Introduction to Organic Chemistry
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Lecture - 12
Metal alkene complexes

So, today we will discuss, metal olefin complexes. For the first time in this series, we are going to look at compounds where the metal is bonded to two carbon atoms simultaneously.

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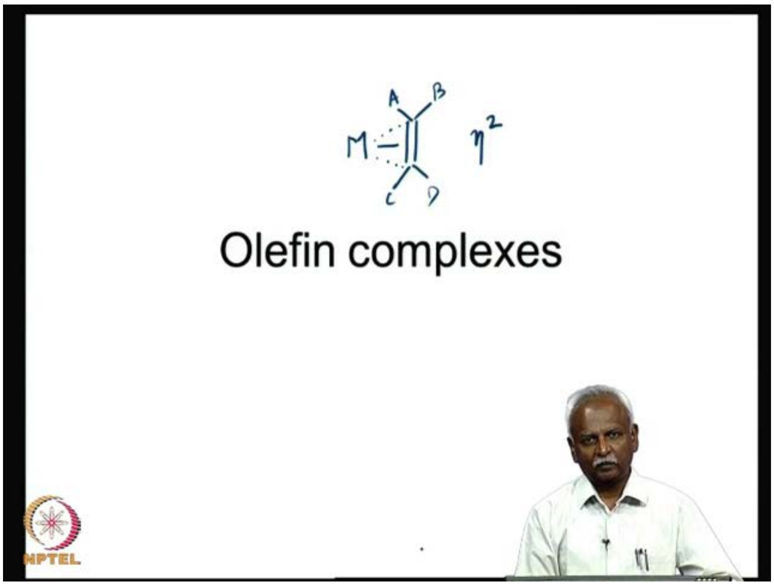
Olefin complexes

In organometallic terms, on often indicates the formation of an olefin complex by writing them as M coordinated to two carbons, by drawing a line in between the two carbons. And in the nomenclature one indicates this as an eta two complex, we need both carbon atoms are bonded at, not necessarily equidistant, but almost in a similar fashion. So that, both carbons are interacting with a metal simultaneously.

So, in these systems the olefin which is usually, if we consider the four atoms, which are bonded to the olefin, and will label them as A, B, C, and D; if A B F and D and the two carbons are in a plane then the metal is in a position below that plane. So, the metal itself is in a plane below the plane which is containing the four, which is containing the four atoms A B C D and the two carbons which are interacting with the metal.

So, let us take a look at some of these complexes, it is interesting that there is a very similar bonding pattern between olefins and metals and carbon monoxide and metals. The give and take of electrons that we discussed with metal carbonyl complexes, exists with metal olefin complexes also. So, the type of synthesis that we encounter in metal olefin complexes are very similar, to what we encounter in metal carbonyls. So, let us take a look at a few of the synthetic methods then, we will examine a few structures and the bonding pattern in these molecules today.

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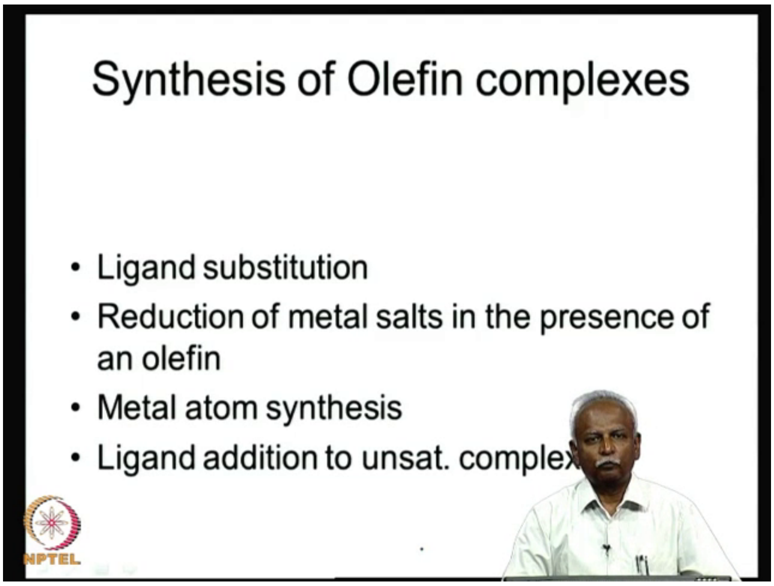

Synthesis of Olefin complexes

- Ligand substitution
- Reduction of metal salts in the presence of an olefin
- Metal atom synthesis
- Ligand addition to unsat. complex

So, synthesis of olefin complexes in general involves, a simple ligand substitution. So, a carbon monoxide ligand can be substituted by an olefin, one can also reduce a metal salt in the presence of an olefin. And this is exactly what we did for carbon monoxide, we used to reduce the metal salt in the presence of carbon monoxide, sometimes at high pressure. And that led to the formation of a metal carbonyl complex.

If you want to make a metal olefin complex, we can do this same trick namely, take the metal in the higher oxidation state, reduce it with a suitable reducing agent, which will not reduce the olefin. And under those circumstances we can prepare a metal olefin complex. There is also a specialized method called the metal atom synthesis and in the metal atom synthesis, one generate a vapor of the metal which will condense with the olefin or any ligand of interest. If you can do that, then the metal olefin complex can generated without interference from any other ligand. Finally, one can in some instances take an unsaturated complex and add an olefin and that will lead to a metal olefin complex.

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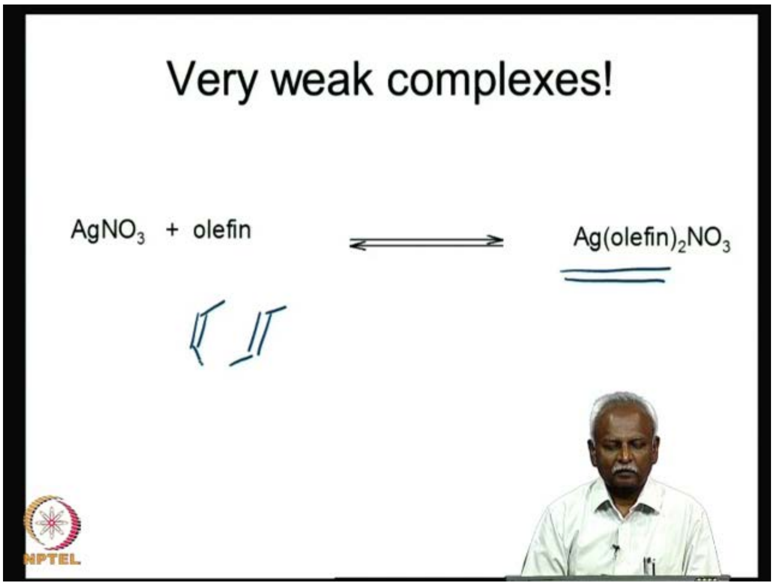

Very weak complexes!

$AgNO_3$ + olefin $\rightleftarrows$ $Ag(olefin)_2NO_3$

So, let us take a look at some very simple methods of generating metal olefin complex, complexes. So, the group 10 elements which are usually the ones having D10, it is actually group 11 which has a D10 complement of electrons. And so, they are oxidized to the plus one oxidation state. So silver1, gold 1 and copper 1 are suitable examples. So, you can very easily make these olefin complexes. Especially the copper and the silver metal complexes by simply taking the metal salt and reacting them with an olefin. All you have to do is to keep a non-coordinating anion and if you take a nitrate. For example, it is quite efficient as non-coordinating anion and you can treat it with an olefin, a suitable olefin a weak complex is formed.

Now, you might be wondering why is it weak complex, you remember that the type of interaction that is involve in this given take of electrons between the metal. The olefin, you need the metal to be present in a state, which is ready to give electrons to the anti-bonding orbitals of the olefin, in this instance. The carbon monoxide case was also similar, to form a carbon monoxide silver plus complex or a copper one complex. It was quite difficult, because the back bonding is poor. So, necessarily you form weak complexes, but never the less these complexes are extremely useful because the weak interaction convenient, for establishing an equilibrium. And any application that requires only a weak interaction, will benefit from such a situation.

So the very, the common application of silver complexes is that one can court chromatographic columns with silver ions and then, this weak interaction is sufficient to distinguish between various olefin complexes. So in other words, the stability constant of two different olefins, if they are different, if you can have the Cis and trans isomers of two butene, they can be very easily separated utilizing this trick.

Because the stability of the trans butene is less than the Cis butene complex and this is some this which we will consider later, but sufficient to say that this stability difference is able to differentiate between these two olefin complexes, in terms of the stability constant. And hence the rate at which the silver coated column, will discriminate between the trans and the Cis butene.

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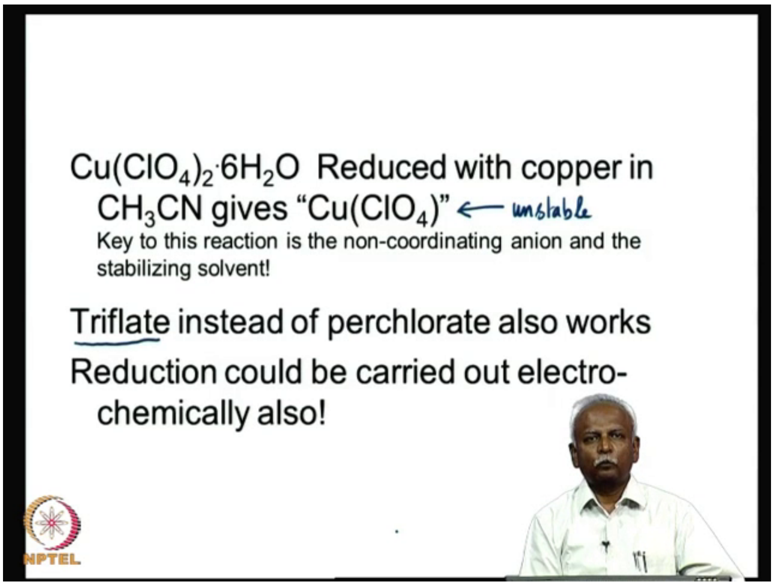

$Cu(ClO_4)_2{\cdot}6H_2O$ Reduced with copper in CH_3CN gives "$Cu(ClO_4)$" ← unstable

Key to this reaction is the non-coordinating anion and the stabilizing solvent!

Triflate instead of perchlorate also works

Reduction could be carried out electrochemically also!

So, a similar situation occurs with the copper complex, if you take a copper two plus ion, you can reduce it with copper metal, in the presence of a solvent like acetonitrile CH3CN. The key to this reaction is a fact that, you have a non-coordinating anion or a weakly coordinate anion, the per chlorate anion. And also the fact that, you have a stabilizing solvent, copper one is stabilized in the presence of acetonitrile, because acetonitrile is a pie accepting ligand. And so, it stabilizes the lower oxidation state of copper, in this case it is copper one. So, it is possible to make copper per chlorate which is in the plus one oxidation, which I have put within quotes, because this itself is an unstable system. This is unstable and it is only stable, if it is present in the, if acetonitrile is also present in the medium.

One can use other non-coordinating anions very conveniently, the other ligand which is very commonly used is a triflate counter ion. So, copper two triflate is taken, the reduction is carried out with copper metal, which is a most convenient because no other interfering metal is present in the medium. So you take, copper two plus reduce it with copper metal and in the presence of the Triflate or the perchlorate or nitrate then, you can reduce it the copper one state. And if an olefin is present, you can form the metal olefin complex Fairley readily. But as I mentioned, the copper and the silver salts are reasonably stable, but they cannot be used extensively because it tend to decompose.

The reduction can be carried electro chemically, this is sometimes convenient, if you use two copper electrodes and to, and try to pass current in the presence of acetonitrile and an olefin. The olefin complex will be formed, when the copper two plus in solution, a copper sulphate solution can be taken and the reduction can be electrolysis can be carried out with copper electrodes. It is convenient to do so, when the anode and the cathode get coated with the copper one compound. Especially, the solvent is sufficiently stabilizing, one can get very good yields of the copper one complex.

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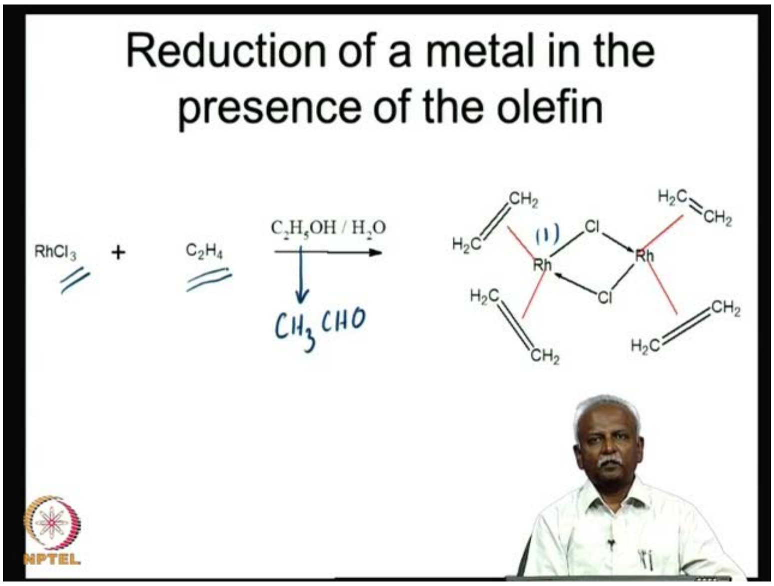

Reduction of a metal in the presence of the olefin

Now, it is not always necessary to reduce the metal from the higher oxidation state to the lower oxidation state, using a metal. Here is an example, where ethanol functions as a reducing agent, ethanol gets oxidized to acetaldehyde. So, ethanol gets oxidized to CH3CHO. In other words, two hydrogens have been removed from ethanol and those are the reducing elements, they reduced the rhodium chloride to rhodium one. Rhodium three chloride, here it is present in rhodium three and here it is present in the rhodium one, oxidation state. And you can see that, because you have two rhodiums with two chlorines.

Now, in the presence of acetylene, if acetylene, in the presence of ethylene, in the presence of ethylene you will form a rhodium one complex and in this case, it is two rhodium atoms coordinating to four ethylene moieties. And this complex is quite stable and because ethylene is quite volatile, this can also be used as a precaution for making other olefin complexes. So, this is yet another way, of reducing the metal salt and generating the metal olefin complex.

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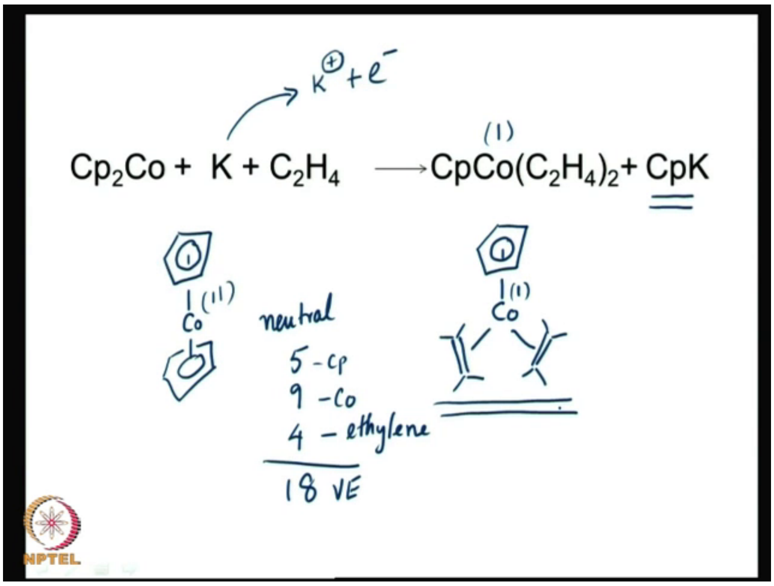

$$Cp_2Co + K + C_2H_4 \longrightarrow CpCo(C_2H_4)_2 + CpK$$

So, let us take a look now at, some other, few more complicated methods. In this instance you have bis cyclopentadienyl cobalt complex. And as you know ferrocene is, the only bis cyclopentadienyl complex that has got an 18 electrons structure, in the plus 2 oxidation state. So cobalt obviously, has got more number of electrons than necessary to form an 18 electron system. Since, cobalt has got 9 electrons, it has one electron more and if you pump in one more electron, using say, potassium. Potassium is a reducing agent, which will become K plus and it will add one electron to the medium and this one electron will add on to the cobalt. And so, cobalt if it becomes cobalt minus 1 this turns out to be a 20 electron complex and it is quite unstable.

What it does is that, it liberates cyclopentadienylanion with potassium as the counter ion and during this process, cobalt from the plus 2 oxidation state, it is present in the plus 2 oxidation state, it has got reduced to cobalt 1. And the cobalt 1 is now coordinated to, two ethylene molecules which are in the reaction medium. So, this complex can be drawn as follows, you can have two ethylene moieties, which are bonded in a symmetrical fashion to two ethylene, to the cobalt one species, which is present in the center. Although, we have not studied cyclopentadienyl complexes up to now, we can understand that because we have 5 carbons coordinated to the cobalt bond.

They will, in the neutral method give 5 electrons so, the neutral method will have 5 electrons from the cobalt and 9 electrons, 9 electrons from the cobalt, 5 electrons from the Cp and 2 electrons to each from these olefins. And so we have, 4 electrons from ethylene so, we have a total of 18 electrons. So, 18 valance electrons form very continently and this turns out to be a stable system. So, this moiety is in fact known for cobalt, rhodium and the rhodium complex is extremely interesting and if time commits we will look at, the structure of the structure of this complex and the type of interactions that can be there in this system.

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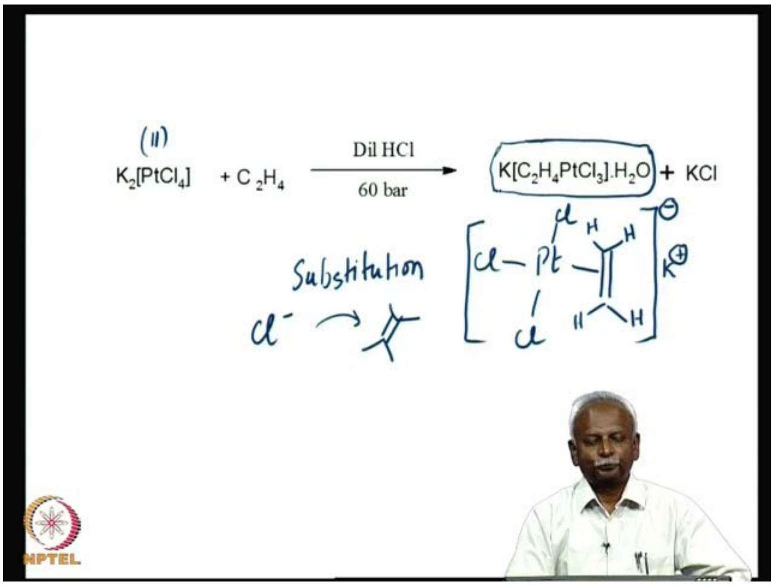

$$\overset{(II)}{K_2[PtCl_4]} + C_2H_4 \xrightarrow[60\ bar]{Dil\ HCl} \boxed{K[C_2H_4PtCl_3].H_2O} + KCl$$

Now, the most famous olefin complex that is present in the literature, that is available in the literature is what is called this Zeise complex. This Zeise complex has, in fact, a very strange complex that was formed. And it was accidentally discovered by Zeise, when he boiled potassium tetra chloroplatinate, with ethanol and finally, it was found out that it was, an ethylene complex that was present in the product. So, there was one ethylene moiety which is coordinated to the platinum and there are three chlorines. Because platinum is present, in the plus 2 oxidation state, it has got a negative charge and this negative charge is now balanced by a potassium ion.

So we started with, a platinum two complex, we have not carried out a reduction here, but what we have done is, we have generated ethylene and we have used ethylene in the reaction medium, and coordinated the ethylene to the platinum, which kicks out one chloride ion and forms an ethylene complex. So this is an example of, a simple substitution there is no reduction involved.

So, this is an example, of a simple substitution reaction, a chloride ion is replaced by an olefin and because the olefin is reasonably, strongly bond to the platinum two. In spite of the fact that, the oxidation state is plus 2 platinum, because it is a lower group element and it has got sufficiently large orbitals. It interacts very continently or very readily with ethylene and it forms a nice olefin complex.

Now, the few words about, now a few words about this complex is pertinent here one of them is the fact that, the complex is found in the presence of water. This whole reaction was done with, dilute hydrochloric acid and notice that the structure of the molecule is also containing the lattice, the crystal structure of the molecule is also containing a molecule of water. So, this is very strange because one often thinks that organometallic compounds cannot be synthesized in the presence of water. And the very first olefin complex that, was synthesized and that was way before the discovery of Ferrocene it had a molecule of water, in the, in the lattice to begin with. And it also was made by boiling it in dilute hydrochloric acid with ethylene.

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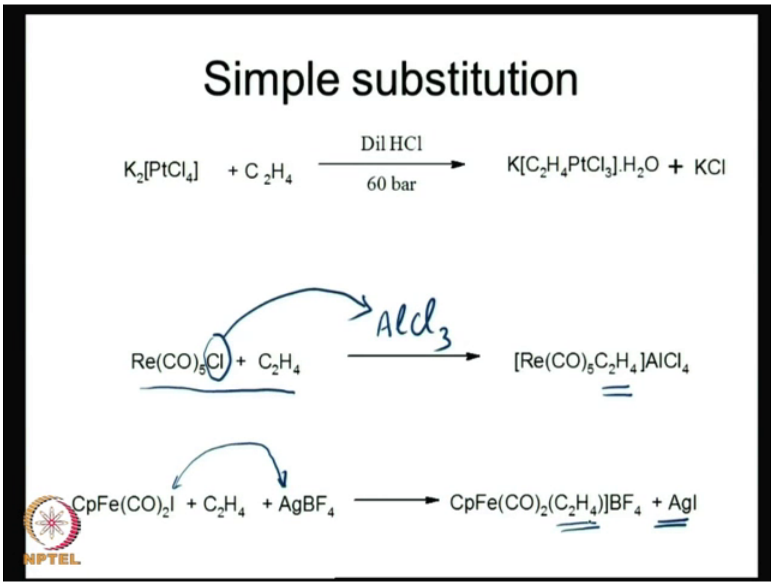

Simple substitution

$K_2[PtCl_4] + C_2H_4 \xrightarrow[60\ bar]{Dil\ HCl} K[C_2H_4PtCl_3].H_2O + KCl$

$Re(CO)_5Cl + C_2H_4 \xrightarrow{Alcl_3} [Re(CO)_5C_2H_4]AlCl_4$

$CpFe(CO)_2I + C_2H_4 + AgBF_4 \longrightarrow CpFe(CO)_2(C_2H_4)]BF_4 + AgI$

So, simple substitution reactions are possible with several elements especially with elements, which have either a D 8 configuration and they have only 4 ligands around the coordination sphere. It is very easy, to add a ligand or to substitute a ligand. So here is an example, here is an example with rhenium we notice that, rhenium is again interacting with ethylene molecule and in this instance what has happened is Alcl3 in the reaction medium, Alcl3 has grabbed this chloride ion.

So, this chloride ion has been grabbed by aluminum in the process an ReCO5 plus moiety has been formed, an ReCO5 moiety will be coordinatively unsaturated. And it grabs the ethylene and forms an ethylene complex and the counter ion is now Alcl4 minus. Another example is, the generation of a vacant coordination site in the complex by using a silver slat, by using the principle that silver 1 ion is halophilic.

It will tend to react very readily, with any halide ion in the coordination sphere of the metal. Here we have taken ion complex, which has got an iodide and the iodide is removed by the silver. So, the iodide and silver react together and form silver iodide and this silver iodide is now removed. And that leaves a vacant coordination sphere on ion, which leads to the formation of an olefin complex, which we have pictured here.

So, in all these examples either there is an assisted of a ligand from the coordination sphere, of a metal complex, and that vacant coordination sphere is occupied by an olefin. Notice, in all these examples we have used simple ethylene, in fact ethylene forms a very strong complex with metals and substitution in fact destabilizes the system, except under some special circumstance which we will look at in a few minutes.

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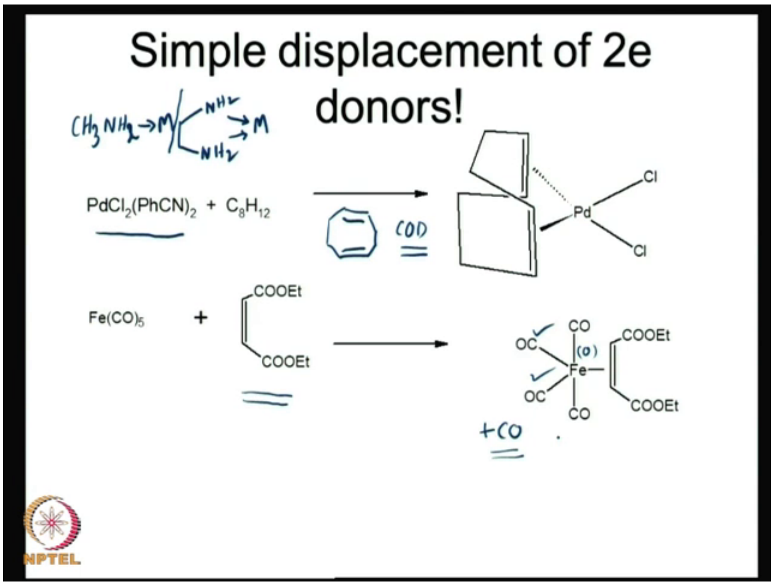

Simple displacement of 2e donors!

$PdCl_2(PhCN)_2 + C_8H_{12}$

$Fe(CO)_5$ +

In coordination chemistry, it is possible to have more stable complexes formed, when you have two places of attachment for the ligand, so in other words, if I have a metal complex where two NH2 groups are present on the ligand. Then, the coordination of both, both NH2 groups to the metal, turns out to be a most stable situation then, when you have a single point of attachment. So, CH3NH2 coordinated to a metal verses, CH2 verses ethylenediamene coordinating to a metal. These two systems are differentiated by, the so called entropic effect, the chelate effect which leads to more stable complexes.

A similar situation can happen, in the case of olefins and here we have pictured cyclooctadiene, which is written in a convoluted form purely because it has to bend in that fashion, in order to bind to the metal. So that, both olefin phases can be facing the palladium atom. So here you have, a weakly coordinating benzonitrile PhCN that leaves the coordination sphere palladium and cyclooctadiene is a chelating ligand. It is a olefin complex, but it is a chelating ligand and it can now continently form a metal olefin complex. Now, it is also possible for us to replace a carbon monoxide as we have mentioned, when we discussed substitution reactions.

Carbon monoxide in metal complexes can readily displaced, especially in the trans position, if one can use a ligand, which will not compete with carbon monoxide for pi accepting property. Although, I mentioned in the beginning of the lecture that ethylene can have pi accepting property. It is not as god a pi acceptor, as carbon monoxide. Carbon monoxide as I mentioned to you earlier, is a ligand par excellence. It is a only ligand, which has got extremely good pi accepting property and it is very convenient to use it in a variety of situations. But when you want to do a substitution reaction with an olefin the trans carbon monoxide gives way.

So that, one carbon monoxide will have better pi accepting property from the metal and a weakly coordinating ligand can be present in the coordination sphere. And here we have, ion in the 0 oxidation state, it is 18 electron complex, where carbon monoxide has been displaced. So that, the other two carbon monoxides, which are present in the same plane will have better pi bonding characteristics from the ion. So, you are replacing one pi accepting ligand by a weaker pi accepting ligand. This again is a general principle and we have managed to do this, in this instance with this diethyl maleate, which is a good ligand for replacing the carbon monoxide.

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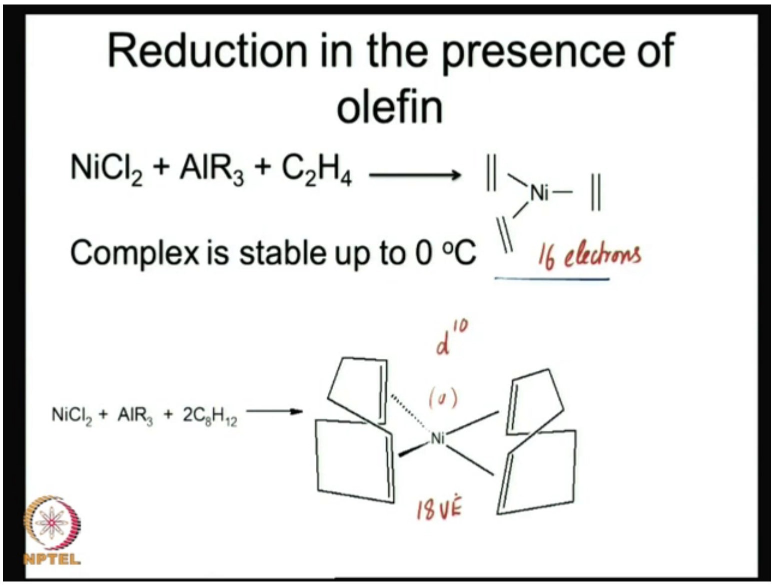

Reduction in the presence of olefin

$NiCl_2 + AlR_3 + C_2H_4 \longrightarrow$

Complex is stable up to 0 °C

16 electrons

$NiCl_2 + AlR_3 + 2C_8H_{12} \longrightarrow$

Now, I have mentioned that ethylene is a good ligand for metal in 0 oxidation state, but very often it is not possible to prepare homoleptic complexes. Where homoleptic complexes I mean, only those complexes, only those ligands which are present around the metal are a same type, where in this case olefin. So, it is possible in a few instances to prepare homoleptic complexes of with olefins.

And one example is, when you can reduce nickel dichloride with tri alkyl aluminum and when you do that, in the presence of ethylene you can prepare a Tris ethylene complex of nickel. Unfortunately, this complex is not very stable, this complex is not extremely stable and is stable only up to a temperature of 0 degree centigrade. So this is useful, but nevertheless it is not in stable system. A slightly more stable system, is bis cyclopentadienyl complex of nickel. Here, because of the chelate effect the stability is increased, nickel is again in oxidation state of a 0. And so, you have a D10 system so, you have a D10 system.

And this D10 system now has got 4 olefins coordinated to it in such a fashion that, it is almost like a tetrahedral complex of ethylene, here you have 2 cyclooctadienes and it is quite, much more stable than the ethylene complex, which is a 16 electron complex. So, the nickel complex with three ethylenes is a 16 electron system, with 2 cyclooctadiene, it is a 18 electron system. And this is 18 electron system is much more stable and this can be isolated and characterized very easily.

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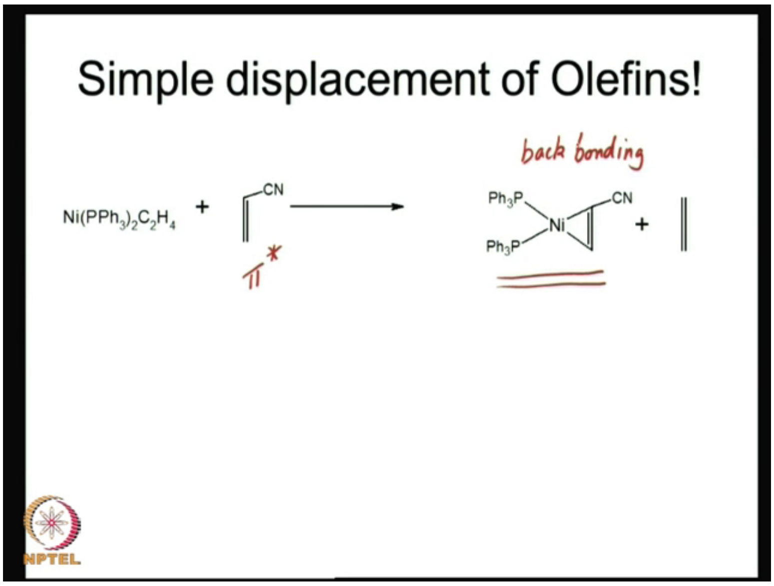

Simple displacement of Olefins!

Now, I want to talk about displacement of one olefin by another olefin, now this is not the method of choice for making olefin complexes. But in a few instances, ethylenes can be replaced by another ethylene or an olefin. Now this has to, if it has to thermodynamically viable, the complex that is formed must be much more stable. The complex that is formed, must be much more stable than the complex that was present initially, and when you replace ethylene, with a cyano ethylene or acrylonitrile then, the stability increases. This must be an electronic effect, because any time you have a substitution on ethylene, the stability usually goes down, but in this instance it has increased.

And it can be seen immediately that, if you put an electron withdrawing substituent on the ethylene, this leads to greatest stabilization. Because, the pi star orbital on acrylonitrile, the pi star orbital is at a lower energy level and from the nickel the electron density can flow into the pi star orbital more readily. And so, the back bonding is greater in this instance. So, the greater degree of back bonding, greater degree of back bonding in these complexes leads to greatest stability.

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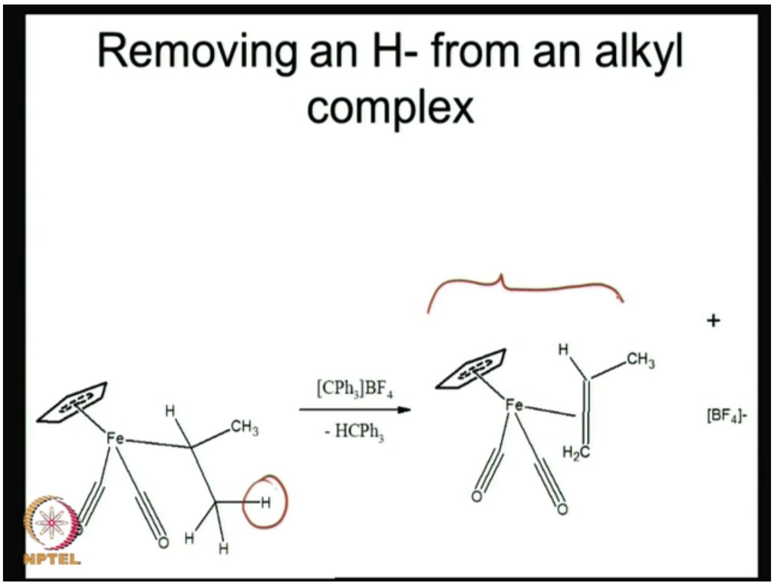

Removing an H- from an alkyl complex

Now, let us move on there is one unusual method of synthesizing metal olefin complex and this is by removing a hydride ion. If you take, the trityl cation, the trityl cation is the one which is, the cation stabilized by the presence of three phenyl groups and this can abstract the hydrogen atom. And if it abstracts the hydrogen atom from an alkyl complex, which you have already learned about.

If this hydride is abstracted with a trityl cation then, one ends up with ethylene complex. In this particular case, it is a propane complex which is formed and this propane complex is quite easy to, or conveniently isolate using this method. So, alkyl complexes can be converted to olefin complexes in a few instances, by the use of this trityl cation.

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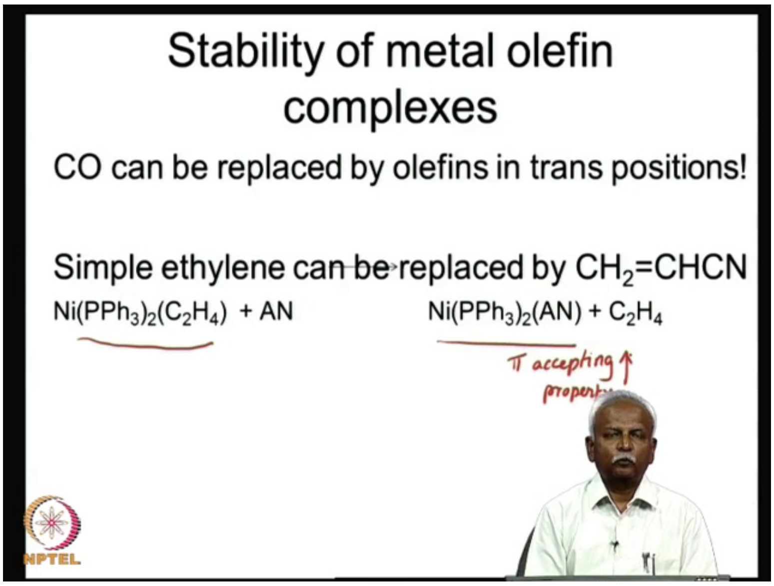

Stability of metal olefin complexes

CO can be replaced by olefins in trans positions!

Simple ethylene can be replaced by $CH_2=CHCN$

$Ni(PPh_3)_2(C_2H_4)$ + AN $Ni(PPh_3)_2(AN) + C_2H_4$

π accepting ↑ property

Now, we have discussed a few methods of making metal olefin complexes and we have discussed in the, during this process the reasons for their stability, but let us just systematize them and collect our thoughts together. First of all we said that, carbon monoxide can be replaced by olefins in the trans position. And this is possible because, carbon monoxide is a stronger pi accepting ligand.

And it will displace or it will displace carbon monoxide in the trans position and replace it with an olefin. And this will lead to greater stability because, the olefin itself is a poorer pi acceptor. So, the metal is, able to donate more electron density to the carbon monoxide. And the end CO bond becomes stronger and this leads to greater stability.

So a second, a second example that I told you about is the replacement of an ethylene, with acetonitrile, acrylonitrile and acrylonitrile because of its greater pi accepting property. It also can replace a simple ethylene, here again we are talking about better pi accepting character of the olefin, but in this instance the pi accepting property of the olefin, that is coming in is much better.

And so, the nickel 0 complex that we had in the, in the, on the reactions side, on the reactants side this complex turns out to be less stable than the acrylonitrile complex. Purely, because on the right side we have better pi accepting property, so the pi accepting property goes up in this instance and so you have greatest stability.

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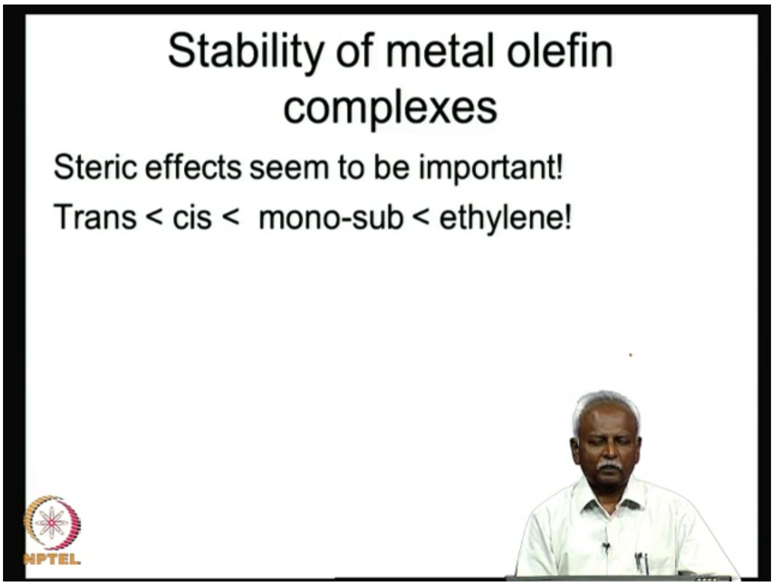

Stability of metal olefin complexes

Steric effects seem to be important!

Trans < cis < mono-sub < ethylene!

So, apart from this electronic effect we also have very significant stereo effects in case of metal olefin complexes and usually it is seen that the trans complex is less stable than the Cis complex, if there are two substituents. And the mono substituted complex, is always more stable than the di substituted complex. And of course, the ethylene was the best ligand when you have no electronic effects to talk about. Then, the ethylene complex is in fact the best system to study. So, this steric effects play an important role and we will see in a few minutes, why this is the case.

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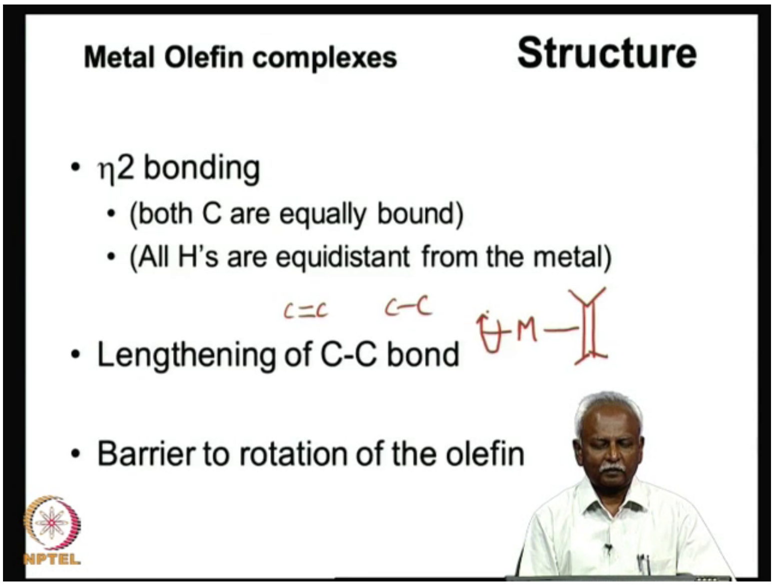

Metal Olefin complexes **Structure**

- η2 bonding
  - (both C are equally bound)
  - (All H's are equidistant from the metal)
- Lengthening of C-C bond
- Barrier to rotation of the olefin

Let us take a look at the complexes, in greater detail the structural aspects. You have eta two bonding, which means both carbons are equally bound and all the hydrogens, if there, ethylene, if it is an ethylene there are four hydrogens. All four hydrogens are equidistant from the metal, the back bonding that we have referred to, which means the metal gives electrons density in to the pi star orbitals, lengthens carbon carbon bond. So, you have a carbon carbon bond which can lie anywhere between a C C double bond, to a C single bond C.

And if there is such a back bonding interaction, we will see in a minute that there is a barrier to rotation of the olefin, with respect to the metal carbon, metal olefin access. So, if this is the olefin that we are talking about then, in this access you can rotate olefin, the, or the metal complex with respect to the olefin. But this rotation as a barrier and this is because of pi interactions between the metal and the olefin. All these factors have to be explained.

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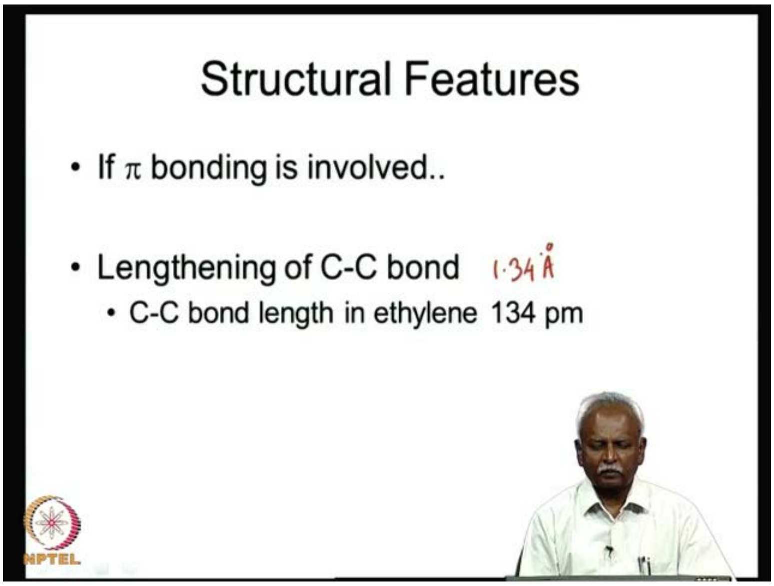

Structural Features

- If π bonding is involved..
- Lengthening of C-C bond 1.34 Å
  - C-C bond length in ethylene 134 pm

And we will be able to explain each one of these factors, each one of these factors using some of our structural features. Here I have indicated, the carbon-carbon bond length in ethylene is 134 picometers or if you prefer the angstrom unit, it is 1.34 Angstroms.

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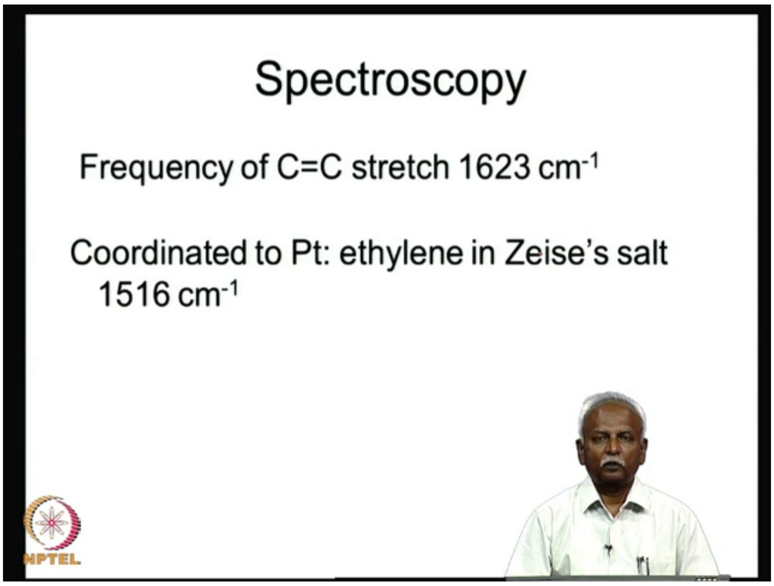

Spectroscopy

Frequency of C=C stretch 1623 cm^{-1}

Coordinated to Pt: ethylene in Zeise's salt 1516 cm^{-1}

And if one forms the complex, when the carbon carbon bond length increases. Similarly, the frequency of the carbon carbon double bond stretch, the stretching frequency in ethylene itself is 1623 centimeter minus 1. And when it is coordinated to platinum, as in Zeise's salt it is reduced remarkably. It goes down by about 100 centimeter minus 1 and this is exactly the ((Refer time: 33:27)) figure, we obtained for carbon monoxide complexes also. When you interact a carbon monoxide with a metal, then if the metal is in 0 oxidation state, the metal is capable putting electron density in to the pi star orbital. And similarly, here in this instance it is putting electron density in to the pi star orbital of the olefin and we will picture that in a few minutes.

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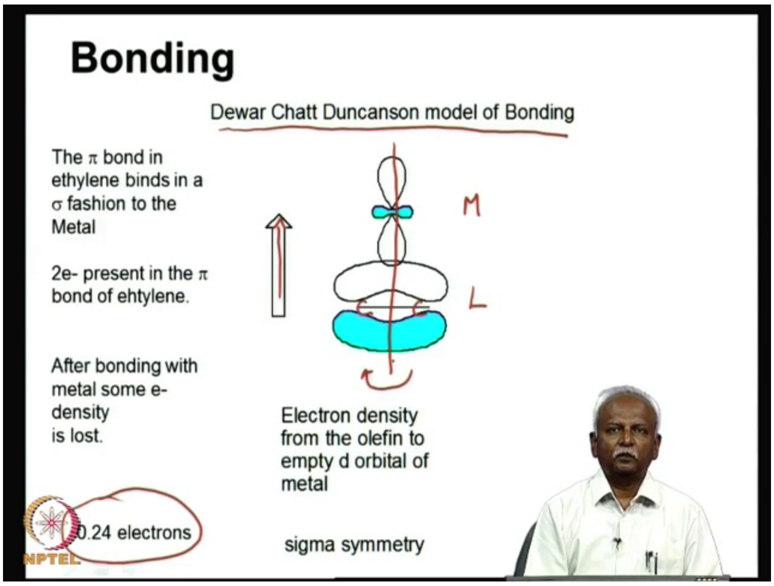

Bonding

Dewar Chatt Duncanson model of Bonding

The π bond in ethylene binds in a σ fashion to the Metal

2e- present in the π bond of ehtylene.

After bonding with metal some e- density is lost.

0.24 electrons

Electron density from the olefin to empty d orbital of metal

sigma symmetry

So, here is an initial interaction and we have already discussed the, people who have discovered this type of bonding Dewar Chatt and Duncanson. Dewar Chatt and Duncanson are the three people, who developed this mode of bonding. So, the primary interaction in this mode of bonding is the donation of electron density from the ligand. So, this is the ligand we are talking about and here is the metal and usually, the ligand donates electron density to the metal. And we have pictured that here, it is giving electron density to the metal, from the filled pi orbitals of the olefin. So, the filled pi orbitals are present and they do not have a note between the two carbons and here are the two carbons.

And the two carbons have a pi cloud, on the either side of the carbon and one side is capable of donating electron density very significantly, in to an empty orbital on a metal. So, this is the sigma bond, people have estimated that this sigma interaction transfer of both 0.24 electrons, 0.24 electrons from the ligand to the metal. So, although we call it two electron donation, the two electrons are present in the olefin.

But approximately 0.24 electrons are transferred or at least 24 percent of the electrons, or about 12 percent of the pi electron density is transferred completely to the metal. So, this is the sigma interaction we call it sigma interaction. Because one can rotate the, one can rotate the olefin about this axis and you will not lose any overlap as you rotate the olefin.

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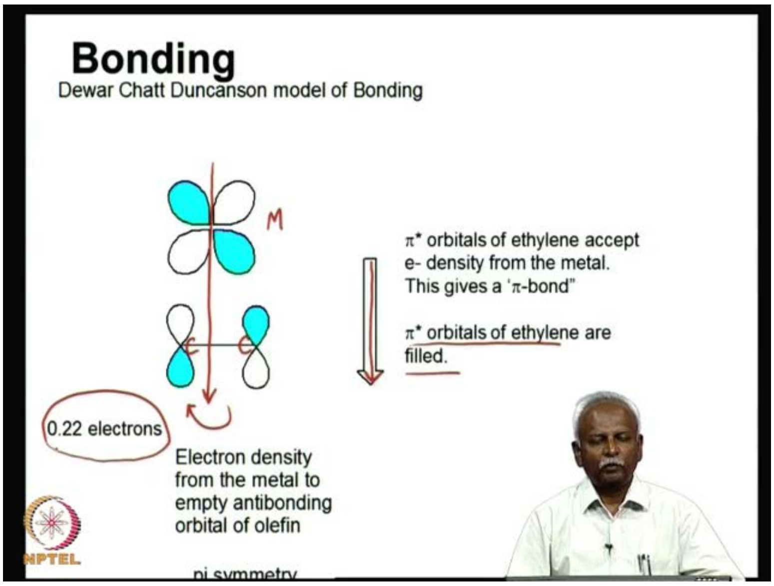

Bonding

Dewar Chatt Duncanson model of Bonding

π* orbitals of ethylene accept e- density from the metal. This gives a 'π-bond"

π* orbitals of ethylene are filled.

0.22 electrons

Electron density from the metal to empty antibonding orbital of olefin

pi symmetry

So, let us take a look now at the pi electron, pi attraction again this is part of the Dewar Chatt Duncanson model of bonding. And what we have is, a pi star orbital of the ethylene now, interacting with a filled orbital on the metal. So, here is the metal and here is the olefin, the two carbons are present here and a pi star interaction involves an anti-phase overlap of the two p orbitals, on the carbon. The ones that are not hybridized to interact with hydrogens and so, this pi star orbital now accepts electron density, accepts electron density from the metal into the empty orbitals in the olefin.

So, the situation is very similar to what we encountered in carbon monoxide, electron density from the metal is going into an anti-bonding orbital. And the symmetry of this interaction is pi interaction, because you will notice that if I rotate the metal or the olefin with respect to one another, around this axis of interaction then the bonding is immediately disrupted and there is a breakage of this bond. So, this must involve pi symmetry, so these are pi interactions and people have estimated that, in this pie interaction about 0.22 electrons are transferred, from the metal to the olefin.

So, almost equal amounts of electron density are transferred from the ligand to the metal and from the metal to the ligand. Now, if one can believe these calculations, then one can say that there is a slight excess of electron density transferred from the ligand to the metal. And so, the sigma bonding is little bit more important, than the pi interaction, but you can see that it has to be a synergistic interaction. If you donate more electron density to the metal then, the metal in turn can donate more electron density to the pi star orbital. So, this Dewar Chatt Duncanson model promotes or suggest that, there is a synergistic interaction between the metal and the olefin.

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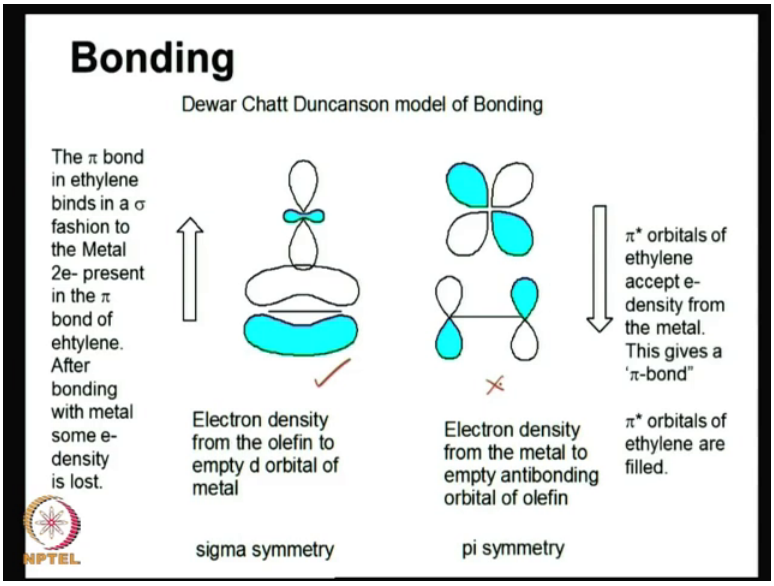

Bonding

Dewar Chatt Duncanson model of Bonding

The π bond in ethylene binds in a σ fashion to the Metal 2e- present in the π bond of ehtylene. After bonding with metal some e- density is lost.

Electron density from the olefin to empty d orbital of metal

Electron density from the metal to empty antibonding orbital of olefin

π^* orbitals of ethylene accept e-density from the metal. This gives a 'π-bond"

π^* orbitals of ethylene are filled.

sigma symmetry

pi symmetry

So, here I have summarized both, pictured both in the same slide. And you can see how the two interactions complement one another and it is a completely synergetic interaction one of course, has sigma symmetry and the other has got pi symmetry. So, rotation does not break this bond, whereas this bond is completely broken, the pi bond is broken when you rotate it. So, that is why you have a small barrier for the rotation of an olefin.

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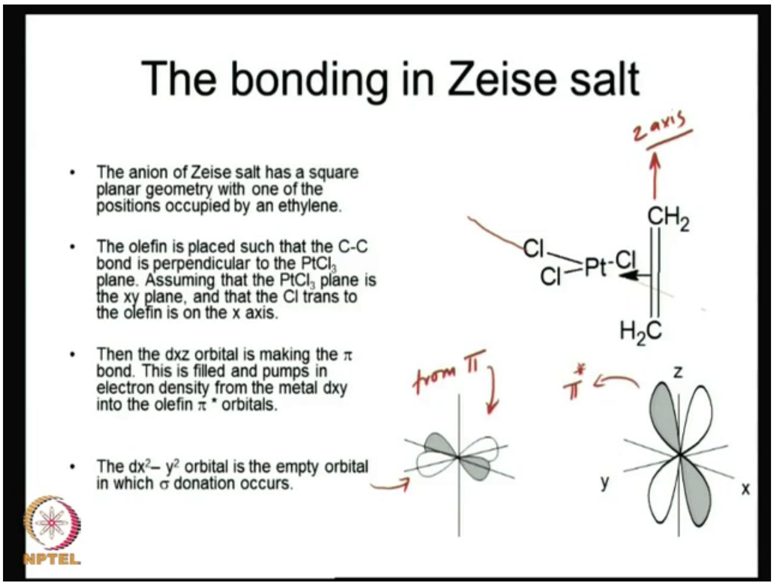

The bonding in Zeise salt

- The anion of Zeise salt has a square planar geometry with one of the positions occupied by an ethylene.
- The olefin is placed such that the C-C bond is perpendicular to the $PtCl_3$ plane. Assuming that the $PtCl_3$ plane is the xy plane, and that the Cl trans to the olefin is on the x axis.
- Then the dxz orbital is making the π bond. This is filled and pumps in electron density from the metal dxy into the olefin π^* orbitals.
- The $dx^2 - y^2$ orbital is the empty orbital in which σ donation occurs.

This barrier can be pictured here, in the Zeise complex, I have illustrated it for you saying that, if the three chlorines around the platinum are in the x y plane. If you think that, this is x y plane then the ethylene is parallel to the z axis. The ethylene carbon carbon axis is parallel to the z axis so, that is how we want to talk about this interaction then, the dxz orbital. If this is the x axis then, the dxz orbital is the one which would be suitable for interacting with a pi star orbital on the olefin.

So, the dxz orbital is pictured here and the d X square minus, Y square orbital will be the orbital which primarily accepts the electron density from the pi, from pi of the olefin electron density flows into this. And from the dxz it flows in to the pi star orbital of the ethylene. So, I hope you will be able to appreciate this Dewar interaction that stabilizes metal olefin complexes very significantly.

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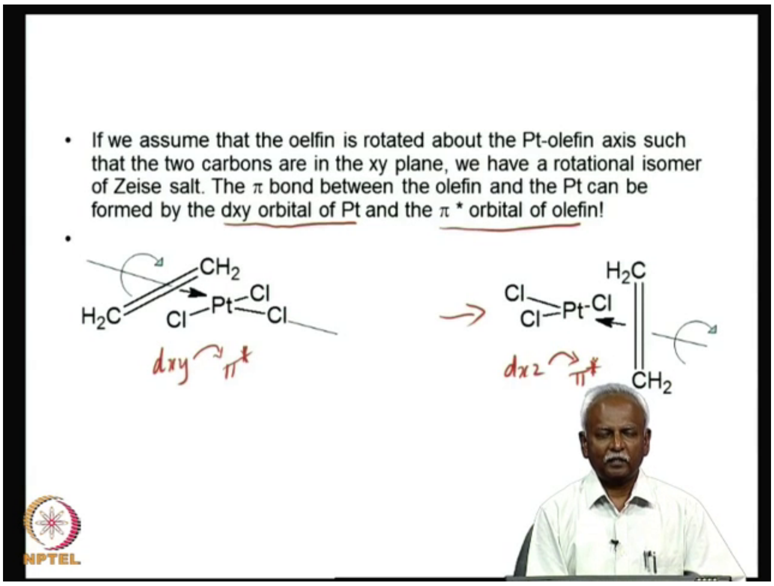

- If we assume that the oelfin is rotated about the Pt-olefin axis such that the two carbons are in the xy plane, we have a rotational isomer of Zeise salt. The π bond between the olefin and the Pt can be formed by the dxy orbital of Pt and the π * orbital of olefin!
-

And as I mentioned earlier, you do have a barrier to rotation this, the original geometry that we talked about. If you rotate it, you will end up with the four carbons, the four hydrogens on the carbon, in the same plane as the PtCl3 moiety. They will all be in this particular plane and when you do that then, you end up with some steric interactions which destabilize this situation.

But you will notice that the dxy orbital on the platinum and the pi star of the olefin, can interact just as much as the dxz was able to interact with the pi star. So, here the d x in this orientation, dxy can pump in electron density into the pi star of the olefin. So, both ways you can have pi interactions the sigma is not disrupted at all, but the pi star can also be there in this orientation, because of the steric influence you do not have a very stable situation.

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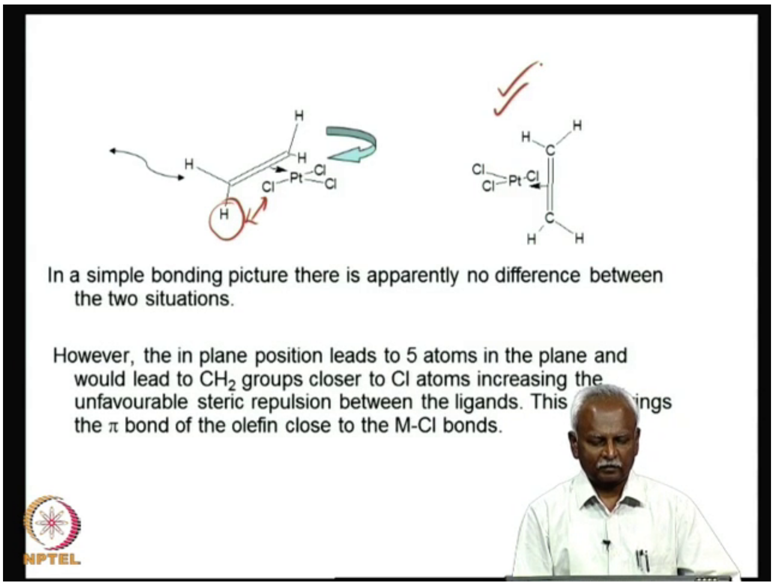

In a simple bonding picture there is apparently no difference between the two situations.

However, the in plane position leads to 5 atoms in the plane and would lead to CH$_2$ groups closer to Cl atoms increasing the unfavourable steric repulsion between the ligands. This ings the π bond of the olefin close to the M-Cl bonds.

So, the steric interaction is pictured here in general, it is more important when you have bulky group in this position. Then, it interacts with the chlorine significantly, but even with ethylene the molecule prefers this orientation much better. And so, that is the more stable crystallographically characterized system.

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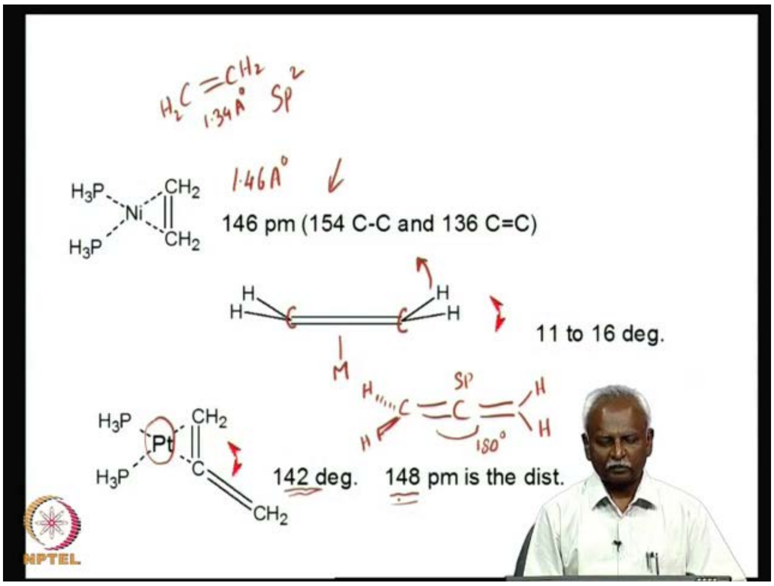

146 pm (154 C-C and 136 C=C)

11 to 16 deg.

142 deg.

148 pm is the dist.

So, let us move on, let us take a look at a few of the characteristics that are significant. One is the fact that, you have slight re hybridization of the carbon, the carbon in the ethylene, in simple ethylene it is hybridized in a SP2 fashion. So, the carbon has got a

SP2 hybridization now, when it is bonded it seems to have a slight re hybridization at the carbon center. And that leads to, a bending of the hydrogens away from the metal.

So, if the metal is boned in this position then, the hydrogens are moved away from the metal and this moving away leads to a slight re hybridization of the carbon. And various explanations have been given for this particular explanations, we just talked about the mild steric interaction. That can be present, is also an electronic effect that makes the carbons bend away, in such a fashion that there can be better overlap between the metal and the carbon orbitals.

So, initially carbon carbon bond distance is around 136 or 134 picometers. Here it is 1.34 angstroms. And it can in the complex, they go all the way from 146 picometers or 1.46 Angstroms, to even 1.54 Angstroms and this is the distance that you have for a carbon carbon single bond. And surprisingly, the back bonding can be more and more significant in some instances, especially if you have electron withdrawing groups and then, the bond distance can increase all the way to 1.54 angstroms. Now, if you have ((Refer time: 43:42)) where you have two double bonds consecutively, then the central carbon, we are talking about systems like this then, the central carbon is SP hybridized.

So, these are alynes and these alynes gets significantly bent when, you are binding them or interacting them with a metal atom. Here I have pictured, a platinum atom which is interacting with an alyne moiety. And the angle in the free alyne is 180 degrees and there is no, there is no difficulty in understanding that. Because, the central carbon is hybridized with SP hybridization, but the moment you have interacted with an olefin then, the strain of the central carbon is released. And it goes, moves towards the 120 degree angle that you would end up within SP2 hybridization. And it becomes close to 142 degrees here. The carbon carbon bond distance is around 148 picometers and it is close to the carbon carbon double bond distance.

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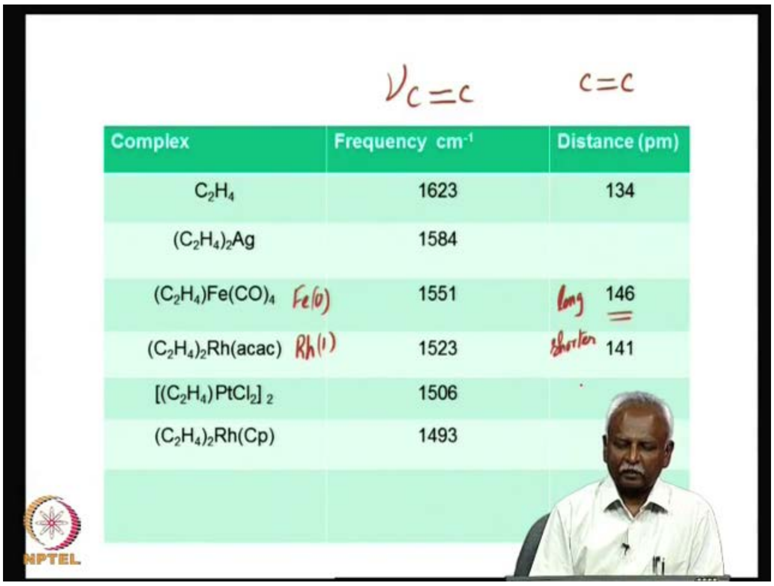

$\nu_{C=C}$ C=C

Complex	Frequency cm^{-1}	Distance (pm)
C_2H_4	1623	134
$(C_2H_4)_2Ag$	1584	
$(C_2H_4)Fe(CO)_4$ Fe(0)	1551	long 146 =
$(C_2H_4)_2Rh(acac)$ Rh(I)	1523	shorter 141
$[(C_2H_4)PtCl_2]_2$	1506	
$(C_2H_4)_2Rh(Cp)$	1493	

Now, let us take a look, at the frequencies of metal olefin complexes because this is also interesting. As I mentioned, the free olefin is 1.34 Angstroms or 134 picometers when it is bonded to a metal then, the bond distance increases and the frequency decreases. So, you can see about 100 or less than 100 centimeter minus 1 decrease, in the metal olefin you have a 100 centimeter minus 1 decrease in the carbon carbon stretching frequency. So, this frequency is stalking about the carbon carbon stretching frequency here, you see C and this, is the C double bond distance that we are talking about here. You will notice that, when you have a 4d or a 5d element then, the bond distance is different that be greater or more pi interaction between the metal and the olefin.

And if you have, a metal in the 0 oxidation state then, the pi interaction the bonding between the two carbons is decreased even further. So, if you have ion in 0 oxidation state, this is ion in 0 oxidation state, the bond distance is 1.46 Angstroms. It is long, where as in the case of rhodium one, this is a plus 1 oxidation state. And so, back bonding is less and so, the olefin has got shorter bond distance.

So, this is less pi interaction in this case. So, the discussions that we had with carbon monoxide, with respect to greater pi back bonding and greater pi binding resulting infrequencies that are smaller or greater reduction in stretching frequencies, whole good in this instance also. If there is less back bonding then, the bond is stronger and the frequencies are higher. So, there is inverse correlation between both of them.

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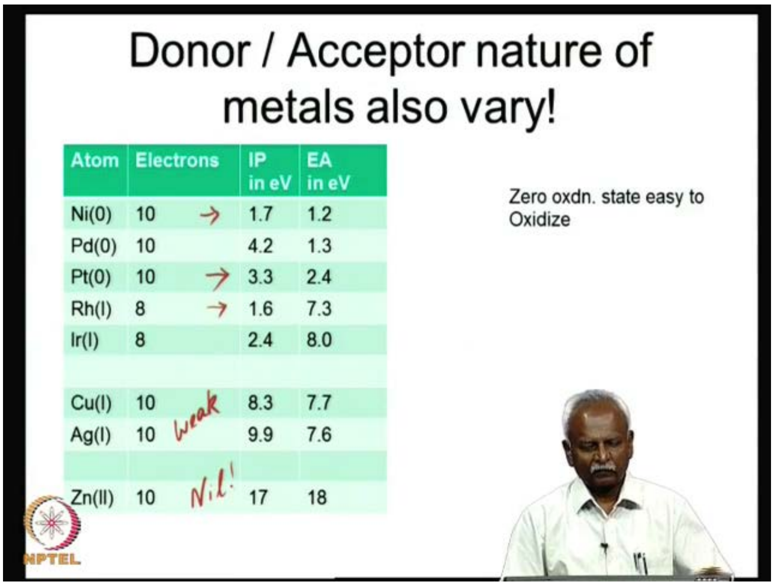

Donor / Acceptor nature of metals also vary!

Atom	Electrons	IP in eV	EA in eV
Ni(0)	10 →	1.7	1.2
Pd(0)	10	4.2	1.3
Pt(0)	10 →	3.3	2.4
Rh(I)	8 →	1.6	7.3
Ir(I)	8	2.4	8.0
Cu(I)	10 weak	8.3	7.7
Ag(I)	10	9.9	7.6
Zn(II)	10 Nil!	17	18

Zero oxdn. state easy to Oxidize

So, how do you know, how much the metal is interested in pumping electron density back into the olefin. One way to measure this is, to look at the ionization potential for the metals and here I have listed a few of the ionization potentials. And you will notice that, as you go down the group you tend to have a remarkable change in the ionization potentials.

Nickel is easiest to ionize, it is easy to remove the electrons from nickel 0, that is also a d10 system, platinum 0 is also a d10 system, but it requires almost the two times the amount of energy to remove electron density from platinum. But the platinum complex is with, olefins are extremely good purely because, in spite of this higher energy of ionization, higher energy required for ionization it is possible to have good overlap between the platinum and the olefins.

In the case of nickel, one realises that it is easy because of the fact that, you have 3d element and this also results in very good, in very good bonding between the two systems. Palladium 0 should not by, what we have seen here in terms of ionization potential, nickel and platinum should form better complexes than palladium. And that is in general true so, let us take a look at the rhodium and the iridium complexes once again, the rhodium complexes is easier to ionize and the iridium complex has got a higher ionization potential.

And so, rhodium forms very good complexes, very stable complexes we have seen a few of them in the last few transparencies. Similarly, copper and silver because they are positively charged, they are already oxidized, they are very high ionization potentials, they form weak complexes. So, these are system where they have weak complexes, and you have no complexes, no complexes with zinc 2 plus.

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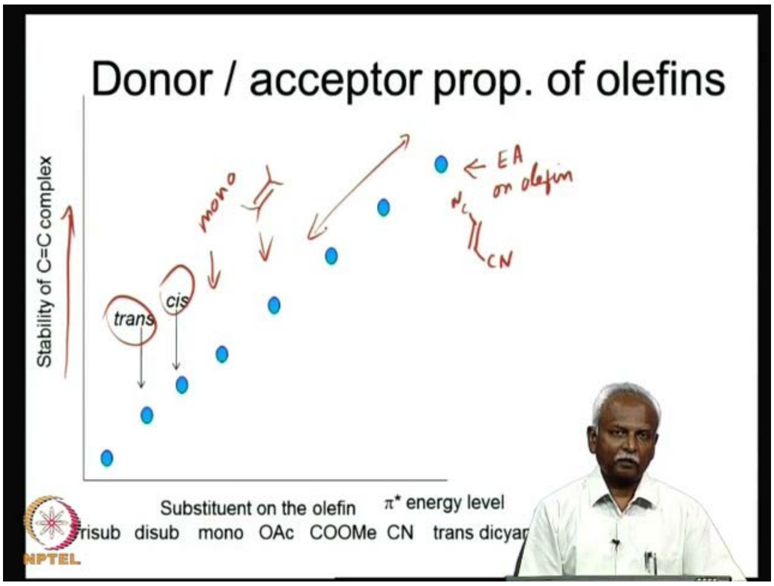

Donor / acceptor prop. of olefins

So, let us proceed further, the time that we have. Let us take a look at the donor acceptor properties, can we correlate the donor acceptor properties, with the pi accepting property under stability of the complex. In general the stability of the complex, if it is plotted on the y axis, if it keeps increasing, if you have very good, if you have very good electron accepting groups, electron accepting groups on the olefin. Then, they form stable complexes so, you have Trans di cyano compounds so, you have CN and CN. Then, it forms a much more stable complex with the metal, because you can have better pi accepting property.

Whereas, if you have a no substituent then, you have a poorer pi accepting property and that is pictured around here. And then you have system, which have got substituents which prevent the close approach of the olefin to the metal. So, if you have Cis it is more stable than Trans, we have already explained this because Trans cannot twist in such a way that, it can approach the metal in a closer fashion.

Whereas, Cis by bending the substituents on the carbon carbon double bond in such a way, it can move it away from the metal and so it can have better interactions. And so, this is the mono substituted systems and then, this is your ethylene itself, simple ethylene and these are both weaker electron accepting groups. The systems which are pictured here, are weaker electron accepting group. So, this is a general tendency will have very poor or unstable complexes, when you have tetra substituted systems and they are not pictured here in this graph at all.

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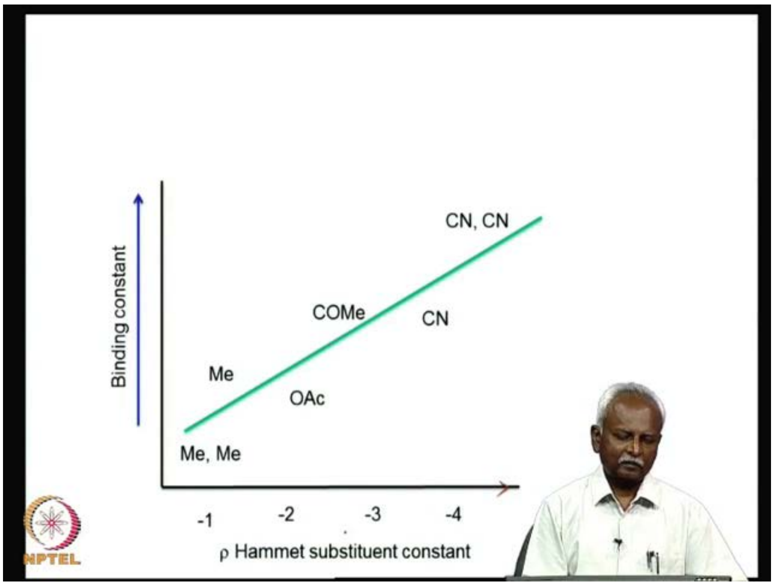

So, here again if you have this electron accepting property is quantified using the Hammet parameter, which you encounter in organ organic chemistry. The Hammet parameter is plotted on the x axis then, we will notice that as, the Hammet constant becomes larger and larger electron accepting property increases and then the binding constant is increasing. So, there is a positive correlation between the two of them.

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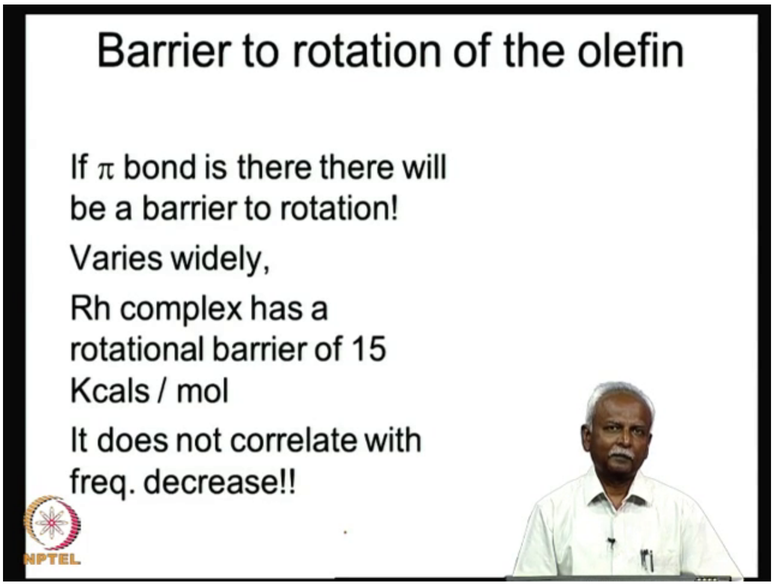

Barrier to rotation of the olefin

If π bond is there there will be a barrier to rotation!

Varies widely,

Rh complex has a rotational barrier of 15 Kcals / mol

It does not correlate with freq. decrease!!

So, the barrier to the rotation is proportional to the accent of pi interaction. In general you have, better barriers to rotation when you have 0 oxidation state metal complexes, the rhodium complex that we are going to talk about, has got a barrier of 15 kilo calories per mole. But this barrier to rotation, need not correlate with the frequency decrease, frequency decrease independently correlates with the back bonding, but because there is a combination of steric effect and pi effect, these two need not correlate one with the other.

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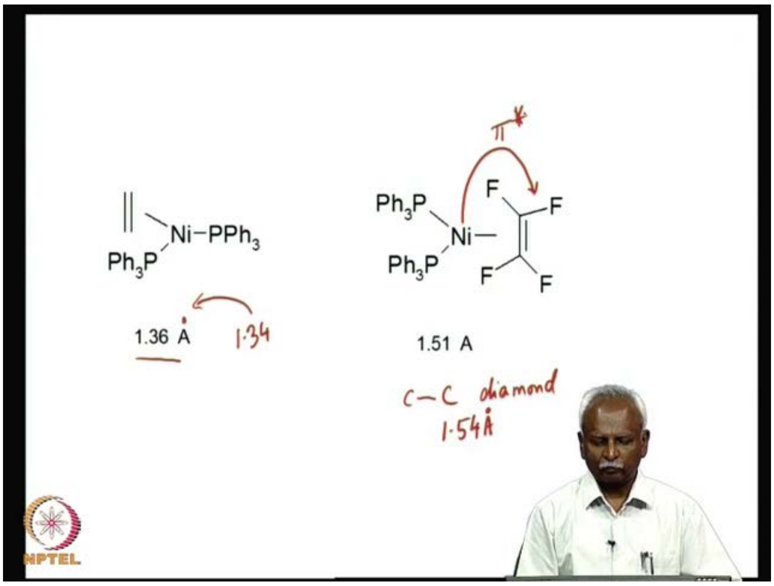

So, here I have pictured for you what happens to the carbon carbon bond distance when you have electron withdrawing substituent. Here I have tetra, 4 fluorines attached to the carbon, the olefins and here I have simple ethylene. This distance is hardly increased from, 1.34 Angstroms, it is gone only to 1.36 Angstroms. So, there is hardly 0.02 angstroms increase, in the case of the ethylene complex.

Whereas, the carbon carbon bond distance in the case of tetra fluro ethylene, is almost similar to what you have for a carbon carbon bond distance, in diamond. So, carbon carbon distance in diamond would be close to 1.54 Angstroms and that is pretty much, what you have in the case of the tetra fluro. So, there is a lot of electron density going in from the nickel to the pi star orbital and this result in a very strong weakening population of the pi star weakening of the carbon carbon bond.

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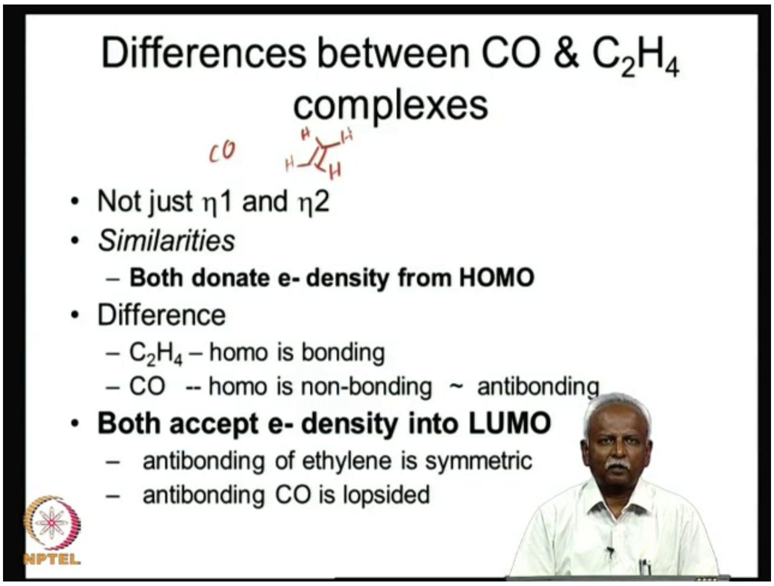

Differences between CO & C_2H_4 complexes

CO

- Not just η1 and η2
- *Similarities*
  - **Both donate e- density from HOMO**
- Difference
  - C_2H_4 – homo is bonding
  - CO -- homo is non-bonding ~ antibonding
- **Both accept e- density into LUMO**
  - antibonding of ethylene is symmetric
  - antibonding CO is lopsided

So, there are some similarities between carbon monoxide and ethylene complexes. It is not just a case where, you have eta 1 and eta 2 coordination modes between the ligand and the metal. Eta 1 in the case of carbon monoxide and eta 2 in the case of ethylene, that is not the only difference or that is not the only similarity in terms of electron density, donation from the homo probably ethylene, is little better than carbon monoxide, homo in ethylene is bonding. And so, when you remove electron density from homo, it weakens the carbon-carbon bond.

So, both carbon monoxide and ethylene accept electron density into the pi star orbital so, this weakens the ethylene carbon carbon double bond. And so, the CO on the other it has got a slight difference because the homo is non-bonding, if not slightly anti-bonding. And as I explained when we are discussing the carbon monoxide complexes, this is a controversial discussion that is been there in the literature. But it is understood that, the carbon monoxide is not a bonding orbital, the highest occupied molecular orbital is not a bonding orbital. And so, removal of electron density does not affect carbon monoxide significantly in terms of the CO stretch.

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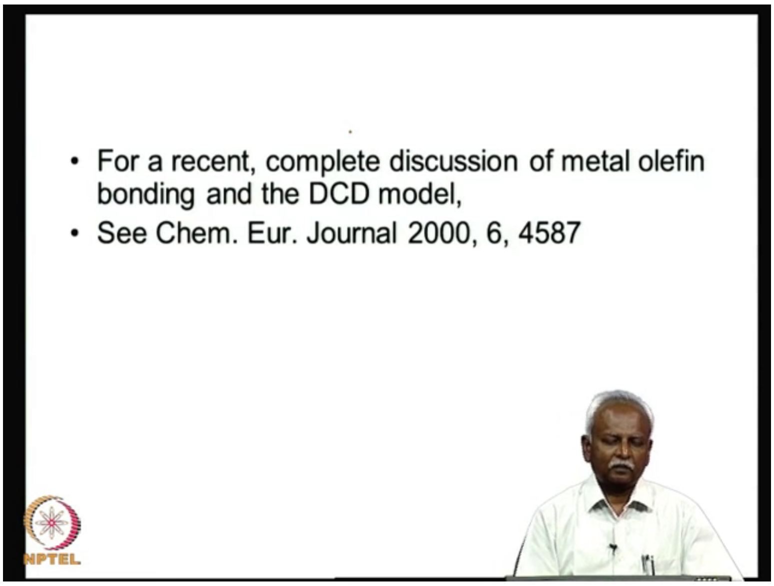

- For a recent, complete discussion of metal olefin bonding and the DCD model,
- See Chem. Eur. Journal 2000, 6, 4587

So, a complete discussion of the metal olefin bonding and what we called as a Dewar Duncanson Chatt model is given in a recent paper, which is pictured, which is reference is given here.

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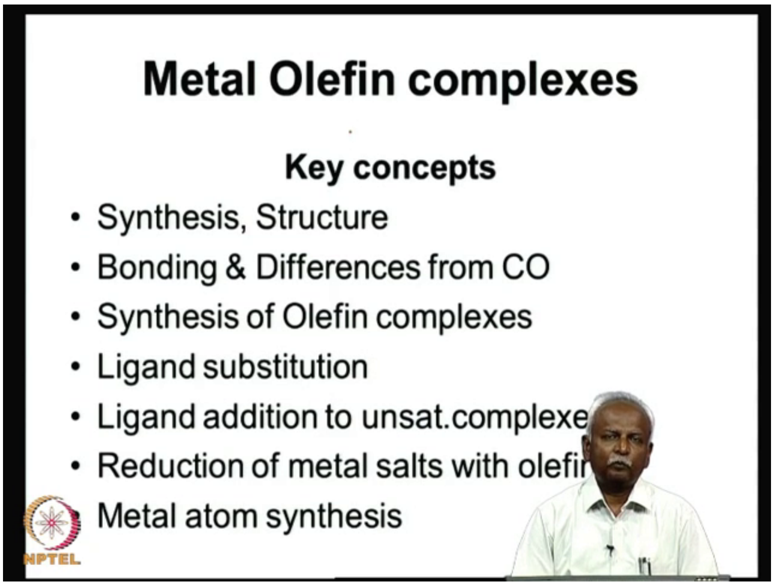

Metal Olefin complexes

Key concepts

- Synthesis, Structure
- Bonding & Differences from CO
- Synthesis of Olefin complexes
- Ligand substitution
- Ligand addition to unsat.complexe
- Reduction of metal salts with olefi
- Metal atom synthesis

And what we have understood from all these aspects is, the fact that it can, olefin complexes can be readily synthesized, structurally characterized. The bonding differences between carbon monoxide and olefins allow one to synthesize them by displacing carbon monoxide. And it is possible to have, the significant reduction in the stretching frequency of olefin complexes, due to pi accepting nature of the olefins. And you can also, you can also use these metal olefin complexes to generate more stable olefin complexes, by displacing them based on the pi accepting nature.