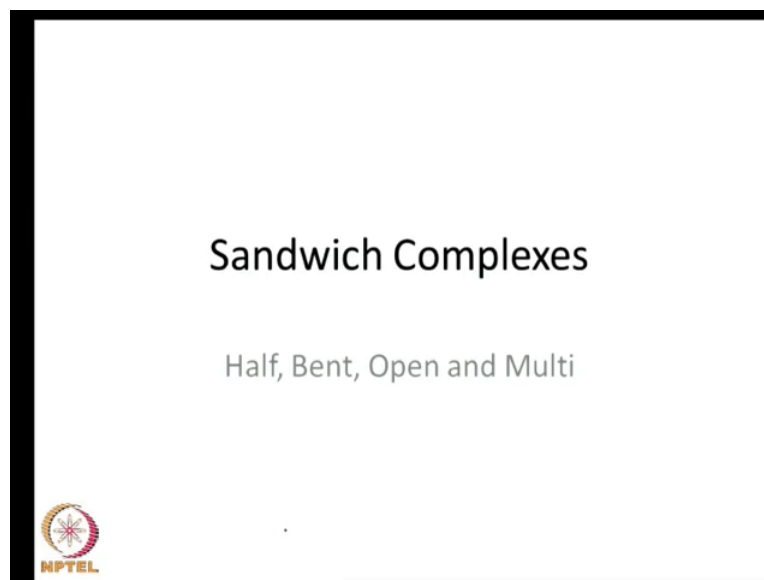


Introduction to Organometallic chemistry
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Lecture - 27
Half sandwich complexes

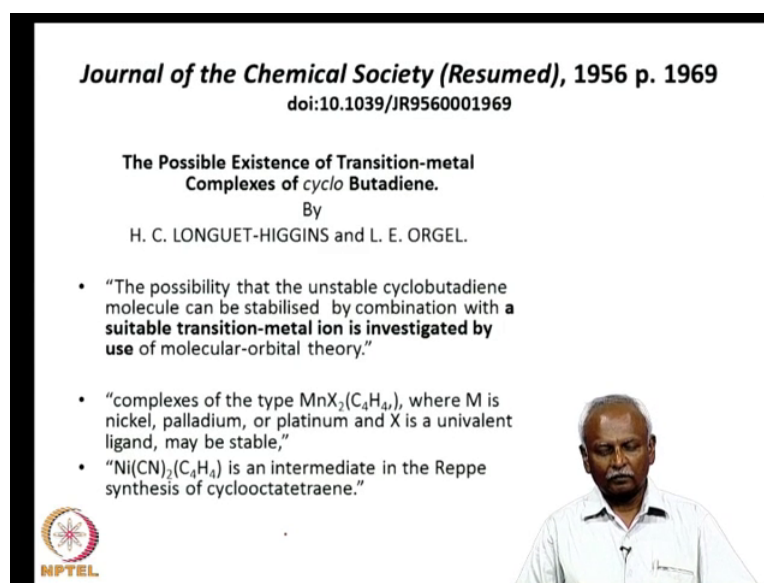
In this lecture we will talk about sandwich complexes again. This is in fact, the third lecture in the series, where we are talking about metal atoms or metals and a few ligands which are sandwiched between two organic pi systems. And these pi systems could be aromatic or could be even anti aromatic, as in the case of cyclopentadiene. Now, in today's lecture we will also talk about some variations in the sandwich complexes, where this sandwich is not complete, as in the case of a half sandwich complex or maybe a bent sandwich complex or even something that is open. Where the cyclic pi system is not there, but it is only an acyclic system, but it is still sandwiches a metal atom and its components.

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And there are still more complicated and exotic structures such as, multiple metal atoms between organic pi systems or even multiple metal atoms, which surround a cyclic pi system. So, the type of complexes that are formed by organic ligands are quite large, and in this category where we classify them as sandwich complexes. And today's lecture we will explore some of these variations.



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The Possible Existence of Transition-metal Complexes of *cyclo* Butadiene.
By
H. C. LONGUET-HIGGINS and L. E. ORGEL.

- "The possibility that the unstable cyclobutadiene molecule can be stabilised by combination with a **suitable transition-metal ion is investigated by use of molecular-orbital theory.**"
- "complexes of the type $MnX_2(C_4H_4)_n$, where M is nickel, palladium, or platinum and X is a univalent ligand, may be stable,"
- " $Ni(CN)_2(C_4H_4)$ is an intermediate in the Reppe synthesis of cyclooctatetraene."

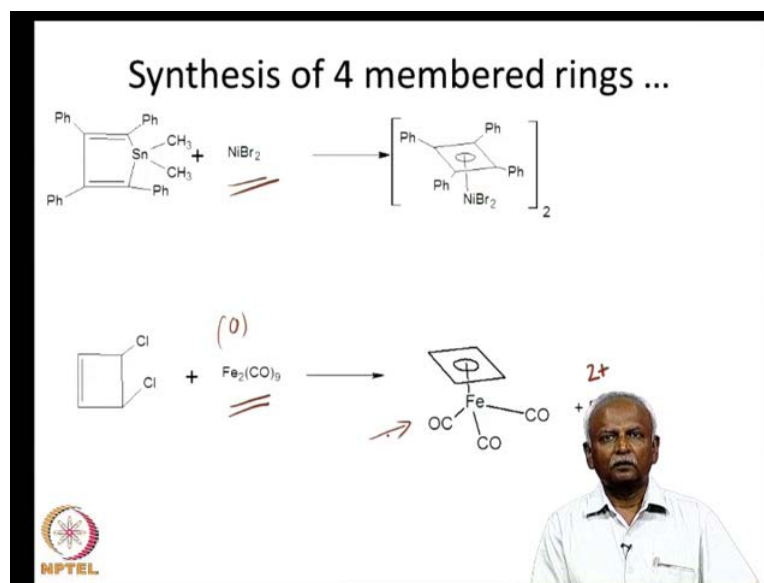
 

To start with, I would like to point out a study that was done by Longuet Higgins and Orgel, way back in 1956. If you recollect the first lecture in the series on sandwich complexes, it was in 1956, that the first sandwich complex was identified. Although these compounds were, several sandwich compounds were known, the correct structure was identified through x ray and through the intuition by Wilkinson Woodward. And the groups in Germany, which correctly identified the double cone structure or the sandwich structure.

So at this time, it was Longuet Higgins and Orgel who studied cyclo butadiene. Cyclo butadiene was already known to be an anti aromatic system. And so they looked at the nature of a metal complex that would be formed by the cyclo butadiene, which is an anti aromatic system with a metal compound. They conjectured that, suitable transition metal ion, for the formation of a sandwich or rather, a pie complex between cyclo butadiene and a metal, would be of the type $M X_2 C_4 H_4$. Where M is nickel, is a nickel, palladium or platinum and X is actually a univalent ligand.

So they arrived at this structure, where they said $Ni CN_2 C_4 H_4$. For example, could be a stable complex or be an intermediate in the Reppe synthesis, which involved acetylene and nickel dicynide. So they predicted, before it was actually synthesized, that a complex of cyclo pentadiene could be in fact formed by ion, the iron group metal atoms.

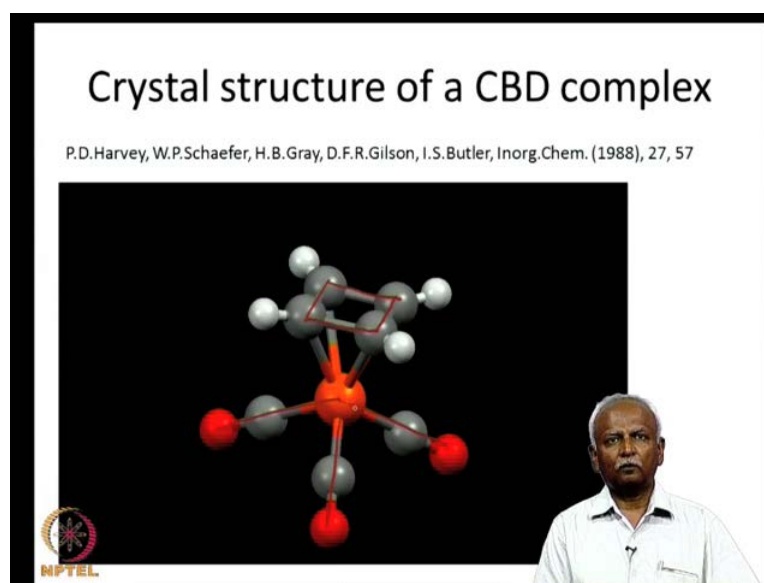
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So, the synthesis of the four membered rings, the cyclobutadiene rings, in the coordination sphere, the metal atom was done in a couple of different ways. And we will just look at a few ways, because it illustrates some different methods by which these molecules are synthesized. You can see here that, nickel literally substitutes for the tin, but there is no oxidation state change on the nickel. You start with nickel dibromide, you start with nickel dibromide and that is, that is replacing the tin dimethyl compound, that is being eliminated in the system. So, you have a dimeric complex of the nickel which is formed, where you have tetrafinayle cyclobutadiene coordinated to the nickel.

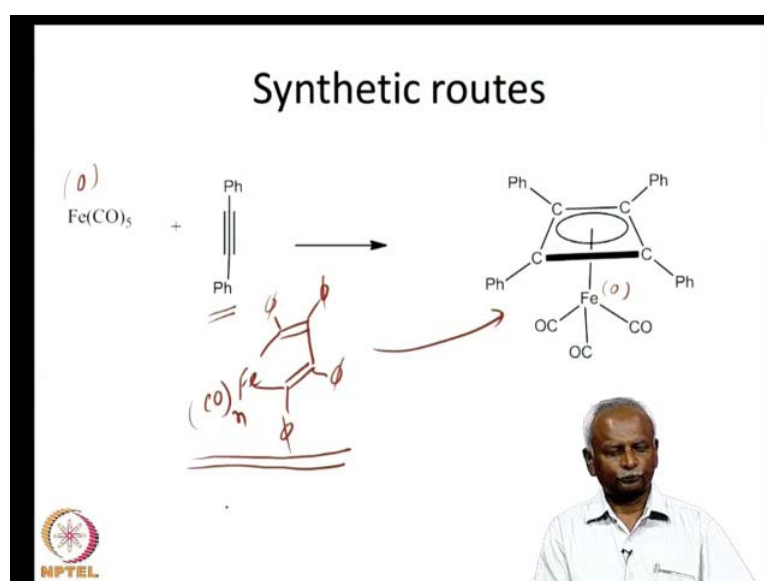
Similarly, you could also have a dichloro cyclobutene, which reacts with iron dicarbonyl. Iron here. However, is in the zero oxidation state, and one iron gets oxidised to iron two plus. This iron gets oxidised to two plus and it forms FeCl_2 , and the cyclobutadiene is coordinated to iron tricarbonyl. So you can see that, a variety of reactions are possible. All of them generate this very stable system where cyclobutadiene is coordinated to a metal complex, no, metal fragment.

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Now, here is a structure of cyclo butadiene. And here it is coordinated to iron tricarbonyl, and you have three carbon monoxide molecules, which are in fact symmetrically coordinate, is, or the carbon monoxides are like a piano stool, which are holding up the butadiene unit. So these are in fact called piano stool complexes, where the butadiene unit is in fact, we can just draw out to show that. So here is the butadiene part, which is the stool of the piano stool, and these are the three legs, these are the three legs of the piano stool. So this is a typical complex that is formed by cyclo butadiene and iron tricarbonyl, which is quite stable.

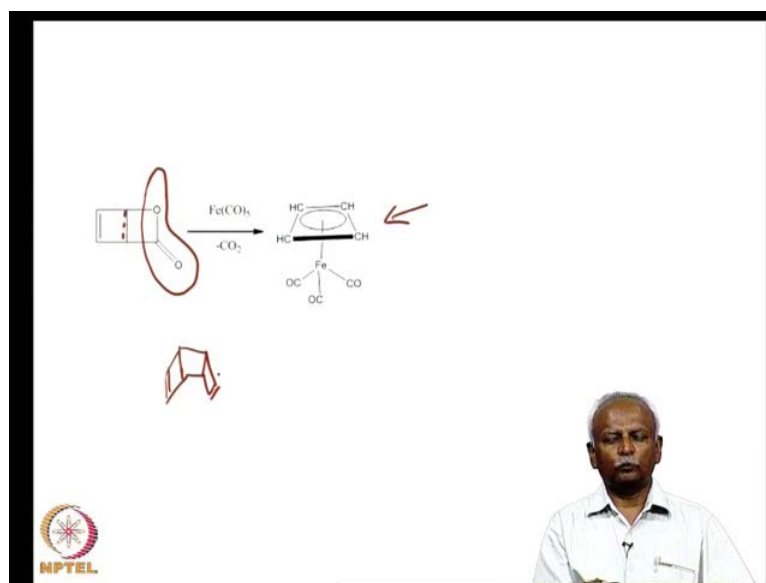
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There are several methods as they told you. Here is a template method, where you would take diphenyl acetylene, and in the coordination sphere of iron tricarbonyl, iron is in the zero oxidation state here, and iron is in the zero oxidation state here, and so no redox reaction is involved. At templated synthesis of the cyclobutadiene, however, is achieved in the coordination sphere of iron tricarbonyl. No intermediates were isolated.

Although one can conjecture that, iron complex would go through any intermediate where ferrocyclopentadiene would be an intermediate and this would collapse, as in the case of the nickel system that we talked about. This would collapse to give you, the appropriate number of carbon monoxide attached to the iron, you would end up with the iron tricarbonyl complex. So in fact, there are examples of complexes where, ferules as they are called and in conjugation with the acetylene is, has been isolated. Such complexes have been isolated and so this is quite an acceptable intermediate in this reaction.

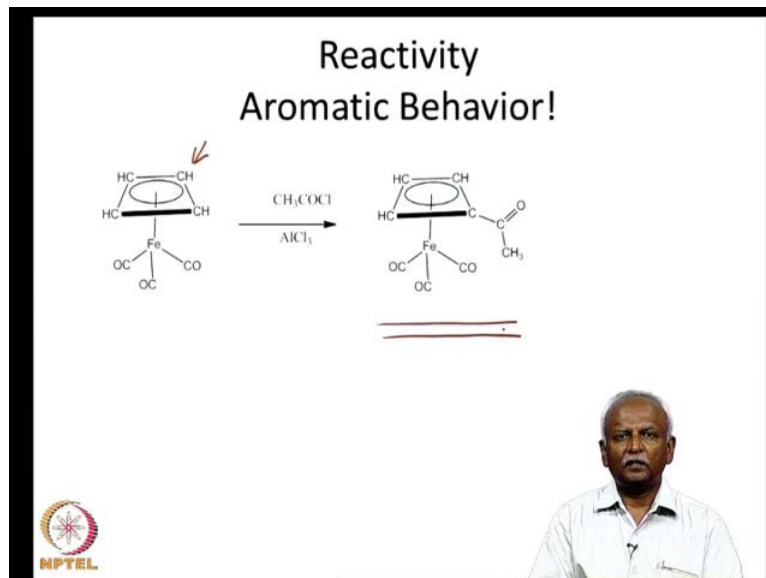
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The generation of cyclobutadiene, which is an unstable molecule, is difficult. So one has to generate it, in the coordination sphere of the metal. That is what we have seen in the last three methods of synthesis. So here, we have a photochemical reaction, in which a molecule of carbon dioxide is eliminated from this bicyclic molecule. So here is the molecule of carbon dioxide, which is eliminated. And that generates a cyclobutadiene.

But now because you are doing it in the coordination sphere of the iron, you end up isolating a stable molecule of cyclobutadiene coordinated to iron tricarbonyl.

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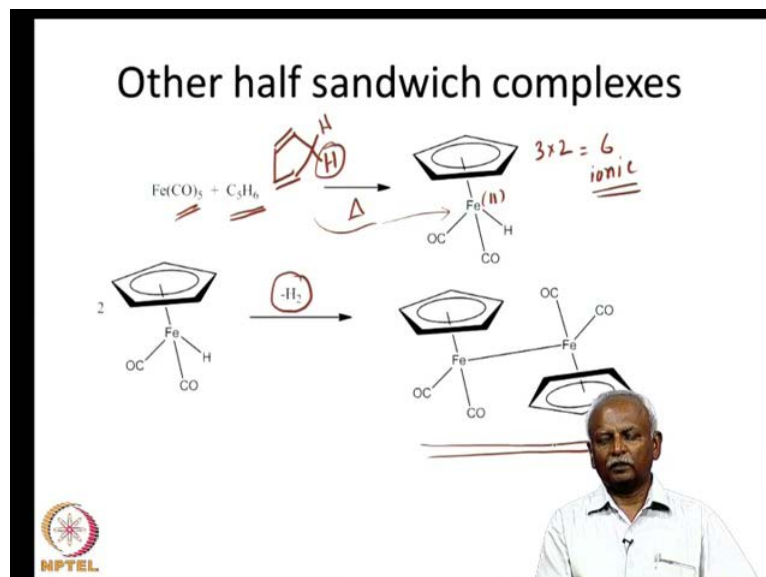
So you will notice that, these reactions have to be carried out, so that the cyclobutadiene is captured by the metal atom before it is too late. Otherwise it dimerizes, and it generates a bi, a molecule which is cyclic. And it is just dimer of the cyclobutadiene. So this is a molecule that would isolate, if you are not careful enough to provide a stabilizing foresight for cyclobutadiene, which is anti aromatic and it would dimerize rapidly. Now, although cyclobutadiene itself is anti aromatic, it seems to exhibit reactivity that is characteristic of aromatic compounds.

One of the characteristic reactions of aromatic compounds is, the electrophilic aromatic substitution. So you would remove one of these hydrogens, which are here on the ring and replace them with another electrophilic group. And that, in this case is the acetyl group, which is generated by AlCl_3 and CH_3COCl . So you end up generating, the acid laden version of cyclobutadiene and which is still coordinated to the iron tricarbonyl.

And the yields in these reactions are quite good. Indicative of the fact that, you can have a smooth electrophilic aromatic substitution of the CH group, on the cyclobutadiene coordinated to the iron tricarbonyl. So this is a very characteristic of the aromatic behavior of cyclobutadiene, which is completely new. It is changed reactivity all the

way from, the anti aromatic behavior of cyclobutadiene to the aromatic behavior, that we have observed here.

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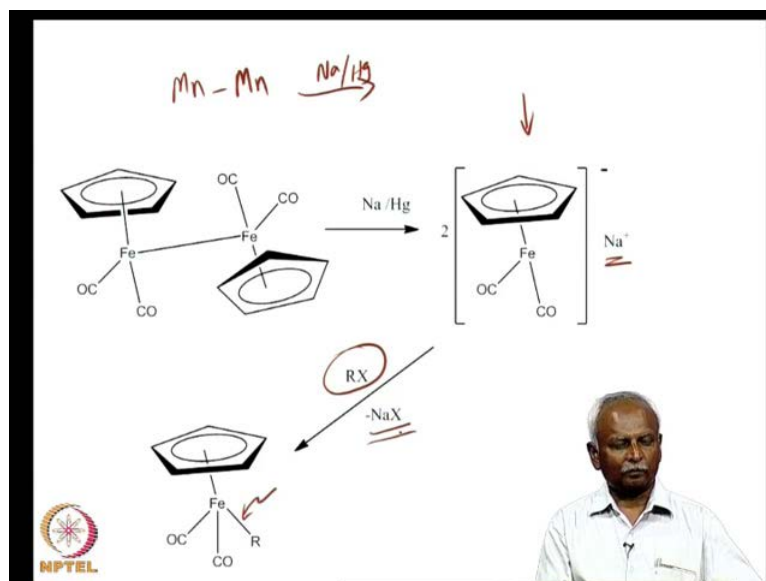


Now, other half sandwich complexes are also known. What we have talked about is cyclobutadiene, because that was the first one which was predicted, even before it was synthesized. A very simple reaction of iron pentacarbonyl with cyclopentadiene. If you remember, cyclopentadiene is the molecule, that has to be generated by cracking dicyclopentadiene. And if you heat the two together, what you end up with, is iron hydride cyclopentadiene molecule, where two carbon monoxides are still retained in the coordination sphere of the iron. You seem to have accomplished an oxidative addition of cyclopentadiene, which of course, is this molecule.

So, you have two hydrogens here and now you have ended up adding one of those hydrogens to the iron atom, and so you have a hydride, which is present on the iron and the cyclopentadiene anion. So, iron is gone from the zero oxidation state, to the plus two oxidation state. This is an oxidative addition, but at the same time there has been substitution of the carbon monoxides on the iron, which is penta carbonyl to start with and it is now become a dicarbonyl molecule. And what you have replaced the three carbonals, is the cyclopentadienyl unit, which in fact will donate 3 into 2, 6 electrons. So this donates six electrons in the ionic method.

And you can do the electron counting to show that this is in fact going to be a stable eighteen electron molecule. Although the system is stable, what happens is, it dimerizes, rather rapidly and loses a molecule of dihydrogen. That means two hydrogens from the two iron atoms are eliminated as H_2 , and you end up with a dimer which is a very convenient source of $CPFeCO_2$ unit, when you need them.

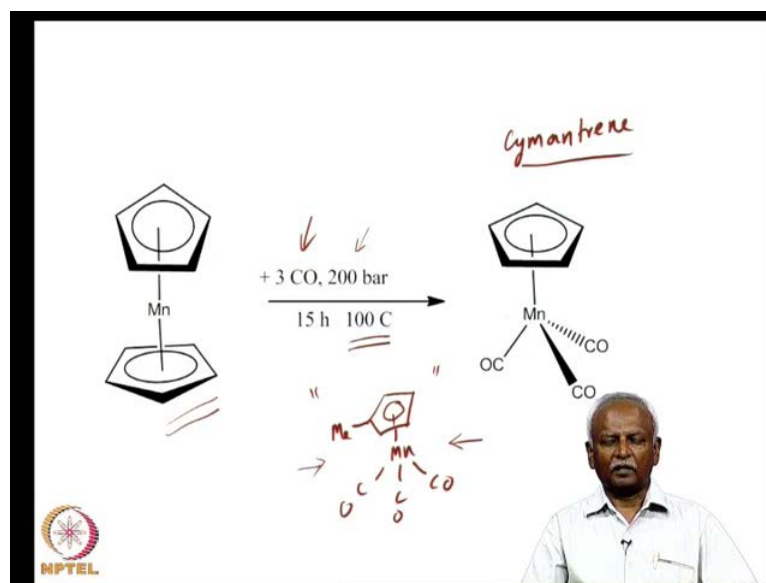
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So here I have shown you, what you can do with this dimeric species. You remember the reaction, which we have encountered several times in the series, which is Mn_2CO_{10} , which has got a manganese manganese bond. And this manganese manganese bond could be reduced with sodium and mercury. And similarly, this system also can be reduced with mercury, and you would end up with a very reactive iron dicarbonyl anion, and this very reactive iron dicarbonyl anion, is been called super nucleophile.

So this is extremely reactive and will react with a variety of electrophiles. Here I have shown you the reaction with RX , and this does simple nucleophilic substitution now, on the r group, and that leads to the iron R bond. So, this iron R bond is formed, and X leaves as X^- . And this X^- and a plus will end up with as NaX in the reaction medium. So, you can see that, there are some very interesting half sandwich complexes and ions that can be generated by simple reaction of iron pentacarbonyl with cyclopentadiene molecule which is shown right here.

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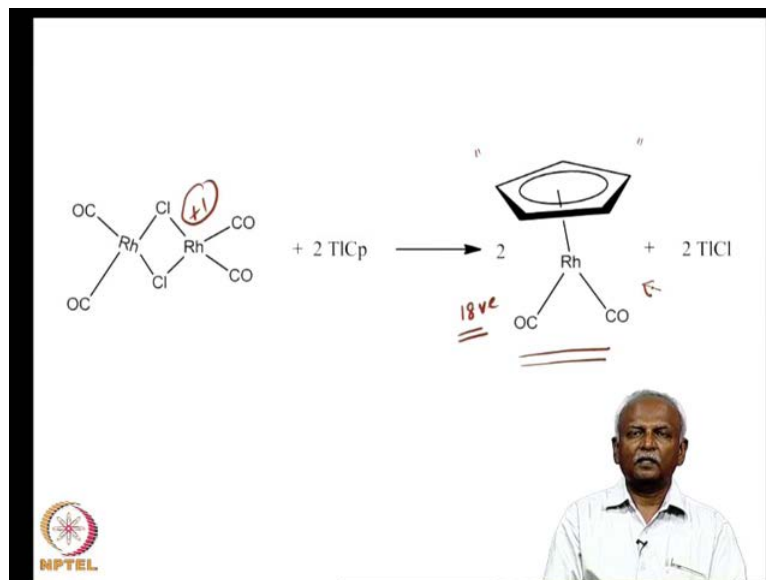
So, let us proceed now. As I told you earlier, it is possible to generate the half sandwich complexes in a variety of ways. One of them is, to treat a sandwich complex which is not an eighteen electron species. So in this case, for example, this is not an eighteen electron species. If you reacted with carbon monoxide at high pressure, then you, at high pressure, this is fairly high pressure, two hundred bar, which two hundred times atmospheric pressure, you treat magnocyne with carbon monoxide at high temperature and high pressure, what you end up with is, a molecule called cymantrene.

And this molecule is a very interesting molecule, because the substituted variety of this, methyl cymantrene turned out to be, possible additive, possible additive for, here is the molecule that I am talking about. This is the methyl cymantrene. You have three CO groups attached to the manganese, and you have, stable eighteen electron system and this turned out to be additive for fuels, so that you can have smooth burning of the fuel, in the internal combustion engine.

Remember, tetra ethyl lead was used for a long time and now it has been completely removed from the market and in between, people were looking for alternatives, as fuel additives, so that there will be less knocking in the fuel. And one of the molecules were cymantrene, and that is this molecule where you have a methyl cyclo pentadiene, which is coordinated to the manganese and three carbonyl units are there along with the manganese to give you stable eighteen electron system. So, this cymantrene molecule

again, has got the familiar half sandwich structure, where you have one cyclic pi system, which is coordinated to the metal and the other side has got ancillary allegiance to support this metal atom.

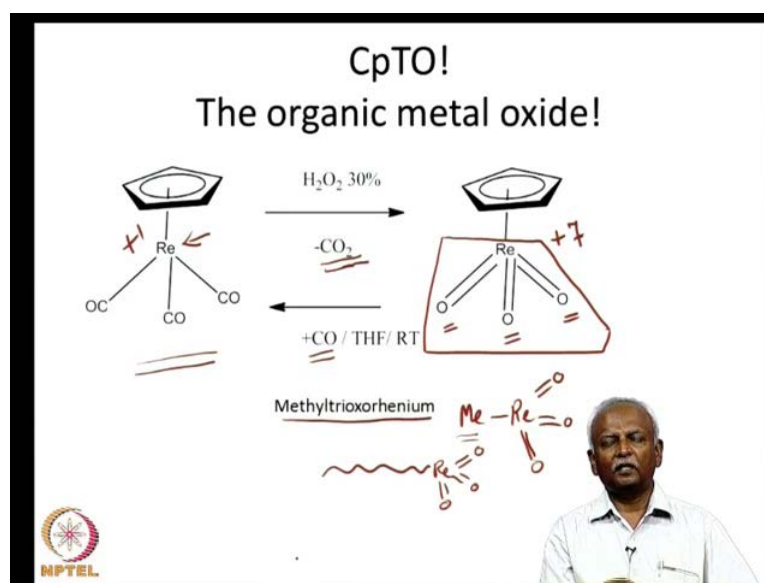
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Now here, we crossover into rhodium one chemistry and this is just adjustment of the number of electrons, rhodium has, in its plus one oxidation state. This is plus one oxidation state, eight electrons in its valant shell. This is got eight valance electrons, and so it would require a total of ten valance electrons and those are provided by cyclo pentadiene anion and two carbon monoxides.

A simple displacement reaction happens of the chloride, but that now generates a monomeric complex, from the dimeric system that we started out with, and it is again a stable eighteen electron complex, eighteen valance electron complex that we isolate. So you will notice that, this molecule is looking very similar to the CpFe(CO)_2^- ion and that is exactly isoelectronic with this molecule, although this is not as good a nuclear file CpFe(CO)_2^- . This molecule also behaves like a nuclear file, and it attracts RX molecules.

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So, before we proceed further with the cyclo pentadiene systems, I should mention that, there are some, as you go down the group, or as you go to heavier transition metals, you end up with some very interesting reactions. And this reaction, which was in fact, discovered fairly recently or at least utilised fairly recently. You have a carbonyl species, the analogue of the cymantrene. So the cymantrene had manganese, here you have rhenium. This molecule surprisingly, reacts with hydrogen peroxide. And hydrogen peroxide is fairly good oxidising agent and it oxidises the carbon monoxide to carbon dioxide.

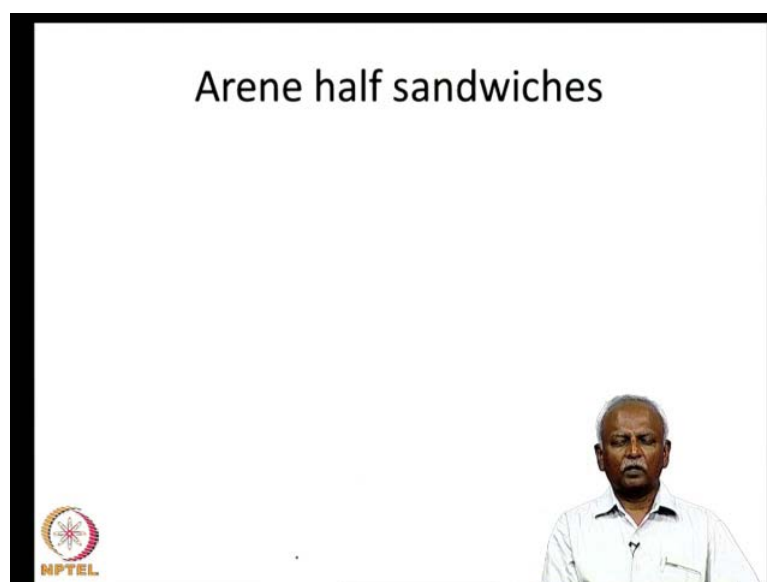
So, carbon monoxide is converted to carbon dioxide and the hydrogen peroxide not only oxidises the carbon monoxide, it also oxidises the rhenium. Rhenium is in the plus one oxidation state here, and it is oxidised to rhenium all the way to plus seven. So here is a metal atom, which is formally in the plus seven oxidation state. And it is got three oxo groups, which are coordinated presumably through double bonds to the rhenium metal. So that makes an oxidation state of seven and this unit, that is ReO_3 , turns out to be a very stable unit.

This stable unit is been found in many of the organometallic molecules. It is doubtful that, rhenium is in fact, in the, has lost all its d electrons, but nevertheless, the formal oxidation state has to be plus seven on the basis of oxygen, which is electro negative and is considered as a O^{2-} ligand, in this case. Surprisingly, very surprisingly, you can

convert this rhenium trioxide, in the presence of carbon monoxide, back to the rhenium tri carbonyl species.

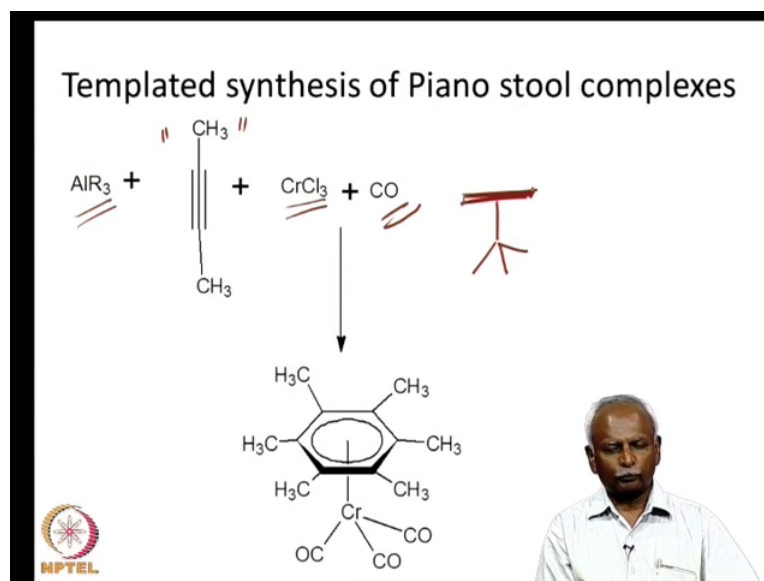
And it is also possible to make methyltrioxorhenium, which means it is Me rhenium, with three oxygens. So this incredible molecule is in fact, not only methyl, but any long alkyl chain can be attached. So this is in fact, strange molecule, where you have an inorganic oxide which is attached to an organic molecule. So this is being called organic metal oxide. The rhenium turns out to perform several catalytic functions and we will look at some of these reactions in a later, in a later talk.

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Now, upto now, we have looked at cyclo butadiene arene and cyclo pentadiene arene.

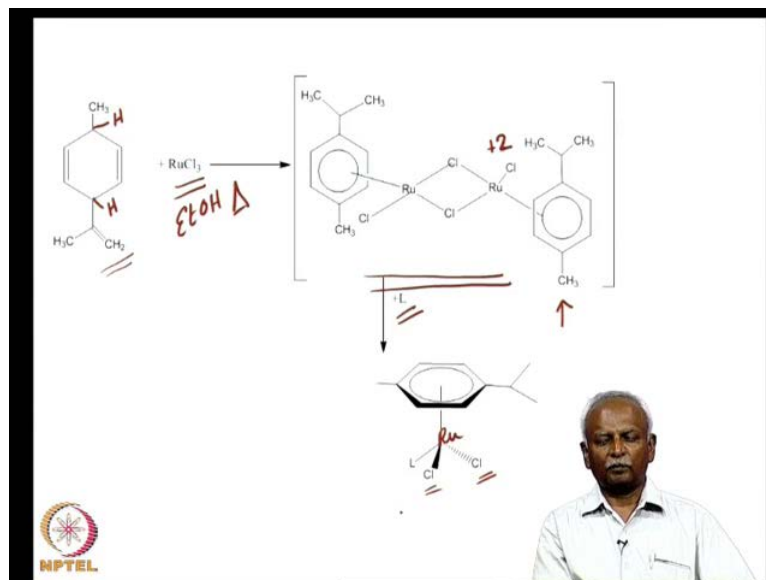
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Let us look at some, arene half sandwich complexes. Arene half sandwich complexes, can also be made by a templated synthesis. Here we have reduced chromium trichloride with AlR_3 . AlR_3 is a very powerful reducing agent and it reduces the chromium from plus three to zero. And, because you have in the reaction medium, dimethyl acetylene. The dimethyl acetylene is quickly polymerised or oligamerised, I should say, to trimerised, to give you hexamethylbenzene.

So this would be a convenient way of making hexamethylbenzene. And if you do this in the presence of carbon monoxide, then you end up with a half sandwich complex where, $\text{Cr}(\text{CO})_3$ has got a hexamethylbenzene coordinated on the top. So all of these molecules have this piano stool, and they have either two or three legs for this piano stool. So that, you have a dissimilar framework and that is why they are grouped together as piano stool complexes.

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Now, the aromatic ring system, that is coordinated to the metal, can in fact be synthesized in the coordination sphere of the metal atom, through a reduction reaction, which is accomplished by the organic ligand. In the previous instance, we used an inorganic reducing agent to reduce the chromium to chromium zero. Here, in this example, what we are doing is, reducing the ruthenium three. We are going to reduce the ruthenium 3 to ruthenium two species, but we will do this, using the aromatic ligand system, that is present here.

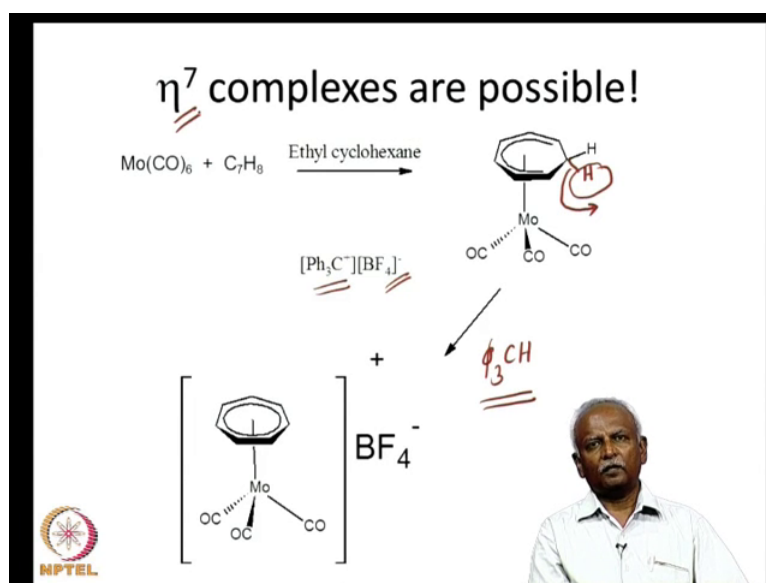
So two hydrogens are here, which in fact, can be used for the reduction reaction and as that is happening, you lose those two hydrogens as HCl . And you end up with an aromatic ring system, coordinated to the ruthenium. Notice that, here ruthenium is in the plus two oxidation state and you will also notice that, this is completely an inorganic compound, except for the organic aromatic ligand, that is present here. It is possible to reduce it in the, or rather convert it from the dimeric state to the monomeric state by using a good ligand.

So, if you add, good L plus by which I mean, a strong ligand, which will coordinate very effectively to the metal. It could be anything from a phosphine or a peridienein or triethylamine or any ligand, you, which is suitable for stabilizing ruthenium, when you end up with piano stool complex, where the aromatic ring system is now coordinated to

ruthenium. So here is ruthenium, coordinated to the aromatic ring system and supported by three legs, two of which are chlorides.

So, two of them are chlorides and one of them is a ligand that you added. This provides a very convenient way of generating the half sandwich complexes, because this reaction is conveniently performed in a refluxing ethanol. You can just heat ethanol and the philanderine, which is this molecule, to generate this cyclic aromatic ring system coordinated to the metal.

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Now, not only is it possible to generate ethyl six molecules. In the previous aromatic ring system we have six carbons, attached to the metal atom. In this case, you have seven carbon atoms attached to the metal. You will notice that, C seven H eight is a cyclic molecule, which is not conjugated to start with. And you have three aromatic or three non aromatic double bonds which are capable of coordination to the molybdenum.

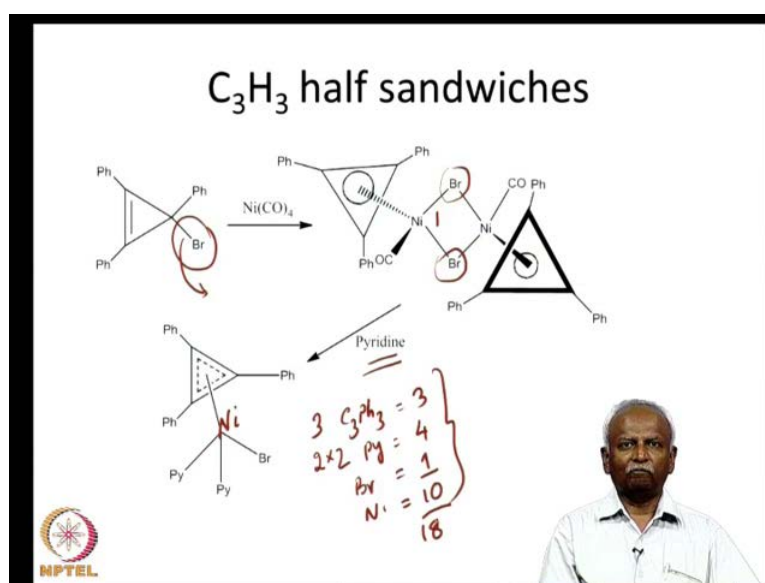
Molybdenum of course, requires only, molybdenum requires only, 3 into 2, 6 pi electrons from the cyclohexatriene and it has got a saturated carbon centre, which is indicated by two coloured hydrogens. Now one of them can be removed as H minus, along with this pair of electrons. So, this is accomplished very effectively with a trityle cation. The trityle cation is a stable cation, which is capable of removing hydrogen hydride ion. So if this hydrogen is removed as H minus, you will end up with a cyclohepta trinyl cation.

This cation would be pseudo, would be aromatic, because it now has six pi electrons and one p orbital which is vacant.

So, you have six pi electrons in a cyclic system and all the criteria required for making an aromatic pi system is satisfied. Only difference is that, you are now attached, you are now attached to the pi system, to molybdenum atom. And, this gives you a cycloheptatrienyl molybdenum tricarbonyl. Now, because you have removed this molecule, you have removed the trityl cation, which has now become trifluoromethane, you have removed trifluoromethane by removing this hydrogen, as H^- and Ph_3C^+ , you are left with BF_4^- , which is counterion present here.

You will notice that, in this molecule all the seven carbon atoms are almost equally bound to the metal atom. So that is why we call it a, eta seven complex. And all of these are again half sandwich complexes, meaning the system has got one pi system, pi ring system, which is coordinated to the metal.

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And, not only is it possible to expand the ring size from six to seven, it is also possible to go down from four to three. Remember we talked about four, five and six being the most popular ring systems, but it is also possible to have 3 and 7. 7 is what we discussed earlier and here we have cyclopropenyl bromide, which now means to lose Br^- , as Br^- minus. It needs to lose Br^- as Br^- minus, to form cyclopropenyl cation, which would be aromatic.

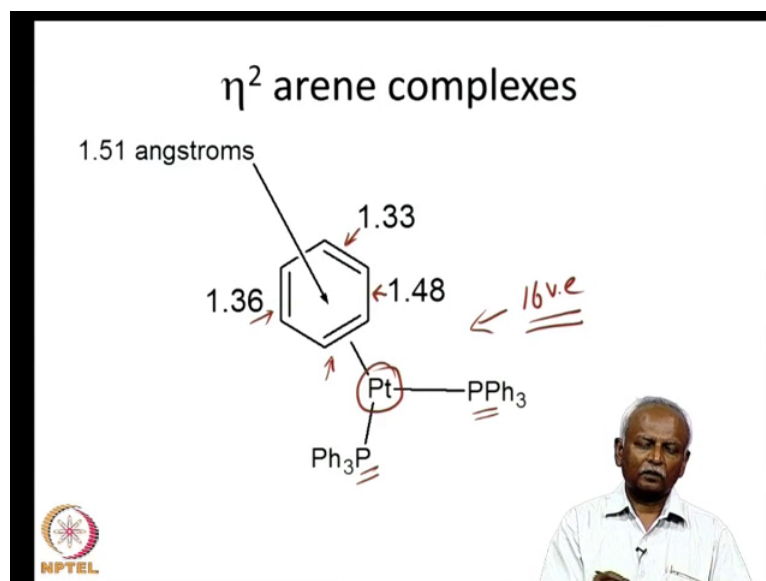
And, in the coordination sphere, nickel tetra carbonyl, you end up with a dimeric complex, where two nickel atoms are interacting with the cyclo propynyle group, and bromide is in fact a bridge.

Notice that, in this molecule, nickel bromide, Ni_2Br_2 , exist in an unusual oxidation state of nickel one. If you only take this fact, but normally by convention you consider the cyclo propynyle cation, which is coordinated to the nickel, as an anionic group. So this confusion is there for most organic molecules because, by convention we take them as the negatively charged species, which would be anti aromatic.

But we know that, from the way in which it was made and in fact, it has been made by generating the cation. Nevertheless, the molecule can be treated with ligand, like pyridine and you can generate, once again generate now, a piano stool which is only three pointed. It has got a three pointed leg and it has also got a three pointed stool, to support the person sitting on it.

So here is the nickel atom. Now, attached to two pyridine ligands and it has got a bromide and a cyclo propynyle group. So if you were to use the anionic method or the, let us use the neutral method this time, you have three electrons from the C_3Ph_3 unit, and you have two into two, from the pyridine units, so that will give you four electrons. And you also have the bromine, which is in the neutral method, giving one electron, so nickel has got ten electrons and so you would form this nice, eighteen electron system. So the total works out to be, eighteen valance electrons.

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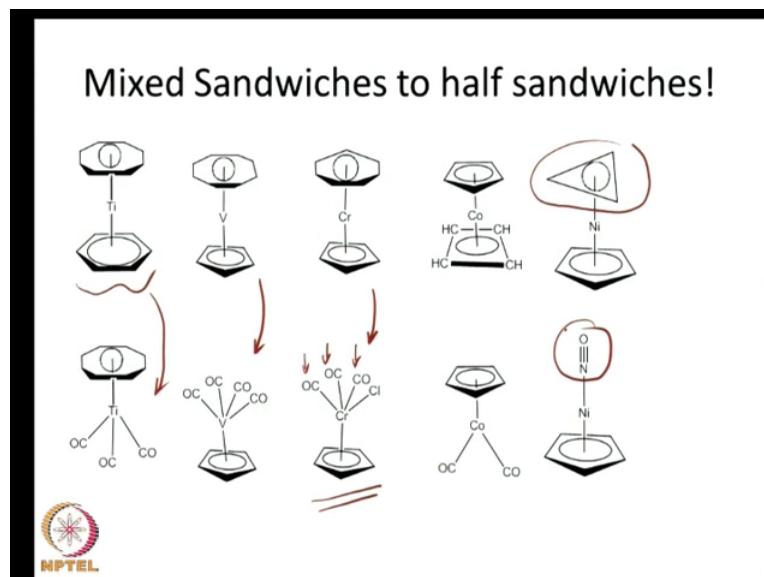
Now, obviously you do not have a cycle, when you have only two atoms, which are coordinated to the metal, but I just wanted to point out here that, the eighteen electron rule turns out to be reasonably important. You can have sixteen electron complexes, but nevertheless, going beyond eighteen is more difficult than having complexes which have less valance electrons than eighteen. So here I have shown you a platinum complex, which looks like a piano stool complex, but only one of the double bonds in the benzene ring is coordinated to the platinum atom.

So, platinum is in the zero oxidation state and you have two try fennel phosphine is coordinated to it so you have sixteen valance electrons system, sixteen valance electron system and you do not go to the twenty valance electrons system which would be formed, if you were to have a symmetrically eta six coordinative benzene ring. You will also notice that, this now has got bond alternation, that is a very clear indication of the double and single bond, there are isolated and are now, not really conjugated with another, with one another.

So this, the bond which is right next to the double bond which is coordinated, is in fact, a long bond and then, two short bonds are there, one is, 1.33 Angstroms and the other is, 1.36 Angstrom units. And the bond that is coordinated to the metal, is in fact, lengthened significantly which is indicative of the fact that the double bond has been weakened quite a bit by interaction with the platinum. Electron density from the pie molecule orbital has been donated to the metal and the pie star orbital has been populated. As a result, this

bond has been weakened significantly. So it is no longer like a double bond, it is almost like a single bond.

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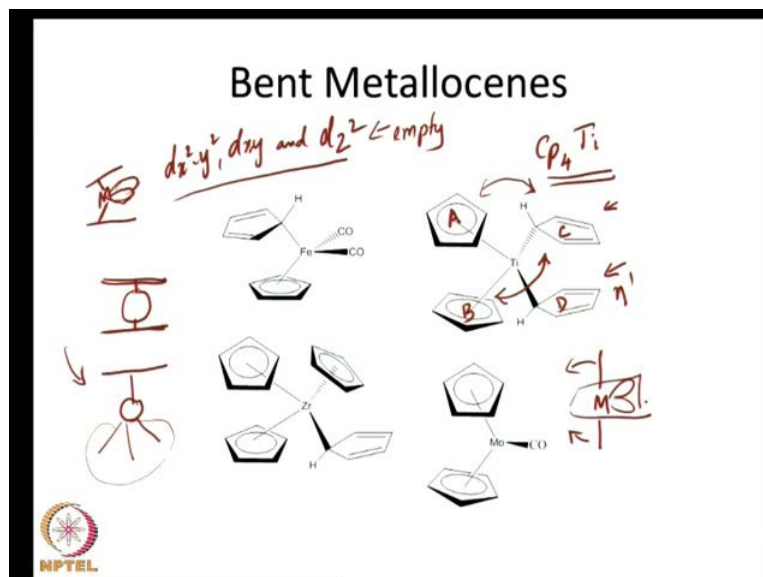
So, this brings me to a conclusion, of the series of half sandwich complexes, that I wanted to talk about. I just want to point out that, this forms the series, were you, were we talked about mixing and matching the number of electrons required on the, for the metal, to form eighteen valence electron systems. And you could do this, by simply replacing the neutral ligands, neutral aromatic or non aromatic pi systems which are present on the metal, by carbon monoxide units. Because each carbon monoxide gives two electrons, you can replace, say, a benzene ring, with three carbon monoxides and that is exactly what we have done here.

And similarly, you can have, here a cyclo octetarine, which is giving you eight valence electrons, we just replace it with 4 and 2. So, 4 carbon monoxides replaces a cyclo octetarine. And if you replace a cyclo hectotrynyle unit, this is a cyclo hectotrynyle unit. So you replace it, with three carbon monoxides and one chlorine. So that also seems to be an acceptable solution.

So, you can just see that, you can have a huge variety of metal complexes, which are formed. Let us just take a look at the last one, which is mentioned here, where I have replaced the cyclo propynyle unit, which will give you three electrons. A three electron donor, among the carbon monoxide type molecules is NO. So, you can simply replace

CH three with NO. In the neutral method, this is so convenient for us to understand this electron, isoelectric substitution. So, C 3 H 3 is just replaced by a NO molecule.

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So, a multitude of metal sandwich complexes can be made, which are all half sandwich in nature. Now I want to move on to bent metallocenes. What are bent metallocenes? The metallocenes of the sandwich complexes are systems, where the metal was in fact, symmetrically held in between two flat pi systems. So, there are two flat pi systems, and the metal was sandwiched between the two units. And just now, we have looked at a series of systems, where the metal is just attached to, attached from one side, with a pi system and the other side is supported by a variety of other ligands.

So, instead of combination, instead of supporting it, in this fashion with three ligands, one can also think of supporting the metal or bending the sandwich in this fashion, so that if you have vacant, if you have vacant orbitals on the metal atom, these can also coordinate. This happens very readily, in the early transition metals. So, early transition metals have in fact, three orbitals on the metal. The dx square minus, y squared, the dxy and dz squared.

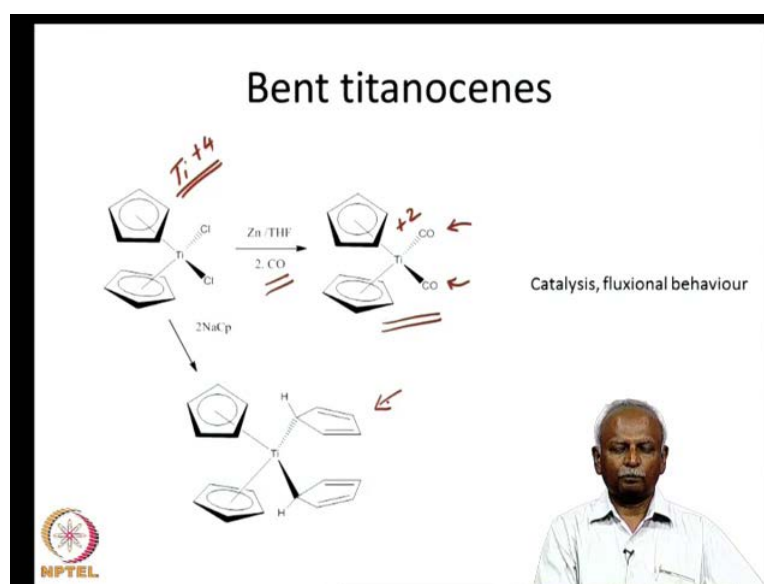
So, there are three different orbitals on a metal, which are available for bonding. If you have a titanium four plus, just interacting with two cyclopentadienyl units. So all of them will be empty. All three orbitals will be empty. So these orbitals are now available for coordination with the metal atom. So here I have shown you, a set of molecules,

which are capable of interacting with more ligands, just because they have got these empty d-orbitals, which are available for interaction. First let us take the tetra cyclopentadienyl titanium.

So, you have Cp_4Ti . So you take TiCl_4 and treat it with four molecules of cyclopentadienyl anion, and you end up with this molecule, which if you want to write an 18-electron structure, it would be difficult to do so. But if you bend the cyclopentadienyl units sufficiently, you can attach the cyclopentadiene unit in a sigma fashion. You can attach the cyclopentadienyl units in a sigma fashion or eta one fashion, in this molecule.

Notice that, there is nothing which distinguishes the ring A, ring B, the ring C and the ring D, other than the hapticity that is associated with them. So there is a very rapid exchange of, A with C or B with C, and that leads to some fluxional behavior, which we will talk about in a future lecture. But these molecules, right now this is a sixteen valence electron system. These molecules are quite stable and turn out to be an interesting class of molecules, where the cyclopentadienyl ring systems are just bent, a little bit backward from the usual orientation. So, this bending back, allows for exposure of these orbitals, which are there in the x y plane and, so allows for interaction with the metal atom, with other ligand atoms.

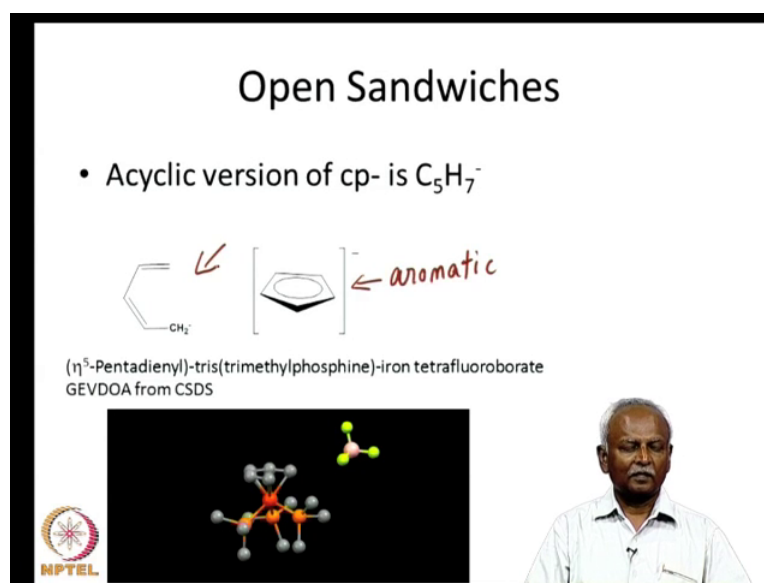
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So, I have shown you a variety of molecules here, but let us take some specific examples now. Let us take Cp_2TiCl_2 and, Cp_2TiCl_2 is titanium four plus. This is titanium four plus, you can reduce it with zinc and use carbon monoxide, in the reaction medium and that gives you TiCO twice. So here is a molecule, which is titanium in the plus two oxidation state. Remember, there are three orbitals that were available on the titanium.

So, we can in fact, add six electrons, if it was titanium four plus. Now you have a plus two system, so you end up adding only two other ligands. So, that gives you, two other ligands in the coordination sphere of the titanium and you have a bent sandwich structure. So, this is a game, the bent sandwich structure, which we just talked about, where the cyclopentadiene units are coordinated in a eta one fashion. This is the way you would end up making it.

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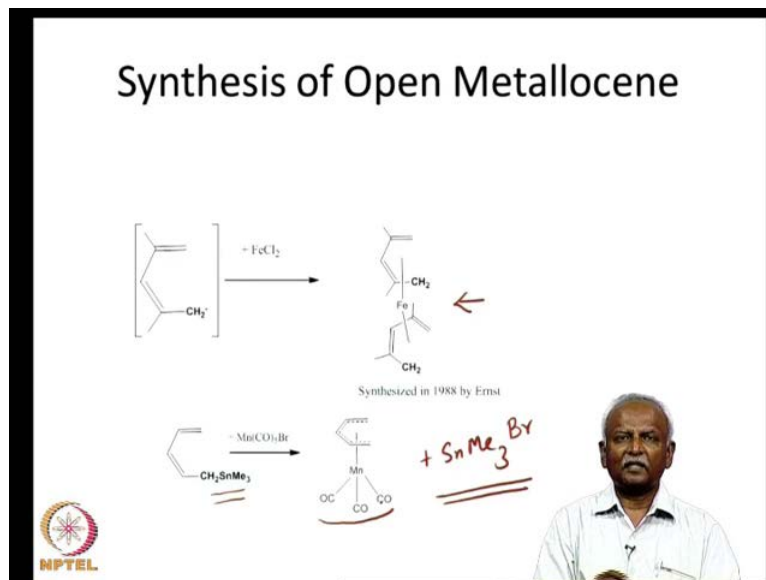


Now having talked about bent sandwiches, species which will encounter later, during catalysis. Let us take a look at, what would happen if you have a open sandwich. These are molecules which are not appreciated a lot, because you do not have a very stable cyclopentadienyl unit, which is aromatic. So, this cyclopentadienyl unit is aromatic. Whereas, if you have a acyclic version.

This is the acyclic version, then it turns out that this is not an aromatic molecule and so, but still, you do have situations, where you have cyclopentadienyl units, which are coordinated to the metal. And these are stable molecules, I have shown for you on the

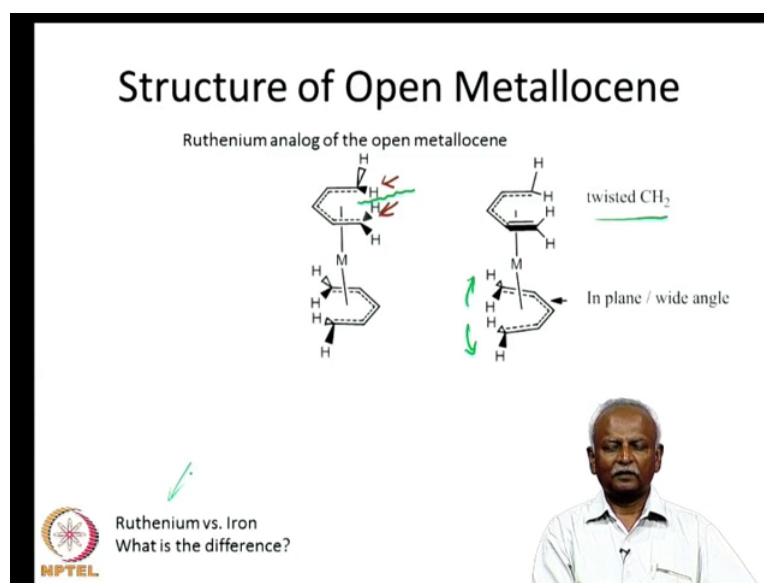
screen, a half sandwich complex. And we can also have this type of a complex, in a, this form, that means two acyclic cyclo pentadienyl units can coordinate to the iron or ruthenium, and those molecules have also been isolated and characterized.

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Let us take a look, brief look at, why these molecules would be different from the cyclopentadienyl molecules. If you treat FeCl_2 with the cyclopentadienyl anion, you end up isolating, a well characterized molecule which is exactly like ferrocene, but it is not as stable as ferrocene because of its open structure. You can also form a half sandwich complex by treating, a thin substituted molecule. So, here you have MnCO_5Br and SnMe_3 reacting together, to form SnMe_3Br . So, you end up with, a cyclopentadienyle unit, sorry, you end up with acyclic pentadienyle unit, which is coordinated to the manganese. So this is the acyclic variety of cymantrene.

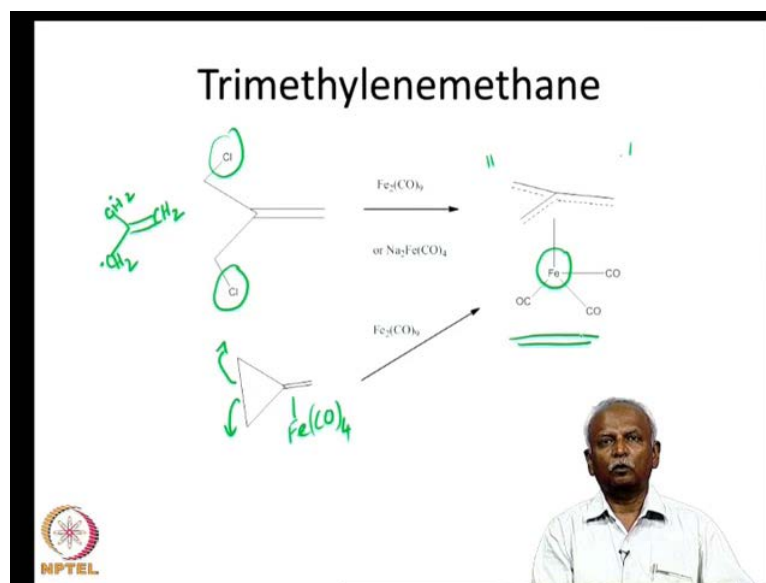
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So, these molecules are not, as stable as the cyclic variety, for two simple reasons. One is a fact that, the cyclopentadienyl unit has got a covalent bond between carbon atoms, one and five. Here the covalent bond is being replaced by two hydrogens. So here are the two hydrogens, and they are pointed towards one another. So as a result, there would be repulsion between the two hydrogens. Let us just indicate the repulsion with different colour here.

So, this is the repulsion that is going to happen, the place where the repulsion happens between the two hydrogens. To avoid this interaction, you would either have to twist the CH_2 group or you would have to widen the two ends of the pentadienyl unit and both of these movements, of these cyclic π systems, would destroy the metal interacting with the π bonds. So what will happen is that, you will end up, weakening the metal pentadienyl bond, and it would make the pentadienyl unit more reactive. And that is probably one reason, why ruthenium complex has been isolated and characterised crystallographically and has been found to be more stable than the iron system itself.

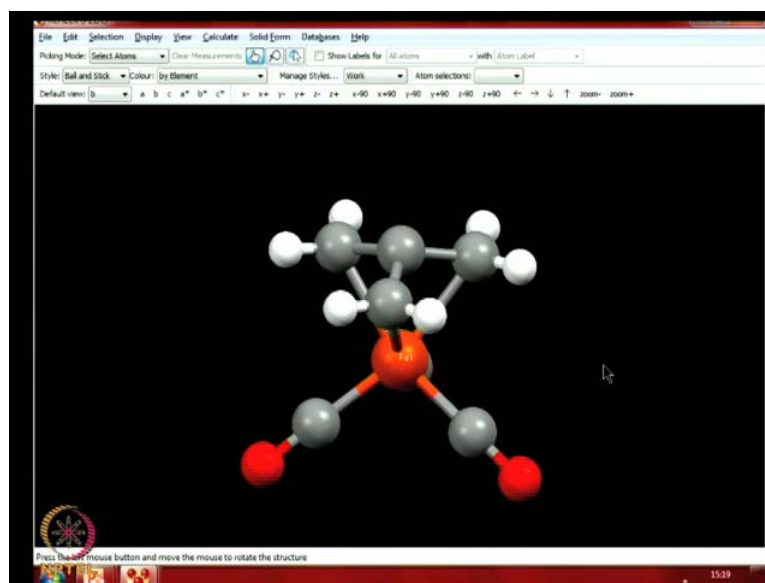
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It is possible to make pentadienyl complexes, but it is possible to make a bifurcated pi system. Here I have shown you, trimethylenemethane. And the trimethylenemethane is formed, by reacting this allylic system. So here is a double bond, which is, here is a chloro atom, which is allylic or just adjacent to a double bond, there are two chlorine atoms. And this forms a y shaped molecule and if you remove the Cl as Cl dot, then you end up with a biradical. So, this is a biradical, which can now react with iron, and it forms a molecule, which is shown here. And this is called trimethylenemethane because, you have three methylene groups, there are three methylene groups, which are attached to the central carbon atom.

So, these three are obviously, in resonance and equivalent. And you can coordinate it to, iron tricarbonyl molecule. Now, you can also do this by, without doing an oxidative addition, you can do a ring opening reaction, where the ring opening reaction can happen by, the coordination of iron tetra carbonyl unit to the double bond first, and then, that allows you to have a ring opening reaction and the trimethylenemethane tricarbonyl complex is formed.

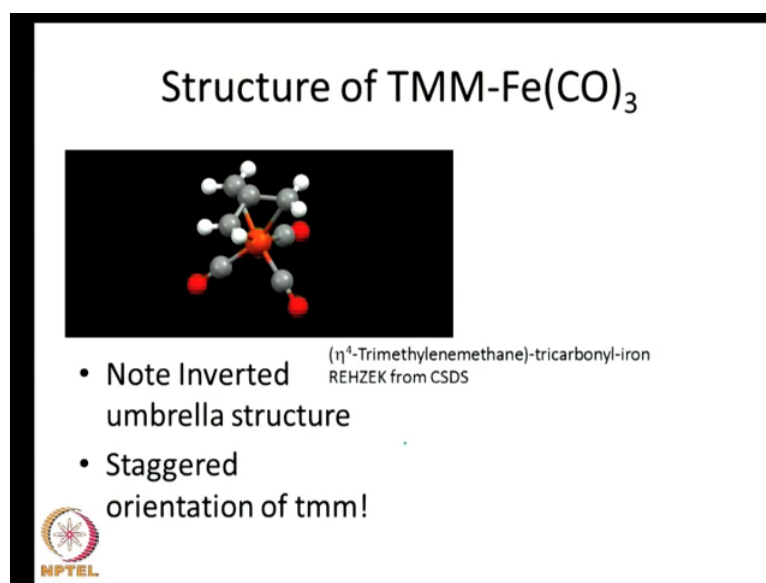
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I will show you this complex. Here is the iron tricarbonyl unit coordinated to a trimethylene methane. Now, you will notice that, there are four carbons which are marked here. These are the four carbons. All of them are within the bonding distance of the iron atom, which is shown here. So, the iron atom which is marked in red, is almost equidistant with all the four carbon atoms, but the central carbon atom is slightly above the plane, which is formed by the three other carbon atoms, which are closer to the iron atom.

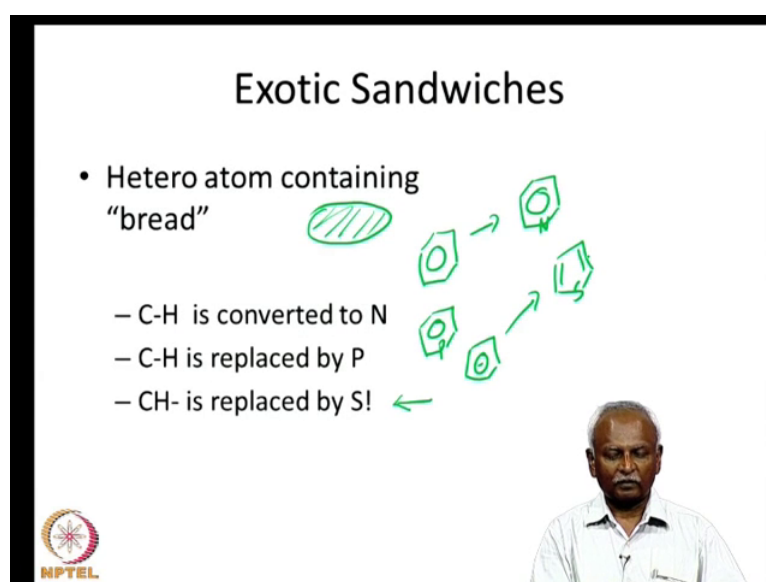
So, three carbon atoms are closer and the central carbon atom is in fact, slightly above the plane. And recently it has been shown that, the bonding nature of these iron, this iron tricarbonyl unit to trimethylene methane is quite interesting. And it is a very interesting molecule, where people have questioned the nature of the bonding between the central carbon and the iron atom. But nevertheless, the bonding distance happens to be slightly more here, the distance is slightly more, but it is still within bonding distance. So, this is the molecule which is called an inverted, it is almost like an umbrella, so it is like an umbrella which is coordinated to the iron tricarbonyl.

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So, let us proceed further now. This molecule is, got this inverted umbrella, or it is also in one sense, it is like an umbrella structure and it is got a staggered orientation of the three carbonyl units, with respect to the three methylene units. So, it is almost like octahedral geometry around the iron, if you consider the three carbons and the, the trimethylenemethane and the three carbons of the carbon monoxide.

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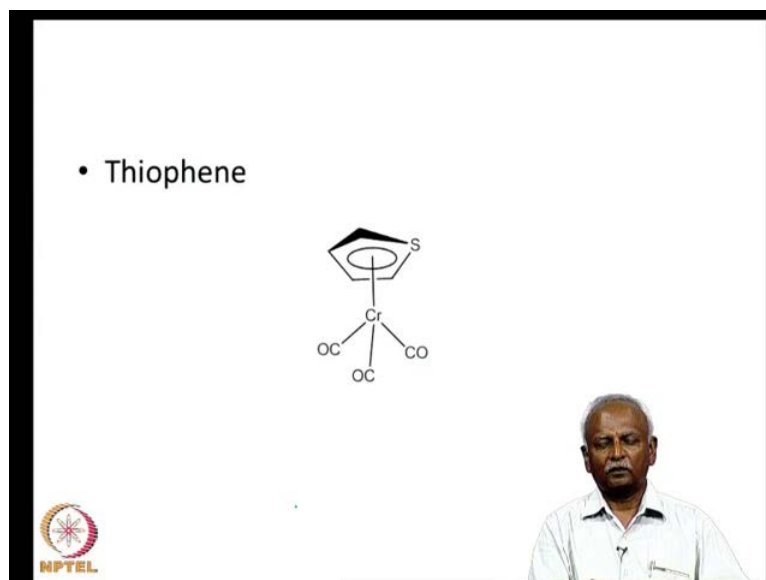


You could also have some exotic sandwich structures, where the heteroatom, which is the bread part of the sandwich structure that we are talking about. So the cyclic pie

system that makes the bread part can be different, it can be heteroatom and some of the simple replacements that we can talk about are, is converting this C H into N. So from benzene, from simple benzene, we can move on to peridene. So that will give you peridene complex, or you can replace it with a phosphorus.

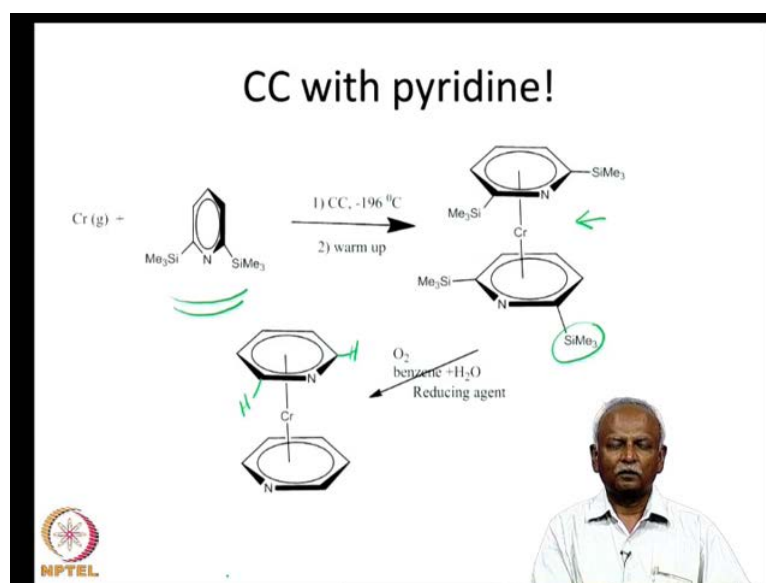
So, this will be phosphor benzene. So we can have phosphor benzene, which is coordinated to a metal atom. Now, it is also possible to replace CH by S. CH minus by S. So in other words, if you can have cyclo pentadienyl anion, you could convert it into thiophene. So there should also be a good replacement to do. So these are possible replacements and you can have these molecules, where you can have substitution, appropriate substitution to make sandwich complexes.

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Thiophene, can replace cyclo pentadienyl units. And here we have chromium, which is coordinated to thiophene and it forms a nice half sandwich complex. So, you can imagine how the cyclopentadienyl unit has been replaced by thiophene, to form this half sandwich complex.

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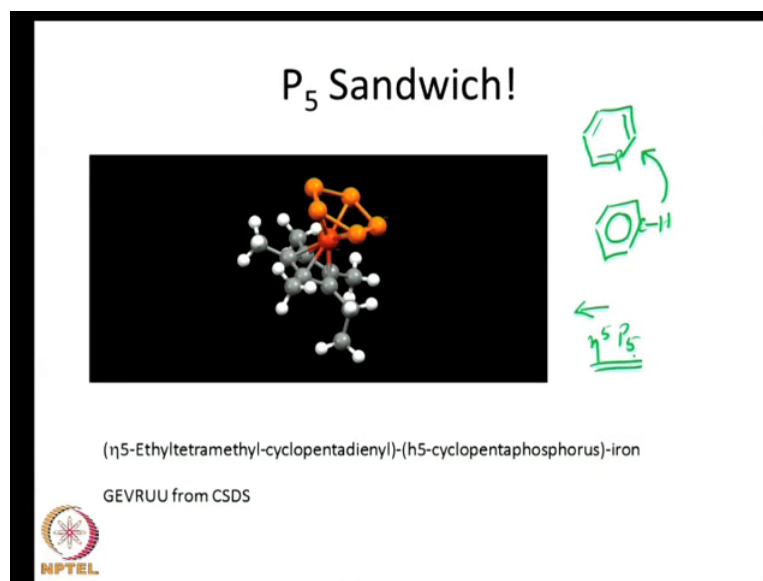


To make a complex with pyridine and, which, something that would be equivalent of this benzene chromium, it has been quite difficult. In fact it was, this was accomplished, fairly recently by ((Refer Time: 51:08)) and coworkers. What they did was, a co condensation reaction of this substituted pyridine, where the two orthopositions were blocked.

So much, so that the nitrogen was not able to interact with the chromium. so this pi system was now able to interact with the chromium in a high fashion, or in other words, it was forced to interact only in this fashion where it forms a sandwich structure. And after the sandwich structure was formed, the SiMe₃ groups were oxidatively removed. Just by bubbling oxygen into a benzene water mixture of this molecule, it was possible to knock off these SiMe₃ groups and replace them with hydrogen.

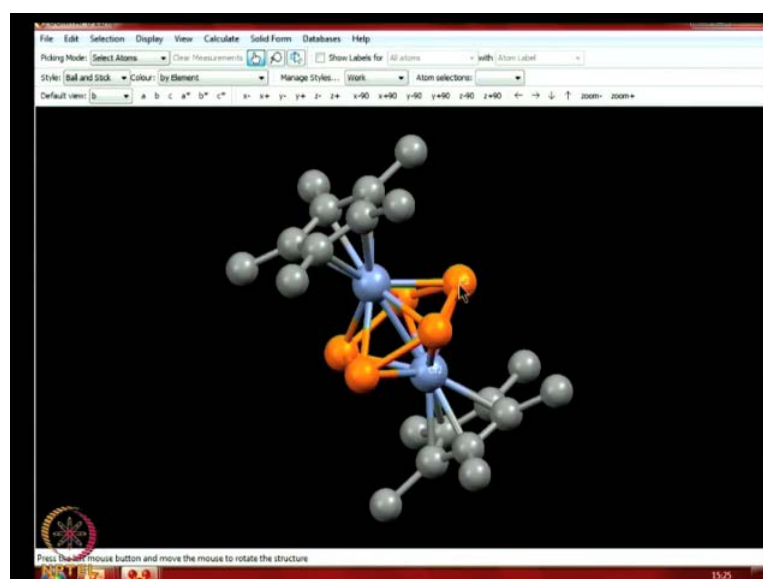
So, these hydrogens were generated from this water molecule, were taken from these water molecules, and you have this nice sandwich structure, where the pyridine is not coordinating with nitrogen. Otherwise it was not possible to make complex, simple complexes of a pyridine, which were coordinated in this benzene type fashion.

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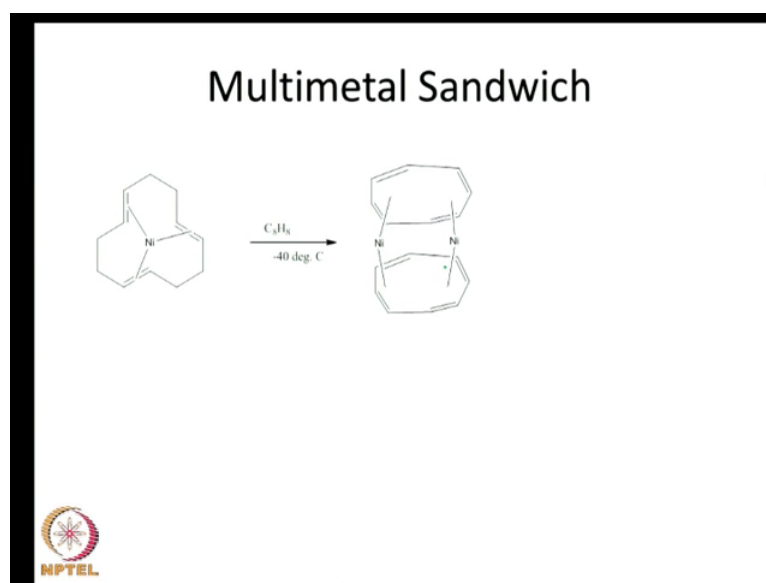
Now, I also told you about making P₅, phosphor benzene complex. Instead of making phosphor benzene, even more exotic structure would be, to replace all the molecules of, all the molecules, all the atoms of benzene, which are all CH units. If you can replace all the CH units with a phosphorus, then you would end up with a molecule which would be phosphor benzene, and in here, I have shown for you, phosphor cyclo pentadienyl system. So here you have eta five, P₅ unit. So let us take a look at some of these structures, because there are several structures where the CH unit has been replaced by a phosphorous molecule, phosphorous atom.

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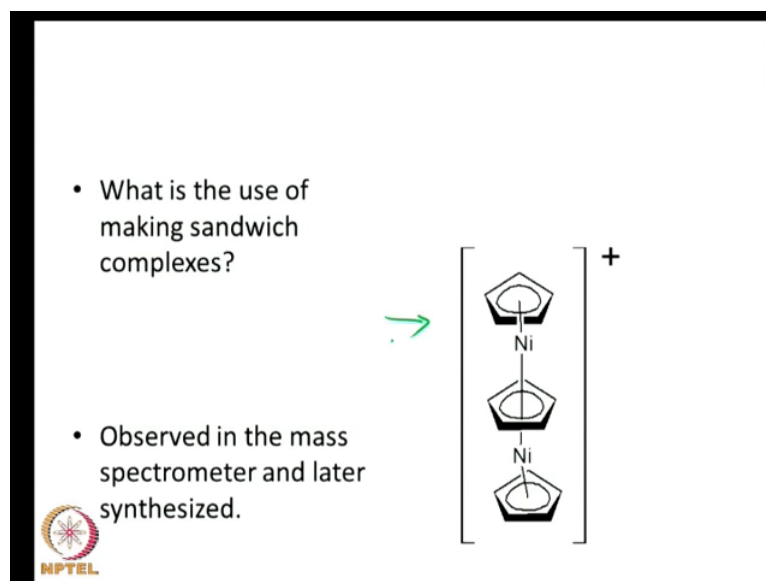
So, here I have shown for you, two chromium atoms, which are interacting with cyclopentadienyl groups here, on one side and five phosphorus atoms. So that is equivalent to C_5H_5 minus. So it is possible to make these molecules. So here is the other molecule, which is shown on the screen. Here we have five phosphorus atoms. So, we have five phosphorus atoms, which are substituting for five CH units and you can have isomorphous replacement over a CH group with a phosphorus atom.

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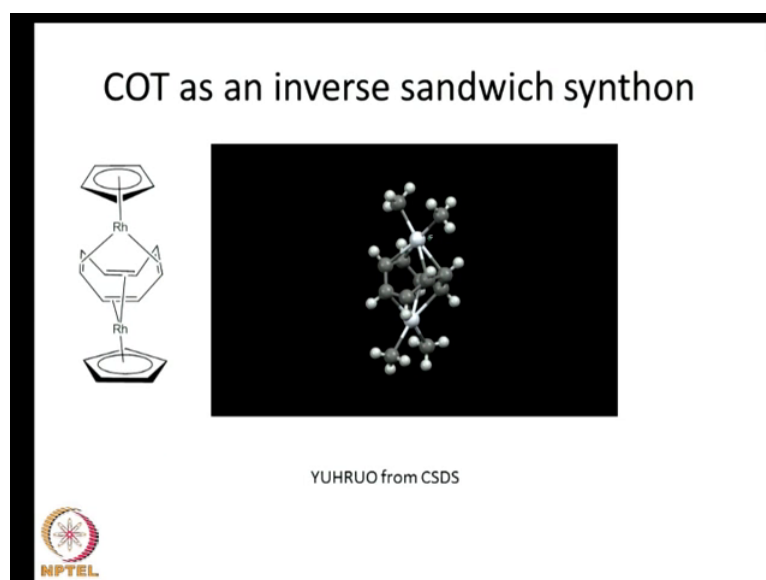
So phosphorus sandwiches are also known, it has also been possible to make, multiple metals coordinating to a single pi system. So here I have a replacement of cyclododecatriene, which is a weak ligand coordinating to nickel zero, by cyclooctatetrene, but because cyclooctatetrene needs less number of electrons. And you have more electrons in the nickel system, you ended up forming a sandwich, where you have more than one metal coordinated to the pi system.

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So, multi decade sandwiches are also being isolated and characterized, but this one was only isolated in a mass spectrometer, which was the first multi decade complex to be isolated, or multi decade sandwich complex to be characterized. Here, there are three nickel, two nickel atoms and three cyclopentadienyl units and has got a net charge of plus one.

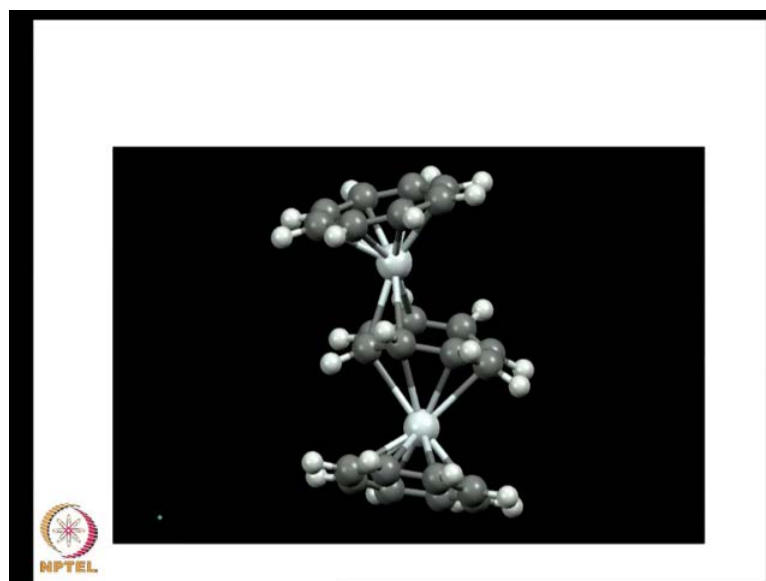
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Now, inverse sandwiches are also possible. Here I have a cyclo octatetrene, which is like a inverse sandwich synthon, because of the stub type structure, the two double bonds on

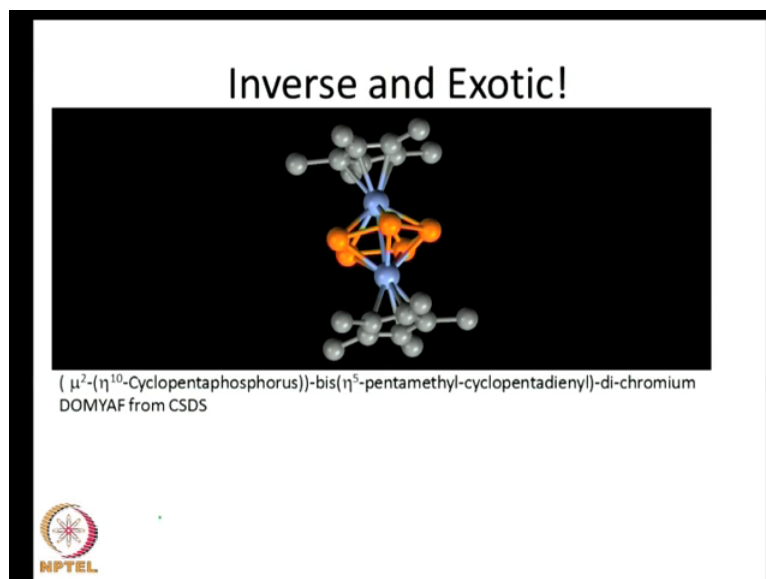
the cyclo octatetrene and can coordinate to one metal atom on one side, and the other side coordinates to another metal atom. I have shown for you on the screen, a structure where you have a metal atom on one side, which is coordinating to, two legands on one side, and the two double bonds are coordinated to the metal atom, which is indicated in the centre.

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So, you have a variety of systems. Here again I have a cyclooctatetrene, which is forming a multiple sandwich type structure.

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You can see that, the cyclo octatetrene is a great synthon for forming multiple sandwiches and P 5 also turns out to be interesting system. Here, I have shown for you on the screen, a P 5 unit, which is coordinating on both sides, to two different metal atoms.

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Summary

- The sky is the limit!
- 18 electron rule is a great guiding principle
- The complexes are useful as catalysts as the “bread” is flexible and can change hapticity!



So, you can have very interesting structures indeed. And let me say that, sky is the limit for making sandwich complexes, and this is a place which is being actively pursued. Most of the time, the eighteen electron rule is a great guiding principle for making the right type of a complex and making, choosing the right of the synthesis. And, very often, it is possible to change the pi system according to your convenience, so that you achieve the right electronic structure. So with this, we will go onto the reactivity of these molecules.