.

Now, let us assume that the orientation of the metal is along the z axis. The butadiene is itself is lying in the xy plane ligand. The metal is along the z axis. So, this is your z axis. So, if the metal is lying along the axis, if the butadiene is along is lying on the xy plane, and then you will have this particular combination. So, this is the e filled orbital again. The second pi orbital is the filled orbital. So, you need to choose an empty metal orbital. So, that will be 4 p y or the 3 d y z in case the metal is early transitional metal and has got empty orbitals.

You will notice there is a slight difference in the type of interaction that is present in the butadiene and the s p and d z squared orbital that we talked about first. If you rotate the butadiene along the z axis, so if you carry out a rotation in this fashion, if you do this particular operation, nothing can happen to the bonding interaction between the metal and the butadiene. On the other hand, if you take this combination, if you rotate along this axis that is the z axis, what you will realize is that you will break the type of interaction.

The favorable interaction that is there between these 2 lobes has got perfect overlap. Now, you have a nice overlap here and a nice overlap here that is stabilizing. You will break this if you rotate the metal with respect to the butadiene. So, this is the pi type orbital molecular orbital that de generate. So, one is sigma where you do not break any interaction if you rotate. The other is the pi because you will spoil the interaction and make it completely 0 if you turn it by 90 degrees. So, let us move onto the third interaction.

Here we have an empty orbital. This is an empty orbital. So, we will call this the lumo. So, it is the lowest unoccupied orbital on the butadiene. So, the psi 3 is an empty orbital. So, you need to take a filled orbital and invariably if you want to have a stabilizing interaction between the metal and the butadiene this is empty. It has to be interacting with a d x z orbital because of 4 p is unlikely to be filled.

So, the 3 d xz orbital if it is filled, then it can interact by pumping in electrons into the empty psi 3 orbital. So, again you will notice that this is the pi type of interaction because if you rotate it with respect to the along the z axis, if you rotate one either the metal or the butadiene with respect to the other, then you will end up breaking the type of interaction that is there between psi 3 on the butadiene and the metal. So, this is again a pi type of orbital.

The last type of interaction is a type of a delta bond, which can be formed between the butadiene and the metal is pictured here. This is the high lying empty orbital. This has got 3 nodes. This is the high lying empty orbital with 3 nodes. This can interact with the d x y orbital. This type of interaction is going to be very weak because d orbital is not pointed towards the diene. It is on the plane parallel with 2butadiene and butadiene and the metal orbital are in 2 parallel planes.

So, the type of interaction that would be there that is delta bond. If you rotate it by 45 degrees, you would lose all the overlap. So, this is a very weak bond. It is possible between the d x y and psi 4. So, d x y is filled. The 3 d xy is filled. So, you can pump electron density into the psi 4, but this is likely to be a very weak interaction. So, these are the types of interaction that you can have between the butadiene and the metal fragment the metal orbital primarily.

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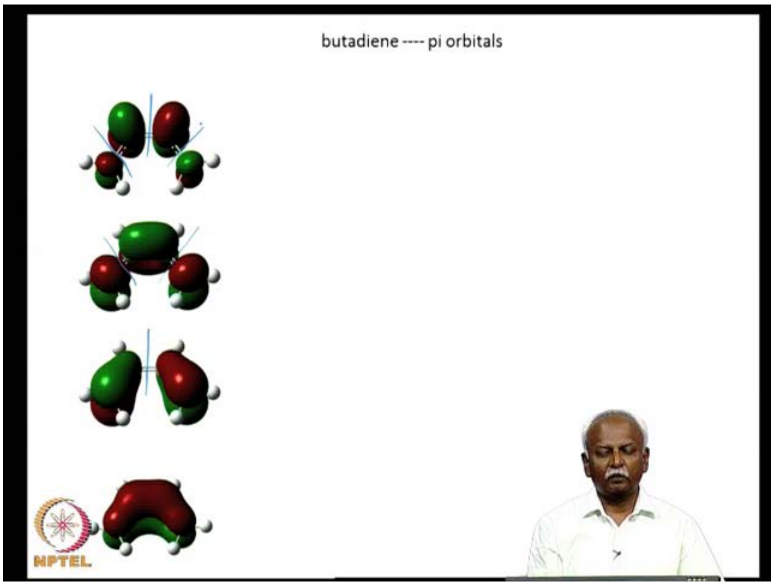

butadiene ---- pi orbitals

So, here I have shown you some pictures, the type orbital pictures that normally would generate using molecular program. So, you have the 4 orbitals and you can see the node here very clearly. There is this single node that you have in between the 2 double bonds. You have 2 nodes in this case and the 3 nodes there are pictured here. So, the butadiene orbitals that are available are kept in one plane and the metal is below the plane. It is interacting with the butadiene.

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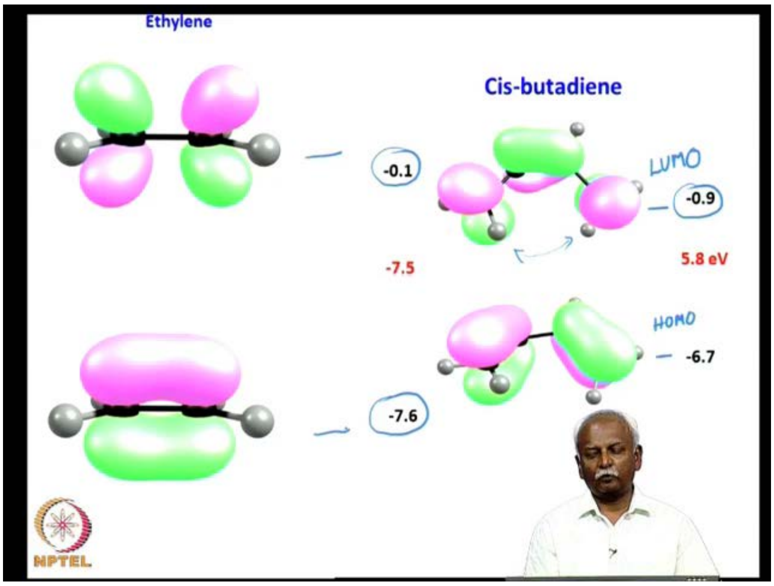

So, if you look, let us take a look at the energies one calculates for the butadiene and compare them with what you have with ethylene. So, if you draw cis butadiene, the butadiene twists itself because it does not like the interaction that is there between the 2hydrogens, which are pictured here. So, what butadiene does is that it twists a little bit. These are the energies of the twisted orbital, but nevertheless, they illustrate some key principles.

If the butadiene is cis, the highest occupied orbital, this is the highest occupied molecular orbital is lying at minus 6.7 electron volts. In the case of ethylene, the energy is at minus 7.6 electron volts. What this means is the 2 electrons, which are lying in the homo can be donated to the metal more readily than the electrons on the ethylene. So, butadiene would in principle be a better donor.

Not only has it had 2 pi bonds to donate electron density to the metal, it also able to donate it more effectively. This is because of the higher lying energy of the homo, higher lying homo orbital. Now, let us take a look at the lumo. You will notice that the lumo is at minus 0.1 electron volts, in the case of ethylene.

So, in the case ethylene, it is at minus 0.1 where as in the corresponding calculation, one estimated minus 0.9 electron volts. So, this energy is lower. The lumo is at a lower level compared to the lumo of the ethylene. So, what this results in is fact that you can put in more electron density or rather you can put in electron density much more easily into the lumo of the butadiene, the cis butadiene. Then, you can put it into the lumo of the ethylene. So, cis butadiene is better acceptor. At the same time, it turns out to be a better donor.

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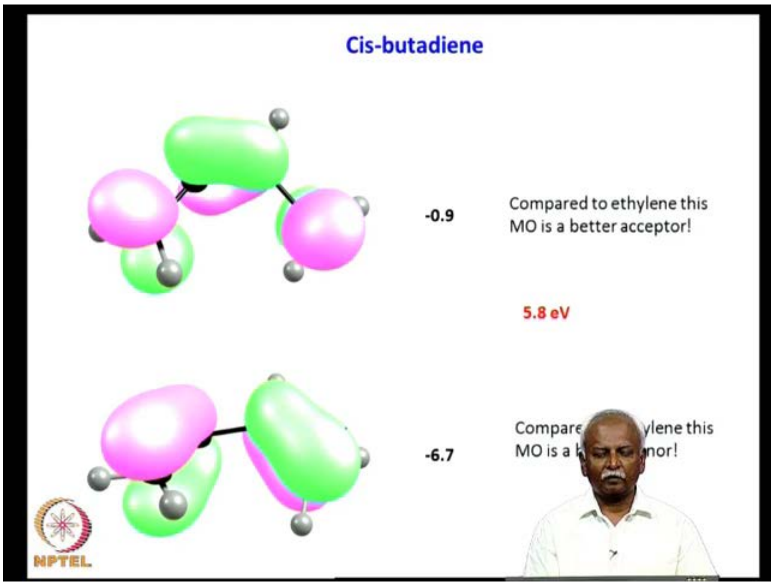

Cis-butadiene

-0.9

Compared to ethylene this MO is a better acceptor!

5.8 eV

-6.7

Compare ylene this MO is a nor!

So, this has got some many important consequences in principle. Then, as you go on from an ethylene to butadiene to triene, you will keep increasing the donor capacity of the ene. You will increase the acceptor capacity also at the same time. So, it will lead to much better bonding not just a matter of interacting to 2 parts of the ligand with the metal. Of course, that leads to something chelate effect.

You have 2 double bonds interacting with same metal. You have something like chelate effect. In addition to that, you also have a situation where you have better donor capacity and better acceptor capacity. So, this turns out to be a key factor in the study of the butadiene or polyene with metal complexes.

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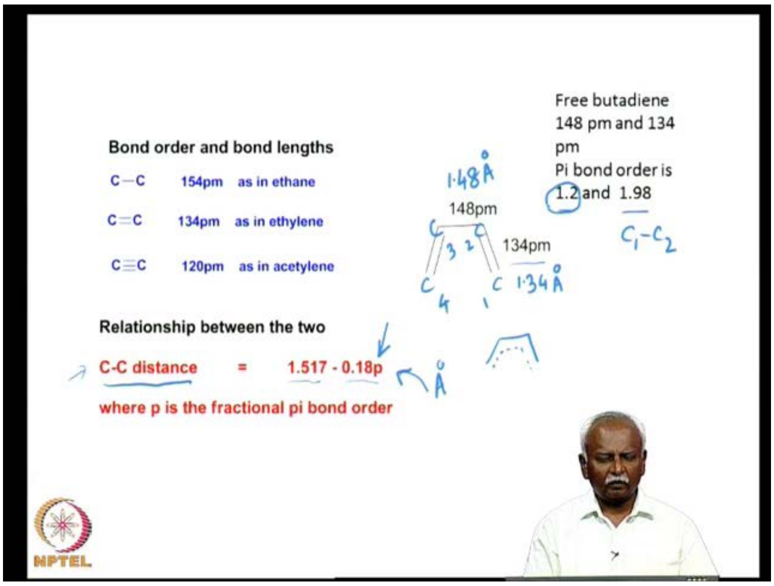

Bond order and bond lengths

C—C	154pm	as in ethane
C=C	134pm	as in ethylene
C≡C	120pm	as in acetylene

Relationship between the two

C-C distance = 1.517 - 0.18p

where p is the fractional pi bond order

Free butadiene
148 pm and 134
pm
Pi bond order is
1.2 and 1.98

So, let us take a look at what happens to the bond distances. First take a look at what happens with ethane. In ethane, the bond distance is about 1.54 angstrom. So, 154 picometeres as it is given here in this projection. You reduce the bond distance to about 134 picometeres in ethylene that is the double bond and double bond between 2 carbon atoms. Then, it further falls to 120 picometeres in the case of tripe bond.

So, these are somewhat like standard we can use and look at partial double bond orders, which will result when you start making cogitated olefins. So, there is an empirical relationship, which is being formed between the bond distance there is observed in the molecule and the bond order.

This is because the bond order is something that we compute and we infer from the bond distance. So, it is the relationship between the 2. It is in fact a linear relationship. If you look at the carbon carbon distance in the molecule of the question, this is the carbon carbon distance in the molecule that we are discussing, and then if you subtract 0.18 p from 1.57, you can estimate. This gives you an estimate of the partial double character that you have partial or fractional pi bond order. So, that tells you how good a pi bond you have between the 2 carbons, which are separated by a particular distance.

Let us take an example. Now, let us take a free butadiene. Free butadiene has got a bond distance of 134 picometeres between the 2 carbons. So, that is 134 picometeres between the carbons and or rather 1.34 angstroms. You have a bond between C 2 and C 3 if this is

1, 2, 3, and 4, the C 2 C 3 distance is 148 picometeres or 1.48 angstroms. So, this equation is actually given in angstroms. So, if you can calculate the pi bond order between the C 2 and C 3, it is actually only 1.2.

The pi bond order between C 1 and C 2 is 1.98. So, it is almost the bond order is almost 2 between the carbon 1 and carbon 2, and the carbon 2 carbons and carbon 3 is 1.2. This means it has got a partial pi bond order of 0.2. So, you know there is a delocalization between the 4 carbon atoms. So, we sometimes indicate it like this. So, that is indicated by this partial pi bond order. The pi bond order is 1.2. The pi bond order is 0.2. The total bond order is 1.2. So, let us proceed further.

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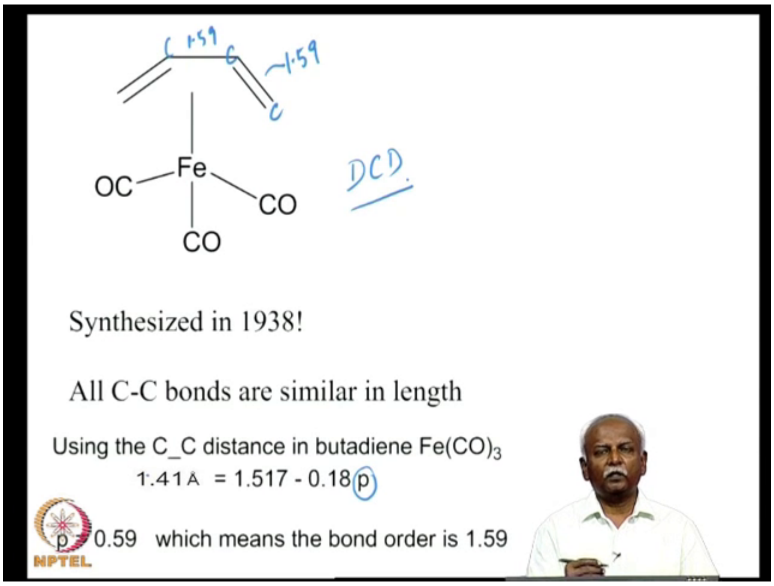

Synthesized in 1938!

All C-C bonds are similar in length

Using the C_C distance in butadiene $Fe(CO)_3$

$1.41 Å = 1.517 - 0.18 p$

p 0.59 which means the bond order is 1.59

Now, let us take a look at the complex that is formed by butadiene and irontricarbonyl. This is probably the first tri carbonyl that was synthesized way back in 1938. Long before it was discovered, this complex or this molecule was known. What is interesting is that the carbon carbon bond length is almost the same. All carbon carbon bonds are approximately 1.41 angstroms. So, this particular equation should be as 1.41 angstroms.

So, this is 1.41 angstroms equals 1.517 minus point 1.8 p. This p is giving you the fractional bond order to which is the pi bond order. So, we get a value of 0.59, which means that the total bond order between Cs, each one of these carbons is 1.59. You will remember that this was close to 1.98 in the case of free butadiene. It is decreased considerably to 1.59. We also estimated 1.2 for the bond order between C2 and C3. Now, we are bringing it. We are increasing it to 1.59.

So, what you will realize is that the bond order between C2 and C3 increases. The bond order between C1 and C2 drastically decreases. So, this delocalization is brought about by the iron atom, which is interacting with the butadiene. So, how does this come about? If you remember the doer chat duckenson model, which we discussed in detail earlier doer chat, and duckenson model DCD model or bonding, you remove electron density from the butadiene from the pi orbitals and push it into the pi star orbitals of the butadiene. So, let us take a look at interactions that we discussed earlier.

So, here we notice that we remove electron density from the bonding orbitals. Electron density flow is from the bonding orbitals into the empty orbitals. This happens for psi 1, psi 2, and the 2 bonding orbitals of butadiene. We are pushing in electron density from the d x z into the empty lowest unoccupied molecular orbital that is the psi 3. So, what we are doing is something like removing electron density from the pi bonds and pushing into the pi star orbitals. So, this results in a weakening of the C1 and C2 bond and strengthening of the C2, C3 bond. This is because the C2, C3 has got some bonding interaction between the pi star or the lowest unoccupied molecular orbital.

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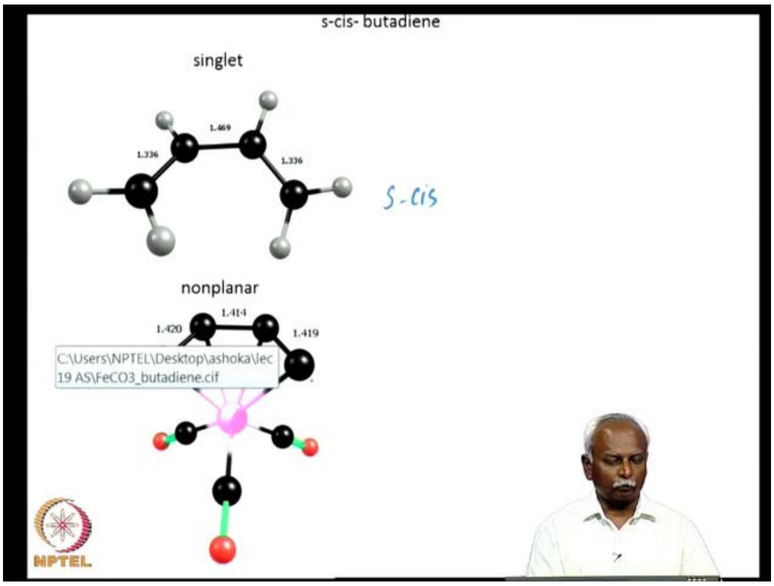
s-cis- butadiene

So, let us take a look at the structure itself. Here is the structure. This is called as s-cis-butadiene because you have in fact, cis geometry along the single bond. So, this is the s sigma cis butadiene complex that you have. So, you notice that the bond distance between C1, C2 is 1.419. It is slightly shorter than the longer distance that is formed between C1 and C2. So, let us take a look at the structure of this molecule in 3 d.

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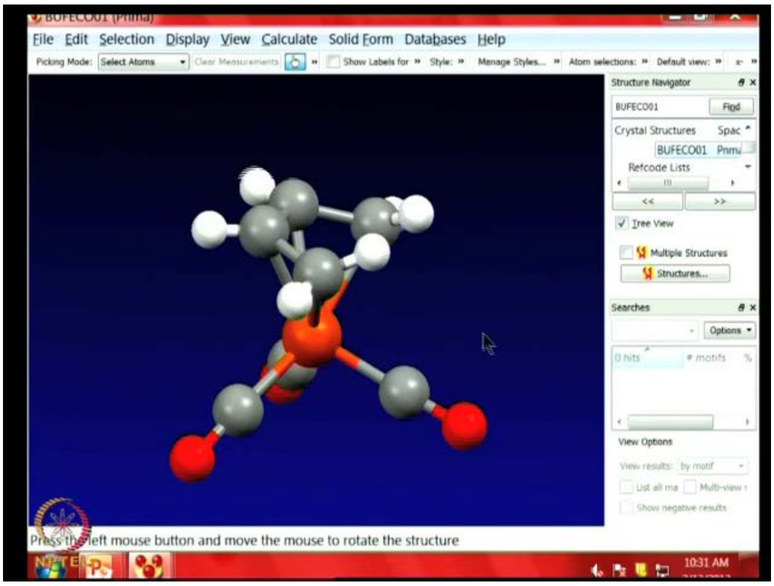

Press the left mouse button and move the mouse to rotate the structure

So, this is the butadiene compound, which is complex to iron. Iron is shown in red. That is the atom in the center here in which the arrow is pointing. The butadiene itself is in a plane which is above the iron atom. So, this is the gray atom here indicated here or the carbon atoms. You will notice that the gray atoms are the carbon atoms.

They are in a plane. They are all lying on one plane. The2 hydrogens at the terminal carbons are slightly twisted away from this place. Nevertheless, the 4 carbon atoms are interacting with the ion atoms, which is below the plane. The 3 carbon monoxides are in like a piano’s stool. They are like a stool for this small table, which is formed by the butadiene unit. So, let us get back to the structure here. So, you will notice that we have a slight widening of the 2 carbons in this geometry. We saw in the complex also.

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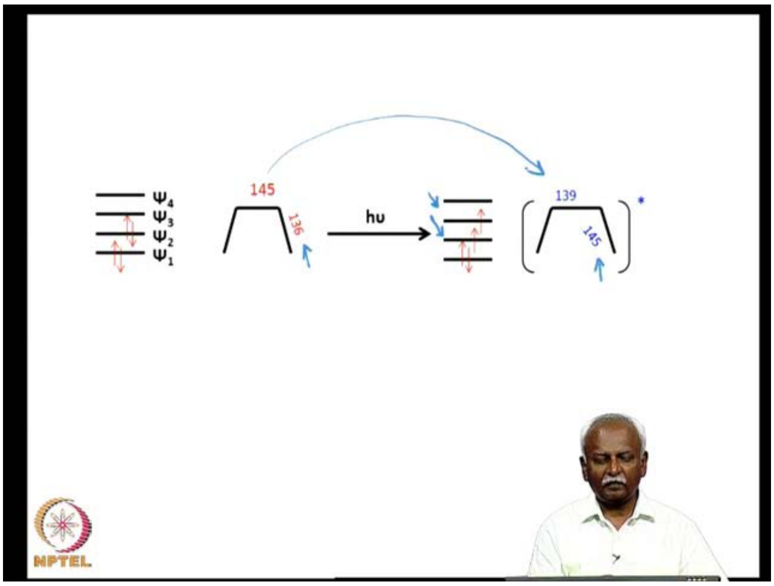

What we have done is remove electron density from this psi 2, its bonding orbital and push into the psi 3, which is the lowest unoccupied orbital. This is exactly what is going on when you have a photochemical reaction with butadiene. So, if butadiene absorbs light, there is an electronic excitation. You are doing exactly the same thing that we are doing when we form a metal complex.

So, here is an example where butadiene is taken and it is photo excited. The first photo excited state, the lowest unoccupied orbital has got 1 electron. The homo is also only having 1 electron because it has lost 1 electron to the lumo. The excited state geometry is predicted to be exactly moving in the same direction. We have lengthening of the C1, C2. So, earlier it was 1.36 angstroms and it has elongated to 1.45 angstroms.

These distances marked on the projections are in picometers. So, it can be 136 to 145 picometers. Similarly, the bond distance between the center carbons C2, C3 has increased from 145 picometers to 1. The bond distance between C2 and C3 has decreased from 145 picometers to 139 picometers. So, this is clearly indicative by the fact that you are pumping in electron density into the psi 3 orbitals, which has got bonding interaction between C2 and C3.

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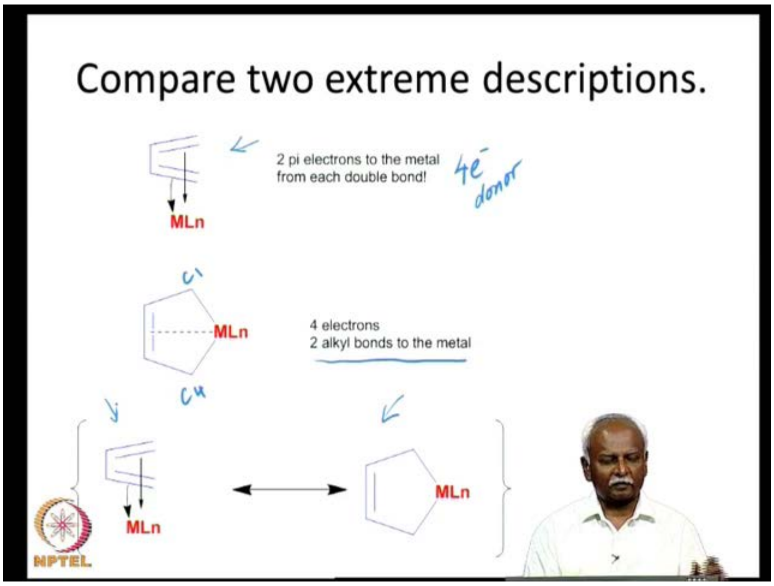

Compare two extreme descriptions.

2 pi electrons to the metal from each double bond!

4e⁻ donor

4 electrons
2 alkyl bonds to the metal

So, let us compare the 2 extreme descriptions of how a metal can interact with the butadiene unit. In the first description, we just had a pi type interaction, pi bond of the butadiene interacting with the metal in a simple sigma donor fashion. That means the 2 pi bonds donate electron density to the metal. This is the primary interaction. If this is the only interaction or the primary interaction, 2 pi electrons are given to each of the double bonds.

So, total it is a 4 electron donor. This is a 4 electron donor. Now, it turns out that if the electron density that is donated to the metal is pumped completely back into the pi star orbital, what you will end up doing is forming a bond between the metal and C1, C4. That would almost look like a covalent bond.

So, the other extreme discussion is to form a sigma, a bond between the C1 and the metal and the C4 and the metal. So, if this sigma bond is formed by completely pumping of the electrons from the metal onto the terminal carbons, then you will have the description that you have a metallocyclopentene. So, here is the metallocycolopentene. So, these are 2 extreme descriptions; either way you have 4 electrons, 2 alkyl bonds to the metal from the terminal carbons. So, you have 4 electrons, which are involved between the metal and the diene fragment. You also have a 4 electron interaction in the case of the pi bond description that I gave you initially.

So, these 2 extreme descriptions are really not completely correct. What is true is something that is in between depending on the nature of the transition metal. You will have different amounts of electron density transferred from the metal onto the pi bond and so into the psi 3. So, you will have either a bond lengthening, which corresponds to this metallocyclopentene geometry or geometry, which is a very slight bond distortion. It is indicative of just the pi bond giving electron density to the metals.

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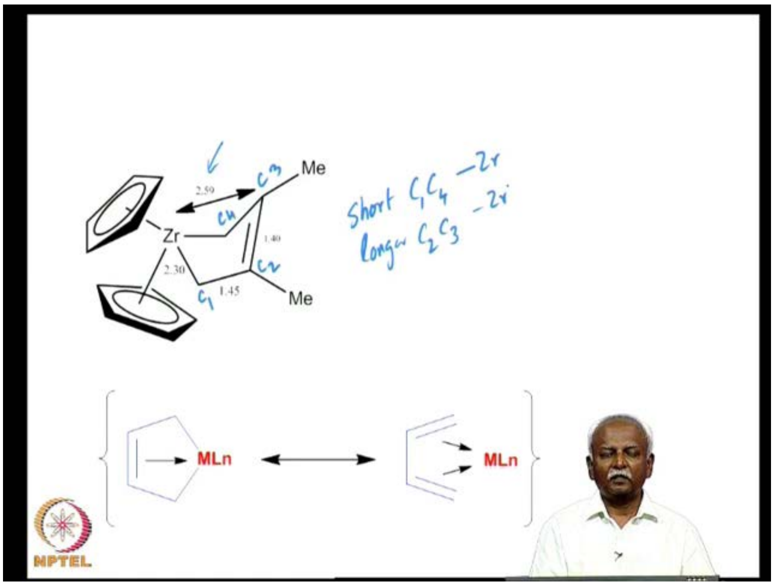

So, here is an example, which is in a zirconium complex. It has got 2 cyclopentadienyl units, which we have not discussed earlier. Let us just take them as flat 5 carbon units interacting. Let us concentrate on the butadiene, which is interacting with this zirconium. You will notice the bond distance between the zirconium and the carbon. So, here is the butadiene. This is C1. This is C2, C3 and C4.

So, these are the 4 bonds, which are interacting with this zirconium. You will notice that earlier the 4 carbons were interacting equally with metal atoms. Now, in this description or in this particular compound, which is a metalloscyclopentene, you have a very long bond between C 3 and zirconium. That is almost 2.59 Angstroms. The zirconium, C1 bond is very short that is 2.30 Angstroms.

So, a short distance between C1 and C4 and zirconium and a longer C2, C3 and zirconium is indicative of other extreme descriptions, which is pumping in all the electrons from the zirconium onto the butadiene. So, you now form a covalent bond between zirconium and carbon. You have a metalloscyclopentene description. So, you can see that this is almost like a cyclopentene envelope, which is common in organic chemistry. Only the flap is occupied by the metal atom.

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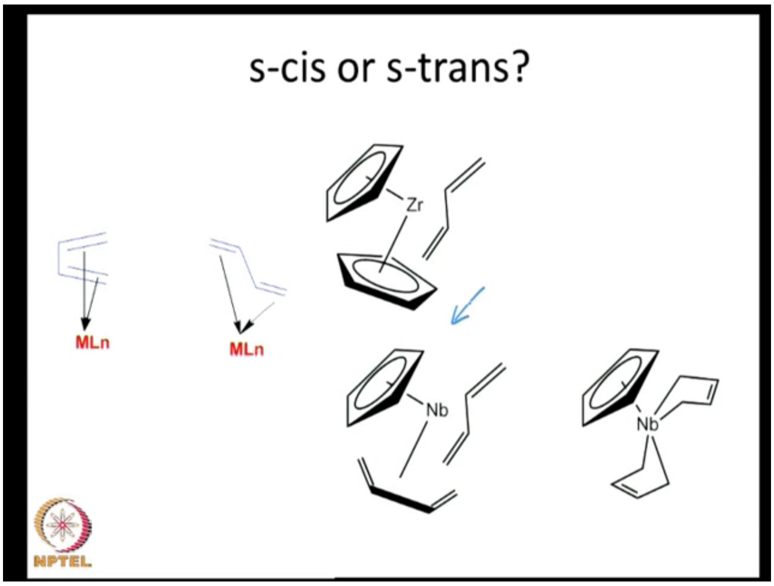

s-cis or s-trans?

So, there are a variety of complexes where you can have both the description that I gave you just now, which are cyclo metalloscyclopentene geometry and also the butadiene geometry. But, in the few cases, the butadiene is not present in the cis geometry. It prefers to interact with the metal when it is in the Trans geometry. This is reasonably rare.

We will take a look at the 3 d structure if time permits. There a few complexes where both the Trans geometry and the cis geometry are co-existent on a metal atom. So, this is very common when you have a very early transition metal. This type of interaction is common. You have the Trans geometry of butadiene interacting with the metal atom.

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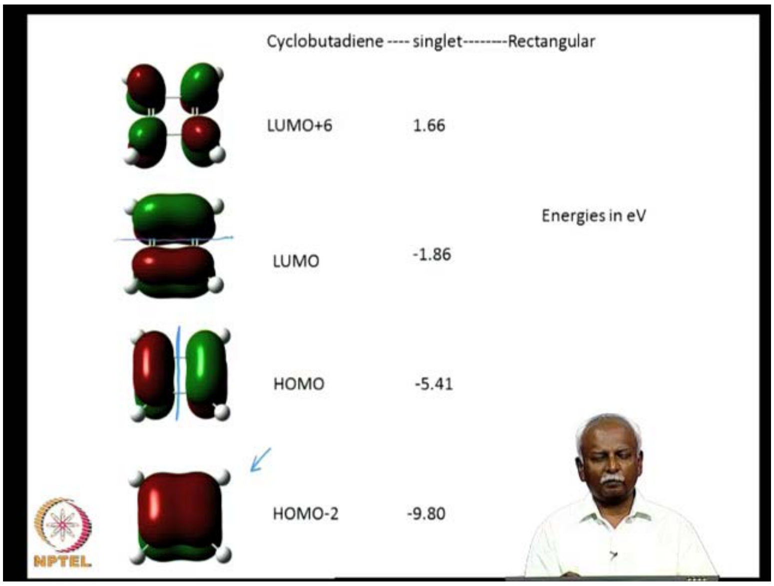

Cyclobutadiene ---- singlet--------Rectangular

LUMO+6 1.66

Energies in eV

LUMO -1.86

HOMO -5.41

HOMO-2 -9.80

So, let us move onto another type of butadiene. Now, in this butadiene, we have joined together the 2hydrogens, which were removed; the 2hydrogens, which were present in butadiene geometry and from the covalent bond. So, that gives us this rather familiar butadiene compound, which is cyclobutadiene. If it is a singlet, it will be the most stable geometry. The most stable is that of rectangular geometry where the 2 double bonds are isolated. It is not a square cyclobutadiene, but a rectangular butadiene.

You will notice that a similar description is good for the pi molecular orbitals. You have a completely symmetric molecular orbital, which can be drawn in this particular fashion. There are no nodes in this pi system except for the node, which is in the plane of the molecule and that is not seen in this particular orientation. Similarly, you have 1 node in the pi system and that is the highest occupied molecular orbital.

Now, if you will notice that there is 1 node here, and then the second one has also got a node, but that node is perpendicular to the first node that we drew. That is the lowest unoccupied molecular orbital. Now, we can in fact take these molecular orbitals and let them interact with the metal orbital just the same way that we did earlier.

You will form a nice molecular orbital picture for the cyclobutadiene metal complex. When the cyclobutadiene interacts with the metal, it very often forms the square geometry.

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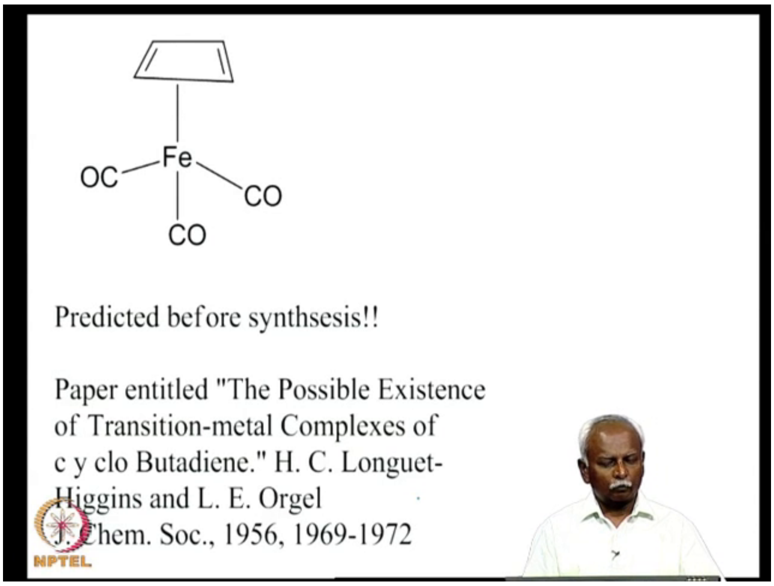

Predicted before synthsesis!!

Paper entitled "The Possible Existence of Transition-metal Complexes of c y clo Butadiene." H. C. Longuet-Higgins and L. E. Orgel J. Chem. Soc., 1956, 1969-1972

In fact, this is one of first molecules that were predicted before the molecule was synthesized. This molecule was predicted before the compound was synthesized. The paper was published in 1956 by Orgel and Higgins. They predicted that it is possible that you have a transition metal complex between cyclobutadiene. This particular complex would have the geometry of having a flat cyclobutadiene interacting with a metal atom.

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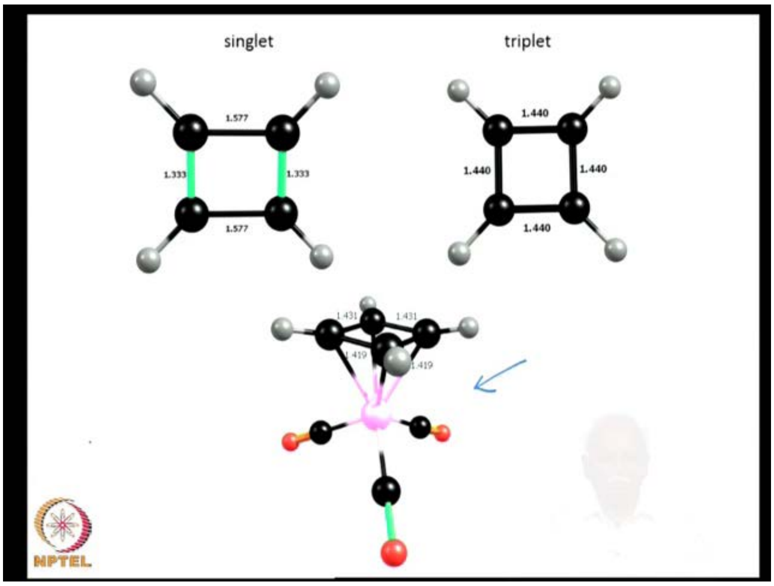

So, right after the prediction, it was possible for people to search for this complex, try and make it sure enough that they were able to make the cyclobutadiene complexes. The metal carbon interaction was quite strong. This was a stable system. It could be isolated and characterized very readily. The bond distance between the carbon atoms was quite delocalized compared to what you would expect for cyclobutadiene. Cyclobutadiene is not stable in the Free State and it readily dimerises.

So, you do not have a experimental structures for free cyclobutadiene bond distances, but you have calculated distances. These are shown here. As I told you, the singlet is the one which would have not cogitated, but isolated double bonds. So, when it form the complex, you have a very nice interaction.

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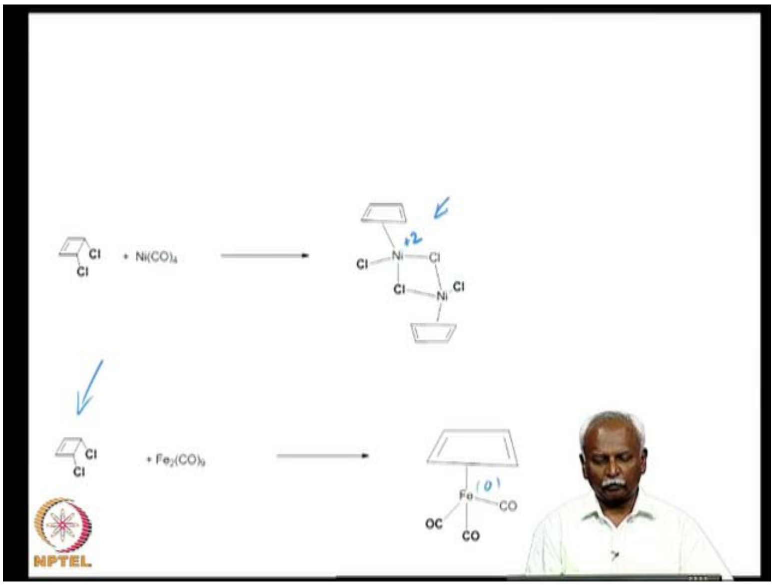

Let us take a look at how one can make these molecules. It is possible to make them by using a compound, which is in a low valence state. In this particular example, we have nickeltetracarbonyl. Nickeltetracarbonyl can be interacted with dichloro 1, 2 dichlorocyclobutene. That gives you nickel 2 complexes, which is cyclobutadiene coordinated to the nickel. So, here you have nickel interacting with cyclobutadiene and nickel is in the plus 2 state. This is again a felly stale complex.

If you want to synthesize the iron complex that we just described, then you can start with this cyclobutenedichlorate that we pictured here. So, this is a very good starting material for making this cyclobutadiene complex. You treat it with F e 2 CO9 in this example. You have an iron 0 complex of the cyclobutadiene interacting with the pi system. So, in this example, it is a plus 2 system either way. You have a very stable complex. Instead of nickel, we can also make the corresponding palladium analogue. These compounds have been characterized fully.

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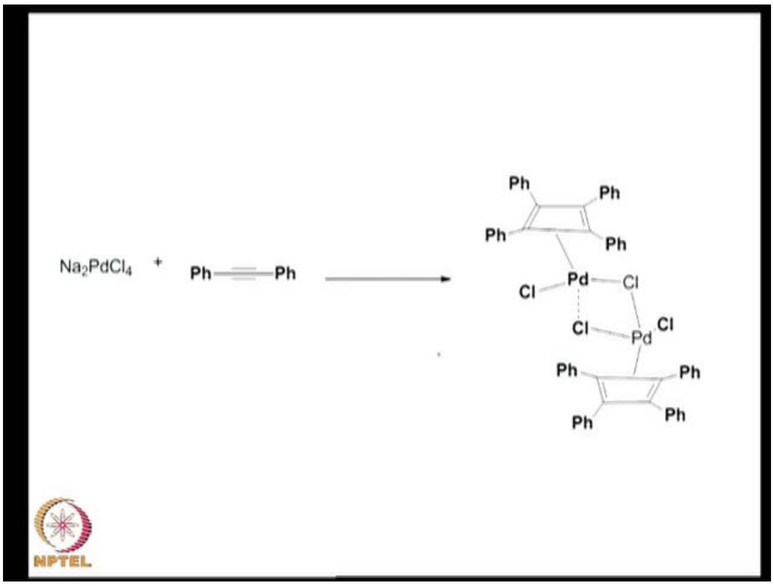

So, here is an example where you can make the palladium complex. If you treat diphenylacetylene with the palladium 2 chloride salts, then you form this very nice palladium complex, which has got 2 cyclobutadiene units. They are coordinated to the palladium. The palladium chlorine palladium bridge connects 2 systems together.

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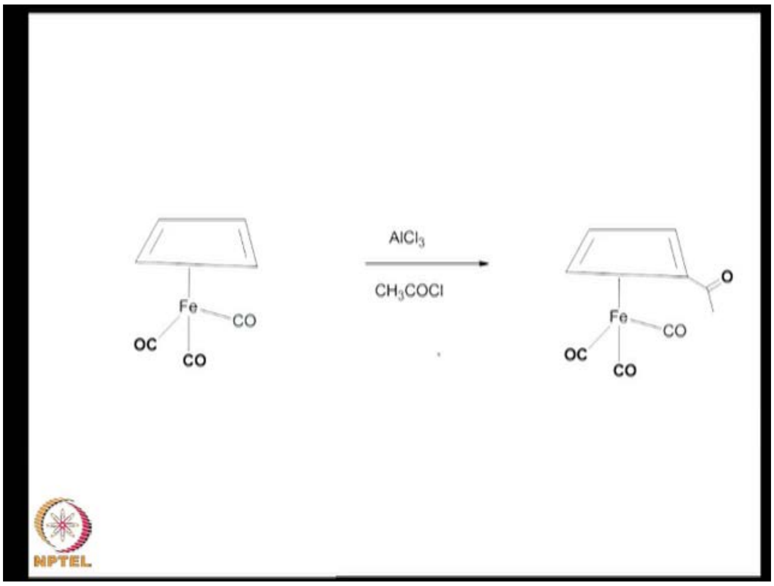

So, you will notice that one can in fact form a very nice cyclobutadiene complex. These cyclobutadiene complexes appear to be pseudo aromatic. So, if you treat them with acetyl chloride that is typical friedal crafts acylation conditions, you end up with acetated product of cyclobutadiene.

So, this would be interesting. This is interesting because cyclobutadiene is supposed to be anti-aromatic or non-aromatic depending on which geometry you choose. If you treat that with acetyl chloride, you have a typical aromatic reaction. What we have done is we have taken an anti-aromatic molecule and converted it into a pseudo parametric molecule by interacting with a metal system. So, this is typical of several cyclobutadiene complexes. One can see some aromatic type reactions for the compounds.

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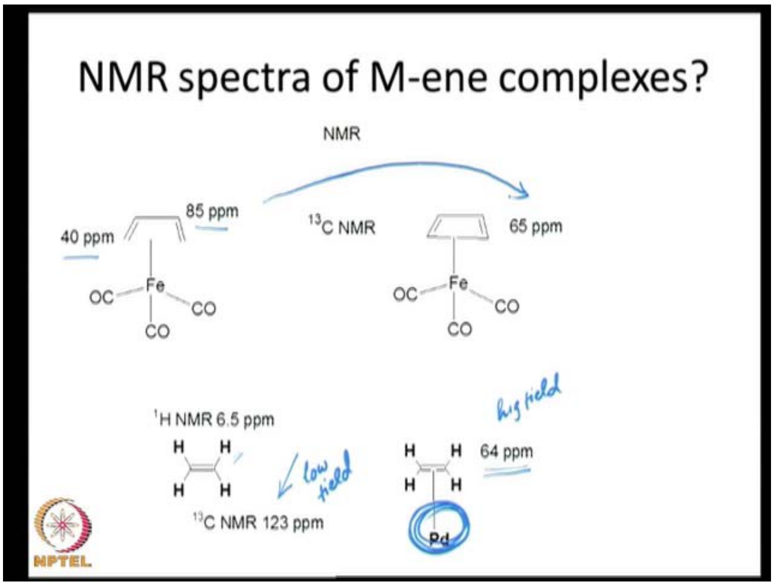

NMR spectra of M-ene complexes?

Let us take a look at the NMR spectra because NMR spectra, especially the carbon 13 NMR spectrum is very characteristic of the electron density on the carbon atom. So, in the case of ethylene, the carbon 13 resonance occurs at 123 p p m. The proton NMR of the ethylene hydrogen is at 6.5 p p m. Now, when you form a butadiene compound or when you form an ethylene compound, what happens?

What happens is that the carbon 13 resonance shifts down to 64 p p m. It is reduced to 64 p p m, which is clearly indicating that you have a low field resonance for the free ethylene and a high field resonance for the complexes form. What you have in ethylene is a pi system that results in carbon 13 NMR peak position at a very low field. This is a low field.

It is a high chemical shift p p m value. It is a low field. What happens is when you put a metal atom next to the ethylene, and then it goes to a high field. It is a high field. It is a low value of p p m. so, this is indicative of the fact that you have a large amount of electron density around the palladium. This electron density is helping the carbon atom from seeing the effective magnetic field. So, you need to apply the high field in order for the resonance to occur.

Now, a similar situation happens when you have a cyclobutadiene complex. It appears that you have in the case of irontricarbonyl complex, chemical shift of 40 p p m for the terminal carbon and 85 p p m for the internal carbons. What happens is when you form the cyclobutadiene complex, this chemical shift turns out to go further low field. It goes to a lower value of p p m and that is to higher field. That is indicative of the aromatic nature of the cyclobutadiene ring system.

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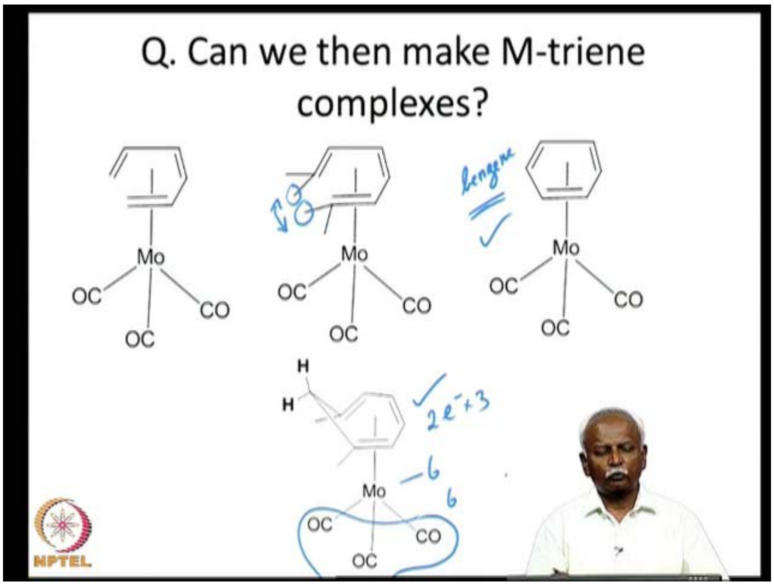

Q. Can we then make M-triene complexes?

Now, we can ask the question can we in fact make a diene complex. Now, there are 2 problems, which we have to encounter when we make a triene complex. First of all, there are 2hydrogens, which are at the terminal position. So, this causes a restitric interaction, which is unfavorable when you try to make a triene complex where the metal atom is interacting with 3 double bonds.

Now, one can circumvent this by forming a carbon-carbon bond. You remove hydrogens and form a carbon-carbon bond. That gives you a benzene complex; a benzene complex with a metal atom. This is in fact a known system. So, this is a known system. The other possibility is to introduce another carbon atom such that the repulsion is removed.

So, this is also in fact known. This is also possible. You can form a molecular tricarbonyl complex where the 3 double bonds are interacting with metal atom. So, each double bond will contribute 2 electrons. So, if you remember, electron counting has got 6 electrons. 6 electrons are given by the triene and 6 electrons are given by the 3 carbonyl atoms. So, you end up with an 18 electron system.

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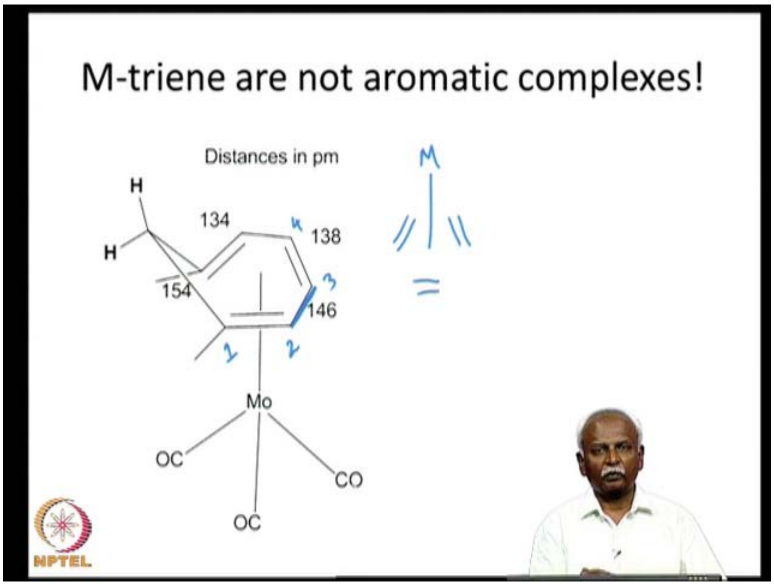

M-triene are not aromatic complexes!

So, we can make metal triene complexes. In these complexes, you find that the bond distances are very clearly indicative of isolated double bond. It is not like an aromatic system. You have removed the aromaticity in the ring by introducing the extra carbon. So, you do not have extra delocalization. You have these bond distances, which are indicative of long bonds between the third carbon and the second and the third carbon.

So, here you have the first carbon that we are talking about. This is the second, this is the third. The carbon atom 2, carbon atom 3 are specked by a long distance. The carbon atom 3 and 4 are having a short distance. So, it seems as if 3 isolated double bonds are interacting with the metal atom. So, 3 isolated double bonds are interacting with the metal atom. There is a long bond or only a single bond between the carbon atoms 2 and 3. So, these are not aromatic systems.

So, it is interesting to note that when you put 3 double bonds together, you can form a complex. That is not like an aromatic system, whereas in the case of cyclobutadiene, you move towards the aromatic system. Although you had an anti-aromatic complex or anti-aromatic compound organic compound, you made it aromatic.

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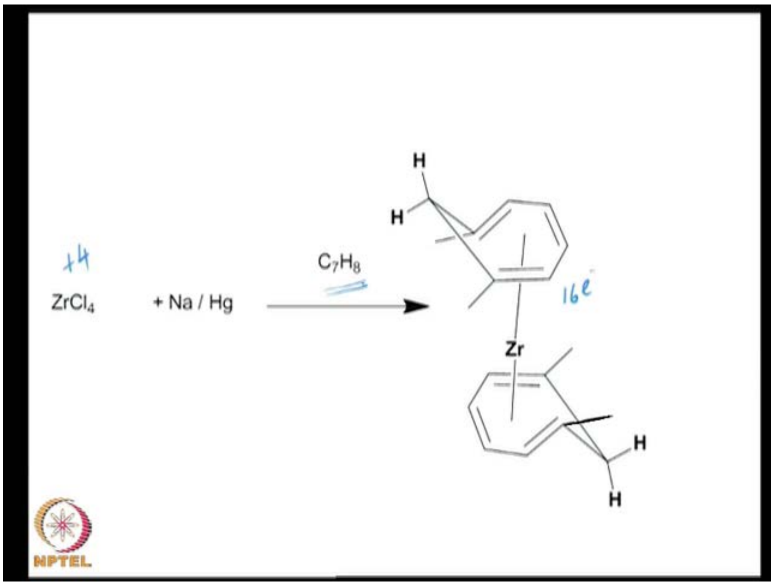

So, here is a way by which you can make another zirconium compound. In this particular example, I have taken 2 cycloheptatrienes and interacted with zirconium. This is because zirconium has got only 4 electrons. This will be a 16 electron complex. This will be 16 electron complex. What you have done is reduce the zirconium from the plus 4 oxidation state in the presence of a neutral ligand C7H8. You end up generating what you have here is a metaltriene complex.

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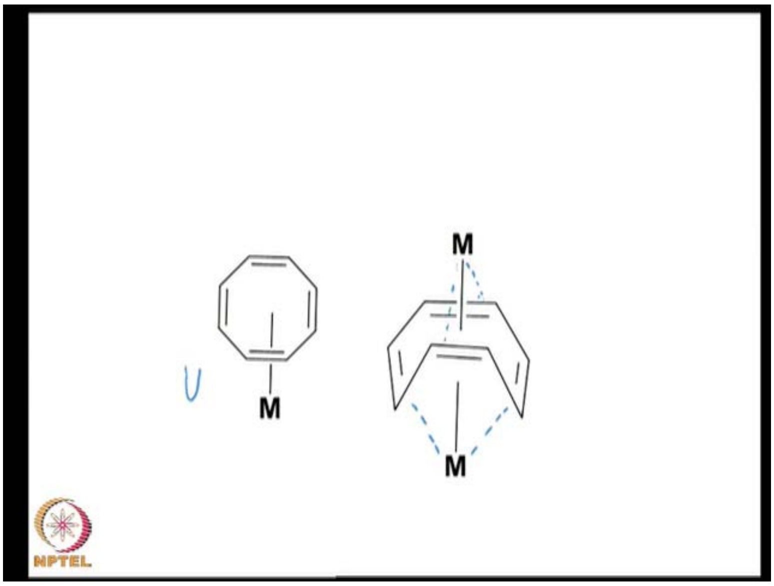

Now, let us proceed further. Since, aromatic benzene ring metal complexes have to be discussed in great detail in the remaining time, let us take a look at what happens when you have a cyclooctetraene. It is a system in which I will have 4 double bonds. Can they interact with metal atom? The answer to the question is yes, but the type of complex that you formed can vary a lot.

This is because you have a large ring system. The distance between the metal and the carbon turns out to be very large. Unless you have a metal atom like uranium or a very 5 d transitional element or a 4 d transitional element, you cannot form a bond which looks like cyclobutadiene metal complex, where the carbon atoms are on a single plane. Invariably, the carbon atom should be in 2 different planes.

Here is an example where the metal atom is interacting as if it is interacting with top and bottom of cyclobutadiene. The cyclobuta cyclooctatetraene, if this is a cyclooctatetraene where the metal is interacting with the top and bottom, it looks as if it is sitting on the same position. In fact, 1metal is interacting with the carbon atoms, which are pointed downward and metal at the top is interacting with the carbon atoms which are present on the top.

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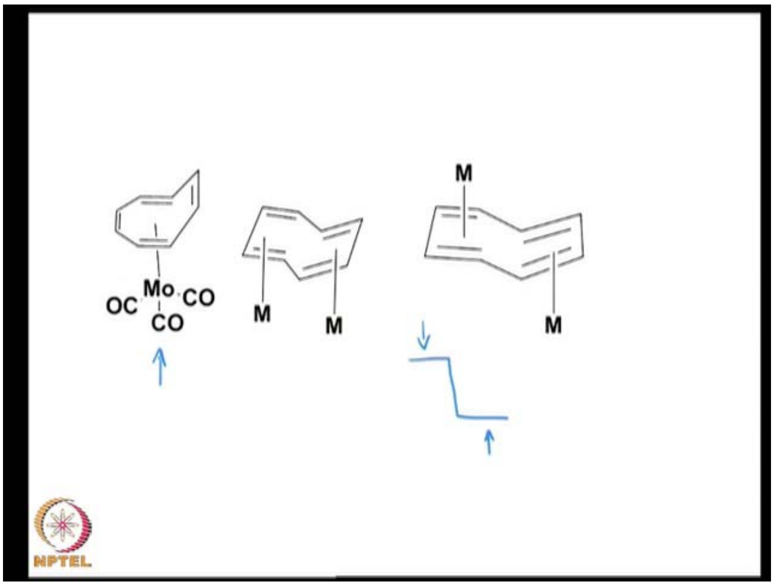

So, this is an example that is been isolated and characterized. Another example is one where cyclooctatetraene is like a step and the metal can interact from the top phase and at the bottom phase. That example is also known. It is also possible to interact with only 3 of the double bonds. So you can form a step structure.

Now, the step is only half step and one double bond is kept non interacting with the metal atom. So, examples of all these types of interactions are known. They are cryptographically characterized. Let us take a look at some of the structures because it will be difficult to explain the nature of these structures otherwise.

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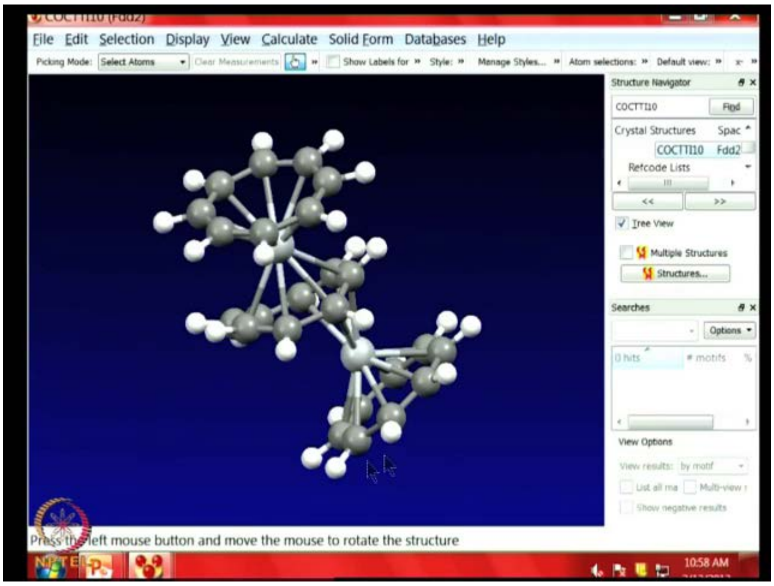

Press the left mouse button and move the mouse to rotate the structure

So, what I have here is an example where you have 8 carbons. Let us take a close look at this central ring. The central ring has got 8 carbons. 4 of the carbons are interacting with this metal atom right here. So, I will label the metal atom. So, that is titanium that is interacting with 4 carbon atoms here. The other 4 carbon atoms of the cyclooctatetraene are interacting with another metal atom, which is one low half.

So, here is 1titanium, which is interacting with 4 carbons. Here is other titanium, which is interacting with another set of 4 carbons. So, cyclooctatetraene has been divided by the titanium equally. One of them is having 4 carbon atoms and 2 double bonds. The other titanium is having the other 4 carbon atoms and 2 double bonds.

So, in this example, you also have a interaction of the second cyclooctatetraene in such a fashion that it is almost looking like a flat ring and oriented such that the left side ring is plain. In similar fashion, you can also orient the right side ring in the plain. You can see that all 8 carbon atoms are interacting with the titanium metal; here in the center.

So, this is one example. Let us take a look at some of the other examples, where it functions like a tub. So, here is an example where you have platinum. The platinum has got 2 metal groups. Here is one metal group with the carbon atom. Here is a second metal group. These 2 metal groups are in a transposition with respect to the double bond, which is present. This double bond is like a hat structure that I described to you.

So, tub geometry is formed by the cyclooctatetraene. The bottom part of the tub is interacting with 1 platinum atom, which I am showing here. The top part is interacting with another platinum atom. So, you have a very interesting tub structure for the cyclooctatetraene.

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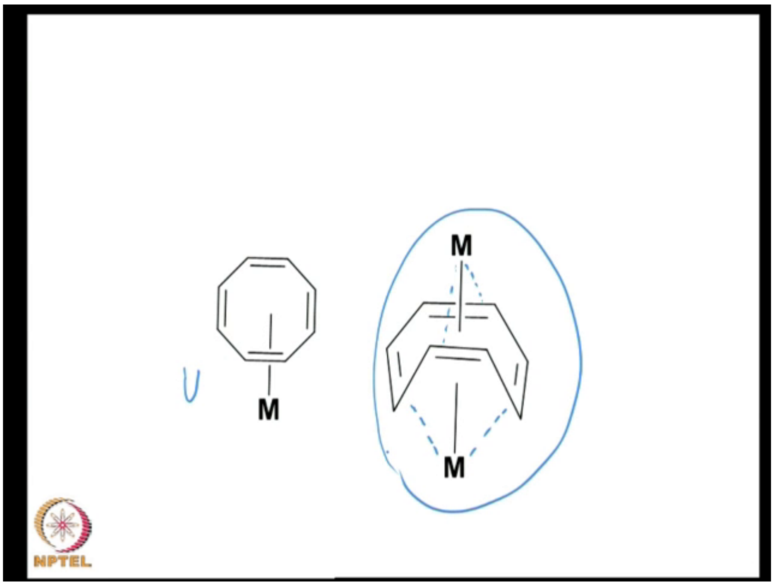

That is what we showed here that you can have a tub structure. This is a tub structure that we are talking about. So, the tub structure is the example that we see here. This is the tub structure where you have 2 platinum atoms interacting with carbon atoms, which are on one side of cyclooctatetraene. So, let us go back now with the cyclooctatetraene structures.

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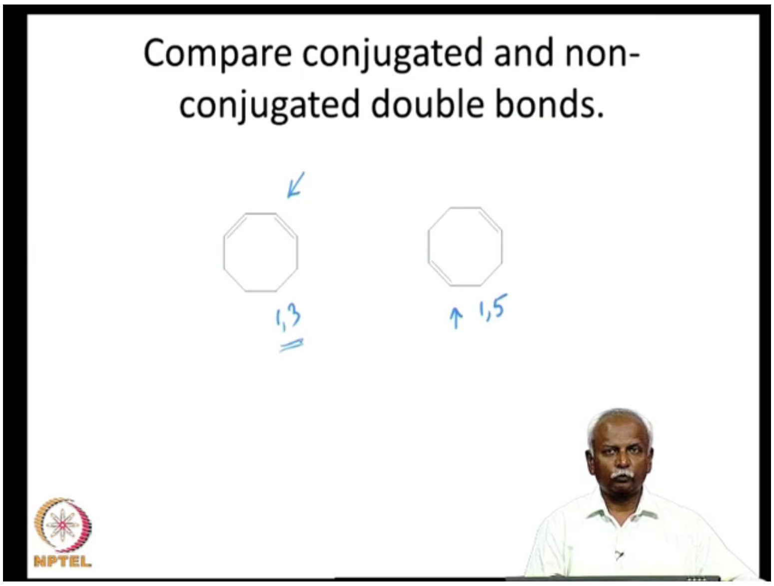

Compare conjugated and non-conjugated double bonds.

So, it is possible to form cyclooctatetraene complexes, but these complexes tend to be varied. You have either a planar structure or you can have a complex in which the double bonds are divided between 2 metal atoms in such a way that whatever forms a bond is with either isolated double bonds or with conjugated double bonds. So, at one instance, the titanium is interacting with 2 double bonds that were conjugated and at other instance the platinum was interacting with 2 isolated double bonds.

This is in fact common in organometallic chemistry. You can either take. Here, I have shown you cyclooctadiene. You can take cyclooctadiene. In 1, 3 cyclooctadiene form that is indicated here, this is 1, 3 structure. You can also have 1, 5 structure. Both of them can interact with metal atoms. Depending on the metal, you will either form a 1, 3 diene metal complex or a 1, 5 diene metal complex. As I told you earlier, this is a better donor.

So, depending on the electron density requirements of the metal atom, you can either have the 1, 3 structure or the 1, 5 structure. It is also dependent on the size of the metal atom. A large metal atom would like to interact with the cyclooctene in a 1, 5 fashion, whereas the smaller metal atom would like to interact with the metal whether 1, 3 cyclooctadiene system. So, it is possible to make these complexes. I will now show you some of the key features of what we discussed.

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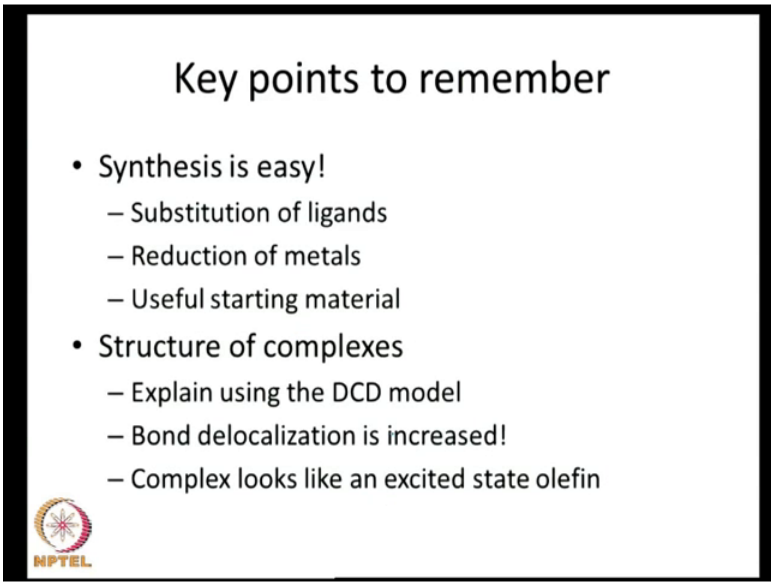

Key points to remember

- Synthesis is easy!
  - – Substitution of ligands
  - – Reduction of metals
  - – Useful starting material
- Structure of complexes
  - – Explain using the DCD model
  - – Bond delocalization is increased!
  - – Complex looks like an excited state olefin

So, let us take a look at the key features that we have discussed today. The synthesis of metal diene complexes or metal polyene complexes is fairly easy and follows the same route that one has to use while making olefin complexes. Usually one takes substitution of ligands, especially carbon monoxide can be substituted. A metal diene complex can be generated because the diene can be conjugated and it can be like a keylate. You can form these compounds fairly reduced. You can also have reduction of the metals.

It is convenient to have a reduction of the metals from higher oxidation state in such a fashion that you can have back bonding between the metal and the ligand very often. The dienes are useful as starting materials. The structure of the complex can often be explained using the DCD model or the bond doer Duckenson chat model. So, the complex often looks like an excited state olefin. That is what we have shown in the bond distances. So, this concludes the talk on the diene metal complexes.