Introduction to Organometallic Chemistry
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Lecture - 25
Eta Five Cynclopentadienyl –Complexes

In this lecture we will be discussing cyclopentadienyl complexes.

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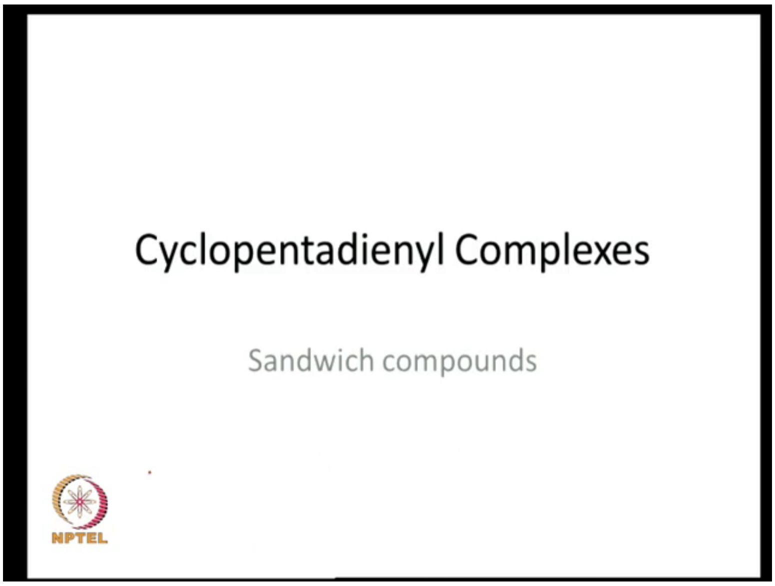

Cyclopentadienyl Complexes

Sandwich compounds

Many of them are called sandwiched compounds but not all of them are one. In fact, cyclopentadienyl complexes initiated the second wave of organometallic chemistry and it is only after the discovery of cyclopentadienyl complexes that there were several new discoveries made. And laboratory started working earnestly on organometallics and realise importance of these compounds.

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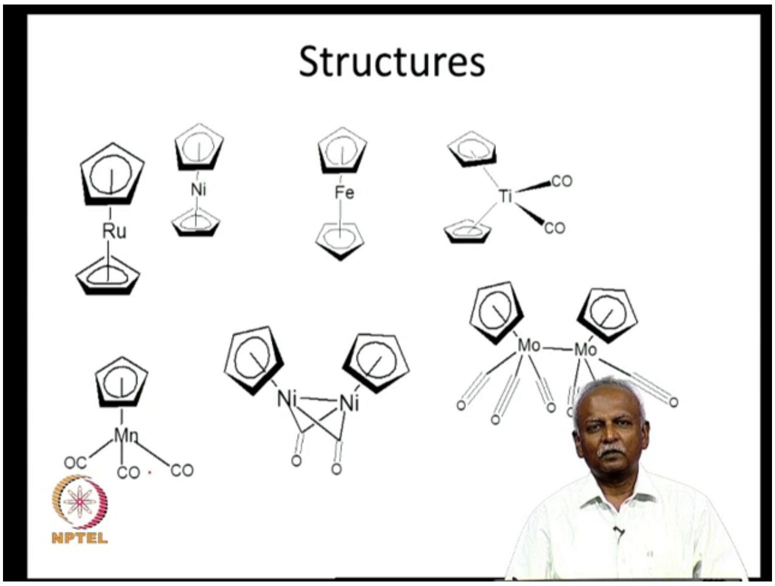
Structures

So, let me just briefly show you a variety of structures that are formed by these compounds. They are ubiquitous in organometallic chemistry, they are very good supporting ligands and many times they are purely supporting but, they can also involve themselves in reactions. In a very subtle fashion and this allows them to be used in catalysis very effectively. So, it is important that we understand how these compounds are formed and how they can be made and how they can be used on organometallic chemistry.

As I mentioned earlier the most important compound or the compound that really started off this new wave of organometallic chemistry is a molecule ferrocene. You are definitely familiar with this particular molecule which was in fact accidentally discovered. The other compounds which are shown here, some of them are dinuclear bridged and having some exotic structures are very common in organometallic chemistry as well. They are probably as ferrocene, but nevertheless because ferrocene initiated this race in organometallic chemistry for making newer and newer compounds. It is very often considered as the icon of organometallic chemistry.

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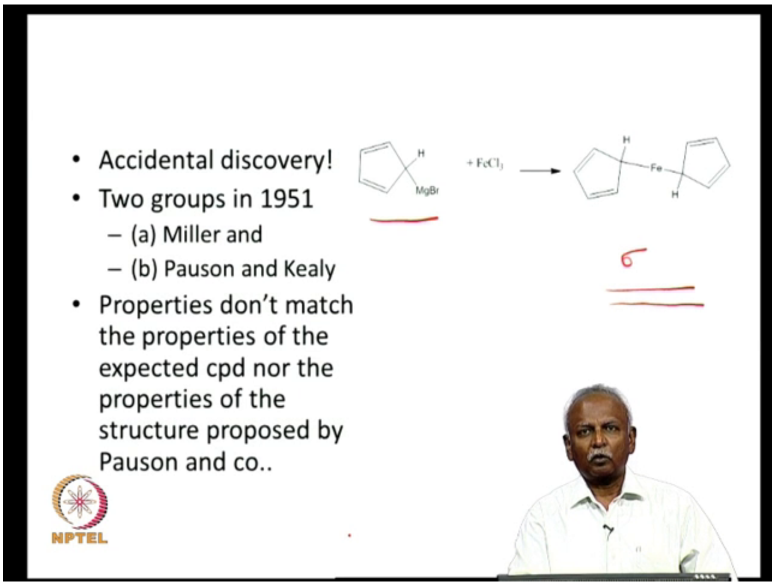

- Accidental discovery!
- Two groups in 1951
  - (a) Miller and
  - (b) Pauson and Kealy
- Properties don't match the properties of the expected cpd nor the properties of the structure proposed by Pauson and co..

So, let us start first with this accidental discovery that I talked to you about. Two groups in 1951, one was a group of Miller and the other was group of Pauson and these two people were trying to make fulvalene. Fulvalene is a simple organic compound which is pictured here. They wanted to make this compound by oxidising cyclopentadienyl anion and to do that they made bromocyclopentadiene and then made the grenade which is shown here and try to oxidise..

The grenade using ferric chloride, ferric chloride is a good oxidising agent and their idea was perfectly sound and surprisingly instead of making this fulvalene molecule they got something where the properties of the compound did not match the expected properties. So, as they were wondering what the structure would be. Pasuon in fact proposed that the molecule was in fact the iron containing compound. It had iron in it by analysis and so he proposed this compound where the iron had replaced magnesium as an electric positive element.

A simple transmetallation compound and he suggested that it was a sigma bonded organometallic compound with iron in the middle between two cyclopentadienyl units. At that time there were no known examples of extended pi systems coordinating to metal atoms. So, this was the beginning and it was natural that they think about a sigma bonded system as a possible organometallic compound that could be isolated through his reaction.

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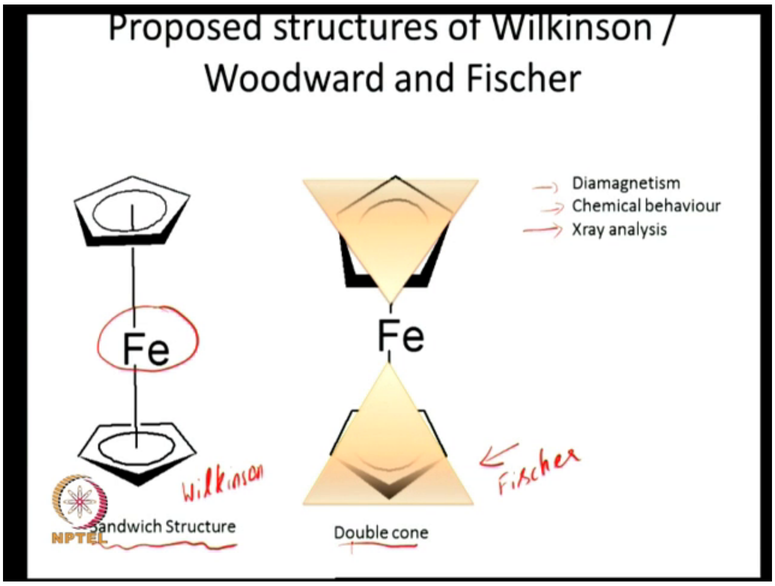
Proposed structures of Wilkinson / Woodward and Fischer

- Diamagnetism
- Chemical behaviour
- Xray analysis

However, all the properties of the compound especially the diamagnetism did not match the type of the diamagnetism was not matched by the structure that they had proposed two people both in England and in Germany and the US and in Germany two groups, two major groups. One was the group of Wilkinson and Woodward and Howard and the other group in Munich headed by Fischer. These are the two people who proposed a different structure. The radical structure that they proposed was the double coned structure which was proposed by Fischer and the sandwich structure.

The sandwich structure was proposed by Wilkinson. Wilkinson and Woodward often had lunch conversations about their research and this was an exciting piece of result that had come out in the literature. Probably the sandwich they had proposed at suggested this new structure for the sandwich structure for the cyclopentadienyl complex. Nevertheless over the years the double cone structure proposed by Fischer do not with that name did not stand the test of time and it was the sandwich structure which always preferred the sandwich structure. The main sandwich structure was preferred by people.

So, we now call most of these compounds where a metal atom is in between two A r molecules as sandwich molecules and the double cone structure. In fact, came from a scientific background he looked at the x-ray density that was there and he found that x-ray density was in the form of two cones and that led to the double cone structure.

So, Wilkinson used the diamagnetic behaviour, the chemical behaviour of this molecule to propose those sandwich structures. Whereas, Fischer proposed on the basis of the x-ray and the infrared evidence that in fact it was a double cone structure and after this structural analysis was completed it was quite clear that the structure of the molecule was indeed unique. It was realised that planar pi systems can coordinate two metal atoms in a symmetrical fashion and the coordination number of carbon which was originally restricted to the value of four may not be preserved in these molecules.

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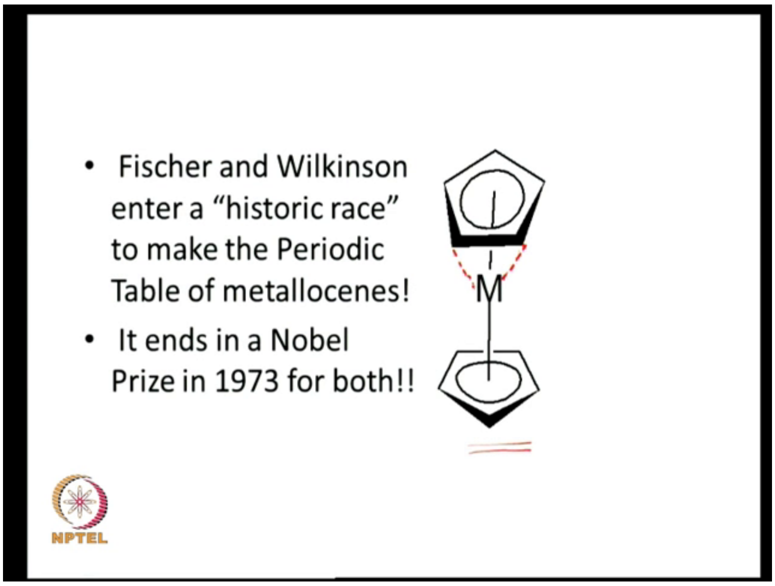

- Fischer and Wilkinson enter a "historic race" to make the Periodic Table of metallocenes!
- It ends in a Nobel Prize in 1973 for both!!

So, with this cyclopentadienyl structure the sandwich structure is pictured here is indeed a celebrated structure, because it was the first one that was discovered with an M equals F e. It was discovered and it was shown that it was in fact a pi system which was extensively demetalised deutilised and at the same time coordinated to the metal. The bond distances between the metal and the carbon the bond distances between the metal and the carbon.

They are all symmetrical and it was also found that in some other structures the cyclopentadienyl groups could be eclipsed or they could be staggered and we will see some of those structures and after a few slides. So, after Fischer and Wilkinson realised that the double cone structure was in fact possible with iron, there was a historic race where both groups tried to make the metallocene of every other metal.

So, they try to make the periodic table of metallocenes with all the transition metals and in fact at the end of this race and after discovering several new compounds and their chemistry they were awarded the Nobel Prize in 1973. It was around 1956 that they had proposed the new structure for cyclopentadienyl, that this cyclopentadienyl iron compound and it was in 1973 the both of them were awarded the Nobel Prize.

Wilkinson was the one who in the group Wilkinson and Woodward. It was Wilkinson who started this race and Woodward who had predicted the chemistry correctly for these compounds did some studies on the organic chemistry of these molecules but then he did not pursue the inorganic chemistry further.

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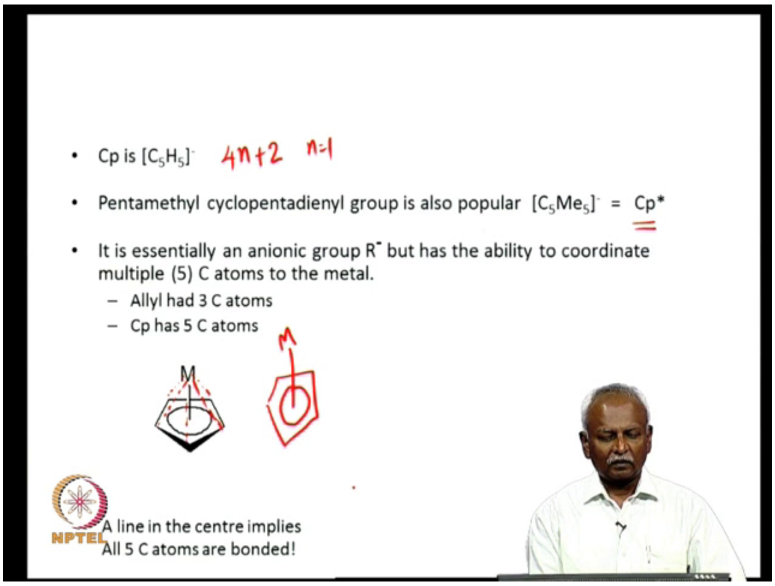

- Cp is $[C_5H_5]^-$ 4n+2 n=1
- Pentamethyl cyclopentadienyl group is also popular $[C_5Me_5]^-$ = Cp*
- It is essentially an anionic group R^- but has the ability to coordinate multiple (5) C atoms to the metal.
  - Allyl had 3 C atoms
  - Cp has 5 C atoms

A line in the centre implies
All 5 C atoms are bonded!

So, what is happening in these molecules. Let us just take a closer look at cyclopentadienyl group C 5 H 5 minus should in fact be an aromatic system. So, cyclopentadienyl has got 6 pi electrons, that is 4 n plus 2 pi electrons and where n equals 1.

So, it should be as simple aromatic planar ring and in fact it is formed as a planar ring in some of the structures that have been characterised in even. In the free state the C 5 H 5 minus as a counter can be found in crystal structures and in fact it is planar and it found to be an in an aromatic system. The chemistry of C 5 H 5 minus is extensive and sometimes it is advantageous to have the hydrogen substituted by methyl groups.

So, it has become very popular to have pentamethyl cyclopentadienyl group and this is C 5 Me 5 minus the per methylated analogue of cyclopentadiene and this group is called the C t star. In fact it is a star ligand, it is used in a variety of reactions where you do not want the cyclopentadienyl group to have any electronic influence or steric influence.

It is essentially an anionic R minus group that but, has the ability to coordinate through all the five carbons. If you have a simple alkyl group al ahalkyl anion, it has only a single point of contact where as the allyl has 3 carbon atoms which can coordinate to the metal simultaneously. The allyl anion which we saw a few lectures ago and the C p as a cyclopentadienyl has got 5 carbon atoms coordinated to the metal atom.

So, if you look at the structure we very often indicate cyclopentadienyl metal structure using this representation, where we have a planar C 5 H 5 unit coordinated to the metal with a metal having a bond to the centre of the ring. There is no atom which is present in the centre of the ring. It is only to indicate that all the 5 carbon atoms are equally bonded. If you were to draw structures where all the 5 carbon atoms are indicated with bonds, then the structure will look very clumsy.

Now, you can see how that representation might look. So, that seems to be a bad representation and so the representation that has come about is usually the representation that is used by the popularly by chemists is a representation, which I just showed you where only the central bond which is to a ghost atom at the centre is indicated by a line. Now, when we indicate it like this we intend to convey the message that all five carbon atoms interacting with metal atom.

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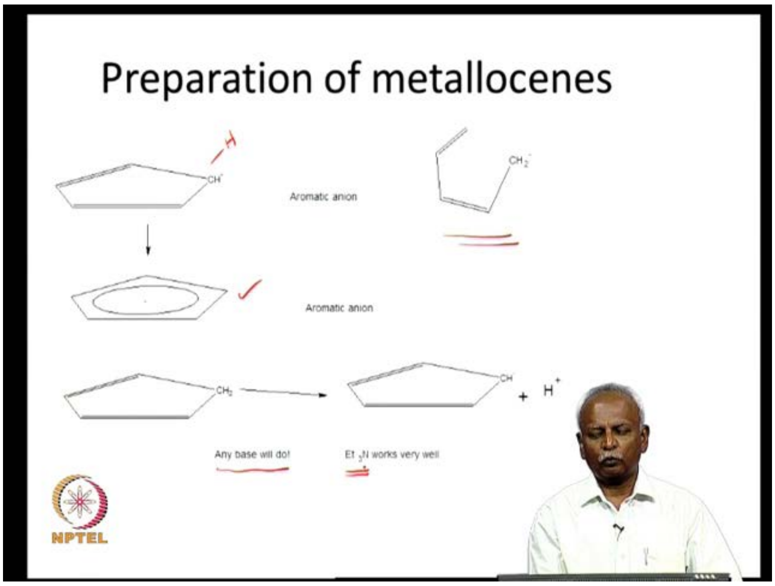

Preparation of metallocenes

Any base will do!

Et $_3$N works very well

So, the preparation of metalocenes a something that is of interest and it is of value for us to consider because it is an aromatic anion, the cyclopentadienylanion is a stable moity and in contrast with the linear or acyclic version of the pentadienyl unit. Pentadienyl anion is also known and that is also known to form complex is that deciding whether the N l and stable because of the artistic and it can be readily generated by removing a hydrogen from this carbon.

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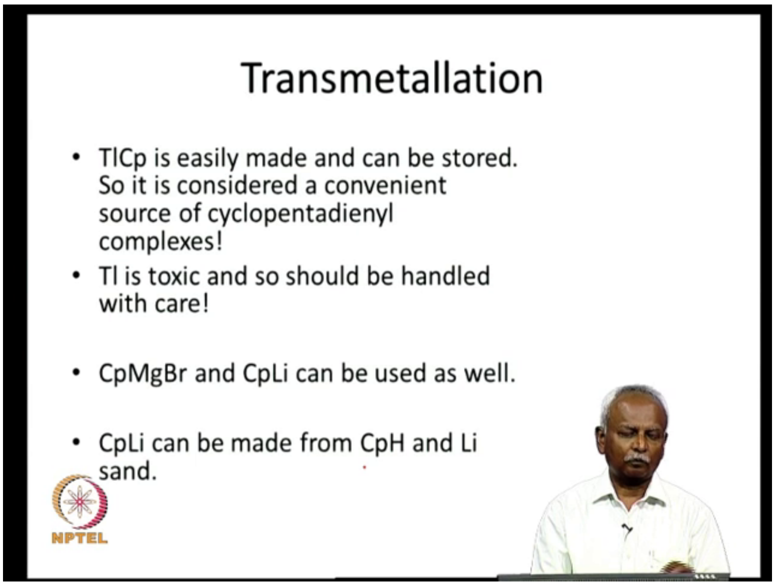

Transmettallation

- TlCp is easily made and can be stored. So it is considered a convenient source of cyclopentadienyl complexes!
- Tl is toxic and so should be handled with care!
- CpMgBr and CpLi can be used as well.
- CpLi can be made from CpH and Li sand.

So, if you have a hydrogen C H 2 groups, cyclopentadiene then you can remove it. Usually is a proton and generate the anion any base will do. In fact a wide variety of dishes can be used, simply organic waste like triethylamine can work very well and can deproteinise the cyclopentadienyl group and generator the anion easily.

We can have several transmetallisation reactions possible. It is possible for us to have Charlie cyclopentadiene made and stood in the laboratory thallium is a universal and metal and so real class city minus is an extremely stable molecule that can be stowed. It is a convenient source of cyclopentadienyl group will probably the thallium is in fact accept the toxicity of valium should be blown in mind and one should handle it with extreme care. If one is using that as a shows of the psychopath, the idea is that it is possible to generate the psychopathic diner.

A rather readily in the laboratory by a simple grenad reaction between cyclopentadienyl bromide and one can also use lithium metal. The cyclopentadiene itself simply ally is usually made from cyclopentadiene and lithium sand. The lithium sanders what is made when you bring lithium to the melting temperature and shake it vigorously when it breaks down to form very fine globules. These globules are so fine that they have a large surface area and can react readily with the cyclopentadiene molecule.

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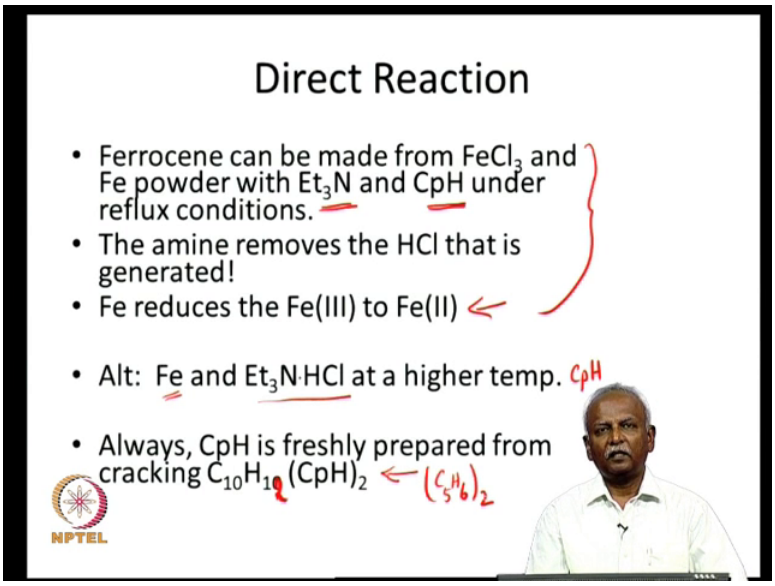

Direct Reaction

- Ferrocene can be made from $FeCl_3$ and Fe powder with Et_3N and CpH under reflux conditions.
- The amine removes the HCl that is generated!
- Fe reduces the Fe(III) to Fe(II)
- Alt: Fe and $Et_3N{\cdot}HCl$ at a higher temp. CpH
- Always, CpH is freshly prepared from cracking $C_{10}H_{12}$ $(CpH)_2 \leftarrow (C_5H_6)_2$

Now, after the discovery of the structure and after understanding the chemistry behind the cyclopentadienyl complexes, pherocene was made fairly rationally and very effective means of making pherocene where a generated the simplest way by which you can generat it in the laboratory is by reacting pherocene. That is the reacting F e C l 3 with iron powder. The iron powder is merely there to reduce the iron reply to this is the purpose of using the iron powder and F e C l 3 together in conjunction with cyclopentadiene and try economy.

One can in fact triethylaminein stoichiometric quantities. One can in fact from the pherocene molecule fairly readily. The amine was there to remove the HCl with his formed between iron trichloride and the cyclopentadiene. So, this reaction is fairly effective and you can replace this whole system by the simplest system but, that requires a slightly higher temperature which required which is a direct reaction between iron and triethylamine hydrochloride at a reasonably high temperature in the presence of cyclopentadiene.

So, if you use cyclopentadiene triethylamine hydrochloride as a catalyst and iron, it is possible in fact to generate this molecule in a very good yield. Now, you always have to generate cyclopentadiene in a fresh fashion. There is no such substitute like the car is having is molecule that can be stored in the laboratory. Unless you want to store it has tallium cyclopentadiene and that is because cyclopentadiene readily dimerises to give you C 10 H 10 and this molecule of C 10 H 10 is readily available.

It can be cracked so to speak by heating it to a high temperature in the absence of any other reactant. When you do that it splits back into C 5 H 6. So, C 5 H 6 is formed fact and see city CpH twice. That is C 5 H 5 H twice provides and nights that that should be 12. Here C 5 H 6 tries to is the time of psychopathic dimer. It is not the one that is readily available in the laboratory.

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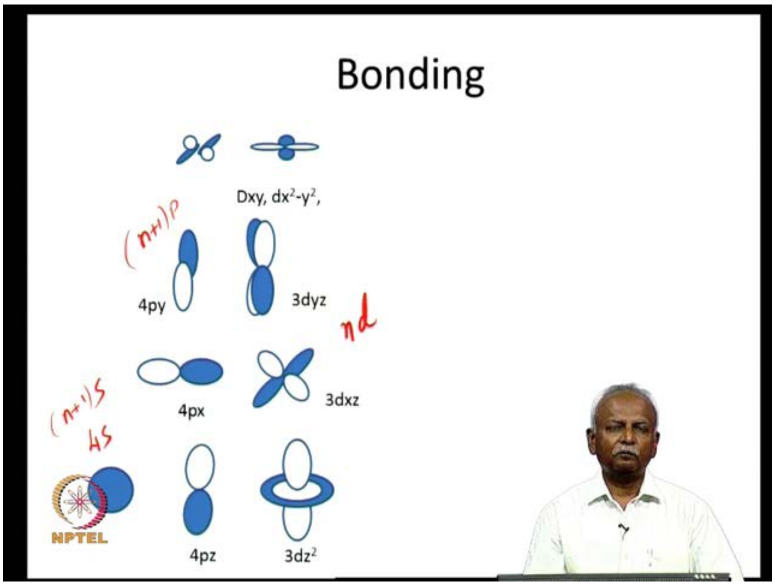
Bonding

So, let us look at the bonding in these molecules. It is possible to make these molecules by simple reaction between psychopathic kind that look at the bonding these molecules. If you remember the orbitals of the iron atom or any transition metal, you know that we have a 4 S orbital. We have a 4 S orbital of the templates want the orbitals and the md orbitals. These are the d orbitals, these are the and the then these are n plus 1 S and n plus 1 P orbitals. So, if you are considering the first row of transition metals then this will be 3 d and this is be 4 S and 4 P. These are the orbitals which are available for the metal atom for interaction with the cyclopentadienyl group.

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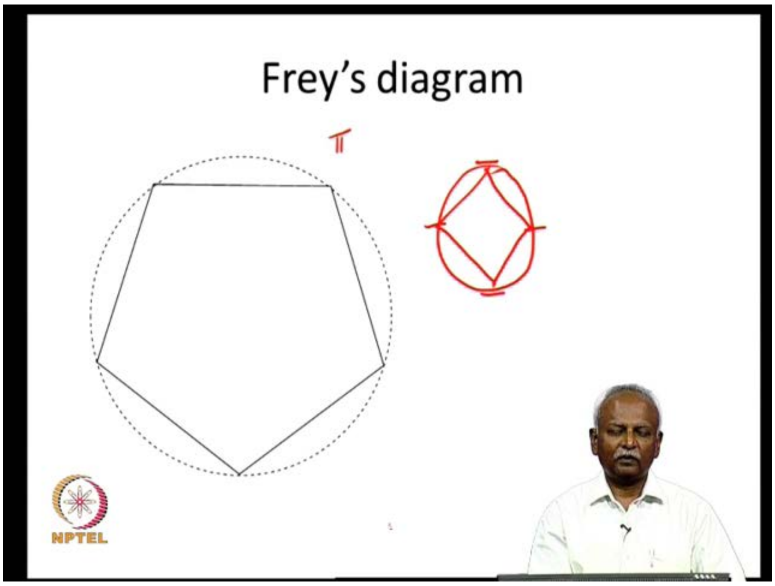
Frey’s diagram

The cyclopentadienyl group itself, the molecule orbitals of the cyclopentadienyl group needs to be simplified significantly. One only needs to consider the pi system which is available on the psychopathic time. One may not look at all the molecule of the molecule orbitals of cyclopentadienyl anion. So, there is a simple way by which one can arrive at the energetics of these molecular orbitals pi. Most of the cyclic ring systems with psychic filing systems that are talking about one has to take a sphere which is shown here on the screen and if you inscribed the appropriate planar molecule that you want to examine.

So, one can in fact, it certainly and inscribed a square. If one wants to find out the energy levels of the cyclo butadiene sushi of esq celebrated 9 inscribed this classic cycle will dine inside a sphere and that give you the energy ordering of the molecular orbitals of the piesystem cycle time. Similarly, benzene and here we have we have to look at today the cyclopentadienyl group.

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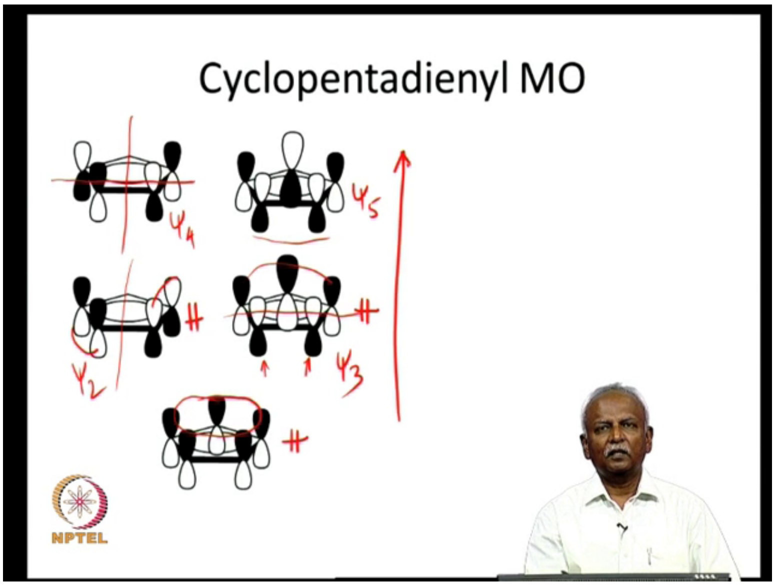

Cyclopentadienyl MO

So, the pi system, the google molecule orbitals can be simply derived by drawing the insider circle and as the phrase circuit. Now, here MO’s now generated from cyclopentadienyl political operatives and if you remember you have 6 C 5 H 5 would be a radical C 5 H 5 miners would be an anion which is got this 6 dialect.

So, these are the 6 pi electrons which are available for the cyclopentadienyl group and you will notice that the pi system is completely symmetrical. In the case of nearly 70 molecule of beauty and the orbitals are all the same phase. That means they are pointing in the same that the p orbitals pointed in this direction, in the upward direction perpendicular to the plane of the molecule have the same phase. The next set of molecule orbitals have got a single node.

So, this note for example, here you will notice that closes the node which is going through an distraction serve to orbitals have the same phase. These two have the same phase and the other two orbitals have the opposite risk but, in the same fashion. The next camera will also have a single plane and minimal clean and that nodal plane is indicated as passing through this molecule. You can do notice that the two orbitals are closer to you. These two orbitals have the same phase and the other three orbitals of the same phase.

So, you can see there is a single node for site 2 and site 3. If one might write is a site 2 and 3 you have a single nodal plain and further site and sci-fi, the number of nodes increase further. So, you have two nodes, one node in this fashion and the other node in this fashion. So, you can see that that is true for this, also this molecule or would you also enough two nodes but, they will make the diagram comes a not drying it, right? Now, that you can see the number of nodes keep increasing as you go up the energy diagram and these molecule orbitals of the highly molecule orbitals of the cyclic systems can in fact be efficiently with a metal orbitals.

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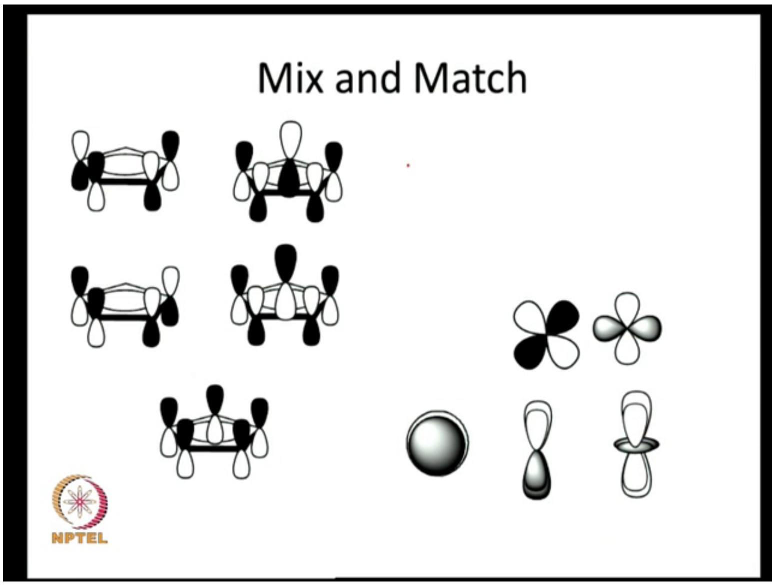

Mix and Match

So, let us can take a look at what is going happen, I will briefly switch the views.

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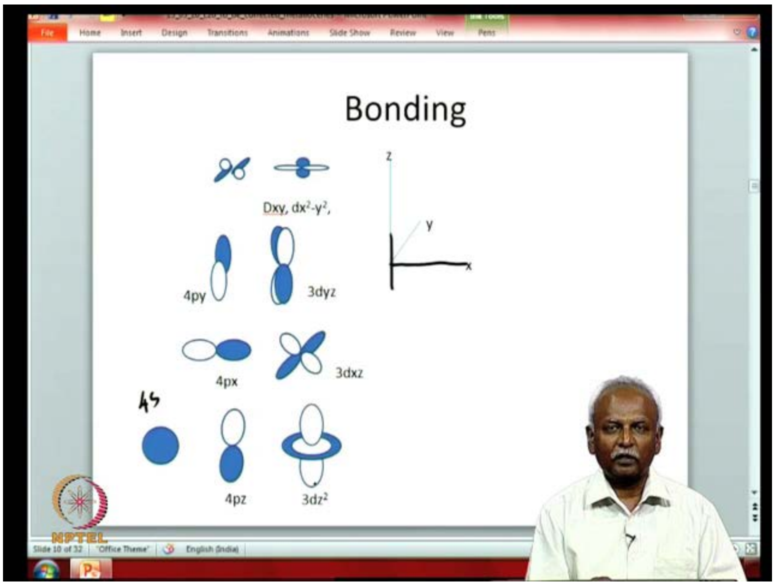

Bonding

So, now let us look at the bonding in these molecules. In order to get the orientation right. Let us just refresh our memories about the nature of orbitals on the metal atom. The metal atom has got an as templates want and the templars contest and an plus 1 p orbitals. These are pictured here for the first row transition element. You would have 4 S that would be 4 P to be and then 3 d orbitals. If these orbitals are arranged in such a way that the d z squared is going to be along the z axis which is in this particular orientation. Now, the x-axis is the one which is the exit, at exit claim is the one which is the plane of the screen and the y-axis is going in and out of the plane of the screen.

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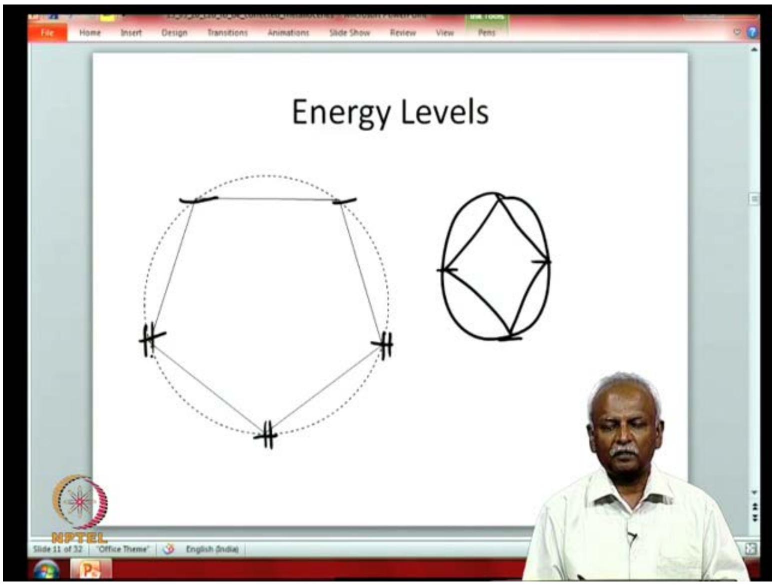

Energy Levels

So, now let us look at the energy levels of the cyclopentadiene night anion or for that matter anyone any of the psychic assistance they can be readily derived by drawing a circle and inscribing the polygram in that circle. So, if you want to drive the energy levels for example, cyclo butadiene, you just draw her figure, you would have to draw a circle and then inscribed the polygram.

In that case this cyclo butadiene would be a square. You would inscribed that and then the energy levels of the various orbitals would be just the places where the squire in the successor to sanitiser cycle butadiene cyclopentadiene night amiens. You would have the orbitals having the energy levels which are indicated here and since you have 6 electrons, you would just fill them up in order to get the appropriate energy level diagram. So, let us now look at the actual form of these molecule orbitals of the cyclopentatide anion and these are pictured here.

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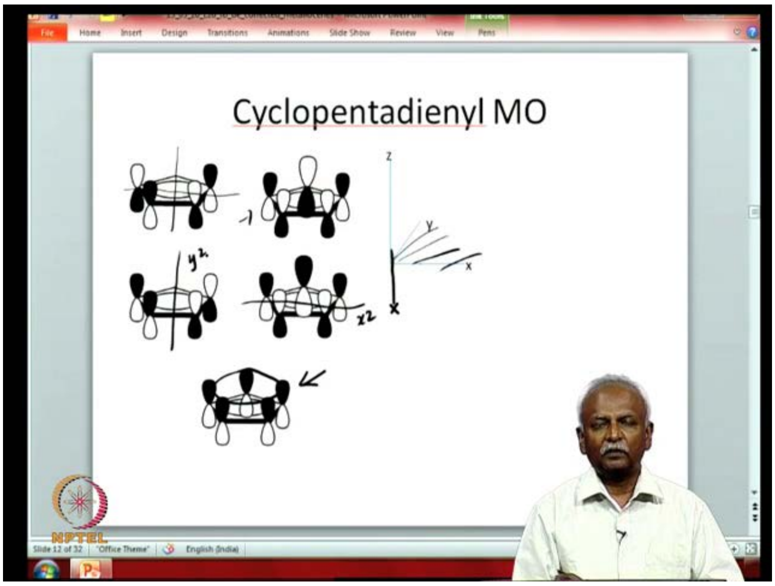

Cyclopentadienyl MO

Notice that the cyclopentadienyl and anion is placed in such a way that it is in the x y plane. The metal atom itself is implicit taxes, this access and so the metal atom is placed along the z axis and that is placed. Let us say at a point here and decided that the time made amiens is placed in the x y plane. So, that would be placed as if it is going in and out the plane of the screen..

So, here the form of the molecule orbitals of cyclopentadienyl anion you will notice that the longest occupied molecular orbital that is this orbital right here has got all the P orbitals oriented in such a way that the inflates, which means that there is no node. When you look at these MO's are these atomic orbitals. All of them are pherocene, the same direction and there is no note the next higher energy molecule orbital of cyclopentadienyl anion has got one node and this note model plane is running perpendicular or it is in the variety z plane to symbolise the plane..

So, the nodal plane is passing the x y plane and it is perpendicular in such a way that you now have a single node in the cyclopentadienyl, the orbitals. Now, you have another set of orbitals which are even higher in energy and these orbitals have got two nodes. Two nodal planes are easy to analyse right here. They would withdraw to nodal planes are going in this two directions, perpendicular to one another and if you look at this molecule or take they would be slightly diagonal but, you consider the to nodal planes right here for this MO also. In this a m MO to nodal plane is running in this direction. So, with that would be the x z, x z plane is a nodal plane here. You have the y z plane as the nodal plane. Now, you see that as a corporal energy the number of nodes increases. Now, these molecule orbitals will now have to be matched with a molecule orbitals, the atomic orbitals of the metal atom. So, let us do this.

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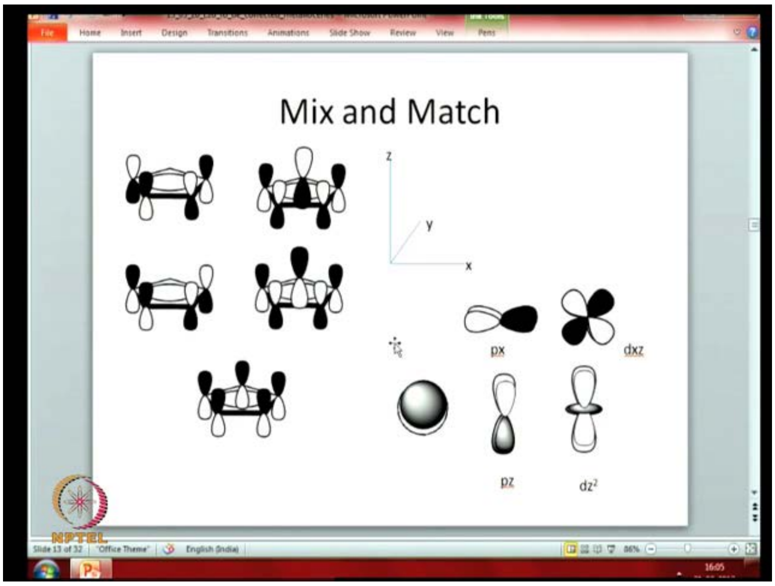

Mix and Match

Let us take a look at the animals that are available for the MAC tool these are pictured here with only one psychopathic time amiens and the is one cyclopentadien anion. So, that we can proceed in a stepwise fashion and see how they match. What you have to do is to make sure the symmetry of these orbitals are well matched. Let us first take the fore as orbital, the folders orbital the case of the 3 d transition series.

So, the forest orbitals pictured here you can see that you can put the metal as orbital and the top lowest average molecule deep. It would have the perfect overlap with all the key orbitals, because all of them are in the same phase and s orbitals also having the same fits. If you look at the p z orbital that also has the mats and you can see that this can be matched so that input in the centre of the cyclopentadienyl anion in such a way that it would have a good match with these orbitals as well.

So, similarly, if you take the d z squared orbital that also has a good match with this molecular orbital.So, in other words the lowest energy molecule orbitals cyclopentadiene anion has got the right symmetry to interact with all three of these orbitals. You will notice that it is god sigma symmetry which means that you can rotate the cyclopentadiene anion as much as you like with respect to the metal atom along the z axis and there would be no break in the overlap between the metal orbital and the cyclopentadiene anion possible to the next step. You see that the p x orbital has got the right symmetry to overlap the cyclopentadiene anion and the metal p x orbital solar metal for picnics will match perfectly in a pie fashion.

This time with one of the molecule orbitals and similarly, if you take the p y orbital that would be matched with this orbital right here the p t y would match with this and the px would match with this molecule orbital the d x z orbital also has the right symmetry. So, in this particular case it is easy to visualise if you place the metal atom in the centre of the cyclopentadiene anion slightly below the plane in which the cyclopentadiene anion is present. You will see that this now has got up I symmetry because we rotate the cyclopentadiene anion some of the symmetry would be some of the overlap would be lost. If you rotated by 90 degrees, it would be completely lost.

So, this two orbitals the exact reaction and the p t y will match with these two orbitals right here and you will notice that the d x z this pointed hoods are cyclopentadiene anion. So, it will have better overlap where is the p x has got only lacked overlap since one orbital is lying in the claim of the metal atom and the cyclopentadiene anion is in a parallel plane.

Now, similarly, there are 2 d exquisite manners were scored orbital which will have a suitable overlap here but, that would be very poor overlap also because the metal is different plane. It is not pointed forwards this set of orbitals. So, these are the orbitals which you can see by matching the symmetry would be able to find out which orbitals on the metal can overlap with the orbitals of the cyclopentadiene anion. Now, let us proceed further we know that in pherocene the two cyclopentadiene anion at the amiens's which are present in two parallel planes.

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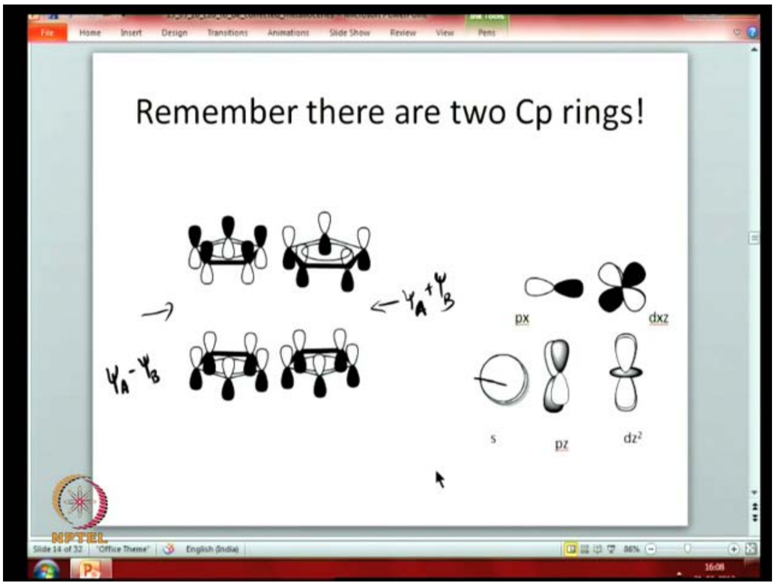

Remember there are two Cp rings!

So, if you take the lowest molecule orbital on the cyclopentadiene anion you can either place them in such a way that the two orbitals are oriented in the same way. So, it sat in such a manner that you will get the shaded portion of the loans pointed towards the unshaded portion of the lobes of the other psychopathic time or you can invert them in such a way that the unshaded portion is pherocene. The unshaded portion of the other cyclopentadiene anion, this is a equivalent to saying that you take site a that you take silently minus side B in order to get this combination and not get this combination you would get side a plus side.

So, these are two combinations that can be present because these two molecule orbitals are far away from one another. The energy of these two orbitals are very close to one another, will see this on the but, now let us mix and match the molecule orbitals. Here is that as orbital fears, the s orbital and if you want to use the s orbital take s orbital. If you take as orbital and place it here you can see that it has got the right face to overlap with the two molecular orbital cyclopentadiene ligand.

Similarly, if you take the desserts squared orbital that also has the right symmetry to overlap with this symmetric political or good variable of combined side A minus side B. Now, if you take the p x orbital then you notice that this political overkill where we have taken inside A plus B, that has got the right combination but, all of them have got the sigma symmetry in order to overlap with these two molecule.

Now, you will also notice that you cannot use a combination of the p x or that the ex-prisoner had to form any combination because the overlap that overlap would be 0. The symmetry of that will not allow you to match the dealings with this combination of this combination. So, as a result you can see that the display just by matching this molecule orbitals you can arrive at a qualitative molecular orbital energy diagram.

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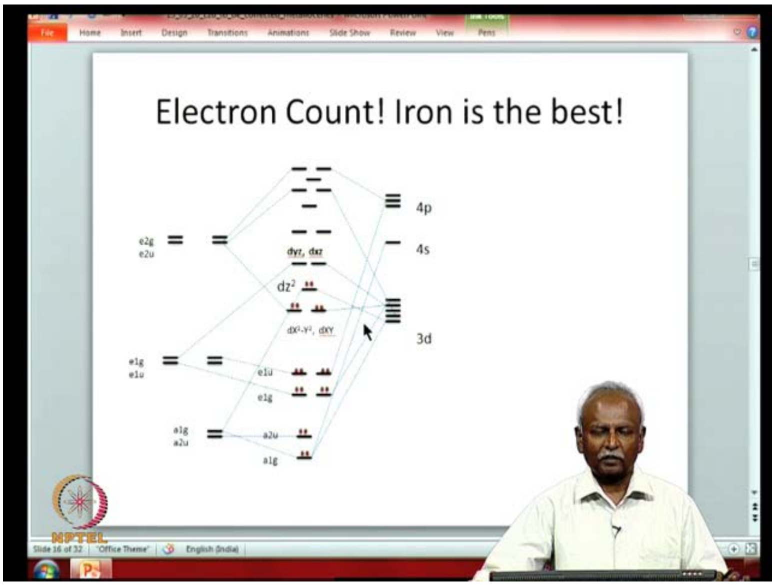

Electron Count! Iron is the best!

So, that is what we have done here. We have filled it up to this level, will notice that because you have 6 electrons here and have 12 electrons from the cyclopentadiene anion. You have filled up upto the energy level where there is sufficient stabilisation. If you fill up more electrons you will end up filling the d y z and that the d x z and those orbitals of the destabilise orbitals and so the system itself will be destabilised..

So, 18 electron rule holds good. In this case also the 80 electrons system which is formed by high-end 2 plus and 2 city minus units from a very stable molecular orbital car setup and it is the one which is the most stable of molecular orbital pitches available for the metal scenes among the greatest metal atoms that can think of..

So, did you can see that the filling up of less number of electrons or if you fill up more number of electrons you would lose the total stabilisation that is present. You can also see with the d z squared is almost present and non-bonding money and you can remove an electron from the desserts quiet and you still have a stable system software cinema fec p 2 can be oxidised to fec p 2 plus and you still have a stable political overkill..

Another interesting feature of this movie global diagram is a fact that the psychopathic time and amiens is a stabilised, mostly by the sigma interaction represent. So, you can have free rotation of the two cyclopentadiene anion groups around the z-axis. If you remember the orientation of the two cyclopentadiene anion is they are located in such a way that the metal is in the z-axis and the two cyclopentadiene anion salon that x y plane parallel to the exciting..

So, they turn out to be freely rotating systems and fought many metallocene. You can rotate the cyclopentadiene anion street and still have the stability of the whole molecule of the phone molecule due to electronic stabilisation. So, this helps us understand the electronic structure. Now, let us look at the filling up of the electrons and the properties and how they come about in the next slide.

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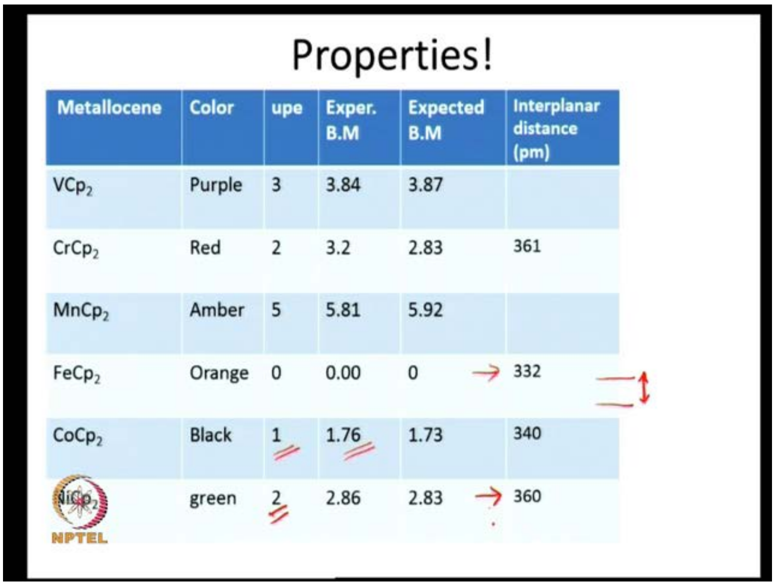

Properties!

Metallocene	Color	upe	Exper. B.M	Expected B.M	Interplanar distance (pm)
VCp_2	Purple	3	3.84	3.87	
$CrCp_2$	Red	2	3.2	2.83	361
$MnCp_2$	Amber	5	5.81	5.92	
$FeCp_2$	Orange	0	0.00	0	332
$CoCp_2$	Black	1	1.76	1.73	340
$NiCp_2$	green	2	2.86	2.83	360

So, the properties of the metal complexes are all satisfied by these. This particular simple quality overkill diagram of the picture that I drew for you here. So, a variety of metal 2 plus compounds can interact with city city -two city minus units and forms and which compounds. Many of them have electron counts of 18 were and when they have more number of electrons then they end up with let us say an extra unpaired electron as in the case of cobalt which has won electron more than iron.

This electron is right here is an unparalleled front leading to a magnetic moment of 1.76 bore electrons and this is exactly what you would expect for a molecule with one unpaired electron. The interplanetary distance between the two city links. So, that means the distance between the two city ranges 332 picometers and in the case of cobalt it ends up with a distance of 340 pico meters.

So, in the case of nickel you have to embed electrons and you are populating some of the antibody orbitals and as a result you have a paramagnetic molecule with two unparalleled trans border climate of the feminism of 2.86 is observed, sorry apparently does not have a paramagnetic molecule is observed having a magnetic moment of 2.86 bye-bye electrons. The distance between the two city ranges also increased to 360 meters to notice that I has got the shortest distance between the two city limits.

So, in other words they are likely the two city minus groups are tightly held to iron. That is natural because that is one way you have the perfect combination of metal electron content organic compound electron manganese and chromium have got less than what is required. Very often they are quiet and extra pair of electrons from another ligament and the stabilised the system that nevertheless cromoscene has been chriscrisler graphically characterised and we will look at this molecule moment and that has got a bond distance which is slightly higher and is as good as nicolosi which is three 60 pico meters.

Without the same as edina molecule which is gutsy unpaired electrons and expected balance of this molecule is exactly what you observe in the system. So, you can see from this list of properties that in fact it is possible to predict the experimental magnetic moment from the molecular orbital diagram that we do this. Now, by mixing and matching the appropriate molecular orbitals.

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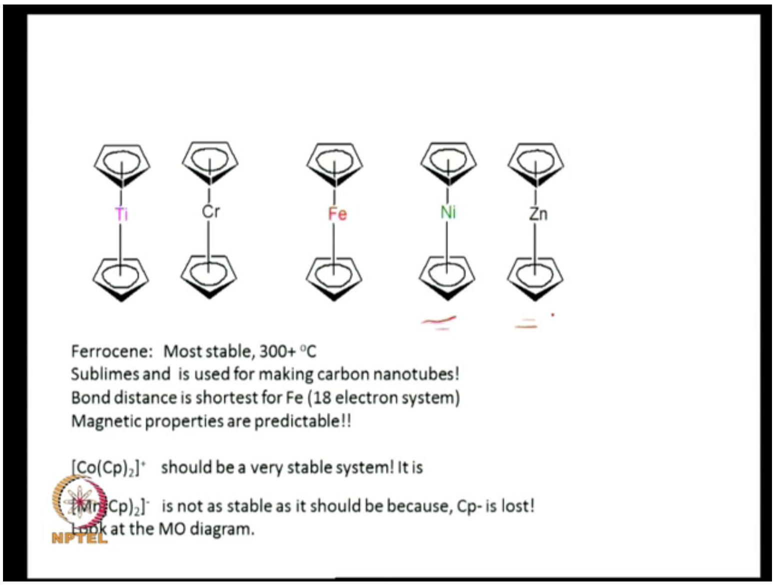

Ferrocene: Most stable, 300+ °C
Sublimes and is used for making carbon nanotubes!
Bond distance is shortest for Fe (18 electron system)
Magnetic properties are predictable!!

$[Co(Cp)_2]^+$ should be a very stable system! It is

$[Mn(Cp)_2]^-$ is not as stable as it should be because, Cp- is lost!
Look at the MO diagram.

Now, ferrocene as a mention to you is the most stable molecule. It is got its stable of 300 degrees which is remarkable for a simple organic molecule. It sometimes and can be in fact if you crack it are treated very to very high temperatures. In the absence of a little not really get converted to carbon nano tubes and that is one of the popular uses were pherocene nowadays but, during this process iron atoms get occluded in it and in the case of servicing the bond distance between asi mentioned earlier the eye and carbon bonuses the shortest.

It is also to be noted that the case of nickel and zinc, you end up with a end up with molecules which are going further and further apart to see things are going further and further apart. There is a different way by which you can move the metal act away from the centre and so reduce the number of electrons that the donated to the metadata. So, let us take a look at some of the structures which we have.

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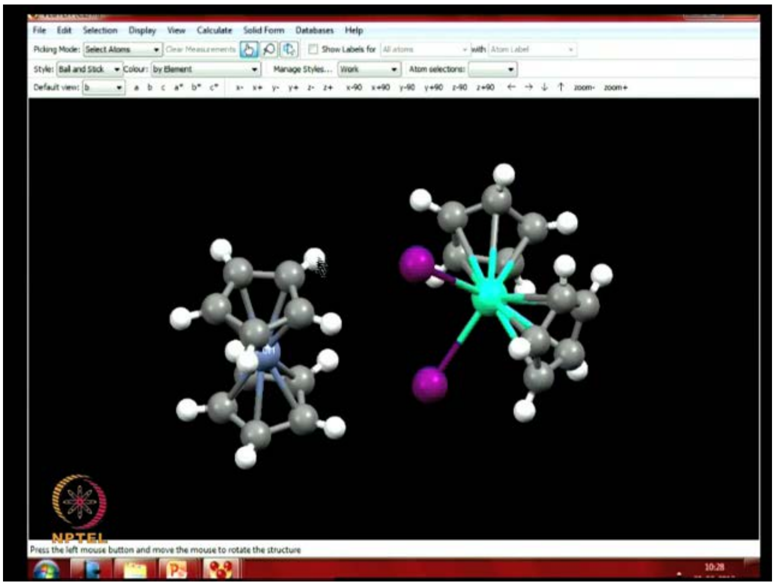

Picking Mode: Select Atoms

Style: Ball and Stick

Colour: by Element

Manage Styles... Work

Default view: b

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

I will first show you the structure which is formed by one of the metal of metal atoms. So, this is a metal atom which is coalescing. So, scene has got a structure where the two cyclopentadienyl units are perfectly stacked eclipsed. So, the two city units are perfectly eclipsed and as a conduit has got electron count which is not perfect and so the carbon carbon into planar distance between the two between the two rings is slightly more than what you have to first seem.

So, nevertheless this shows you how the structure can exist and here is another molecule which is co-crystallised with scene and this molecule is in fact to disclose him lament which I will show you in moment. The distro cm is also forming a cyclopentadienyl complex but it is got to either winds which are shown in purple here is to atoms are also coded disclose him but you will notice that because the distro cm requires the number of collections it has got.

The cyclopentadienyl units coordinated to it in addition, it is got to idle molecules also coordinated through it. So, this is the species which is caught and amiens in charge and the crime scene has lost an electron to the species and so this is how you have an animatic cationic co-crystallised in this particular molecule. So, let us take a look at another molecule.

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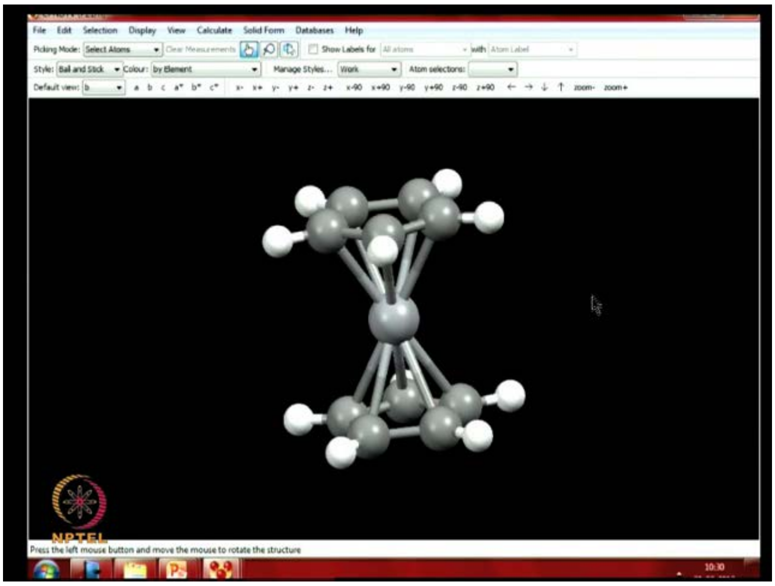

Press the left mouse button and move the mouse to rotate the structure

Now, we first looked at the social is here is another molecule. In this case the molecule is evident when addressing and you will notice that the winner receiving a standard with two city links which are present in it clear parallel to each other. Here you can see with your perfectly parallel, the plane in which the C 5 H 5 units of placed a perfectly parallel with one another but in this instance they are perfectly standard and in the case of the previous structure st we found that it was perfectly eclipsed.

So, the nature of these molecules allows for very easy rotation of wondering with respect to the other ring, so that said cyclopentadienyl ring is very easy to rotate along this vanadium cyclopentadienyl centroid accents. So, it is possible to spend the cp molecule very fast and as a result it is this has some consequences for the spectroscopy of these molecules. You usually end up saying equivalents for all these five hydrogens which are percent of the second amendment might.

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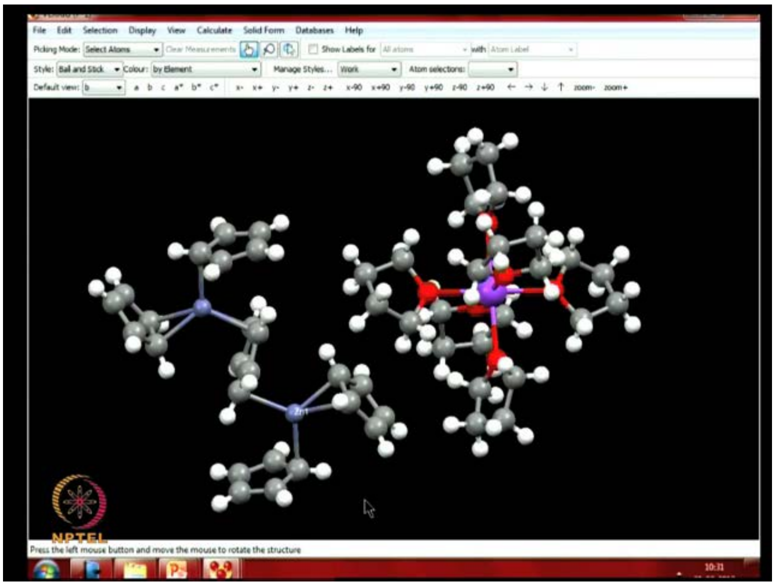

Picking Mode: Select Atoms

Style: Ball and Stick

Colour: by Element

Work

Default view: b

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

Now, let us proceed to yet another molecule. If you do have two systems when you have more of than the required number of electrons and matlack. In other words if you take a molecule exec, you should take a molecule like zinc. Zinc is also true plus matlacktom and here you have zinc coordinated to the sydney ratings. So, if you have two city thinks it will and should be having the right number of the charges. To balance that in this species it and see that there are three city rings which are coordinated to losing and distressing feelings coordinated to the zinc rendering an extra electron to system and as a result as a counter ion which is sodium which is present in this molecule.

So, here is a sodium atom which is sodium ion which is present as a counter ion for this C P 3 zinc 2 plus molecule. The city precinct 2 plus molecule is also not symmetrical coordinated as we saw in the previous kids. So, let us just take a look at the close look at all these include interacting with the C P U. So, here I have rotating it in such a way that you can see that this seed intellectual. This cyclopentadienyl unit is interacting mostly to the zinc which is labelled as zinc 1 here to only a single carbon I will market.

So, that you can see the type of interaction that you have, let us measure this distance between this carbon and zinc. It is 2.06 armstrongs, this is 2.06 armstrong. Whereas, if you take this carbon which is much further away from the zinc you can see that it is 2.3 armstrong sure. The cyclopentadienyl group is displaced from the centroid of the psychopathic dining unit president is displaced from the centroid in such a fashion that it is interacting with only one carbon atom is that if you look at the second cyclopentadienyl unit. That it is interacting with you see that carbon atoms interacting with.

So, here is one carbon atom which is at a distance of 2.4 armstrongs and here is another carbon atom which is at a distance of 2.08, that these three carbon atoms which I marked out for you. These three carbon atoms are at a much longer distance from losing. So, in one site zinc is interacting with two carbon. On the other side its interacting with only one cup and with yet another c to at its interacting with only one. So, you can see that you can have very an symmetrical bonding with the cyclopentadienyl units, when you have metal atoms which have the number of electrons. Then necessary for forming a stable battle scene structure but nevertheless these molecules have fascinating structures.

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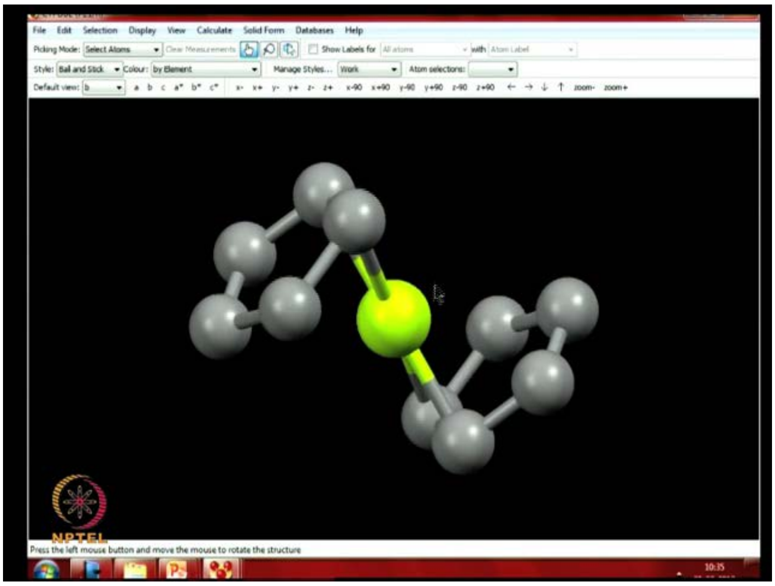

Press the left mouse button and move the mouse to rotate the structure

Now, in the case of the religion where the it is a main group element, here I am showing you the listing. The leucine is a case where you have the class and 2 C P minus units and these two city minus you retain a perfectly planar structure. So, you have only C 5 H 5 units which are into planes and these two planes are parallel to one another. Also, luxurious scene where the two cyclopentadienyl units are eclipsed standard. You will notice that these two C P rings are slept with respect to another.

So, they move away from one another and the beryllium is interacting with only two's second-seeded beryllium is interacting with two comments and the remaining carbons not interacting with the beryllium as much as the show. You can see whether a fascinating range of cyclopentadienyl structures that can be found in many cases. Cyclopentadienyl unit is interacting in a data file fashion.

That means all five carbon atoms are interacting together with the matlack but when the metal is a little small as in the case of zinc, when it is got to many electrons zinc is it true than plus detailed system. So, that means that an electrons then the metal slips from the centroid of the CP minus annual survey show that the number of carbon atoms. It interacts with is less and are nevertheless many of these molecules are stable and from interesting molecules for study.

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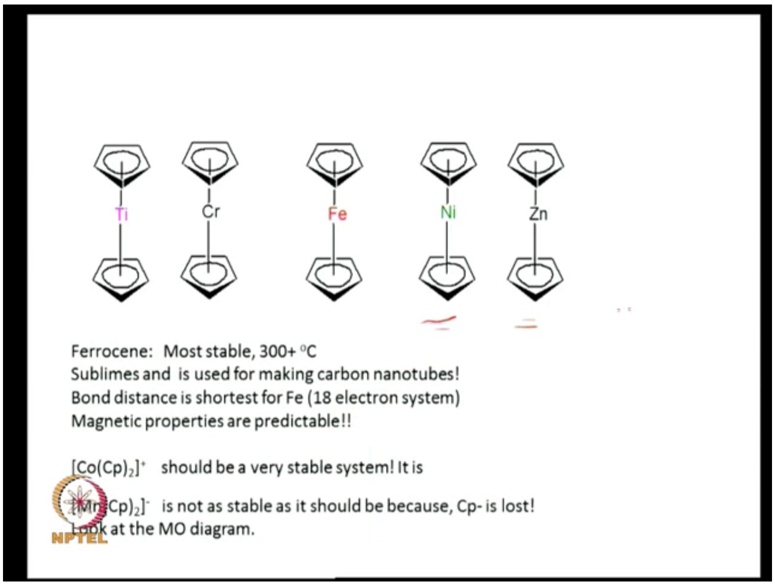

Ferrocene: Most stable, 300+ °C
Sublimes and is used for making carbon nanotubes!
Bond distance is shortest for Fe (18 electron system)
Magnetic properties are predictable!!

[Co(Cp)$_2$]$^+$ should be a very stable system! It is

[Mn(Cp)$_2$]$^-$ is not as stable as it should be because, Cp- is lost!
Look at the MO diagram.

So, let us get back now to the structures.

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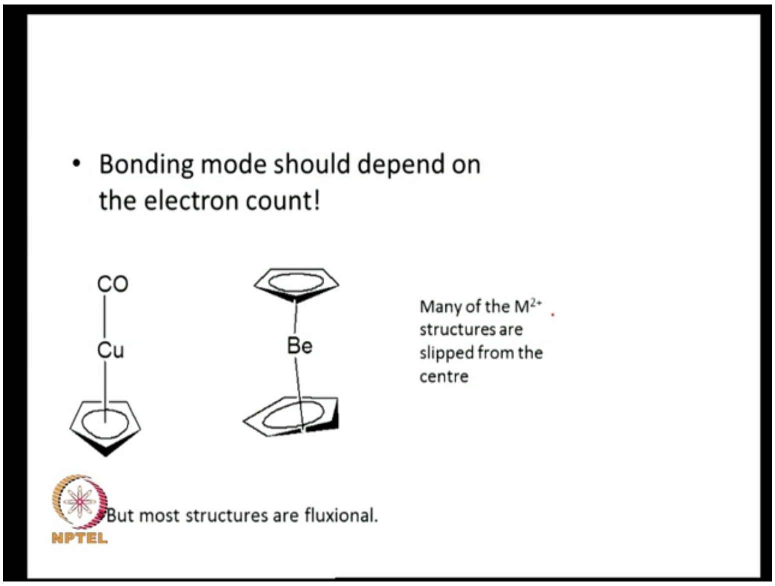

- Bonding mode should depend on the electron count!

Many of the M^{2+} structures are slipped from the centre

But most structures are fluxional.

The bonding as a mentioned depends very much on the electron count, if you have then it tends to interact with only one part of the cyclopentadienyl ring and the because it has got only sft orbitals to interact with the psychopathic dining unit. In fact, the leucine is a fairly very complex system because you have different structures and the one that I showed you had to carbons interacting with beryllium. You also have the leucine is where one of the carbons is interacting strongly with the beryllium and on the other side to carbons are interacting with a brilliant.

So, there are also molecules that you have for example which is a detailed system game. This structure turns out to be completely fractional where it appears as if one carbon is interacting strongly with copper but the copper is not oriented in the centre of the closest central rain. As far as crystallography is, so many interesting phenomena observed in the case of cyclopentadienyl metal complexes.

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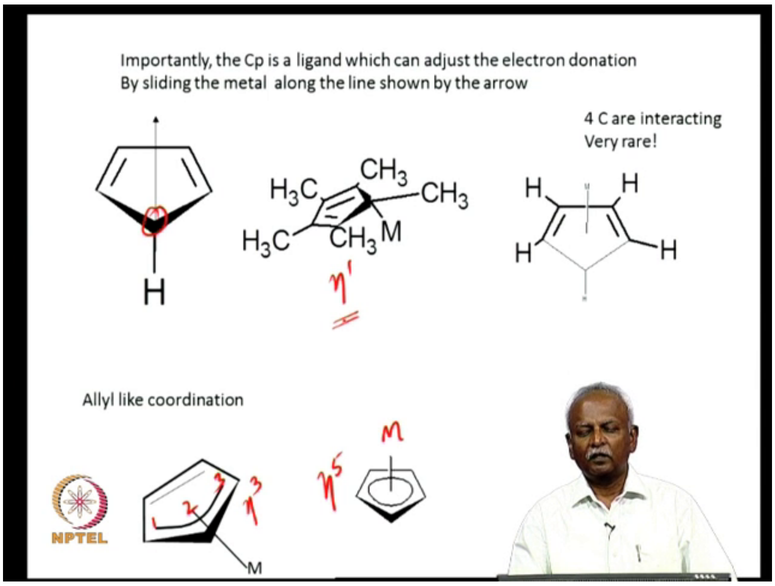

Importantly, the Cp is a ligand which can adjust the electron donation
By sliding the metal along the line shown by the arrow

4 C are interacting
Very rare!

Allyl like coordination

Importantly the CP ligand can adjust the number of electrons. It can give to the Mccain shoulder should draw. For example, you draw a line which goes in between the cyclopentadienyl ring in this fashion, like an arrow that shown you. You can only entertain such a way that only the first carbon atom which is only this carbon atom is interacting with. Then you would have eaten one structure and you can have systems were allowing liquid nation’s present.

So, that means the molecule is oriented in such a way that three carbon atoms are interacting with a map. Then you would also have systems where you have five carbon atoms which are interacting with the metal. In which case of course, we draw a circle and then we indicated as paedophile structure or if it is like an unlikely, we say it is indeed a three cyclopentadienyl unit or we can say that it is at it.

So, it is very rare to have a 4 carbon atoms interacting with the metal atom but as I just showed you one structure with the leucine rich possibly even to have structures where you have two carbon atoms after the cyclopentadienyl unit interacting with the metal atom.

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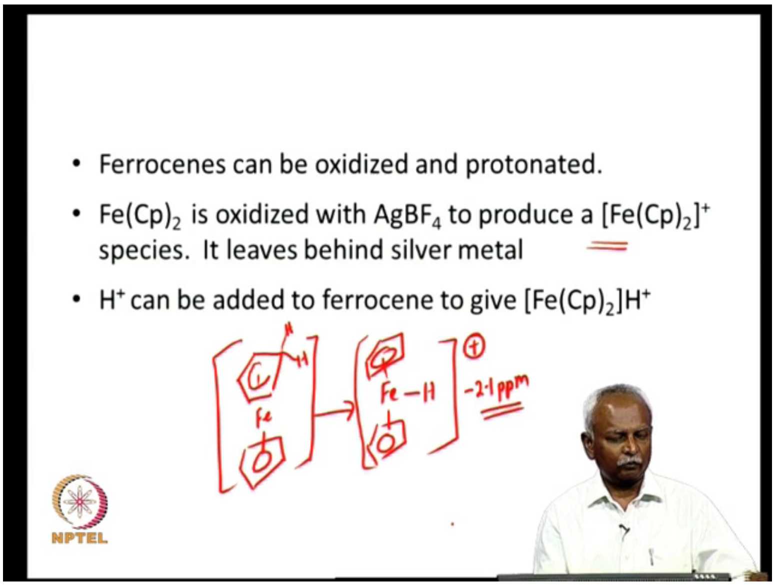

- Ferrocenes can be oxidized and protonated.
- $Fe(Cp)_2$ is oxidized with $AgBF_4$ to produce a $[Fe(Cp)_2]^+$ species. It leaves behind silver metal
- H^+ can be added to ferrocene to give $[Fe(Cp)_2]H^+$

So, let me just and the this lecture by telling you the story of adenosine. We did not discuss the internecine extensively but it was a structure that was in fact the fascinating story, because it was synthesised quite early in the game. That it structure was a mystery for a very long time and it was solved only recently and it turned out to be a structure where direct to bridging hydrogens and the adenosine cyclopentadienyl units with titanic. The title since the capitoline hill units had in fact I am pleased to form a full internet structure.

So, this is the real structure, so the same can be oxidised and appropriated F a C p too. For example, is very readily oxygenates inverted favourite and that generates F a C p 2 plus and this species is quite stable. One of the few ionic psychopathic dimethyl molecules, one of the few sandwich molecules patio scenes that can be very readily oxidised and studied and go and read, processing unit can also be terminated. Proton is at its plus can be added to give you F e C p, to which class it is not very clear. Whether hydrogen is present in these molecules lineages show you one option for this molecule.

It is possible to have fallacy in pictures like this and the proton can come from the top face of the Sydney. So, in fact it was suggested that it has a structure where you end up with a appropriated species like this and then the those seen migrates the proton migrates on the first link so that you end up with a appropriated species which is shown right here.

So, initially the proton arrives at the psychopathic dire unit as one would imagine because that is a negatively charged species and then the proton migrates from the top cyclopentadienyl unit to the metal atom to give you ion proteinated species and propagated a species and this is in fact a resonance of 21 parts per million suggesting the fact that the sitting next to the metal at some show. You can see that there is some very interesting chemistry what is important is that the highest occupied molecular opportunities in fact located on the ion.

So, you have expected the proton the electron to go away from the island and you would have an unparalleled electron on the island that is exactly what you say that you would expect the proton. Also tomorrow directly to the island because that is the highest occupied molecule orbital that in fact it seems to go to the setup and dynamic breakfast and then migrate to the next that’s in fact a kinetic phenomena.

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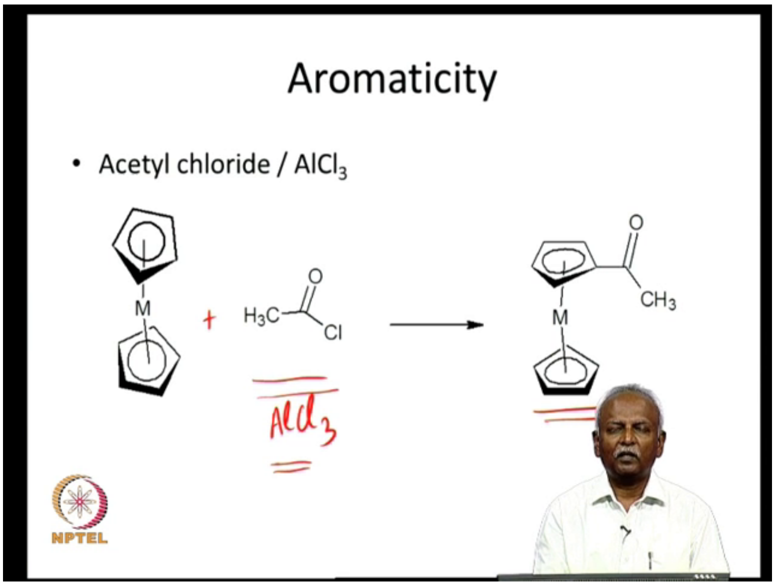

Aromaticity

- Acetyl chloride / $AlCl_3$

Now, it is also possible to a group of also possible to do aromatic type reactions with ferrocene and that is what was predicted by Woodward after looking at the structure because It is a cyclopentadiene anion which is aromatic and the disco nickel metal and he treated it with delicate pastel chloride and aluminium trichloride. The classic combinations of February, the frilly cuffs reaction and he used the seen and treated it with pastel chloride and learn with well. You could do a reaction on the cyclopentadienyl unit as safe, the rain is an aromatic benzene. So, that is another reason why the name kerosene stuck, because it was like benzene. So, you have an aromatic ring system which is present.

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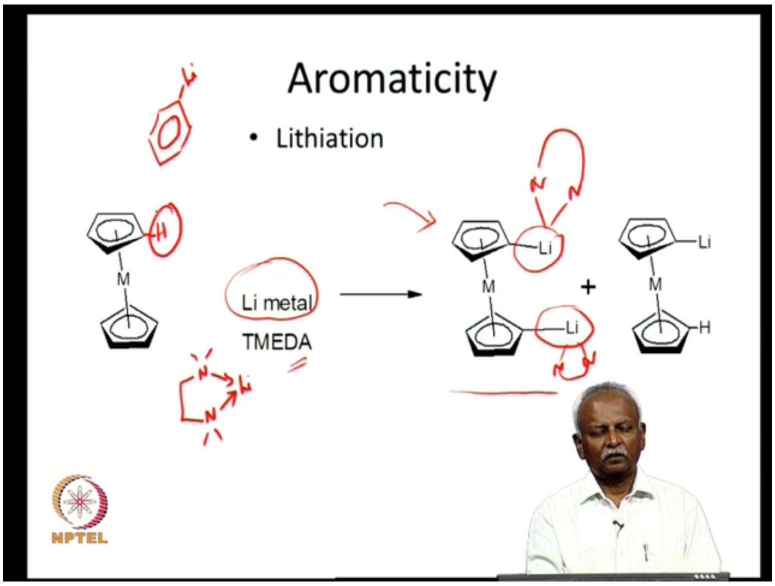

Aromaticity

- Lithiation

So, that another reaction to show you how the molecule is. In fact, if you take the same and treated with lithium metal and detrimentalthe mean, that immaculately diamond is an extremely good complexing agent. So, the full methyl groups on the tonight agents and that makes the nitrogen extremely electron rich and it coordinates to lithium very friendly and stabilises the lithium when it is attached to the cyclopentadienyl ring. So, this lithium atoms are in fact established by the ring system that I just talked about.

So, here is the ring system that is coordinating to the lithium and stabilising. In fact, that three of them, three better with little diamond units coordinated travel to lithium of this system is so stable that you can hardly created and included within even one equivalent of lithium and you will end up with the diversity. Its species just as much as you have communicated species very difficult to prepare fewer fans of the communicated species but nevertheless the guy located species can be prepared to form with treating it with an excess of lithium metal in the presence of dimethyl ethylene.

So, this is a game and aromatic behaviour of the first you will remember that molecules like benzene can be defeated very readily give you with your lipiobenzene. So, this is again an aromatic property and that is coming about because the acid there is some acidity associated with the hydrogens on an aromatic ring system.

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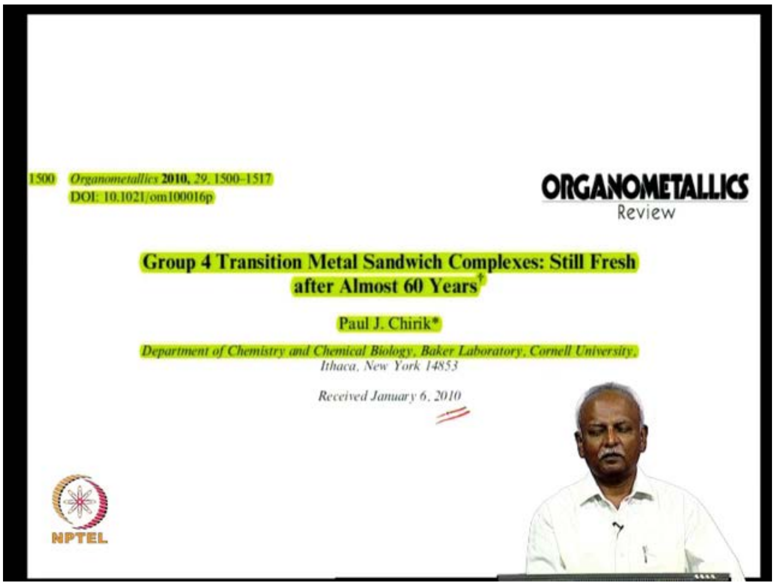

1500 Organometallics 2010, 29, 1500-1517
DOI: 10.1021/om100016p

ORGANOMETALLICS
Review

Group 4 Transition Metal Sandwich Complexes: Still Fresh after Almost 60 Years†

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Received January 6, 2010

So, this brings me to the end of today’s lecture where we have looked at a variety of sandwich complexes and as I told you the chemistry of the sandwich complexes are still fresh. In 2010, there was the review article that was published by Paul Sherik And that talked about how for 40 years the transition metal complexes of by of titanium and fasinated.

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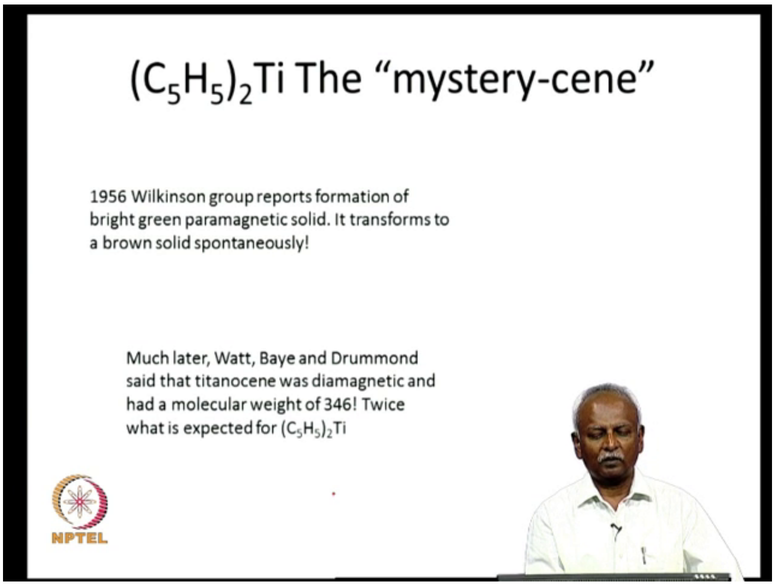

$(C_5H_5)_2$Ti The “mystery-cene”

1956 Wilkinson group reports formation of bright green paramagnetic solid. It transforms to a brown solid spontaneously!

Much later, Watt, Baye and Drummond said that titanocene was diamagnetic and had a molecular weight of 346! Twice what is expected for $(C_5H_5)_2$Ti

This is the interesting story, because in 1956 he had the cyclopentadienyl. The secretary-general titanium synthesised Wilkinson, that the many people could not reproduce. That result there was in fact the green paramedic compound that was a retrograde neutron. It was shown with a molecular weight was tries as what was expected.

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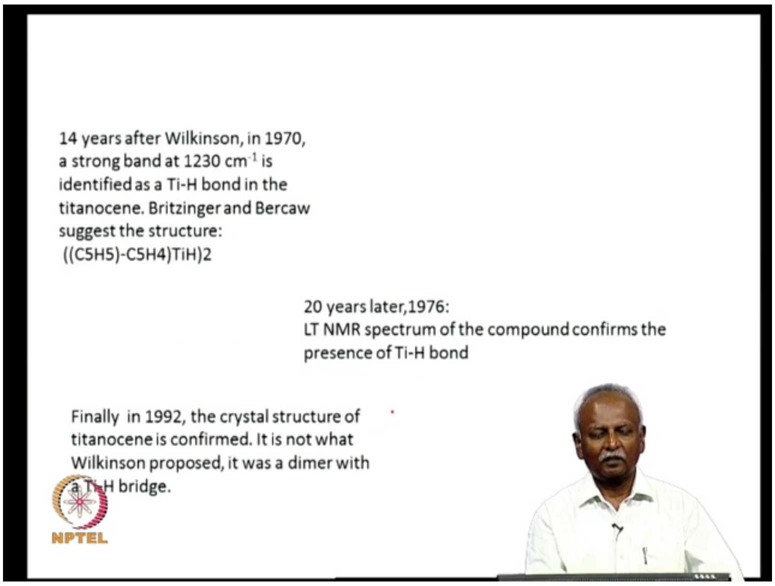

14 years after Wilkinson, in 1970,
a strong band at 1230 cm^{-1} is
identified as a Ti-H bond in the
titanocene. Britzinger and Bercaw
suggest the structure:
$((C_5H_5)\text{-}C_5H_4)TiH)_2$

20 years later,1976:
LT NMR spectrum of the compound confirms the
presence of Ti-H bond

Finally in 1992, the crystal structure of
titanocene is confirmed. It is not what
Wilkinson proposed, it was a dimer with
a Ti-H bridge.

Then it was after nearly 20 years that the N M R spectrum showed titanium hydrogen bond.

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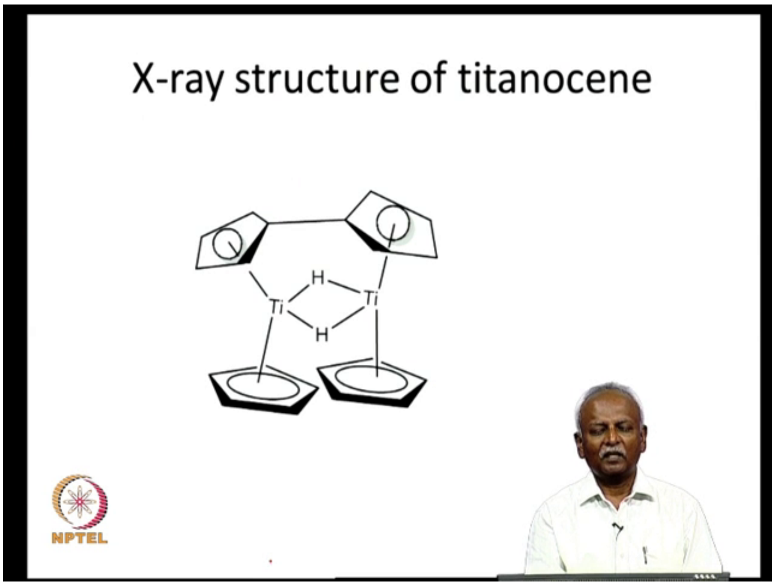

X-ray structure of titanocene

Finally in 1992 the structure of the molecule was solved and it was shown that it was in fact a fascinating dimeric structure. So, this brings us to the end of a brief introduction to cyclopentadienyl complexes of metal atoms as a truly business like periodic table. All the metal atoms have been synthesised and studied. So, we continue with this in the future.