Introduction to Organometallic Chemistry
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Lecture - 26
Eta Six Arene Metal Complexes

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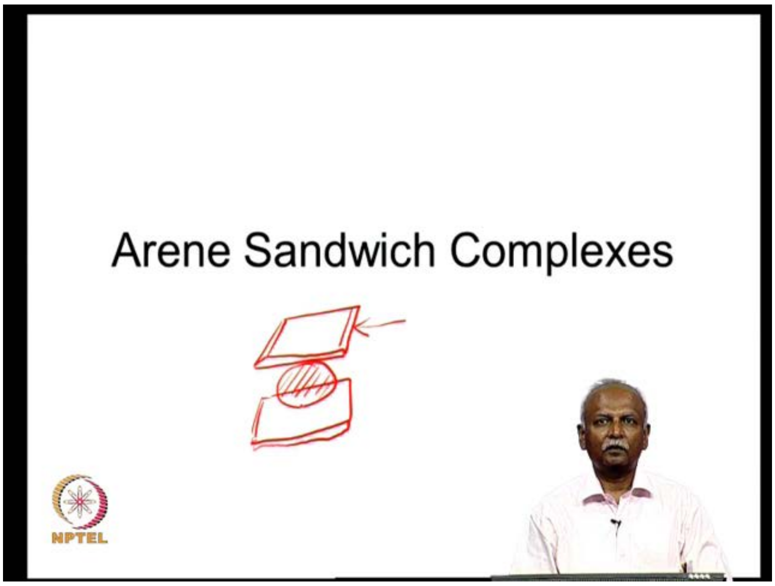

Arene Sandwich Complexes

In this lecture we will discuss arene sandwich complexes. The analogy to sandwiches because an arene ring or a site click pi system is a flat object pretty much and between two flat objects you have a metal atom, which is sandwiched between the metal atom, is sandwiched the two flat objects and. So, we call this a sandwich complex. One often encounters cyclopentant diagonal sandwich complexes and the next probably the most common sandwich complex is the arene complex, where you have a benzene or benchnoied ring which is sandwiching a metal atom.

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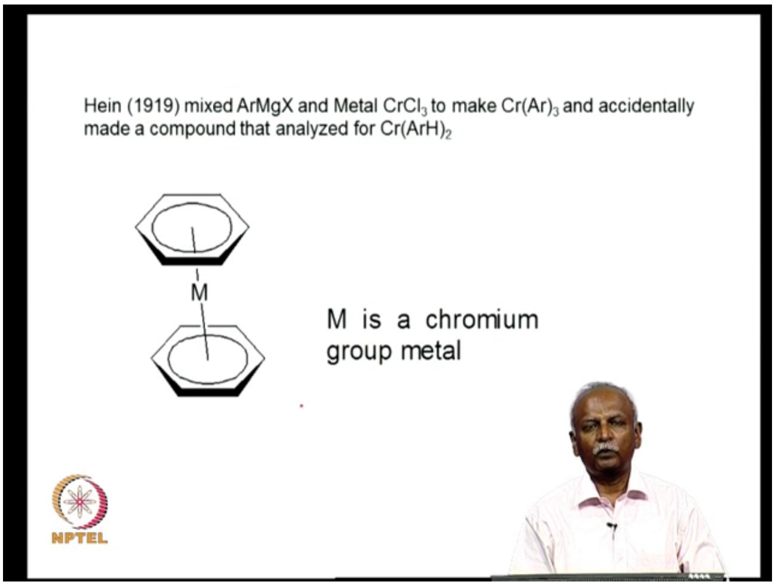

Hein (1919) mixed ArMgX and Metal CrCl$_3$ to make Cr(Ar)$_3$ and accidentally made a compound that analyzed for Cr(ArH)$_2$

M is a chromium group metal

The first time someone made a sandwich complex, although not intentionally was as early as 1919 and that is when Hein mixed Grignard agent and chromium trichloride and he isolated a compound that analyzed for dispensing chromium. Now, there are a lot of complexes where the two arene brings or the pie layers are surrounding a metal atom and metal atom happens to be the chromium metal shields. So, we will see little later why this is the case and why it is stable when you have the chromium group metal atom in between the two sandwich slices.

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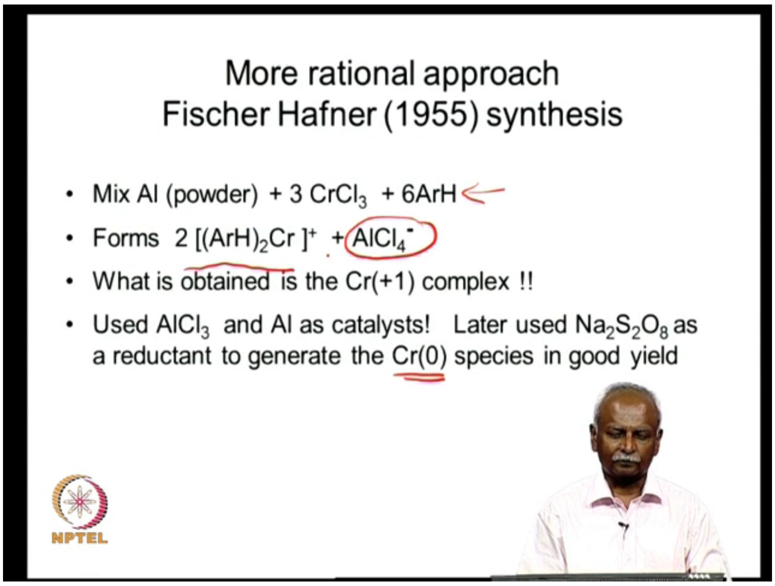

More rational approach
Fischer Hafner (1955) synthesis

- Mix Al (powder) + 3 CrCl$_3$ + 6ArH
- Forms 2 [(ArH)$_2$Cr]$^+$ + AlCl$_4^-$
- What is obtained is the Cr(+1) complex !!
- Used AlCl$_3$ and Al as catalysts! Later used Na$_2$S$_2$O$_8$ as a reductant to generate the Cr(0) species in good yield

So, more rational synthesis of question emerged after the synthesis of phorosene and analysis of the structure. Fischer realize that it is possible it should be possible to make metal complexes, where a benzene ring would be used in several ((Refer Time: 02:24)) which is of course, aromatic and is having six by electrons, who the two systems cyclo and benzene ring should be isolable or similar enough to replace one another. So, Fisher Hafner synthesis as it is called was carried out in 1955 and directed by Fisher.

It was simply release reaction in which aluminum powder and chromium trichloride were used in the presence of an aromatic ring. That is the aromatic ring that some limitations will come to that and what was formed in the reaction mixture was in fact the cationic form of the sandwich complex. So, this is a cationic form is a sandwich complex that was isolated as A l C l 4 minus salt, but then it had to be reduced because it was the chromium of class one state. It had to be reduced and this was done using N a 2 S 2 O 8 and generated chromium zero complex in fairly good yield.

Aluminum trichloride in fact was used as a catalyst and also serves as a suitable way by which you can form a large anion, very often the larger the anion the better it is when you have a very large cat ion to stabilize the crystal structure. So, this is how the first Fisher Hafner synthesis was carried out. There are some serious limitations for the special Hafner synthesis.

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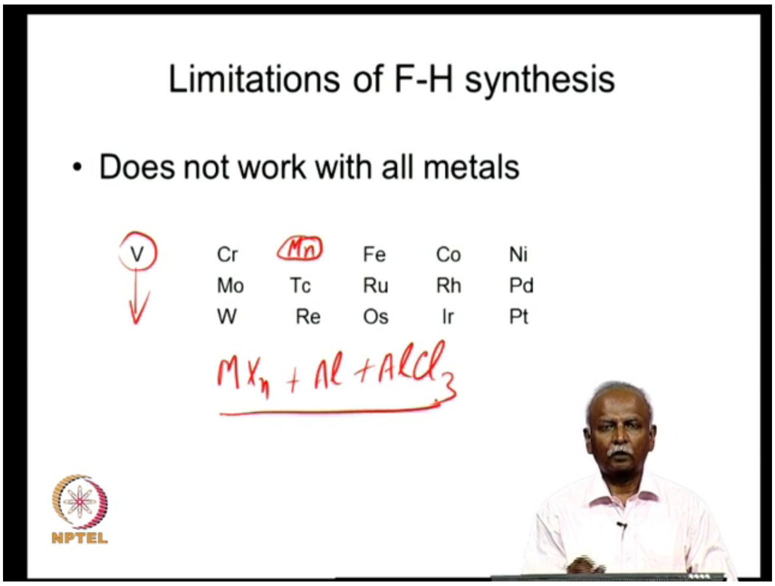

Limitations of F-H synthesis

- Does not work with all metals

V	Cr	Mn	Fe	Co	Ni
	Mo	Tc	Ru	Rh	Pd
	W	Re	Os	Ir	Pt

$MX_n + Al + AlCl_3$

There are limitations in terms of the metal it works pretty much most of the metals in the transition series, but there are some surprising gaps. For example, manganese, manganese is a metal atom which is not found in this series. So, also the vanadium series only vanadium is a suitable candidate for a metal in this Fisher Hafner synthesis. So, you take the metal chloride, and then reduce it with aluminum reduce it with aluminum in the presence of A l C l 3. So, that is the Fisher Hafner recipe for making a metal sandwich complex with arenes.

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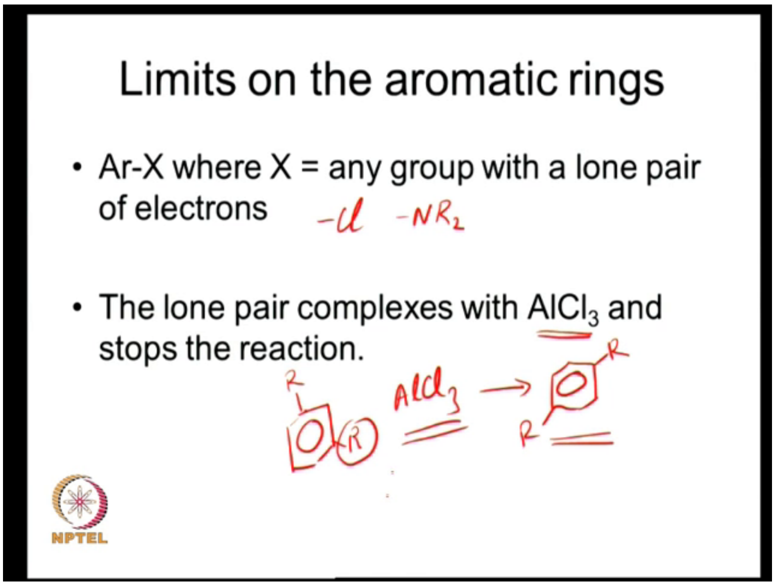

Limits on the aromatic rings

- Ar-X where X = any group with a lone pair of electrons $-Cl$ $-NR_2$
- The lone pair complexes with $AlCl_3$ and stops the reaction.

Now, apart from the fact that you have some limitations in the metal, there are also some limitations on the type of aromatic rings that you can use for making the metal scene complexes that we are talking about. Whenever there is a substitution on the aromatic ring, if it has a lone pair intends to coordinate to the aluminum and it stops the A l C l 3 from functioning. As a result you cannot use aromatic compounds which have got lone parable electrons.

So, that means the cloro group and the N R 2 groups cannot be used as a substituent's any halogen or any amine cannot be used if the aromatic ring will become inactive. Now, the reason for this is a given here, it is the coordination of such groups A l C l 3. There is also another set of compounds which will stop the reaction or cost complications and that are the presence of an alkyl groups on the benzene ring. Surprisingly because this alkyl group and A l C l 3 are the right combination for doing a retro fringe reaction.

If you have a couple of alkyl groups you could have isomerization reactions. So, you might end up with molecules which usually started out with peta or also and you might end up with para substituted. The alkyl para substituted aromatic drain as the red part of the sandwich.

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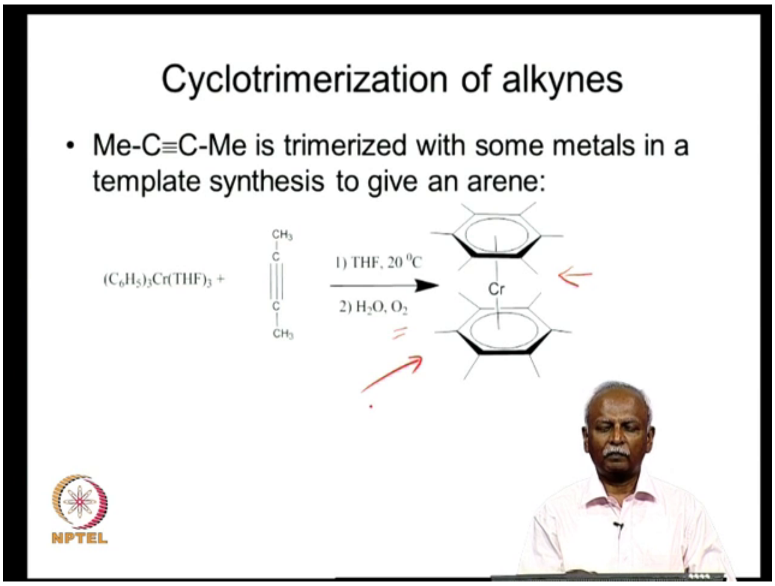

Cyclotrimerization of alkynes

- Me-C≡C-Me is trimerized with some metals in a template synthesis to give an arene:

So, there are some limitations in terms of the Fisher Hafner synthesis, but it is still one of the simplest and most convenient ways of generating a aromatic sandwich complex metal sandwich complex. One can imagine a reaction between an alkaline and here I have shown you an alkaline simple alkaline reacting with a chromium senile compound that is C 6 H 5 tries chromium reacting with this dimethyl acid link, to give you hex methylbenzene, complex to the chromium.

In a sense this is a templated reaction where in the coordination sphere of the metal which is chromium, the three dimethyl acid lanes are trimerised. You end up with the hexa methylbenzene as the as a aromatic ring system which is sandwiching the metal. So, you also need little bit of oxygen required to carry out the reaction. It is not entirely clear how you would end up with an oxidation material, but you can readily produce it in the presence of sodium thiosulphate to back to the chromium zero species.

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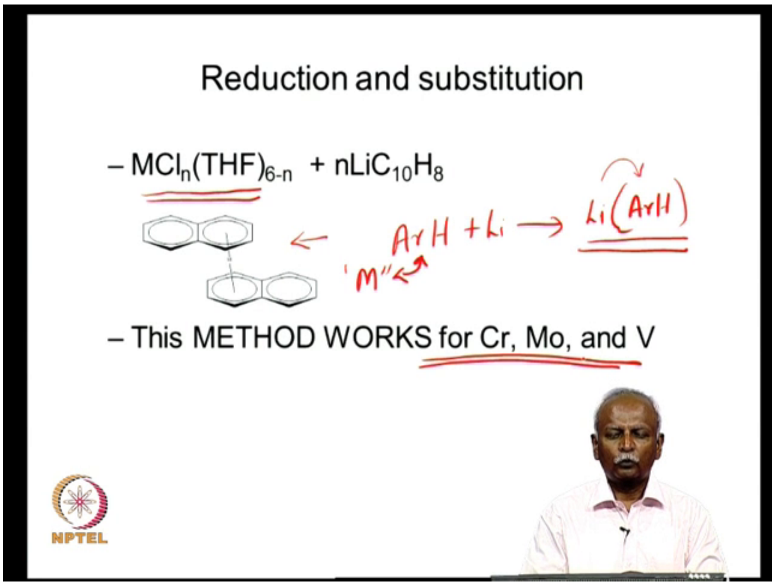

Reduction and substitution

– $MCl_n(THF)_{6-n}$ + $nLiC_{10}H_8$

– This METHOD WORKS for Cr, Mo, and V

So, here is another rational probably more rational way of making it, but it has got limitations because it will not work with benzene. If you have large aromatic systems which are unrelated rings then it is well-known that they stabilize electrons. You can in fact reflux sodium lithium preferably a lower boiling; lower melting alkali metal in the presence of an analytic ring and it generates highly colored solutions, where the electron has been transferred to the aromatic ring system.

So, if you have A r H as aromatic system and lithium and you are heated then you end up with a l i complex to this A r H which will presumably the electron is in fact has been transferred from the lithium to A r H. You can now use this as a reducing agent because it is the source of electrons and reduce metal halide. So, you take metal halide which is complex and conveniently complex with T h F, it dissolves them and tetrahydrofuran, then you can reduce them with this lithium salt.

It is literally solvated electron where the solvent is naphthalene. So, what happens is you end up with the reduced form of the metal in the presence of A r H and the reduced form of the metal is a very reactive state. So, it reacts with the aromatic ring fairly easily and generates a sandwich complex. Now this method is most suitable for the early transition metals right next to chromium molybdenum for which of course, the most number of sandwich complexes are known.

So, you can see that the reduction and substitution is also a fairly common synthetic methodology that is employed from making a variety of gram tally compounds. Any time you need organovetlic compound, you realize that there has to be a low oxidation state metal. And so you generate the oxidation state metal using a suitable reducing agent. And if you have an organic ligand in the presence of this as the reaction is being carried out, you can capture the Novell and metal. In this case it is metal zero in the presence of your organic ligand to generate the complex.

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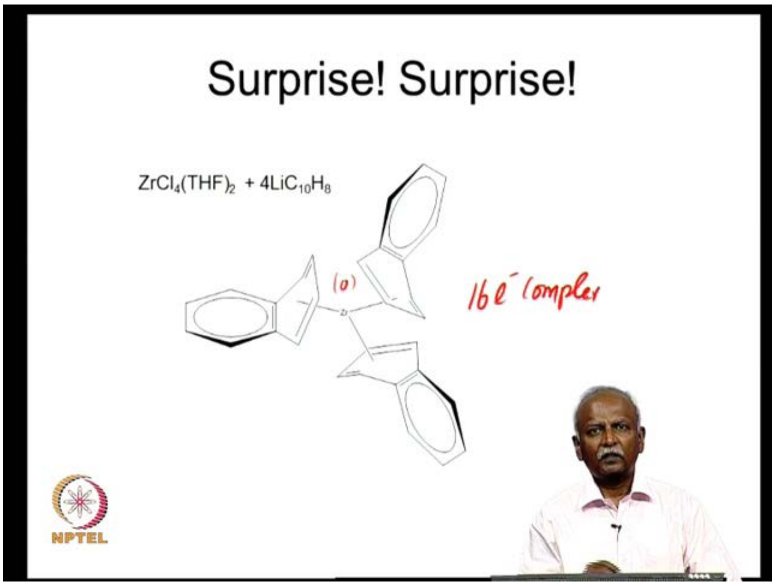

Surprise! Surprise!

$ZrCl_4(THF)_2$ + $4LiC_{10}H_8$

So, it is not divide the surprises. Here is a surprise, which should have generated the base naphthalene zirconium compound, but surprisingly it generates a very strange compound. And you do not have Arlene rink, but you have the naphthalene which is a kind of lost it is majesty in one of the links, so that two double bonds or conjugated dyne systems. Now, coordinating to the zirconium now, one can imagine why this would happen because if you have 2 naphthalene surrounding the zirconium you still does not have enough number of electrons.

We will come to that in a moment. And this can lead to an unstable situation and the formation of this trimetric trisnefthylene is Nichronium. And this here again zirconium is in the zero oxidation state and it is got 4 into 3 4 pi electrons and 3. So, a total of 12 electrons donated to the zirconium. Totally zirconium had 4 electrons and so this is a 16 electron complex. So, let us proceed further.

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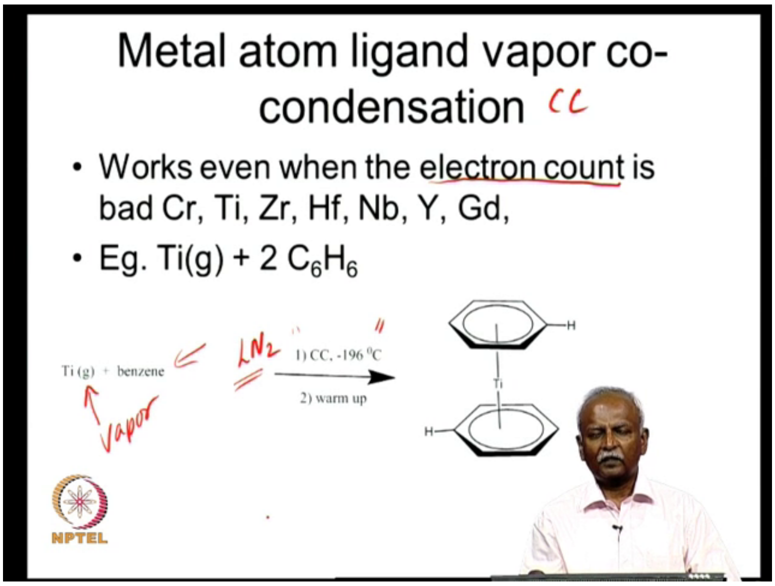

Metal atom ligand vapor co-condensation CC

- Works even when the electron count is bad Cr, Ti, Zr, Hf, Nb, Y, Gd,
- Eg. Ti(g) + 2 C_6H_6

With the most convenient way of the most general method for making sandwich complex between arena ring and metal turns out to be the co condensation technique. The co condensation technique very often abbreviated as CC. Co-condensation technique works even when the electron count is not appropriate. So, even if you do not get anything electron complex by using the arene ring and the metal you will still form a nice sandwich complex as a result of this reaction.

This reaction turns out to be a reaction where you have the metal in the vapor state the vaporized metal. And the aromatic ring also as a vapor, which is condensed onto the sides of the vessel will show a schematic diagram of the imminent. And these two are allowed to react at a very low temperature at the temperature of liquid nitrogen. This is typically a liquid nitrogen temperature that is used and then one slowly warms up the reaction mixture and ends up with very nice sandwich complexes, which are pictured here.

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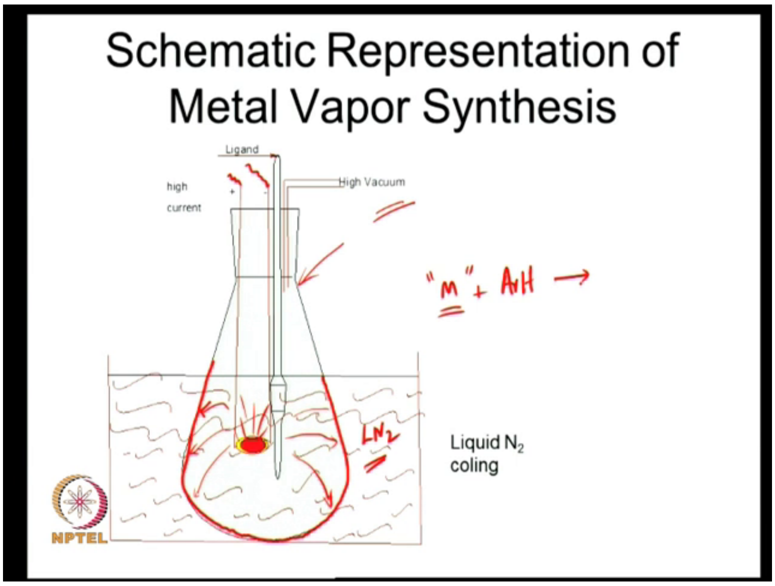

Schematic Representation of Metal Vapor Synthesis

So, this turns out to be an extremely general method. Here is a schematic of a schematic diagram of this setup. You have a way to vaporize the metal under very high vacuum this whole reaction vessel is kept under very high vacuum. And that temperature when you have a very high vacuum, you can now pass the ligand, so that the ligand is now quoting the sides of this vessel.

So, if you have a very thin film of the ligand coating the vessel and this you have done at very low temperature, this is liquid nitrogen as i told you and are very high vacuum. You can evaporate a variety of ligands and then if you resistively heat metal like chromium then, you tend to have vaporization of the metal. So, this vapor tends to grow and law itself in the sides of the vessel and that is what will happen when you start heating this resistibly.

So, here you can see the red hot metal, which is getting vaporized and it goes on deposits itself in the sides of the vessel, which is at a very low temperature. So, now what happens is you have a vapor of the metal condensing on to the sides of the vessel, which already has the aromatic ligand. And at that temperature when the metal has got nothing else as to satisfy with electron count to get an octets and you have only the aromatic species, which is present in the medium. Then you tend to have a reaction very convenient reaction between the two, which leads to the formation of sandwich complexes.

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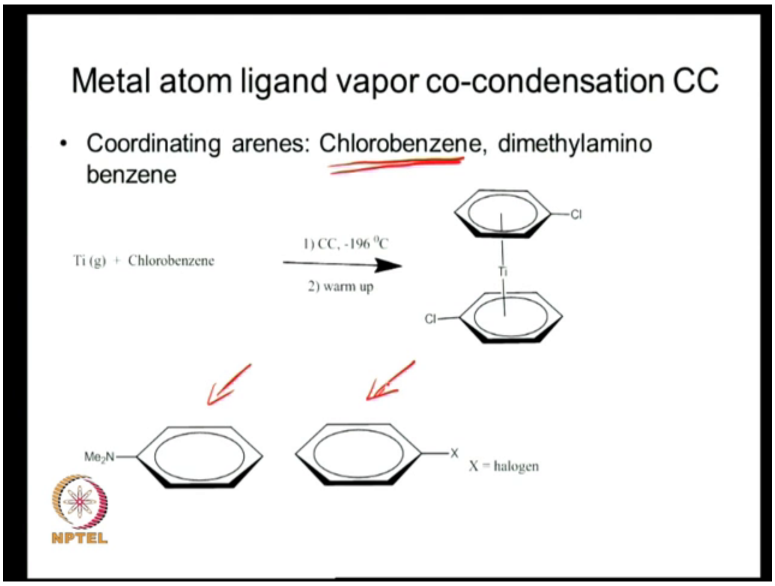

Metal atom ligand vapor co-condensation CC

- Coordinating arenes: Chlorobenzene, dimethylamino benzene

Now, the interesting thing is you can even use compounds like Chlorobenzene or dimethylamino benzene as suitable substrates for this co condensation technique. Here you do not have the complication of requiring Aluminum tri-chloride in the reaction mixture. So, you can mix the two species conveniently even if it is a very strong ligand for aluminum chloride. Here you can use them in the co condensation technique and form nice sandwich complexes.

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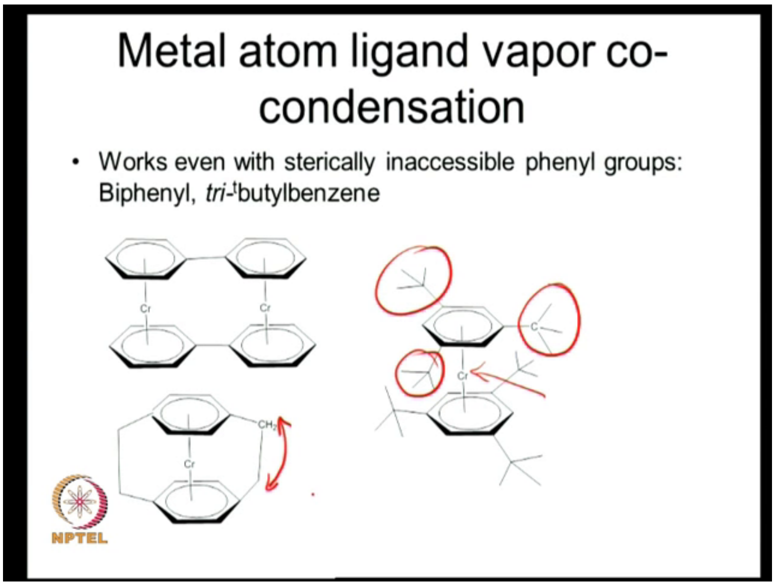

Metal atom ligand vapor co-condensation

- Works even with sterically inaccessible phenyl groups: Biphenyl, *tri*-ᵗbutylbenzene

Now, using the metal ligand vapor co condensation technique you can also use a ligand, which are strictly constrained. Here are couple of examples where you have the metals sandwiched between two aromatic pie systems where, the aromatic pie system is constrained either by an alkyl chain. As we have not pictured here you have an alkyl chain which is constraining the two of pie systems or you have tri-butyl groups.

So, these are very bulky trash in butyl groups, which are present on aromatic ring system. And still you managed to push in chromium between the two ring systems. So, these are systems where you have difficulty in making these molecules with the traditional Fisher half synthesis, but using the metal vapor co condensation technique, you have generated the metal complex rather readily. Much of this work was done by one of the students of a Fisher, who originally initiated the Fisher half synthesis and that is ancient ((Refer Time: 17:28)) who worked in Marburg. And he was responsible for making a large number of metal sandwich complexes using the co condensation technique.

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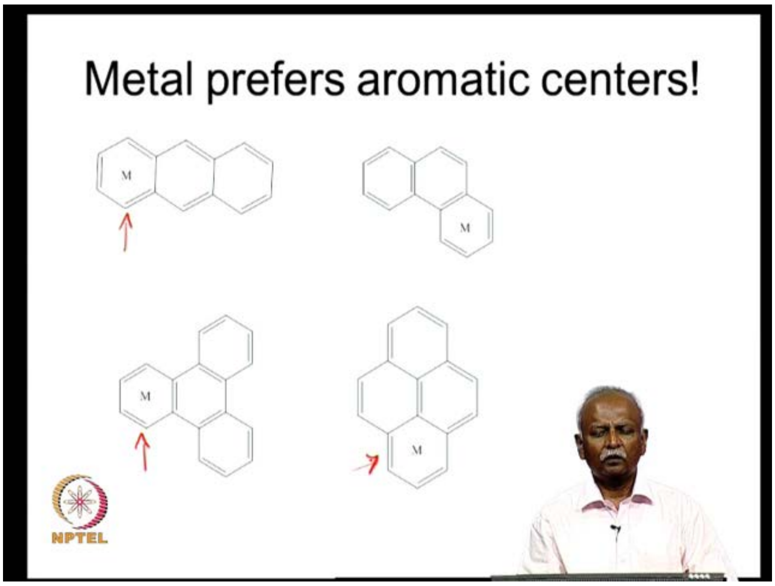

Metal prefers aromatic centers!

I mentioned that a variety of aromatic ring systems can be used in fact unrelated ring systems were very commonly used for these are metal co condensation techniques. And when there is a choice the metal tends to prefer the aromatic ring rather than a ring system, which has got only partial aromatic testing. So, here are a series of ring system where, the aromatic is more complete in the terminal ring and that is where the metal ends up. So, you can see that the metal prefers some of these rings, which is got greater majesty than the middle ring which is got lesser testing. So, this brings us to the end of the synthetic section for these molecules. And now let us talk about the bonding and the structure in these molecules.

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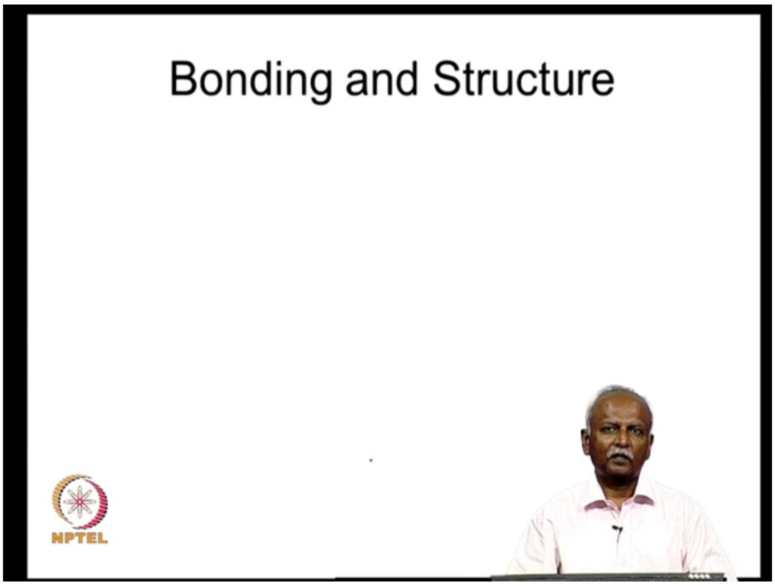

Bonding and Structure

Now, it turns out that the type of interaction between the metal and the benzene ring is best explained by using the molecule of green theory of the molecule framework. So, we will use that and what we are going to do is to use a technique called at giving the ligand group orbitals. And we will do that using a particular orientation of the metal and the ligand. Here I have shown you the M O treatment of the metal ligand in this particular orientation and unique. And you need to remember this orientation always if you have to understand the type of interaction represent.

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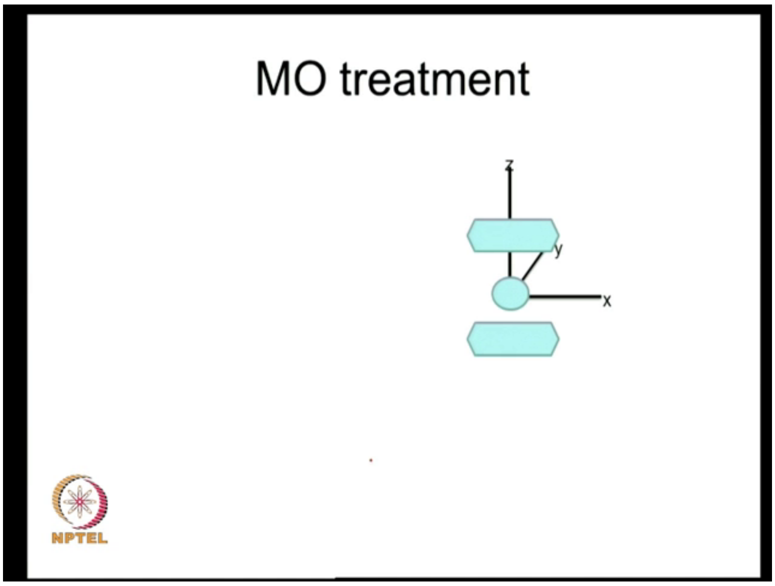

MO treatment

The metal is present at the origin of the Cartesian coordinates. So, that will be a 0 0 0 and the two aromatic ring systems are parallel to the x y plane. So, one of them is displaced along plus z axis and the other aromatic ring system is displaced along the minor z axis. And it is parallel to the x y plane; the ring system is parallel to the x y plane.

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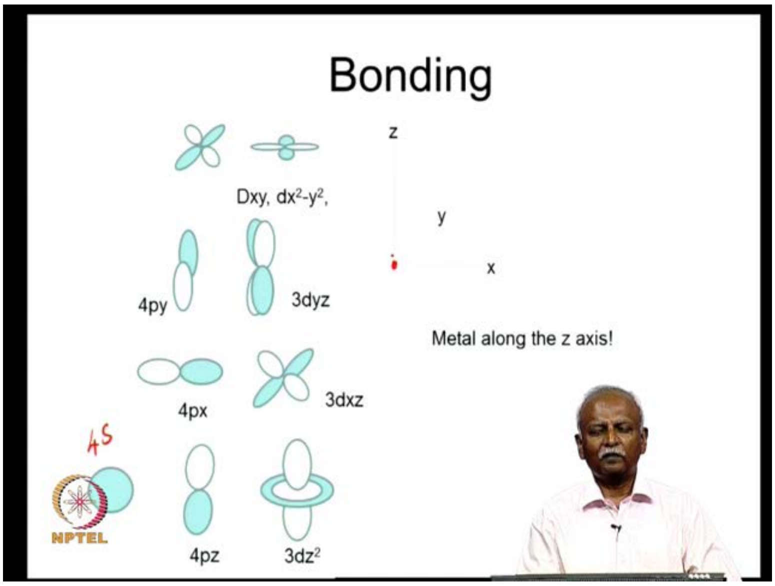

Bonding

Metal along the z axis!

So, let us take a look at the metal d orbital’s refresh our memories. So, here we have the 4 S, if it is the earth 3 d series with 3d transition to announce. It will be the 4 s, which has the 4 p x 4 p y and 4 p z and the 5 d orbital’s which are the 3 d series. So, here the orbital’s also listed and now what we have to imagine is to imagine the presence of these orbital’s at the origin of the Cartesian coordinates. And then see how they will interact with the benzene ring. So, the Frost energy level diagram is a convenient way of generating the various energy levels of an aromatic pie system.

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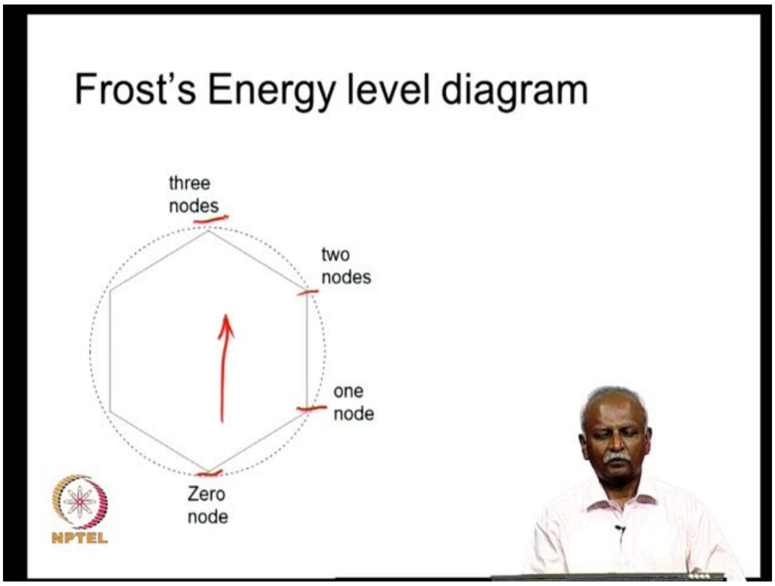

Frost’s Energy level diagram

You will remember that the number of nodes has to keep increasing as you go up in energy. As you go up in energy in the Frost diagram you go from zero nodes to one node to two nodes to three nodes. So, even without solving the vocal molecule orbital you can fact write down the various notes that are available for benzene.

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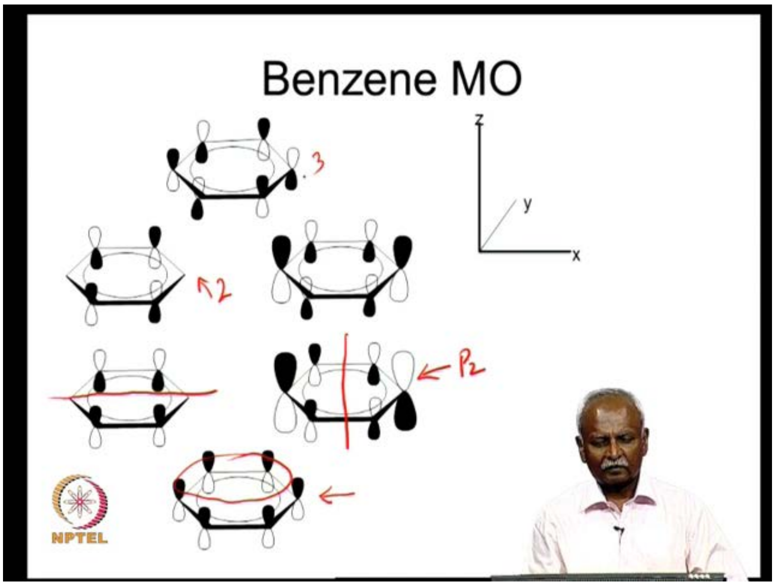

Benzene MO

Today we are going to discussed benzene and so here is the MO of benzene, a pictorial representation of molecules orbital of benzene. Now, the pie MO is formed if I have oriented them correctly along x y plane. The pie orbitals will be completely made up of p z orbitals. So, the p z on each carbon will be contributing to the pie molecule orbital framework of the benzene ring.

So, here is a benzene lowest energy molecule orbital and that has got all 6 p orbitals of aligned together, so that they have the right result oriented in the same direction and the same fields. So, that will form a very nice zero node molecule orbital, which is represented here. If you go to the next higher energy level, you now have a system where you have claimed a nodal plane, which is cutting across the benzene train and that is in perpendicular to one another, but along the x or along the y axis. So, you would now have two molecule orbital both of them having one node each and then the next molecule orbital will have two nodes. So, this will have two nodes and this will have three nodes and so on.

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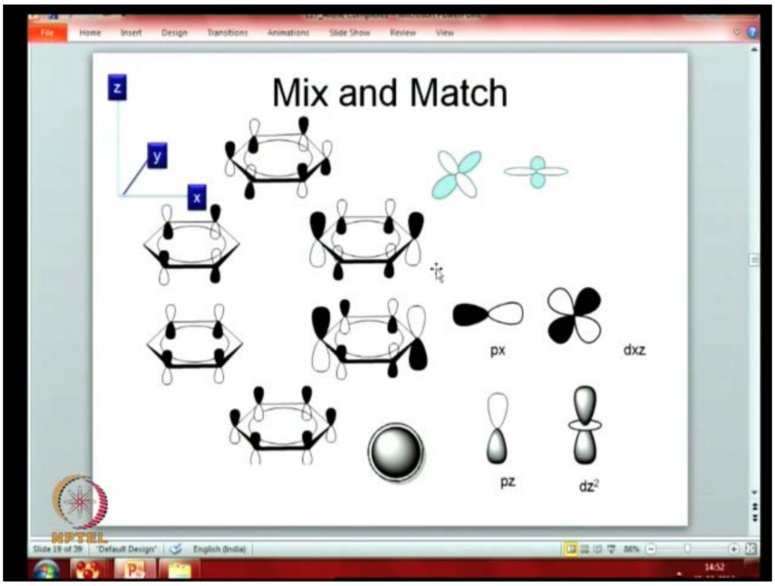

Mix and Match

So, let us proceed further. Let us take a look now how we can match these orbital’s one after the other. So, in order to do that I am going to switch the mode and show you how you can overlap these orbital’s. So, here is the 4 s orbital and if I place it in the centre you can see how that it will have the right orientation to overlap with all the six lobes of the p orbital. So, all the six lobes of the p orbital have the right orientation in order to overlap with the s orbital.

So, the s of suitable combination, 4 s suitable combination and similarly, the fourth p z if is the metal is placed at the centre of the ring that also has got a suitable combination and forms a nonzero overlap with the lowest energy molecule orbital. And the similarly, you can in fact use the three d z square orbital and that also has got the right symmetry to overlap with all the p z orbital’s of the benzene ring.

So, you can see there are three combinations that we can make with the metal orbital and the lowest energy molecule of globe benzene. Similarly, we can in fact overlap the p x orbital and here I am showing you how the p x orbital of the metal can overlap with the benzene ring orbital’s. The highest stock bed molecule orbital is degenerate and there are two number and the benzene ring metal orbital combination that is suitable is a p x and this side 2.

We can also in the same way you visit the x z. So, here I have shown you a combination of d x z. So, if I place the metal in such a way that the d x z can now overlap with the site

2 of the benzene ring. So, you can see that by suitable combinations of these molecule orbital’s of benzene and the d orbital’s and the p x orbital’s, you can form several molecule orbital’s. This particular molecule orbital is very similar to interactions that we showed here except that this now requires p y and the d y z. So, the d y z and the p y orbital’s will be suitable for interacting with this molecule orbital. In order to show the interactions with the next set of molecule orbital’s, I want to change over to another view.

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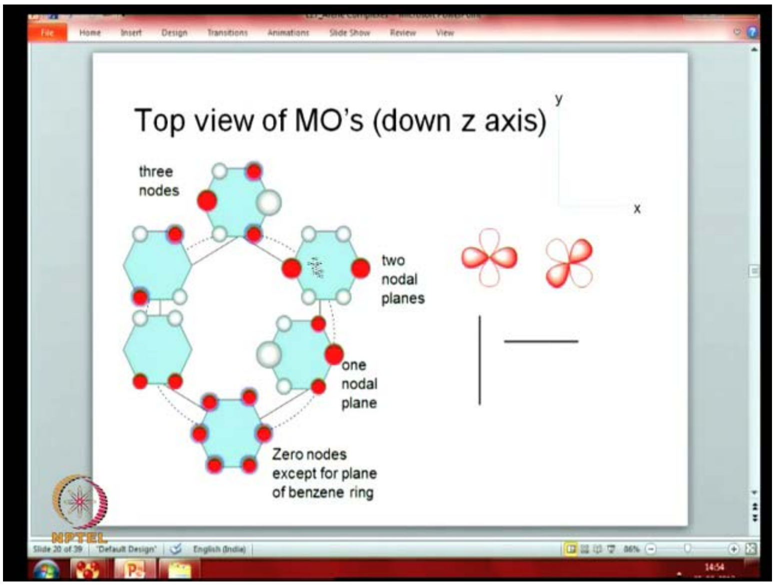

Top view of MO’s (down z axis)

Now, we are looking at the molecule orbitals from the top as if you looking down the z axis. So, this is the orientation with using, here is the y axis and here is the x axis. And now my benzene rings are in the plane of the screen and so these are the same molecule orbital that we looked at earlier. Now, just as shown in a different color, but nevertheless it helps you to imagine how psi 3 can interact with these of molecule orbital’s right here.

So, here is a suitable combination you can see this overlap is perfect when you have psi three and the d x y orbital and the d x squared y squared orbital is suitable for overlap like this. So, you can see that psi 3 and this is psi 4 psi 4 and psi 5 have got suitable combinations with a d squared minus y squared and d x orbital’s. Now, you will also notice that these metal d orbital’s are in the x y plane. So, they are in the x y plane and so the benzene ring is also parallel to x y plane.

So, these are weak interactions that are happening between the metal d orbital's and the pie orbital's of the benzene because although the pie orbital's of benzene appointed towards the metal d orbital's are from the same plane that is in the x y plane. So, you can see very clearly that the type of interactions that you have between the metal and the pie orbital's of benzene can be visualized by using a simple overlapping scheme like this.

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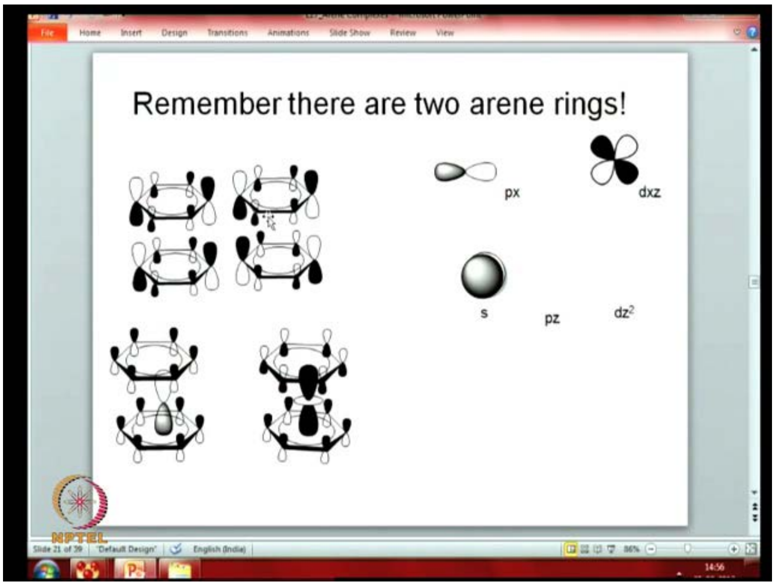

Remember there are two arene rings!

This leads us to draw a molecule orbital scheme where, you have interaction between the metal orbital's and the pie systems of the benzene. As I mentioned in the case of metal scenes, one should remember that there are in fact 2 benzene rings and they can be combined into different fashions. In one fashion you would have the lobes the same face lobes of the benzene ring pointing in the same direction. So, this is the orientation where they pointed in the same direction.

So, the clear lobes of the p z are pointed towards the shaded lobes of the p z. So, this is suitable for combining with the p z because I can place the metal p z orbital in such a fashion that on the top face, it will have the clear lobes interacting with the clear lobe of the p z and the shaded lobe interacting with the shaded lobes of the of the pie system in the lower plane. So, in the same fashion I can also interact this molecule orbital with the d z squared orbital because that will have the shaded lobes on both sides interacting with the shaded lobes of the metal atom.

So, you can see that whether it is s and d z square they will interact with this molecular orbital group of benzene ring. These molecule orbital groups of the benzene ring where the faces are pointed in the opposite direction that means the clear lobes are pointed toward the shaded lobes that will interact with the p z orbital. So, now in a similar fashion you can imagine the type of interaction that will be there between the p x and d x z orbital here. So, you can mix and match these molecular orbital's in such a fashion that you can have all of these 5 orbital's interacting with the s p and the d orbital's of the metal atom.

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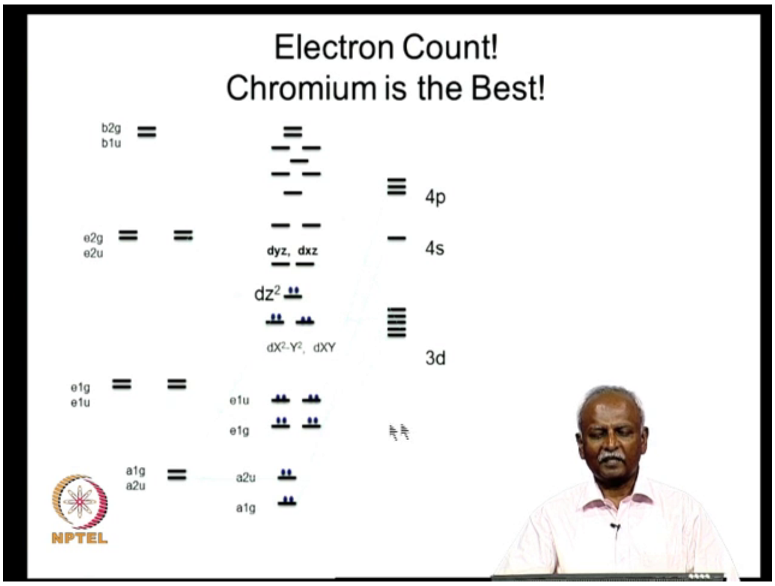

Electron Count!
Chromium is the Best!

So, this gives us now at complete molecule orbital picture an energy level diagram where, we have interact everything other than the highest unoccupied molecular orbital of the benzene ring that remains non-interacting. Everything else has got some interaction of the other although some of them are weakly interacting in a delta fashion. So, they have got weaken contractions, but all of them interact with one another and form this MO picture, which have drawn here.

You will remember that the benzene ring is got six electrons in each binary and, so 6 into 12 electrons will be filled up to this level. And from the metal one now needs to fill up only the molecular orbital's that are not destabilized. So, that turns out to be six electrons can be filled in these three orbital's, which are primarily metal character, but nevertheless they have interacted with the benzene ring and so they now molecule orbital’s.

So, as the original d x squared minus d x y which as explained to you just now, they are interacting in a weak fashion and so this stabilization is not too much and then the d z squared. So, if you fill up these MOs now you will end up with 6 electrons here. As a result you will have the most stable system where chromium and to benzene rings are interacting with one another. If you wanted d 6 systems, obviously you choose an element from the chromium group. So, this gives us a total electron count of 18 and so once again we encounter even in this arene metal complexes and electron count of 18 is ideal for forming a stable metal complex.

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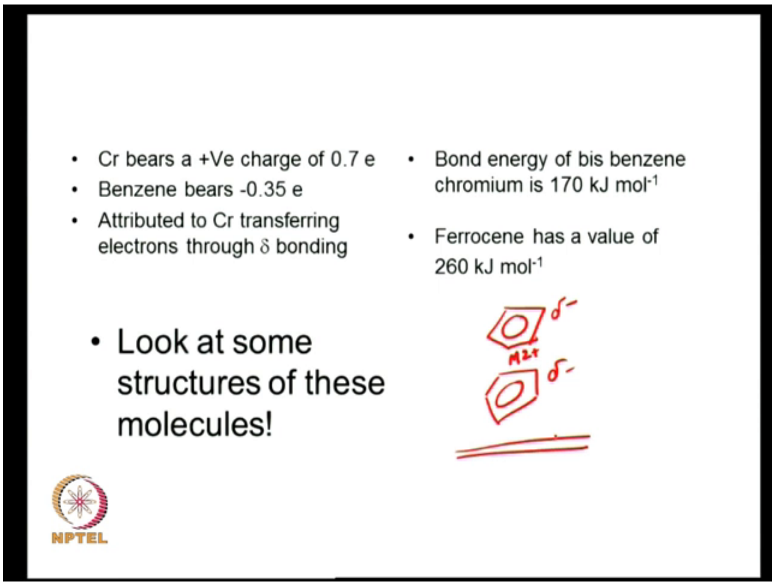

- Cr bears a +Ve charge of 0.7 e
- Benzene bears -0.35 e
- Attributed to Cr transferring electrons through δ bonding
- Bond energy of bis benzene chromium is 170 kJ mol^{-1}
- Ferrocene has a value of 260 kJ mol^{-1}
- Look at some structures of these molecules!

Sometimes the highest occupied molecule orbital reset d z squared can lose electron and the system is still stable because, the destabilization of the d z squared is not significant enough to make a great dent in the electronic stabilization energy. So, experimentally it has been found that this particular MO picture I showed you is the most satisfactory in terms of explaining all the characteristics that people has observed.

It is also interesting that the chromium there is a slight positive charge of 0.7 funds and the benzene ring bears a small negative charge, which means that the net transfer of electron density has happened from the metal to the benzene ring. Surprisingly, usually pointing expects the ligand and to give electron density to the metal. Surprisingly, in this case we have transferred electron density from the metal to the benzene ring and this small transfer of electron density is because of the transfer of electron density from each one of the metal filled orbitals into the benzene ring.

Especially even the delta bonding that we talked about earlier. So, one other factor before we look at some of the structures of these molecules is that the bond energy of this benzene chromium is 170 kilo joule per mole. And this is significantly less than what we have observed for ferrocene, which is stabilized almost 260 kilo joule per mole. So, you can see that the stabilization of benzene is significantly less.

And compare to ferrocene where you had significant electrostatic interaction between the metal and the ligand, which is negatively charged. Southern ligand was negatively charged in the case of the cyclopentadianyle cases. You have a large negative charge on the ring system and the metal very often was a two plus cation. So, this was the stable system whereas, in the case of this benzene chromium you have lesser stability. Let us take a look at some of those molecules now.

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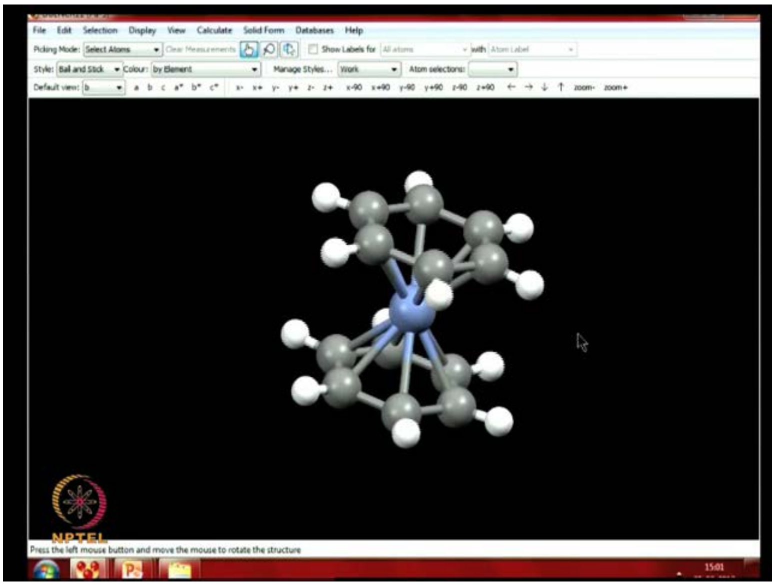

Press the left mouse button and move the mouse to rotate the structure

I am going to show you two or three complexes where you have a benzene ring sandwiched between metal atoms. Here this benzene chromium itself is chromium sandwiched between two benzene rings. And you can see that they are perfectly eclipsed you can see that the two benzene rings are perfectly eclipsed. The difference between the two benzene rings is in fact 3.21 angstroms.

And since a perfectly plain it is convenient to measure just the distance between the two carbon atoms as 3.2 angstroms and all six carbon atoms are perfectly born or symmetrically born to the chromium. So, you have this very nice symmetrical structure between the benzene ring and the chrome atom. So, let us look at one more structure where you have a cation this time.

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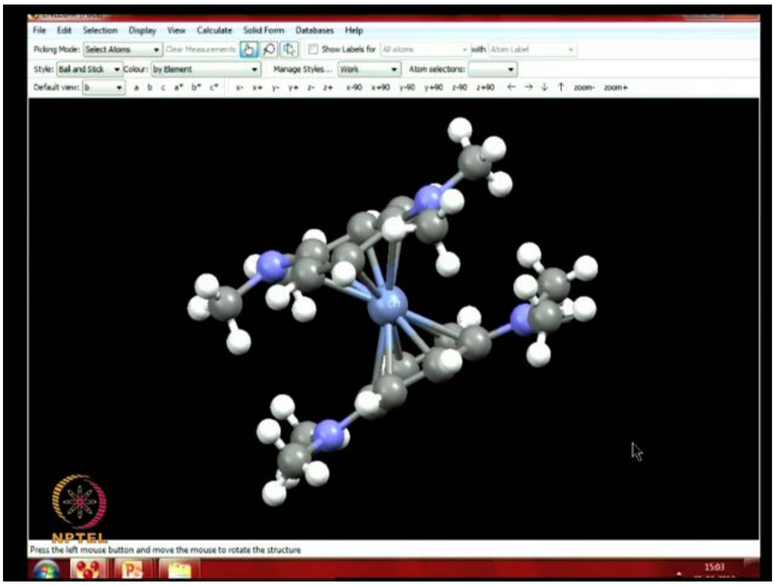

Press the left mouse button and move the mouse to rotate the structure

Here is a dimethylamino group, you have a dimethylamino group which is sandwiched between a dimethylamino substitution in the aromatic ring. Here is a C 6 ring system and the C 6 ring system has got two dimethylamino groups, which are shown in blue here. And these two ring systems are sandwiching the chromium atoms this is again chromium atom here. I will show the label, this is again a chromium atom which is sandwiched and it is got two of rings systems. And the structure of this molecule is being collected for the oxidized species and it is got a counter around, which is not shown in the structure.

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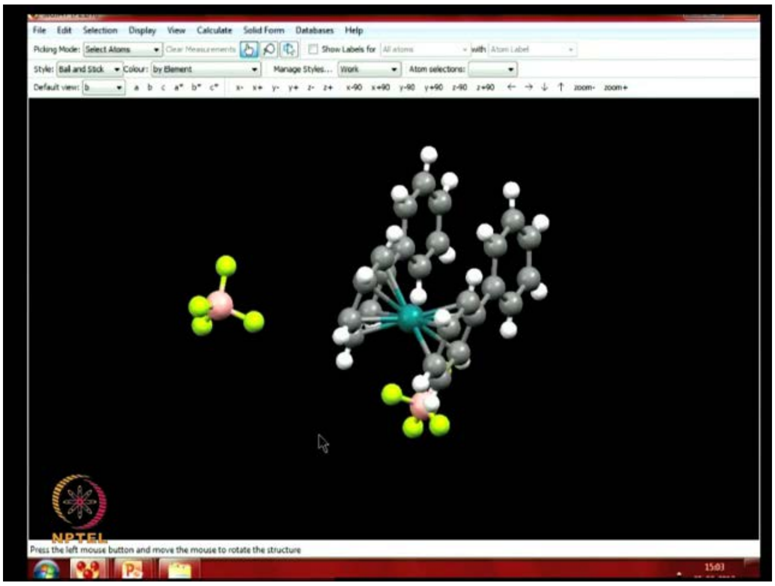

Press the left mouse button and move the mouse to rotate the structure

So, let us take a look at one more molecule, which is this. In this molecule it is the two atoms of biphenyl. Now, biphenyl is just C 6 H 5 C 6 H 5. So, you can see with two phenyl rings connected together by a single bond and that is the single bond, which connects these two carbon atoms, which have highlighted for you. Now, there is one ruthenium atom which is sitting in between the two phenyl groups. You will notice that ruthenium was got 8 electrons.

So, if in order to fall into the chromium group, you have to remove twelve electrons from the ruthenium. So, this is di-cationic molecule where two counter ions present in the crystal structure, but nevertheless this is identical to what we would have generated if chromium was present. Once again you see that the C 6 rings are eclipsed whereas, the two other benzene rings are not oriented parallel to each other whereas, the light angle with respect to each other.

So, these are three structures just to illustrate the fact that you can have very nice complexes where the metal is sandwiched between the two automatic rings. So, let us proceed further now. Look at the structure of these aromatic molecules let us take a brief look at the properties.

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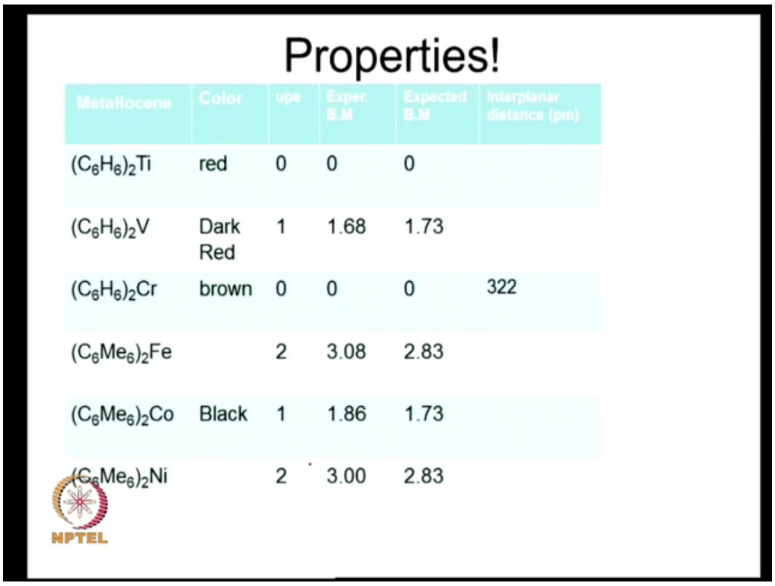

Properties!

Metallocene	Color	upe	Exper. B.M	Expected B.M	Interplanar distance (pm)
$(C_6H_6)_2Ti$	red	0	0	0	
$(C_6H_6)_2V$	Dark Red	1	1.68	1.73	
$(C_6H_6)_2Cr$	brown	0	0	0	322
$(C_6Me_6)_2Fe$		2	3.08	2.83	
$(C_6Me_6)_2Co$	Black	1	1.86	1.73	
$(C_6Me_6)_2Ni$		2	3.00	2.83	

You have once again based on the molecule orbital energy level diagram that we saw a prediction of the magnetic properties of these molecules. You would have for the titanium species at high magnetic molecule and indeed you observe a dynamic species. And you have zero magnetic moment, excremental magnetic moment and predicted moment is also zero whereas, for the vanadium would have one electron and that indeed is what is expected and what is observed.

The bis-benzene chromium itself you would expect zero magnetic moment, it should be diamagnetic and in fact it is a dimeric as it is predicted many of the other molecules. You will notice they have metal groups is on the aromatic ring and that gives use climatic stability for the aromatic ring system that you have. So, the most stable system that you have is for the chromium. Other metals do form sandwich complexes, but they are not as stable as the bis-benzene chromium that was first isolated and characterized.

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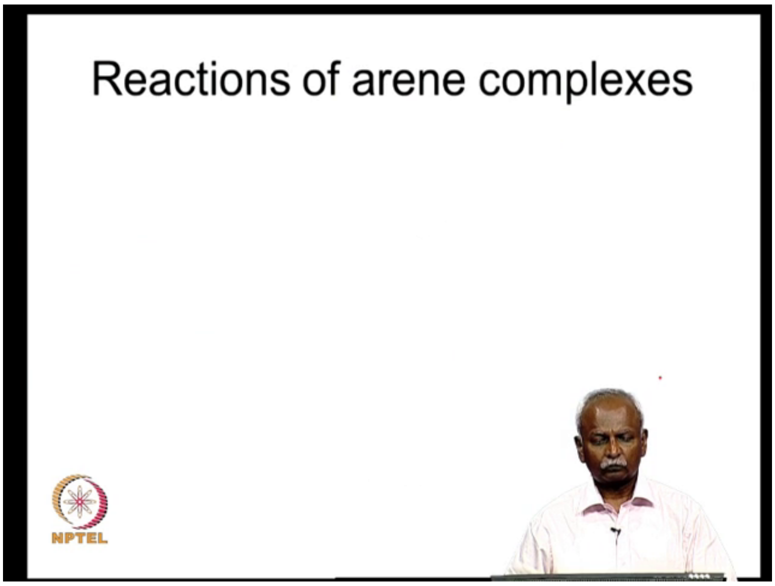

Reactions of arene complexes

So, let us take a look at the brief look at the reactions of these arene complexes eating sandwich complexes.

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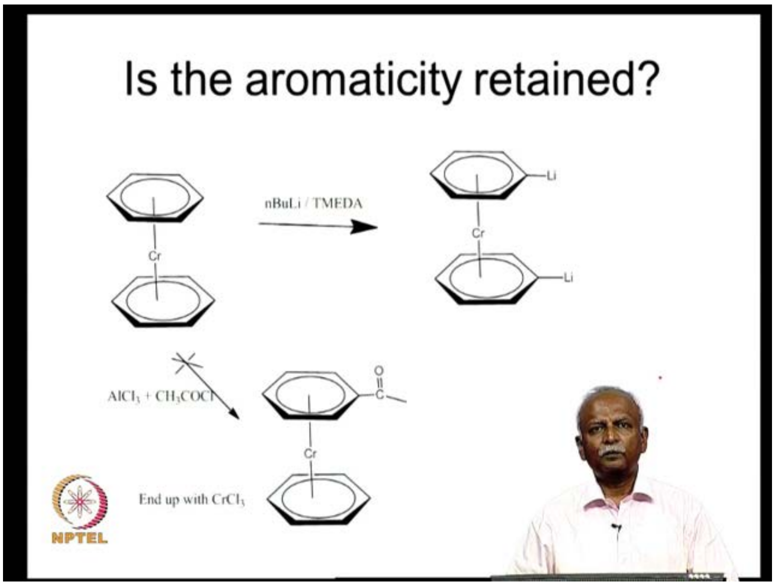

Is the aromaticity retained?

End up with CrCl$_3$

If you treat this benzene chromium with n-butyl lithium, which is known to metal eight aromatic rings and butyl lithium will metal eight rings and generate irritated American links. You find the same reaction happening with this benzene chromium also. Here is a product that you would isolate for this benzene chromium. You end up with both the monolith created species, monolith species and the di-lithium species.

So, this is a typical of these reactions because the touring seem to behave independently and there is not much communication between the two. Unfortunately, the A l C l 3 fielded class reaction that we were able to carry out with ferine is not possible in this instance. So, although you have six members C 6 H 6, which is aromatic coordinates, aromatic bartering system coordinate to the chromium. You do not get the ice you do not isolate the ring instead you have you end up with the chromium being oxidized and you end up with system, which is a mixture of several compounds.

And you do not get the expected acid related compound. So, this suggests that the aromaticity is not completely retained in these ring systems. You do have constable laws on aromaticity and we saw that some negative charges being transferred from the metal to the aromatic ring system. So, it is indeed it should be less aromatic than what you expect for a local forum plus two pie systems.

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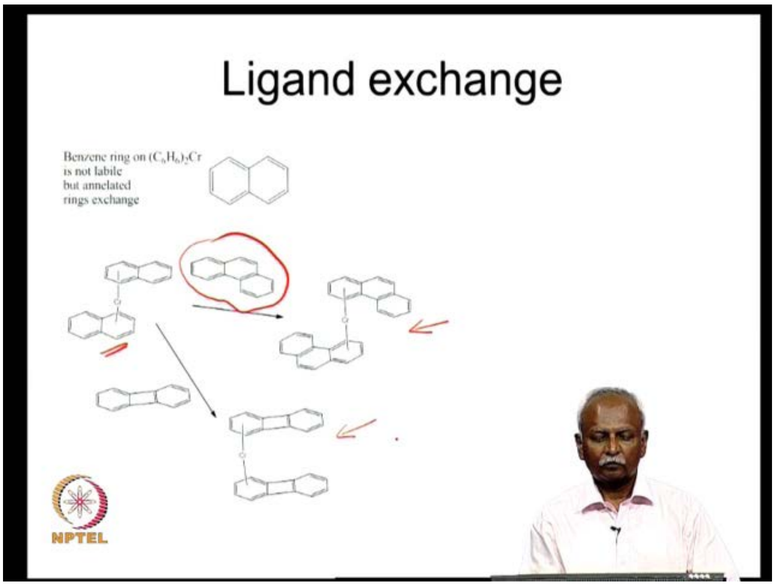

Ligand exchange

Benzene ring on $(C_6H_6)_2Cr$
is not labile
but annelated
rings exchange

So, there is another reaction also with just that you do have some laws on aromaticity and that is the fact that the benzene ring if especially if it is unrelated can exchange. So, there is a quick dissociation of the benzene ring and a recombination and if you have a different aromatic ring system in the medium. There are two aromatic ring systems were pictured here one is frentherene. So, you get di-frentherene chromium complex instead of the naphthalene that started out with.

You can also have this unrelated system reacting to give you a different this aromatic complex because naphthalene tends to go away and you have these ring systems where you greater degree of her Majesty. So, whenever a ring system is partly aromatic it can be replaced by a more aromatic system, but nevertheless we can see clearly that net complex that is formed as got lesser aromatic character than the ligand itself.

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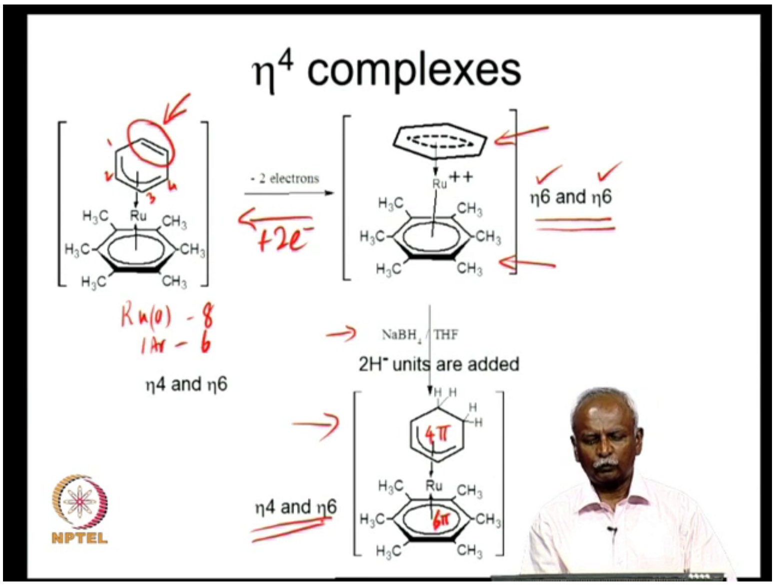

η^4 complexes

- 2 electrons

η6 and η6

NaBH$_4$ / THF

2H$^-$ units are added

η4 and η6

η4 and η6

So, before we proceed further we should mention that the 18 electron system that we worked out for chromium is the ideal complex. So, here is a case complex which we saw in a crystal structure. It is a ruthenium two plus system, which is a sandwiching which is being sandwiched by two aromatic 6 pie electron systems. And here are the two 6 pie electron systems, which are stabilizing the ruthenium two plus.

If you remove or add electrons then, this system tends to show characteristics of the destabilization. So, here is a situation where, if you add to electrons to this plus two electrons and this can be done reversibly. When you add to electrons, this system behaves in such a way that the two electrons, one of the double bonds of the benzene ring of move away so that there are only 4 pie electrons donated to the ruthenium. If you remember ruthenium energy zero oxidation has got 8 electrons.

So, if one aromatic ring gives 6 electrons then you need only 4 pi electrons to reach the 18 electron magic number. So, this pi electron moves away so that is no longer coordinated to the ruthenium. So, you have only these 4 atoms which are coordinated to the ruthenium and it forms energy electron system. So, you can remove to electrons from this complex and go here where both are either six or six. And you can also add to electrons and change the electron count.

So, it is very clear that this ring system is unstable. In fact you can add sodium borohydride, which is h minus source and because it is two plus it will readily add 2 Hydrogen. And here is a complex, which is formed as a result of adding 2 hydrogen remove the double bond and convert them into single bond and found two CH bonds. And as a result you have 4 pi electrons on the top ring and these 4 pi electrons classic s pie electrons from here result in a stable eta 4, eta 6 geometry for the ruthenium.

So, it is very clear that it is possible to shift between the aromatic ring systems to the non-aromatic ring system when you have electron count that is not the expected 18 electrons count.

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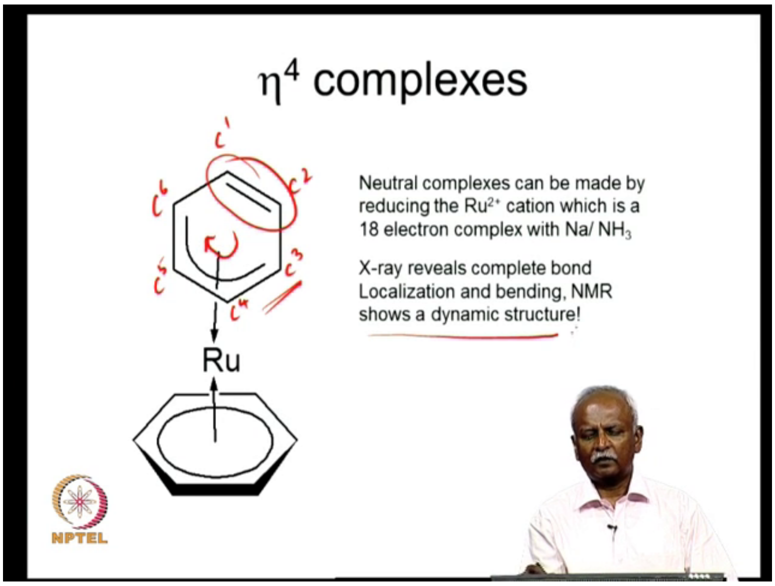

η^4 complexes

Neutral complexes can be made by reducing the Ru^{2+} cation which is a 18 electron complex with Na/ NH_3

X-ray reveals complete bond Localization and bending, NMR shows a dynamic structure!

In fact the x ray crystal structure of this molecule reveals that this double bond is completely moved away from the plane of the a six member ring and so you do not have conjugation with this 4 pi electrons. I should also mention that the NMR structure however is dynamic that means this C 1 and C 2 rapidly inter convert with C 3 C 4 and C 5 C 6 positions. So, there is a rapid rotation around this bond are resulting in an NMR structure that suggests all carbons are equivalent. So, we will come to that later in the later lecture.

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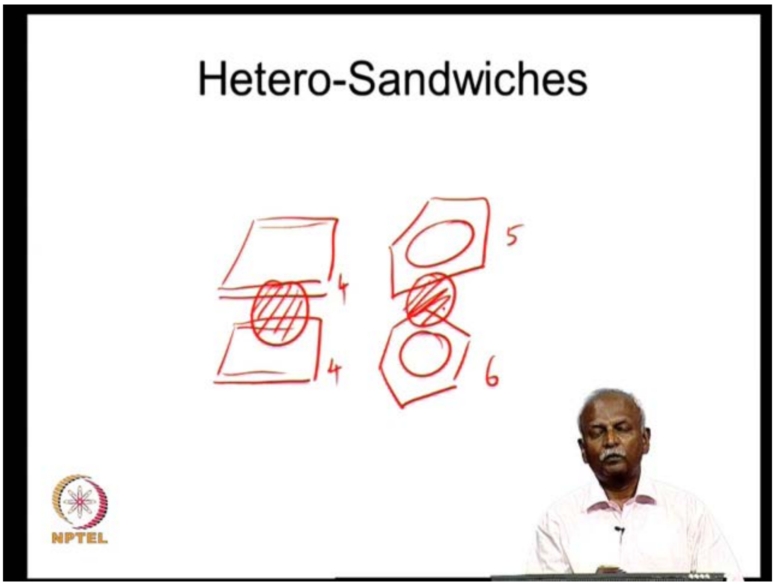

Hetero-Sandwiches

Now, for in the remaining few minutes will talk about hetero sandwiches. By hetero sandwiches I mean the bread part of the sandwich, which we had pictured which hired pictured as a slice of bread. Sometimes can be large and sometimes it can be small. So, for this lecture we were talking about hexagonal slices. We can also have 4 member rings or we can have 5 member rings in combination with 6 member ring.

So, this type of sandwiches where you have 5 and 6 and 4 and 4 are sandwich complexes, which can be formed by metal electrons, which have the suitable number of metals, which have the suitable number of electrons. So, all we have to do is to do the electron counting properly.

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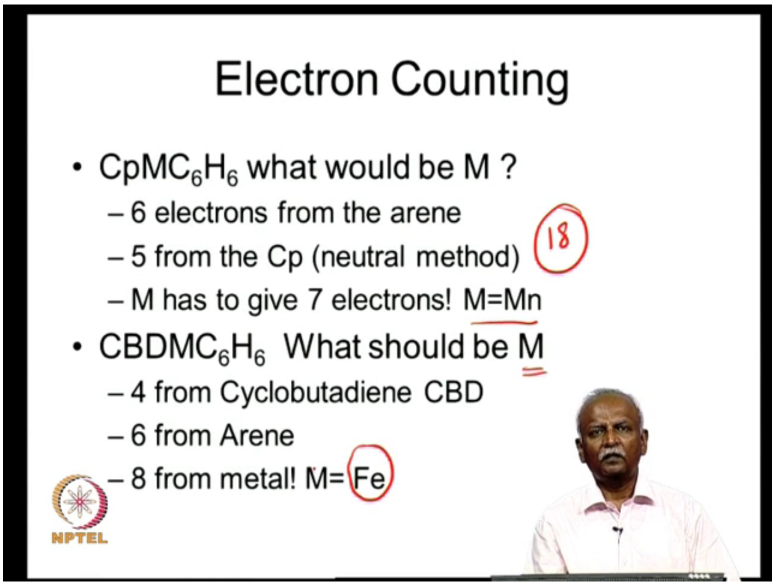

Electron Counting

- $CpMC_6H_6$ what would be M ?
  - – 6 electrons from the arene
  - – 5 from the Cp (neutral method)
  - – M has to give 7 electrons! M=Mn
- $CBDMC_6H_6$ What should be M
  - – 4 from Cyclobutadiene CBD
  - – 6 from Arene
  - – 8 from metal! M=Fe

18

So, if you want to figure out what would be the ideal complex to form a C p M C p cyclobutadiene and C 5 H 5 M C 6 H 6. Then we just need to remember that 6 electrons are given by arene and in the neutral method and five electrons are given by C p. So, that leaves 7 electrons, which has to be given by the metal if one has to attain the magic 18 electron rule. So, that metal would have to be Manganese.

So metal which has got 7 electrons zero oxidation state is Manganese, we are using the neutral method to do electron counting here. So, cyclobutadiene metal C 6 H 6 we can asked the question what should be M, cyclobutadiene will give you 4 electrons. Similarly, 6 will come from the arene and so eight electrons left come from metal and so the metal will have to be in the ion group or it has to be metal, which gives 8 electrons.

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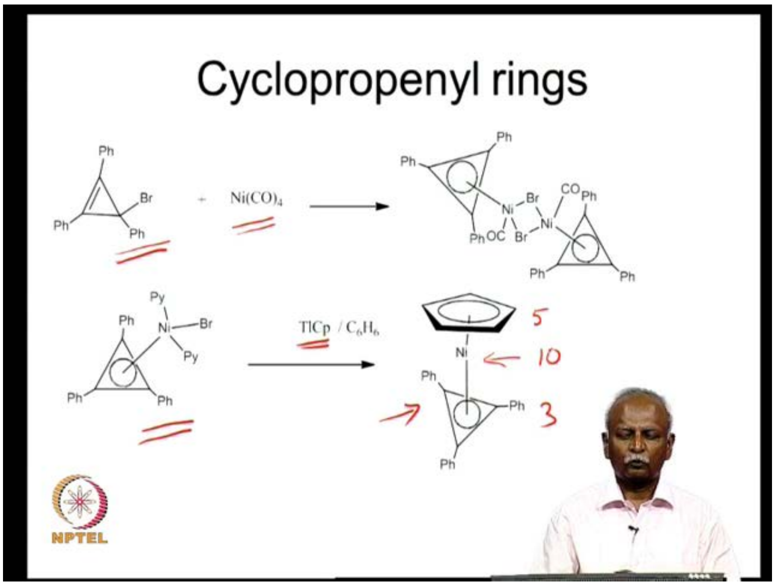

Cyclopropenyl rings

So, here are some few examples of metal sandwich complexes, which are formed by a various molecules and this synthesis involves reacting cyclo propenyl rings system cyclo propenyl bromide with nickel tetra carbonyl. That gives you a molecule in which it is the dimeric complex where, you have the two cyclo propenyl units sandwiching Ni Br 2 Ni Br 2 unit. A more easy to understand system is formed by reacting this dime with a paradigm and then we isolate a nonnumeric complex, which can be treated with thallium cyclo propenyl.

As I mentioned earlier cyclo propenyl and thallium is a good source for C 5 minus. It now forms a very nice sandwich complex where, you have a five member ring on the top and three member rings on the bottom. So, these will give you five electrons and three electrons respectively and the nickel gives you n electrons.

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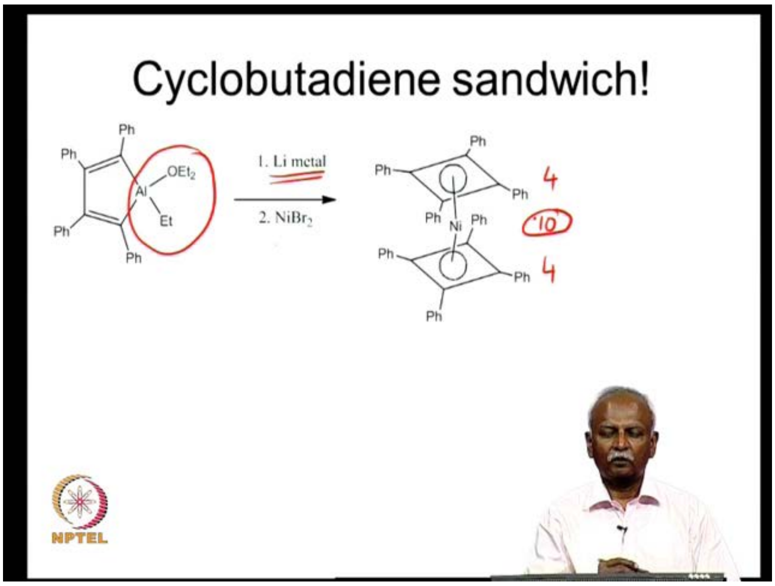

Cyclobutadiene sandwich!

So, this forms a nice 18 electron complex a similar situation happens with cyclobutadiene. This of course, turns out to be a rather unusual synthesis where and alumina cyclo pentadiene is reacted with lithium metal to reduce it in the presence of nickel bromide to give you a elimination of this group to give you two 4 member rings. And this also gives you 4 plus for 4 8 electrons. So, nickel is an ideal element because it has got 10 electrons it is 3 d 8 4 s 2. So, it will give you 10 electrons and a nice cyclopean dimeric complex cyclobutadiene complex is formed where you have two bis two cyclo pentadiene groups.

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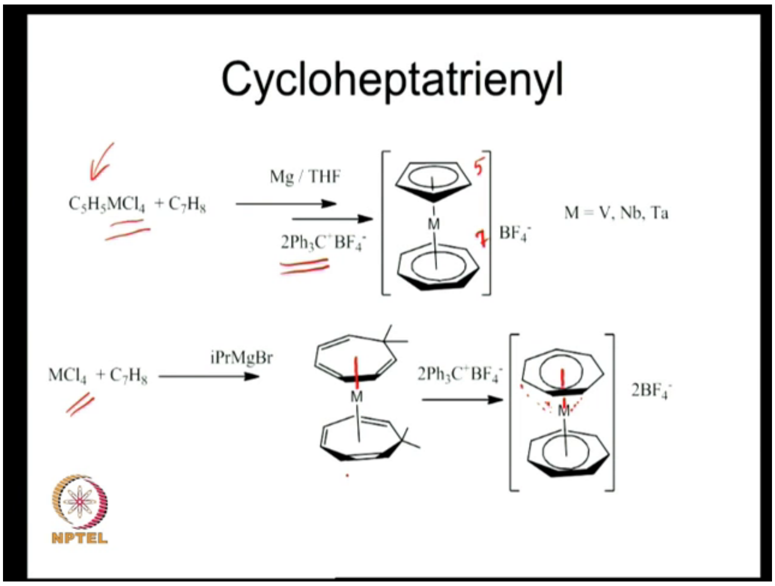

Cycloheptatrienyl

So, it is the best cyclopean mile nickel complex that is form now can be go beyond six other and answer is yes. And here is an example where you have a vanadium group metals interacting with a pentacle a vanadium halides. And you already treated the metal with C 5 H 5 minus and it treated with C 7 H 8, which is cyclo heptatrienyl and then you remove h minus using heptatrienyl then you end up with a metal complex where, you have a five member ring on the top and a seven member ring in the bottom.

This gives you a hetero sandwich structure where vanadium is conveniently located between these two ring systems. If you do electron counting you will notice that this in fact is not an ideal system, it has only 16 valance electrons. Here you have a another case where you end up with another complex, which is in the titanium group M c l 4 that also reaction C 7 H 8 and reforms 16 balance electron complex with cyclo heptatrienyl units coordinated to the metal atom.

So, here there is a game bond, which is present between the metal and the central ring. In fact each of these carbon atoms bonded to the metal and we do not draw it because then it becomes very congested. So, the metal just as shown with a bond to central ring to indicates that all of the atoms are bonded. So, here again p H C 3 plus removes h minus.

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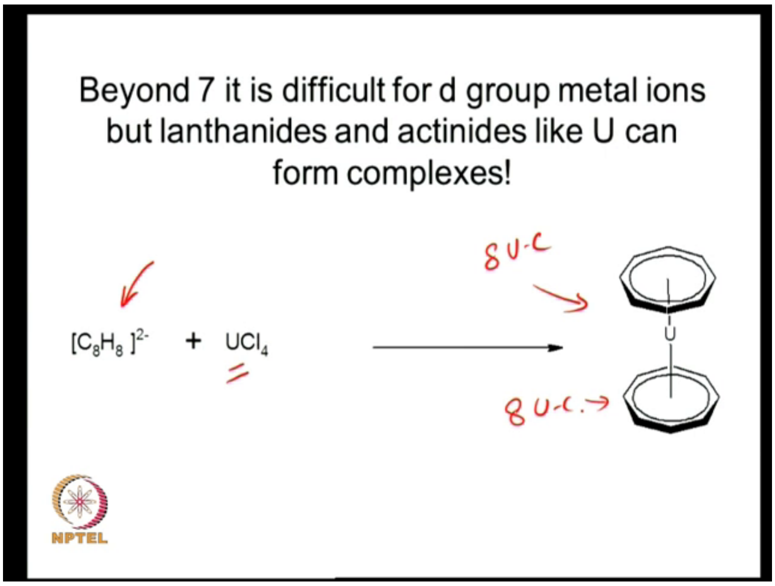

Beyond 7 it is difficult for d group metal ions but lanthanides and actinides like U can form complexes!

$[C_8H_8]^{2-}$ + UCl_4 $\longrightarrow$

Now, beyond seven it becomes difficult in order to form sandwich complexes cyclic pi systems are conjugated to the metal. But when you increase the size of the metal itself like we go to the lanthanide or the actinide systems then, it is possible to generate cyclo octatrienyl complexes. Here the cyclo octatrienyl has been reduced prior to this reaction with two electrons. So, you have C 8 H 8 two minus, you will remember that C 8 H 8 two minus is now aromatic.

It is a ten pi electron system that reacts with uranium tetrachloride to give. You have seen that has got 8 uranium carbon bonds on top and 8 uranium carbon bonds on the from the bottom ring. So, this is the very interesting complex where uranium because of its large size is able to react with 8 pi electron cyclic system.

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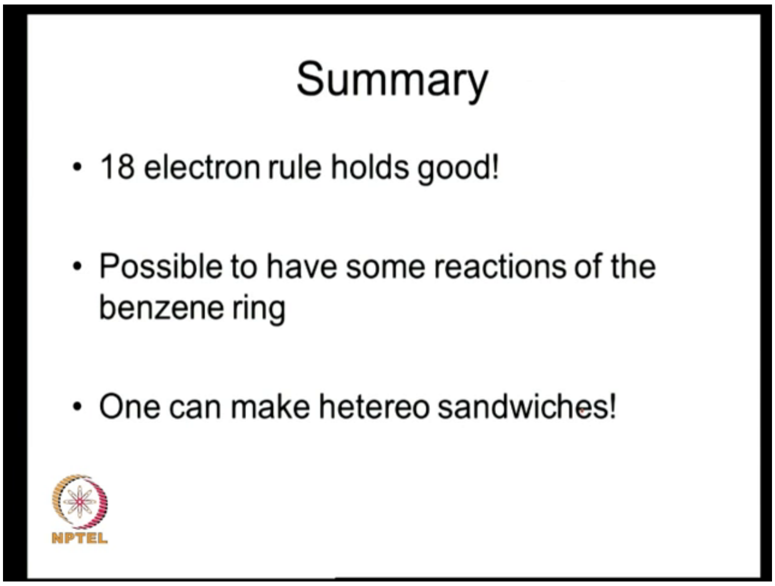

Summary

- 18 electron rule holds good!
- Possible to have some reactions of the benzene ring
- One can make hetereo sandwiches!

So, in summary one can say that the 18 electron rule holds good even in these complex molecules where, you have pi systems interacting with the metal atom. And the 18 electron rule stems from the fact that if you fill up more electrons than 18 the molecule orbital skin. You tend to fill up the electronic energy levels, which are higher in energy which is the ones which have been destabilized. So, it is comfortable for the molecule to stop 18.

Anything more than it is bad, but as you seen in this lecture, there are several systems where the 18 electrons may not be filled and you can have 16 electron systems and they will still be stable. It is also possible to have some reactions of the benzene ring, but not as much as we saw in the cyclo pentadiene alkynes. Cyclopentadianyle is more robust it is interacts with the metal and at the same time carries out is able to with stand feudal craft reactions.

Here we do not have feudal craft reactions, but they can have location reactions. Lastly we can make hetero sandwich complexes where, the pi systems on both sides need not be the same. One can have a cyclo propenyl pi complex system on the top of the sandwich and one can have a six-member ring on the bottom of the sandwich. So, you can have a variety of very interesting molecules and we look at some of the properties of these molecules in a future lecture.