Introduction to Organometallic Chemistry

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Lecture - 40
Special Properties and Applications

Organometallic chemistry is extensively used in catalysis for the synthesis of small molecules, for large molecules like polymers and in day to day applications in the laboratory. However, one always wonders whether it can be used for other purposes and whether it has been used and this question is answered in today’s lecture and presentation here.

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Special Properties & Applications

Sensors, MOCVD, Non-Linear Optics,

We will talk about some special properties and applications, in fact the number of instances where organometallics have been used is quite large, but we will consider only a few of the topics like sensors, metal organic chemical way deposition and non-linear optics.

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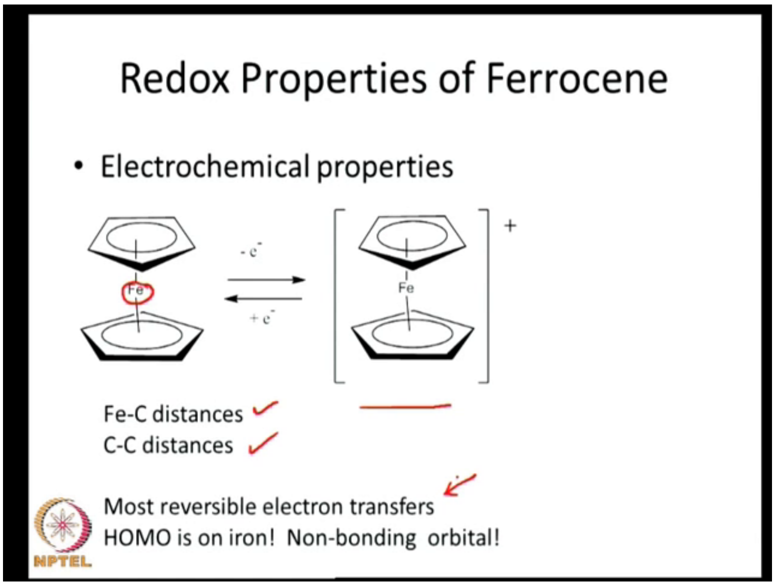

Redox Properties of Ferrocene

- Electrochemical properties

Fe-C distances ✓
C-C distances ✓

Most reversible electron transfers
HOMO is on iron! Non-bonding orbital!

So, let us start off with the special properties of ferrocene which makes it really suited for electro chemical applications. If you remember, the molecular orbital of ferrocene is such that the highest occupied molecular orbital is completely delocalised on the ferrocene, on the ion atom of the ferrocene. So it is at the ion atom, that the electron density is maximum in the ferrocene molecule. And if you remove an electron it is the ion which is depleted of the electron primarily and it is in a nonbonding orbital, an orbital which is not interacting significantly with the cyclopentadienyl rings. In spite of that we will see that there are some effects of the cyclopentadienyl ring.

But this nonbonding nature of the highest occupied molecule orbital gives the ion atom, tendency to have very little change when it goes from the ferrocene to the ferrocenium cation. So, the ferrocenium cation which is pictured here has got very similar ion carbon distances, it has got very similar carbon-carbon bond distances. And so it allows for reversible electron transfers and this property of reversibly transferring of electron to a molecule is possible only if the highest occupied molecular orbital is non-bonding. And that is accomplishing ferrocene.

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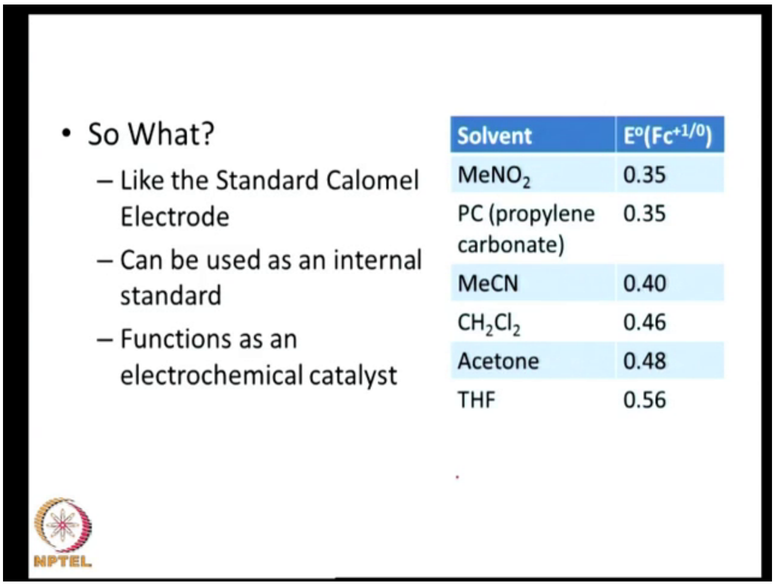

- So What?
  - Like the Standard Calomel Electrode
  - Can be used as an internal standard
  - Functions as an electrochemical catalyst

Solvent	$E^o(Fc^{+1/0})$
$MeNO_2$	0.35
PC (propylene carbonate)	0.35
MeCN	0.40
CH_2Cl_2	0.46
Acetone	0.48
THF	0.56

You might always wonder so if it not having changes in the bond distances and if it going to be reversible transfer, what is the use. If you recollect in electro chemistry, we usually use the standard calomel electrode as a reference point. And in some systems where the standard calomel electrode cannot be used, it is necessary to use secondary standard. And ferrocene serves exactly that purpose, in many instances ferrocene can even be used as an internal standard. That means, during the course of electro chemistry one can in fact add ferrocene into the solution, carry out the electro chemical experiment without ferrocene interfering, with the processes that are going on.

In other instances, ferrocene actually functions as an electro chemical catalyst. In other words, it permits the rapid transfer of an electron, from say the electrode to the solution to the species in solution. So, this kind of a rapid electron transfer or the catalysis of electron transfer is very important for electro chemical processes. On my right side, I have shown you couple of electrode potentials and all of them belong to the ferrocenium cation being reduced to the ferrocene neutral molecule, in a variety of different solvents. And you will notice that although, there is a variation in this potential as long as a solvent is kept reasonably constant, in other words if it is not contaminated with water or very polar compound. This voltage is reasonably close to the value that is indicated here. So, one can be sure that ferrocene can be used as a secondary standard in electrochemical applications.

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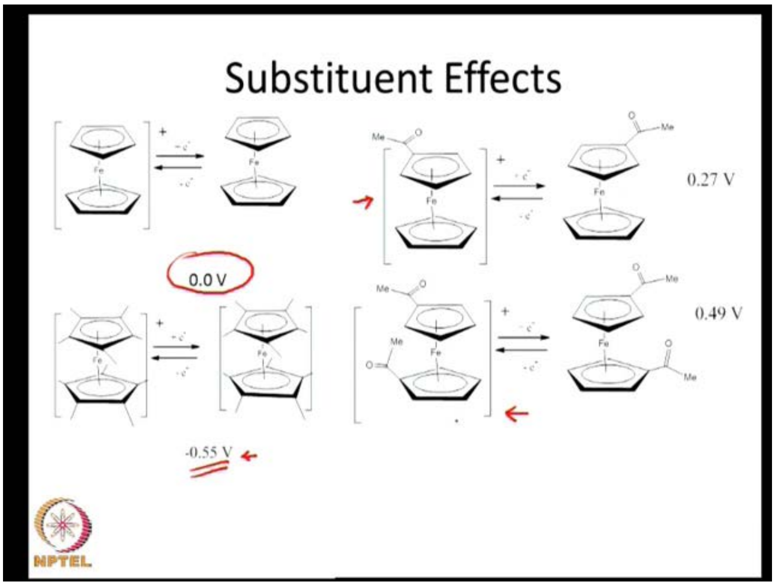

Substituent Effects

I told you that, there are some effects of the substituents on the cyclopentadienyl rings. Here I have shown you four different molecules with respect to ferrocenium, cation ferrocene and this electrode potential is marked as 0 volts because it is reference to the ferrocenium, ferrocene coupled. And you will notice that if I add a very electron donating substituent such as, a metal group on a cyclopentadienyl ring. In this particular case, of course we have added ten metal groups, five on the cyclopentadienyl ring on the top and five on the cyclopentadienyl ring on the bottom. And because we have added it, added so many electrons donating groups this molecule becomes very difficult to reduce. So, it requires about minus 0.55 volts with respect to ferrocene, to get reduced from the cationic species to the neutral species. So, here we are talking about a single electronic transfer.

Now, if you do a substitution on the ring with an electron withdrawing group, as in the case that I have shown here that is an acetile group is added. Then of course, it becomes easier to add electrons. Now, this seems to be slightly contradicting what I started out with namely, the electron is completely localised on the ion and it is in an nonbonding orbital, and this would require that you have no changes in the electrode potential. When you add or remove an electron withdrawing group, but never the less you can see that there are changes. But all these changes happened to be in a reversible fashion. In other words the acetyl for same, always has potential of 0.27 volts with respect to ferrocenium, ferrocenecation coupled.

So, if you make at the diacetyl group, as I have indicated here then of course, it becomes even more easy to compare an electron and it gets reduced at 0.49 volts with respect to ferrocene ferrocenium cation coupled. So you can see that there are substituent effects, but they all are still reversible electron transfers and one can depend on these chemical shift or electrode, electro chemical potentials changing in a systematic fashion.

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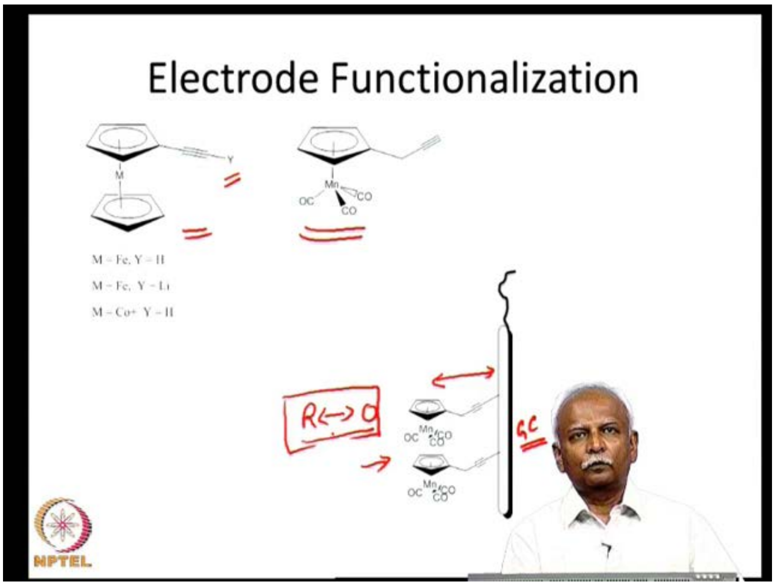

Electrode Functionalization

M = Fe, Y = H
M = Fe, Y = Li
M = Co+ Y = H

So, this has been utilised for functionalising an electrode as I have shown you, here I have an electrodewhich is sometimes a carbon electrode which, is attached to a cyclopentadienyl containing molecule. We talked all the while about ferrocene, but it can be several cyclopentadienyl complexes. There can be half sandwich complexes, as I have indicated here or these cyclopentadienyl complexes, as I have shown on the left hand side. So, if I have attached to cyclopentadienyl ring, then depending on the group which is there on the terminal position of the cyclopean alkaline group.

It can be oxidised and oxidatively coupled to the glassy carbon electrode. This has been very recently shown to be easy method for functionalising the glassy carbon electrode. So, this is a glassy carbon electrode, which is generallyan inert electrode where, you can carry out electron transfers, but the transfer itself has a high barrier, but when you attach an organometallic moiety.

As I shown here, then the electron transfer between the reduced and the oxidised species, the reduced and the oxidised species transfer electrons to the organometallic species.

And so transfer the electrons to the glassy carbon electrode. So, this transfer turns out to be a very facile transfer and the electro chemical reaction is facilitated, because of the functionalised electrode.

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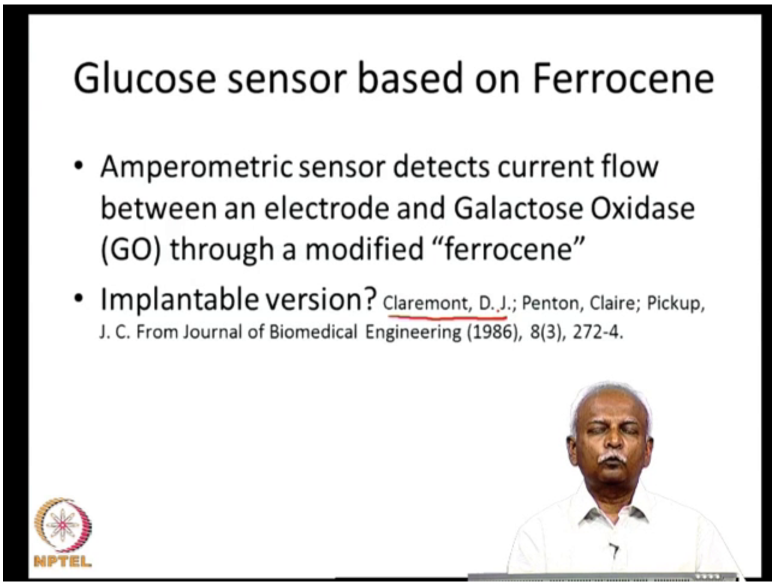

Glucose sensor based on Ferrocene

- Amperometric sensor detects current flow between an electrode and Galactose Oxidase (GO) through a modified "ferrocene"
- Implantable version? Claremont, D. J.; Penton, Claire; Pickup, J. C. From Journal of Biomedical Engineering (1986), 8(3), 272-4.

Now, this is exactly the principal on which, this is exactly the principal on which the glucose sensor. For example, has been designed these are amperometric sensors, in other words they measure thecurrent flow that is there in the electro chemical set up, in order to detect the presence of a species and to quantify the species. So you have an enzyme which specifically oxidises glucose, but the enzyme itself is not capable of transferring that electron to the electrode.

And so you need a modified electrode and the electrode is modified using ferrocene substituted species. And this is what is allowing Claremont and co-workers to even develop an implantable version of a glucose sensor, which would be extremely useful of course, for patients suffering from diabetes. They would have real time monitoring of glucose in the blood.

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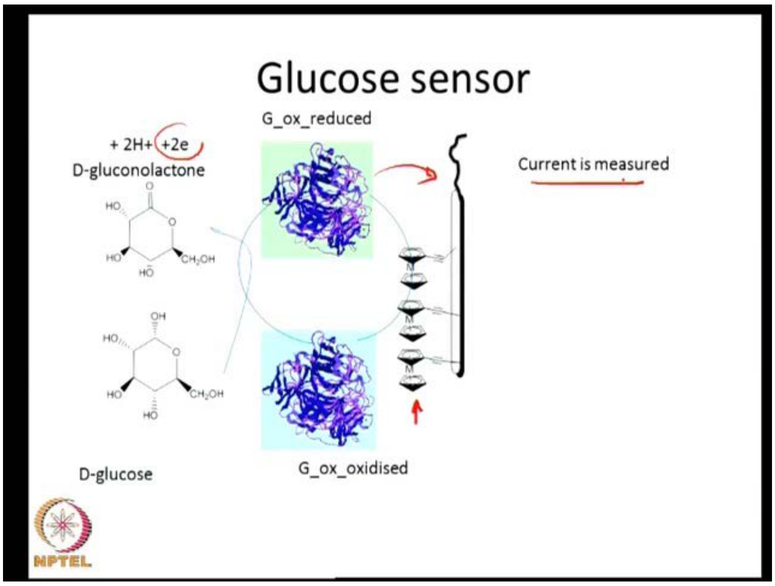

Glucose sensor

Current is measured

So this has, this is possible because you can have an electrode which is functionalise with say ferrocene or a substituent of a ferrocene and the glucose is oxidised glucose, oxidised enzymes, oxidises the glucose to a gluconolactone. And this gluconolactone when it is formed it releases two electrons and these two electrons are now transfered to the enzyme.

The enzyme in turn, transfers it to the electrode, but a direct transfer turns out to be difficult. And it is the ferrocene, which is attached to the glassy carbon electrode or a suitable electrode is a one which is necessary for conveying this electron from the enzyme to the electrode. So, you have a very easy way of measuring the amount of glucose that is present in the system, using this type of an electro chemical set up. Normally one usually, one measures the current that is being generated as a result of this electro chemical reaction.

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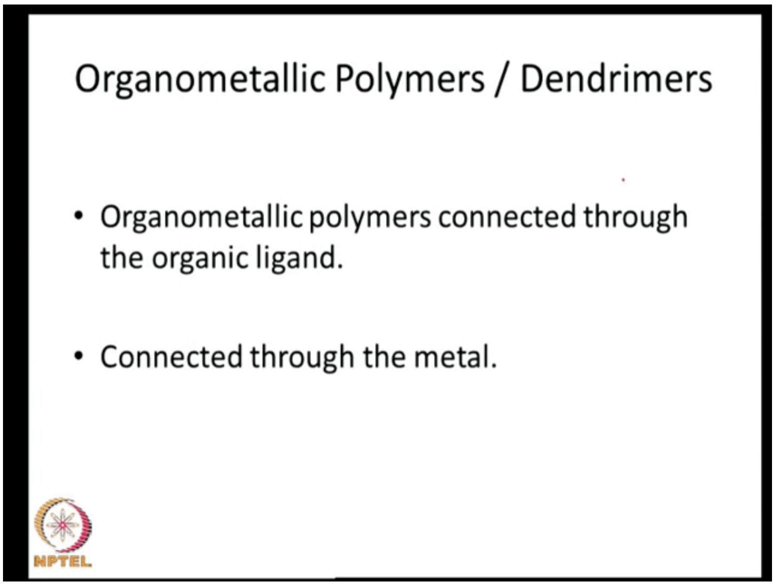

Organometallic Polymers / Dendrimers

- Organometallic polymers connected through the organic ligand.
- Connected through the metal.

And this is conveniently monitored. Now, you can, you might have realised that if I can use ferrocene as a catalyst, for an electro chemical reaction there must be a way of coating this electrode with the organometallic species. And one can use a single molecule functionalised and coated onto the electrode, or one can think of polymers, which are either polymers because they are connected through the organic ligand, that is the cyclopentadienyl ligand, that is present on the ion or one can think of connecting it, through the metal. In other words, is it possible for us to generate a polymeric species where the metal atoms are linked one after the other.

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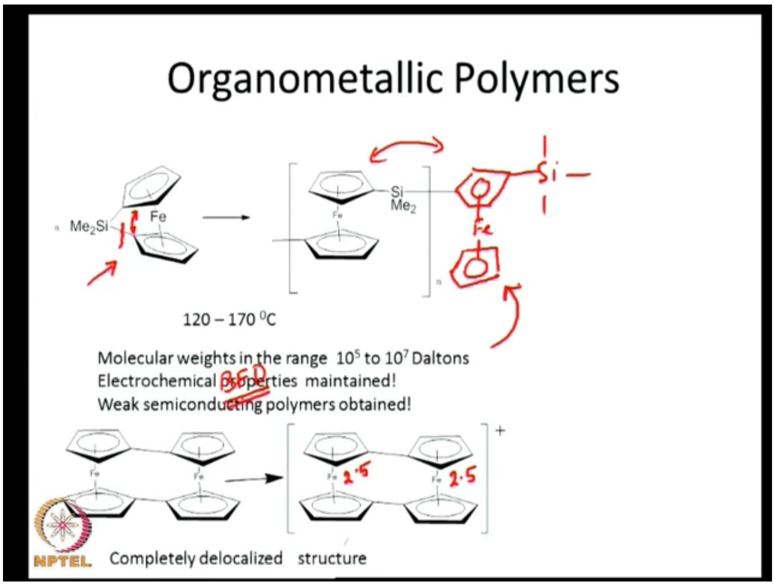

Organometallic Polymers

120 – 170 ^{0}C

Molecular weights in the range 10^5 to 10^7 Daltons

Electrochemical properties maintained!

Weak semiconducting polymers obtained!

Completely delocalized structure

So, here I have shown for you some organo metallic polymers and these organometallic polymers, are generated in a couple of different ways in the first, in this first example that I have shown to you. There is a unique way of linking the polymers and that is what is called a ring opening polymerisation. It is analogous to ring opening polymerisation, but in this case it is, it is assisted by strain that is caused when you link two cyclopentadienyl rings, through a very small bridge. So this bridge opens up and when this bridge opens up, it can link to another molecule in such a way that you can release this train.

And so this train that is there, because of this acute angle it should have been 180 degrees and it has made acute because of the bridge. When it reopens you end up with a very nice polymeric species, where there is no strain and ferrocene is linked to another molecule,to another molecule of the ferrocene, and a nice chain. So, this is the chain that is generated and this chain propagates. Now, what is the advantage of such a system, you have a processible polymer and this polymer can now be coated on to the electrode and so it forms an electro catalyst, which can reverse fully transfer electrons. And the transfer between these two systems also is reasonably facile, so that one can have very nice electro chemical reactions. Now, this transfer of an electron from one ion atom to the other although, I have presented as if it is easy, it is not always a completely reversible electron transfer.

And the system where it is completely reversible, is the bisfuleone di ion this is shown here, this is called bisfuleone di ion molecule. Where, the two cyclopentadienyl units are directly conjugated and if you, if both ion atoms are linked through both cyclopentadienyl rings, then it forms a completely delocalised system. So much, so the oxidation state of each ion is 2.5 and no property of the ion atom distinguishes it as plus 3 and plus 2 unit.

They are completely delocalised and completely equivalent and any time scale, that you can think of... So it is not as if, an electron is hoping back and forth, it is the electron is sitting in an delocalised molecular orbital on the two ion of the atoms. Now, the molecular weights of these molecules, when they are linked directly to each other or turns, turn out to be reasonably small.

But molecules like this, species can be fairly large they can be as high as 10 power 5 to 10 power 7 Daltons. And still the electro chemical properties of these molecules are maintained and they are weak semi conducting polymers. So, in other words, these organometallic polymers are useful species they turn out to be extremely valuable for electro chemically coating, some electrodes and also in some speciality applications, where you need a conducting surface for a particular application.

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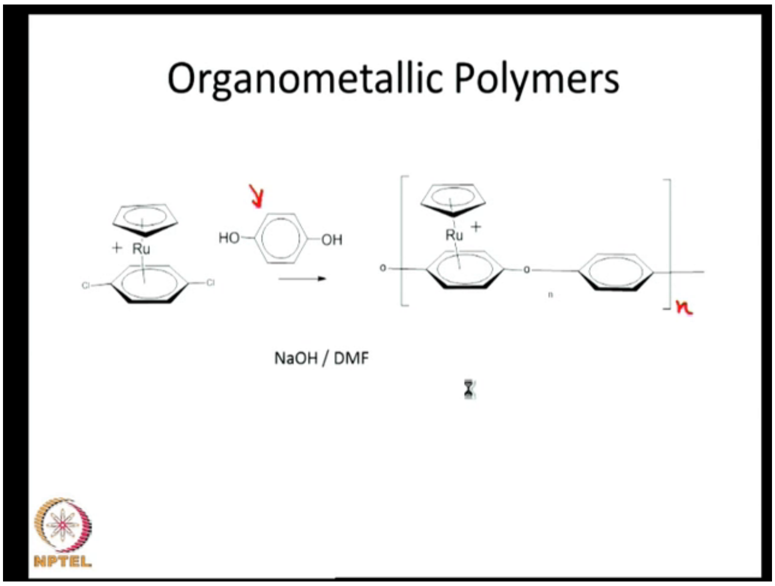

Organometallic Polymers

Here is another way, a second way which I want to illustrate for making an organometallic polymer. In this instance you have, you have a molecule which is a sandwich structure, but the sandwich structure has two different types of breads on either side of the metal atom, which is in the centre because you have aromatic ring. The aromatic ring has got two chlorine atoms and now you will remember that, because of electron withdrawal from the aromatic ring. It is now possible to carry out nucleophilic substitution of the aromatic ring with the phenoxy group.

So, any nucleophile will do, but if you have phenol which is a diol, then a disphilonic compound can do substitution with two different molecules of ruthenocene, which is now an polymeric species, because we are going to repeat this unit several times and so you have a nice processible polymer, which is linked directly, which is linking directly two different ruthenocene atoms or entities. So, this kind of substitution reaction turns out to be extremely useful.

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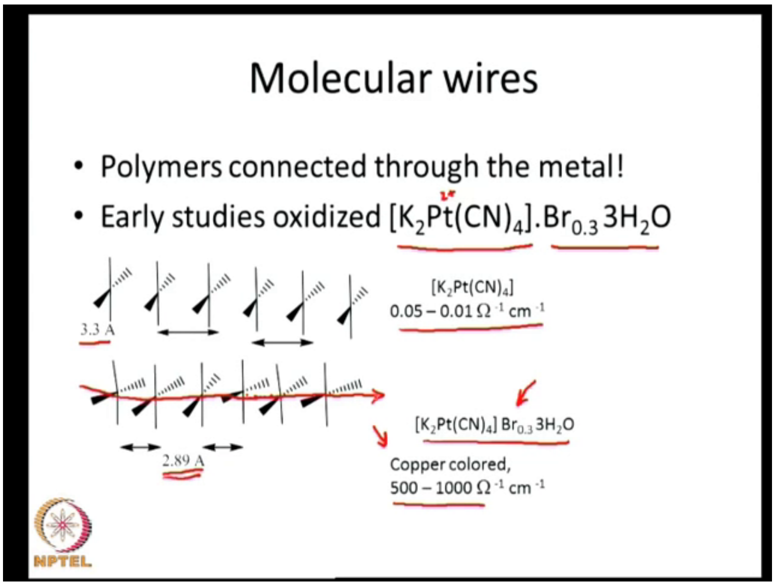

Molecular wires

- Polymers connected through the metal!
- Early studies oxidized $[K_2\overset{2+}{Pt}(CN)_4].Br_{0.3}3H_2O$

$[K_2Pt(CN)_4]$
$0.05 - 0.01\ \Omega^{-1}\ cm^{-1}$

$[K_2Pt(CN)_4]\ Br_{0.3}3H_2O$
Copper colored,
$500 - 1000\ \Omega^{-1}\ cm^{-1}$

And it can be used for several applications in electro chemistry, when it very small, say when it comes to an applications which requires a very small contact, people have thinking about making molecular wires. In other words, if I attach two electrodes through onlysingle molecular entity, then I can have a molecular wire, but very often these single molecules do not conduct electricity. And they turn out to be a very poor conductors. One of the early studies, which successfully made a molecule which almost look like a molecular wire, starts out with a platinum two species, which is a sign of complex although, we do not consider this entity as strictly as a organometallic compound.

It illustrates the purpose, it illustrates the principle that we are talking about and that is a making of a molecular conductor. So, this platinum two plus unit, can be partially oxidised with bromine to generate this oxidised species, which turns out to be extremely interesting. Here is the oxidised species and here is the neutral species, the neutral species the platinum the PtCN for 2 minus are separated by 3.3 Armstrong. Distance is significantly reduced, when you oxidised the platinum, oxidisation of the platinum leads to shorter platinum platinum interactions, this distance turns out to be reduced significantly. And that is being attributed to removal of electron density from d z squared orbital, which is along this axis.

So removal of an electron from this axis and formation of a platinum platinum bond along this axis, leads to the formation of a molecular conductor, because it is only going to be a half filled orbital, both electrons are not removed. This is a partial oxidation and this gives you exactly the features of a conducting material. Turns out, that this can be made with a variety of different oxidants, with platinum oxidised in such a way that the anionic species is not there, but the cation is presented in non stoichiometric amount.

Whatever be the procedure you end up with a copper coloured, metal coloured compound which has got a reasonably high conductivity. Of course, this does not have the good property of polymer, that we talked about earlier, but never the less this is a molecular wire because the conduction is extremely high along this axis. And this conductivity is also a nice attribute very clear indication of the fact that, it is delocalisation of the electrons on the platinum along one particular axis.

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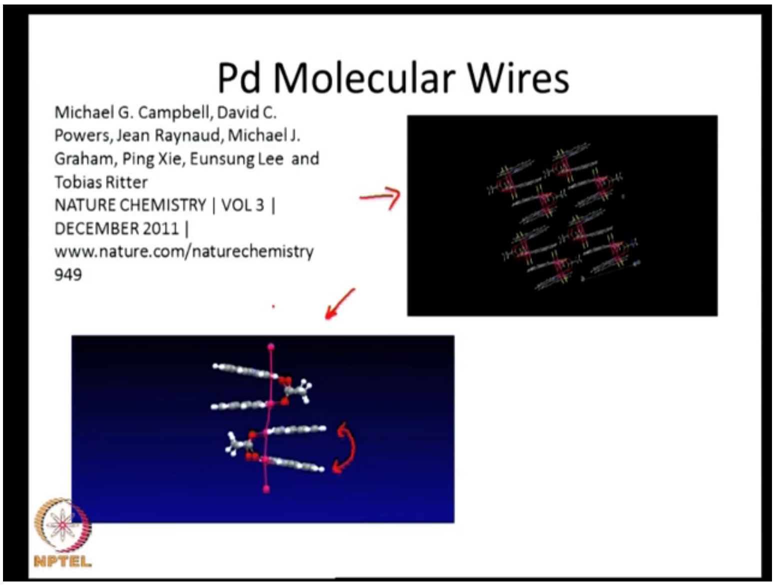

Pd Molecular Wires

Michael G. Campbell, David C.
Powers, Jean Raynaud, Michael J.
Graham, Ping Xie, Eunsung Lee and
Tobias Ritter
NATURE CHEMISTRY | VOL 3 |
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www.nature.com/naturechemistry
949

Now, in a very dramatic development recently palladium molecular wires have been made. Now turns out that platinum, turns out that platinum was the only example where such a molecular wire was made and here for the first time the palladium has been utilised to make a molecular wire. Once again palladium two plus complex, is a complex to start out with and these molecules are pictured on the top. These are discrete molecules they are stacked, but nevertheless they are not aligned with each other in a solid state.

So, they are palladium two plus complexes, but if you oxidise them very strange thing happens, a palladium-palladium bond happened is formed, just like you have in the case of platinum. Now, there are two different things that are happening, one is that the aromatic ligands, which are interacting with the palladium align themselves. And also the palladium-palladium atoms are aligned so what so that this compound is likely to be a semiconductor or a conductor at best. Let us take a look at oxidisation reaction that are been carried out.

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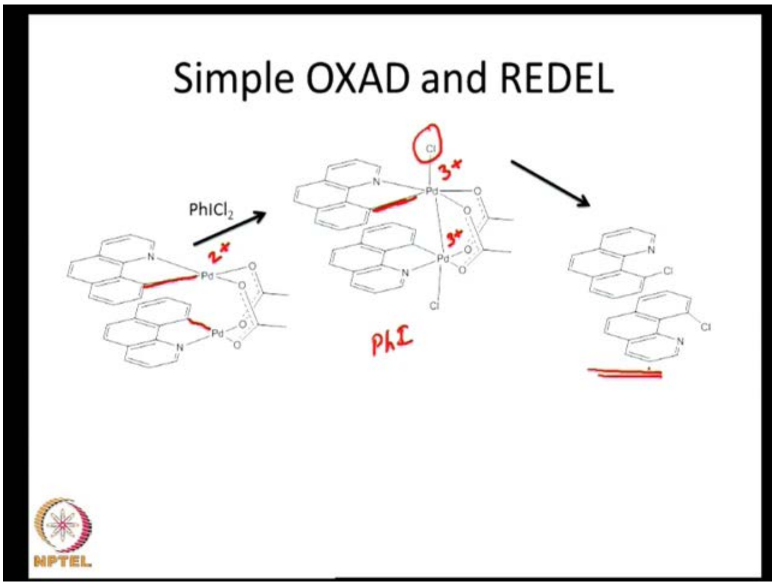

Simple OXAD and REDEL

This was a interesting case of a dinuclear system undergoing, oxidative addition when the researchers Tobias Ritter used PhiCl2. PhiCl2 has a tendency to become Phi, Phi and Cl 2 oxidises the palladium. During the course of this oxidation, each palladium atom which was originally a palladium 2 plus centre became palladium 3 plus centre. But, because there are two electrons coming from the two chlorines, you have both palladium oxidised to palladium three plus centre. You will notice that, there is a palladium carbon bond in this molecule so that accounts for the second source of electrons for this molecule.

So, you have palladium two plus to begin with and have three anionic ligands. So, you have a palladium three plus dinuclear oxidised centreand surprisingly this molecule when you heat it, it only gives you a reductive elimination, where this chlorine is removed along with this palladium, along with breakage of this palladium carbon bond and formation of a chlorine carbon bond, which gives you this molecule, two units of this molecule. So, this is a case of a simple oxidative addition under reductive elimination.

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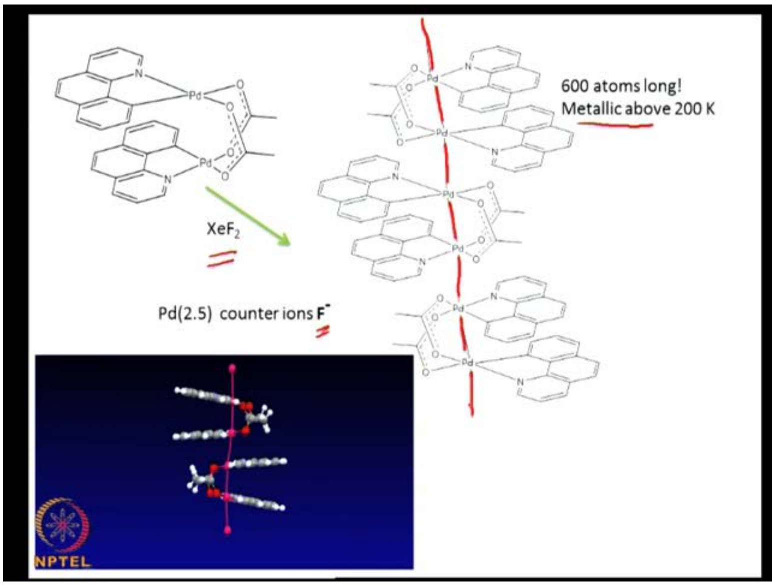

XeF_2

Pd(2.5) counter ions F^-

600 atoms long!
Metallic above 200 K

Surprisingly when the, when the workers used xenon fluoride di fluoride, they formed this very interesting molecule which had counter ions of fluoride, which is what you would expect. But a very strange alignment of the palladium and the formation of a palladium-palladium bond and this palladium-palladium bond is close to 600 atoms long in the crystals that are available. They are so long that needle like crystals which are metallic about 200k and it is very clear that there is de-localisation of the palladium orbital, in such a way that you have this nice molecular conductor been generated because of this orientation. So, this is the same molecule we showed you earlier and here it is shown as the line diagram.

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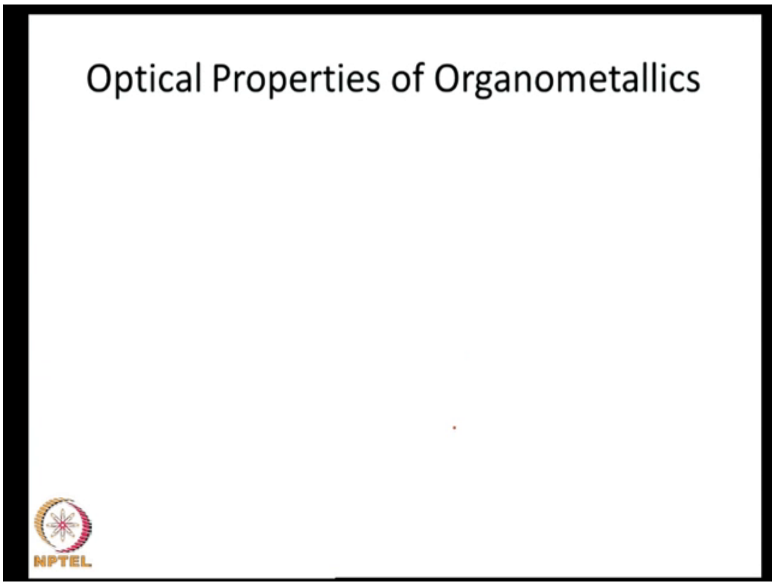

Optical Properties of Organometallics

Now, let us move on from electrical properties to electronic properties of organometallics. The optical properties of organometallics are very similar to the optical properties of many organic compounds.

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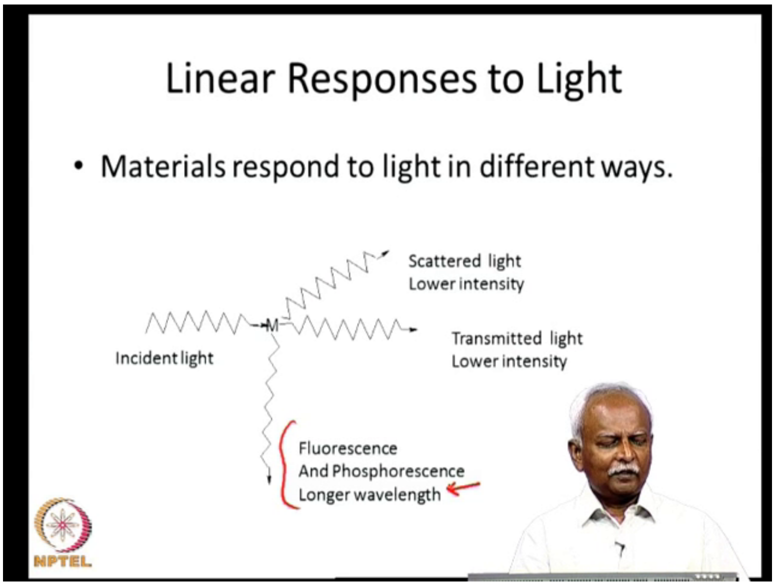

Linear Responses to Light

- Materials respond to light in different ways.

Scattered light
Lower intensity

Incident light

M

Transmitted light
Lower intensity

Fluorescence
And Phosphorescence
Longer wavelength

More often the material respond to light in a linear fashion. If you have a light falling on a molecule, the molecules scatters the light and that light comes out with a lower intensity. It also transmits the light and that also comes out with a lower intensity because some of the light, some of the photon are absorbedthe molecule, if they have the right energy to excite an electron from the ground state to the excited state.

In some instances, in few instances when you can have excitation, the excited electron coming back to the ground state. You can have fluorescence or phosphorescence because there are some changes in the vibrational state of the excited state molecule, you do have changes in the wavelength of the light. Usually the light that comes out is of a longer wavelength. So, in most properties that you have observed for molecules, the incident light frequency and the light that is transmitted or scattered is usually of same wavelength or of a longer wavelength.

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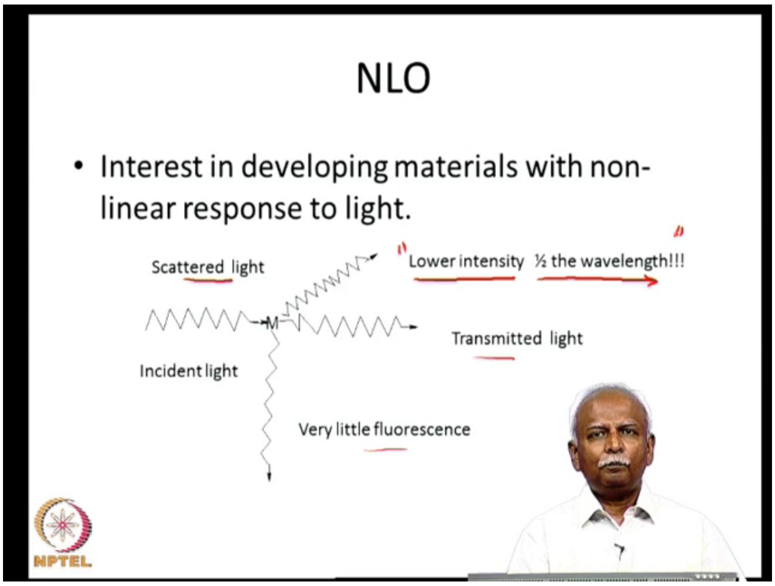

NLO

- Interest in developing materials with non-linear response to light.

Scattered light

Lower intensity

½ the wavelength!!!

Transmitted light

Incident light

Very little fluorescence

There are very few instances, where molecules interact with the light in a non-linear fashion and here also the intensity of the light that is coming out is of a lower intensity. But it turns out to be half the wavelength of the light that is incident on the molecule. Now, as energy is inversely proportional to wavelength, you will notice that the light that is coming out is of a higher energy than the light that is coming in. And so the intensity obviously is going to happen, two photons coming in and both photons have interacted in such a way in the molecule, such that lower wavelength or energy containing photon is coming out from the molecule.

During these processes, all the other processes we have talked about fluorescence, transmittance of light etc, all of them, scattering of light, all of them are happening. But in addition to these properties, you have this non-linear response. Now this non-linear response is very interesting, because you can use light of a low wavelength to convert it to a light of even smaller wavelength, but higher energy. So, this turns out to be very interesting and one has to maximise it and the whole rays or the challenge is to maximise it and the intensity of this half wavelength light that is coming out. So, how does one do it, people have been working on this particular property for a long time now.

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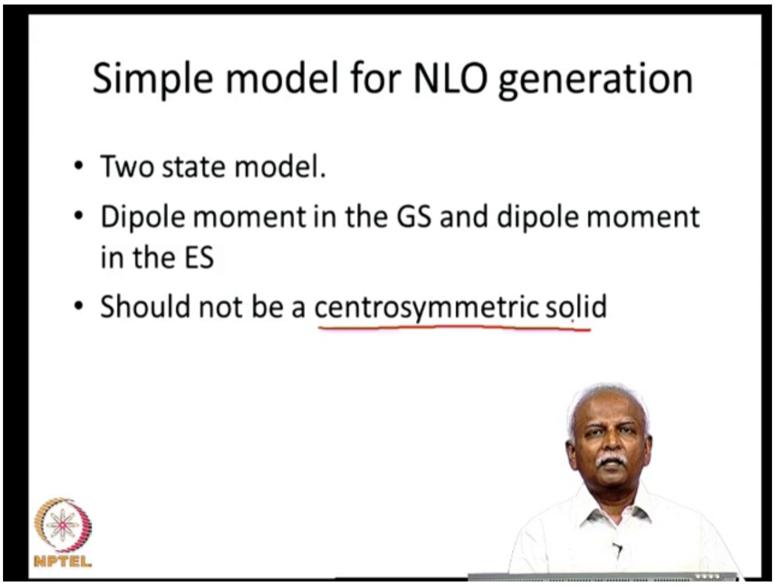

Simple model for NLO generation

- Two state model.
- Dipole moment in the GS and dipole moment in the ES
- Should not be a centrosymmetric solid

And a few simple thumb rules can be derived from, what is called the two state model. According to the two state model, it is the difference the dipole moment between the ground state and the excited state, that is important. So, can we manipulate organometallic molecules such that, they have a very large change in the dipole moment. This can be done with organic molecules also and it has been done and what one can do with organometallic molecules, however is slightly different. And that is what we going to talk about. Second point that one has to note is that, in solid state it should not be a centrosymmetric solid, which will result in cancellation of this dipole moment and results in a zero response for the non-linear optical property.

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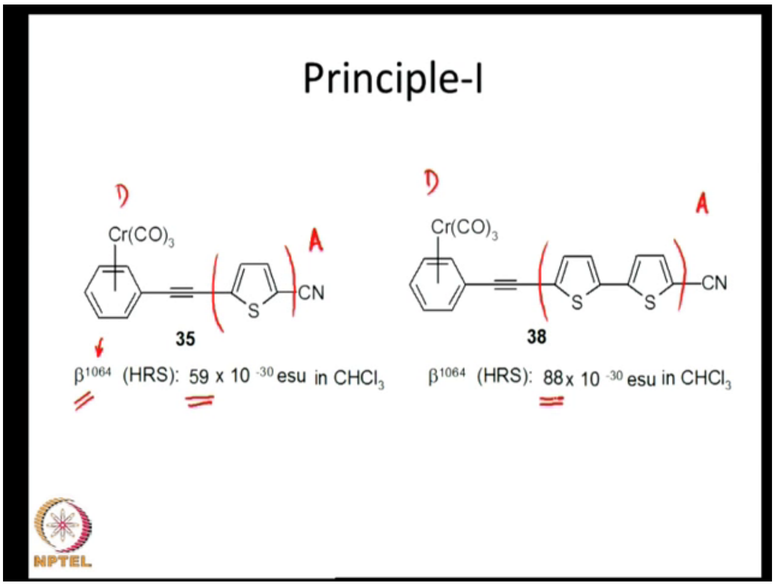

Principle-I

35

β^{1064} (HRS): 59 x 10^{-30} esu in CHCl$_3$

38

β^{1064} (HRS): 88x 10^{-30} esu in CHCl$_3$

So, this nonlinear optical property is measured as the coefficient beta, and if the incident light is having a wavelength of 1064 nanometres. It is indicated as the superscript because the non-linear is dependent on the wavelength of the light that is coming in. So, if you have 1064 nanometres light the beta value would be different from what you have. If you have 532 nanometres light that is coming out. Usually these measurements are made, are made with a high powered lasers because the intensity of the low wavelength, high energy light that is coming out is reasonably small. So, you need a laser in order to measure the wavelength and intensity of wavelength coming out.

So, here are two molecules and the first principle that one can see is that, when you increase the conjugation and the conjugation has been increased by adding this thiophene group. So your one thiophene group here, here you have two thiophene groups and you will notice, you have two different groups. You will make it a donor and an acceptor. So, this donor acceptor units are separated by a larger distances in this molecule and that leads to a larger value for the non-linear response. So you can see that this is just one example, but a multitude of examples can be given. Where, it is very clear that if one increases the conjugation between the donor and the acceptor then it is possible to increase the non-linear responsive in the molecule.

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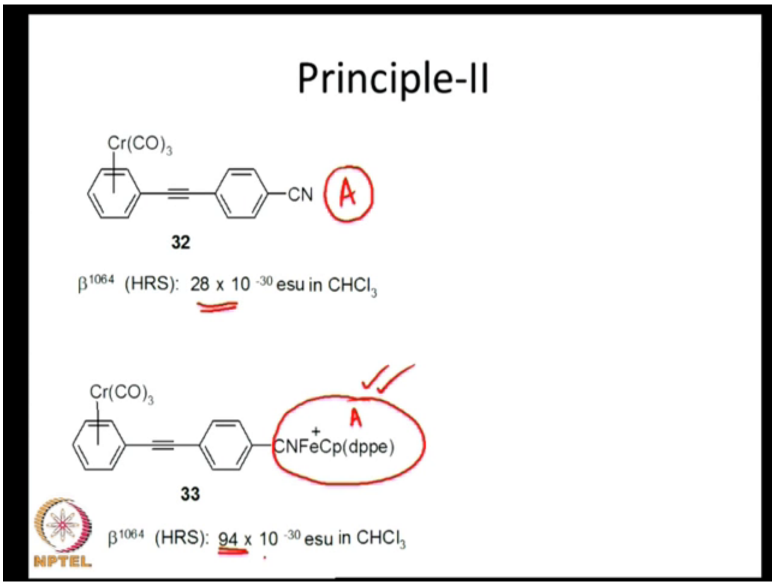

Principle-II

32

β^{1064} (HRS): 28 x 10^{-30} esu in $CHCl_3$

33

β^{1064} (HRS): 94 x 10^{-30} esu in $CHCl_3$

The second principle that is clear, is that if on hasa better acceptoror a better donor, it is possible to have a better non-linear response. And again illustrating it with a similar molecule, but you will notice that there is a tremendous increase in the non-linear optical property, by attaching a molecule next to the sign of group, which makes the sign of group a better acceptor. So, this is an acceptor to start with, but this acceptor is much, much better. So because of the increase in the accepting property of the ferrocene half sandwich that is attached here, you have been able to increase the non-linear response by more than two fold, close to threefold increase in the non-linear response has been achieved. So, these are two simple principles which are shown to you using organometallic examples.

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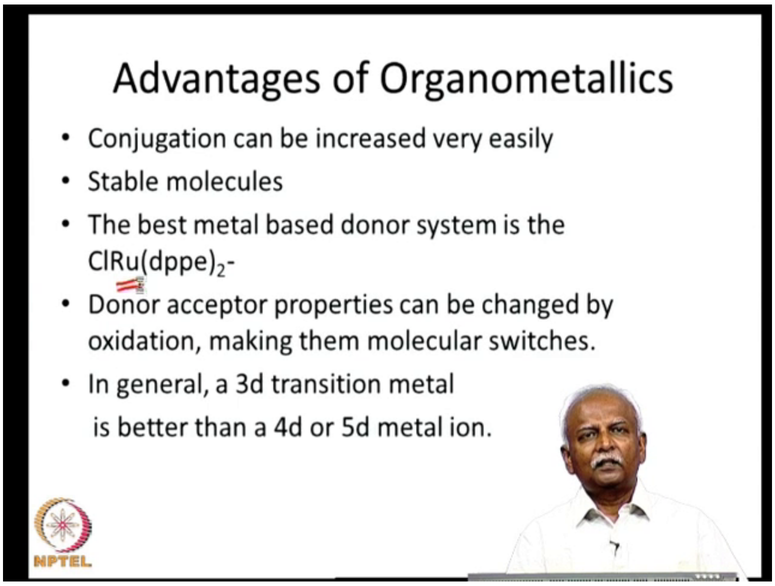

Advantages of Organometallics

- Conjugation can be increased very easily
- Stable molecules
- The best metal based donor system is the $ClRu(dppe)_2$-
- Donor acceptor properties can be changed by oxidation, making them molecular switches.
- In general, a 3d transition metal is better than a 4d or 5d metal ion.

But it is clear that some generalisations can be made on the basis of a large number of studies that have been done. Firstly, conjugation can be increased in order to achieve larger non-linear response and this is increased very readily in organometallics molecules. Secondly, they have to be stable because high intensity lasers come in and so if the molecules are not very stable on heating they, can decompose and loose the response. So, far the best molecule or the unit that has been found to be a donor has been this diphenyl phosphino ethanemole the attached to a rutheniumcentre and the donors are better as we go down the group.

It is also possible that, donor acceptor properties can be changed by oxidation. That is one advantagein an organometallic non-linear optical material, because you can make molecular switches by reducing and oxidisingthe ruthenium centre, you would be changing the redox properties of the molecule in question. Now, in generala 3 D transition metal is better than 4 D or a 5 D transition metal. And because you can polarise the 4 D and 5 D transition metal, one would have expected the opposite to be true, but in general it is been found the 3 D transition metal are better. So, the organometallic compounds provide a very clear advantage for making new non-linear optical materials.

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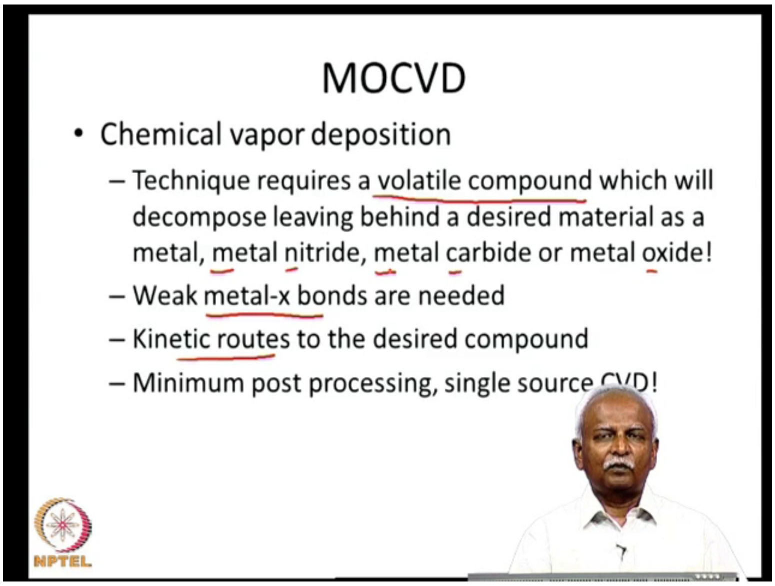

MOCVD

- Chemical vapor deposition
  - Technique requires a volatile compound which will decompose leaving behind a desired material as a metal, metal nitride, metal carbide or metal oxide!
  - Weak metal-x bonds are needed
  - Kinetic routes to the desired compound
  - Minimum post processing, single source CVD!

And this is been reviewed several times in the recent literature. Now we proceed to the properties of materials, other properties of materials and let us take a look at how, some materials are made using chemical vapour deposition. This is a root which is used to make for example, titanium nitrite which is a gold coloured compound. It can be used for coating watches or ornaments and they might look like gold, but they are not really gold and this material titanium nitrite is extremely hard, it is conducting, looks very much like a metal. But unfortunately if you want to coat a metal or a material with titanium nitrite, it is not easy to carry out that process, because it is not a volatile compound.

But you can take an organometallic compound which is volatile so you take a volatile organometallic compound and then you decompose it on a substrate, leaving behind the desired material, which is a metalor a metal nitrite, a carbide or and oxide all these possibilitieshave been realised. And the trick is, to use anorganometallic compound where the metal x bond, whether it is to nitrogen or to carbon or to oxygen, the metal x bond has to be weak. And you can generate desired species on the substrate and if you have reasonably easy ways of decomposing the material, then the kinetic parameters are suitable for carrying out metal organic chemical vapour deposition.

And we do not have a very high temperature, that is required for carrying out this chemical vapour deposition. The advantage of chemical vapour deposition is that, you need very little post processing of the material and if you can make a molecule, which has got both metal and nitrogen, metal and carbon. Then you can have, what is called the single source processor for carrying out the cyclo chemical vapour deposition. This turns out to be an extremely useful parameter, because if you have two different processer, materials giving you the metal. And giving you the nitrogen, then the processes for the required for controlling the two molecules at the substrate become very difficult.

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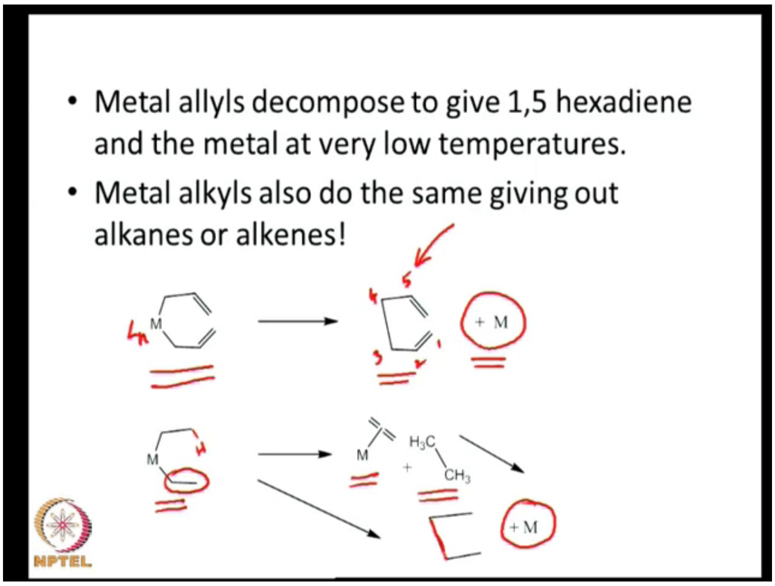

- Metal allyls decompose to give 1,5 hexadiene and the metal at very low temperatures.
- Metal alkyls also do the same giving out alkanes or alkenes!

So, let us take a look at metals if you want to deposit a metal for example, you could take a metal allyl complex. These metal allyl complexes have got a very easy decomposition route, they undergo reductive elimination of the two allyl groups and form these 1, 5 hexadiene. So these are 1,5 hexadienes, so you can see that they are 1, 5 hexadiene and they are easily formed on decomposition of a divalent metal allyl complex. These species even if there are allyl molecules, they turn out to be reasonably volatile. So, at very low temperatures you can volatile these Picasso and in a substrate which is kept hot, it undergoes decomposition and deposits the metal in a pure form.

Because this molecule is volatile, it will be lost very readily and you end up with the deposited material, which is in a pure state. One can not only use metal allyls, one can even use metals alkyl species and in this case, the decomposition might be slightly more complex. You can have a variety of decomposition routes, you can have the ethyl group here, this ethyl group reacting with one of the hydrogens here and giving you ethane and olefin complex.

And in the subsequent step the olefin might be lost and the metal might be deposited on the substrate. In other, in another scenario one can also think decomposing the molecule in such a way that, the two ethyl groups are attached to each other and bond is formed and butane is eliminated. So either way, it is easy to make metals on top of a substrate using chemical vapour deposition of metal alkyl components.

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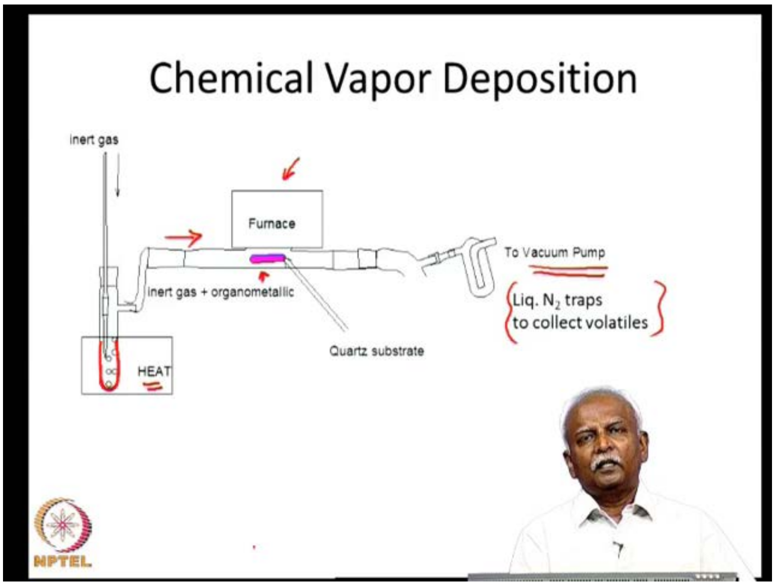

Chemical Vapor Deposition

Here is a schematic representation of how, one do this reaction or how one would carry out, you can have this metalalkyl species sitting in a, in a container which is volatilised using some heat. And sometimes it also nebulised using, an inert gas and this carries, this material on to a glass tube where the substrate is kept. A simple substrate would be a quartz substrate and usually it is kept hot, the temperature of this furnace is kept at temperature, above the temperature which this material would decompose.

So, it decomposes only here, the organometallic species decomposes at this point, deposits the metal on the top of the substrate and the organic compounds are pumped out. And the liquid nitrogen traps to collect the volatiles and the organic compounds that come out. And then the whole thing is kept under high vacuum usually the, in such a way that the organic species do not stay in the region where, you want to have pure metal deposited on the substrate.

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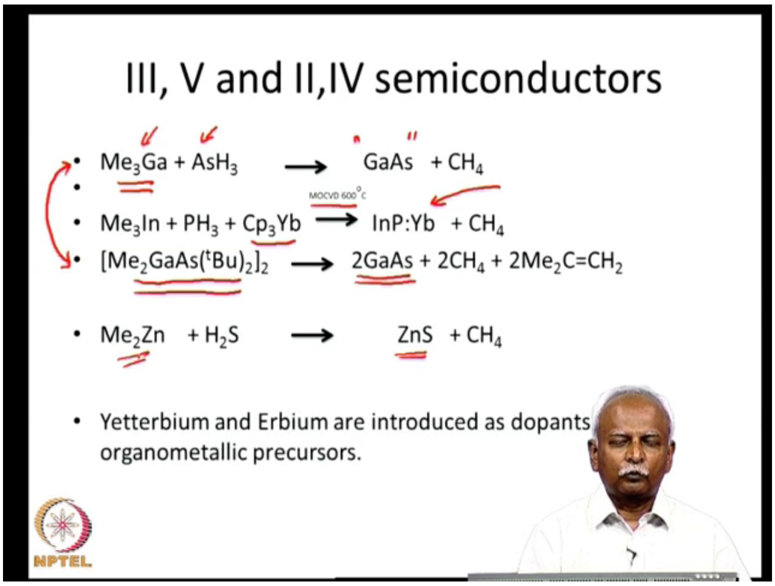

III, V and II,IV semiconductors

- $Me_3Ga + AsH_3 \longrightarrow GaAs + CH_4$
-
- $Me_3In + PH_3 + Cp_3Yb \xrightarrow{MOCVD\ 600^{\circ}C} InP{:}Yb + CH_4$
- $[Me_2GaAs(^tBu)_2]_2 \longrightarrow 2GaAs + 2CH_4 + 2Me_2C{=}CH_2$
- $Me_2Zn + H_2S \longrightarrow ZnS + CH_4$
- Yetterbium and Erbium are introduced as dopants organometallic precursors.

Here is an example where you have some semiconductors made, these semiconductors are called 3, 5 semiconductors or 2, 4 semiconductors. And many of them have been made or deposited on a substrate using this chemical vapour deposition method. The temperatures are rather high, it is about 600 degrees. But relatively lower than what you would end up with, if you have to use a completely inorganic route from making these molecules or making these alloys.

So, here is a gallium arsanite deposition, using trimethylgallium, which is an organometallic species. You can also have, a single source processor which I was telling you about where, there is a gallium arsanite bond. And you can vaporise this gallium arsanite bond directly on to the substrate, and deposit the required amount of gallium arsanite. The advantage of using a single source precursor or a two source precursor is, at the vapour pressures of these two molecules are different.

And as a result, it would be very difficult to adjust the amounts of gallium and arsenic and you should not end up with excess of arsenic or excess of gallium on the substrate, so to avoid that a single source processor is always preferred. One can also dope for example, here in the case of Indium Phosphite, one has doped it with yetterbium and this yetterbium is delivered as a cyclopentadienyl complex. So once again you see that organometallic lanthanite, organallanthanite is used in order to dope the semi-conductor appropriately.

So, Yetterbium, Erbium have all been used as dopants and as organometallic precursors and here is a 2, 4 semiconductor, which is also generated using an organometallic compound. So, you can see that chemical vapour deposition is very useful tool, it can be used for generating a wide range of semi-conductors, both in the pure form and in the doped form.

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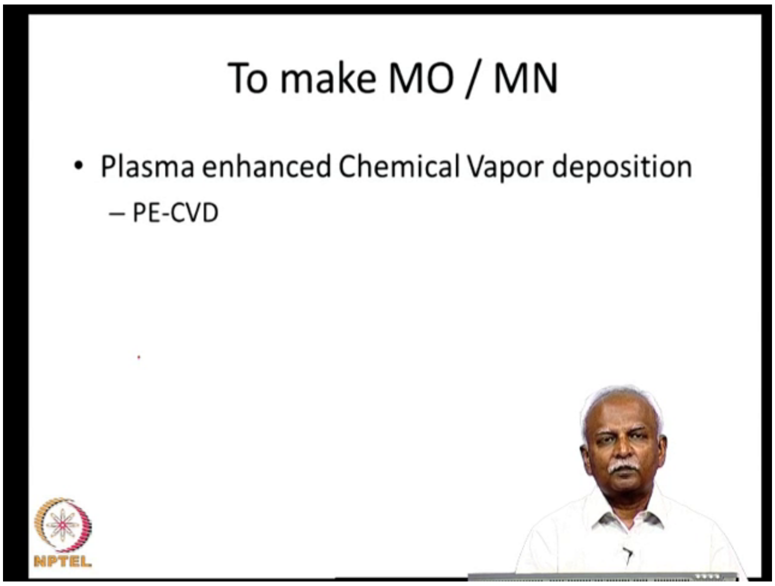

To make MO / MN

- Plasma enhanced Chemical Vapor deposition
  - PE-CVD

In order to make a metal oxide or a metal nitrite, one can also use what is called plasma enhanced chemical vapour deposition. Where there is a plasma which is, which contains a reactive gas and in this plasma, the chemical decomposes and this leads to the appropriate deposition of the appropriate material. This is also been found and it is being utilised very advantageously.

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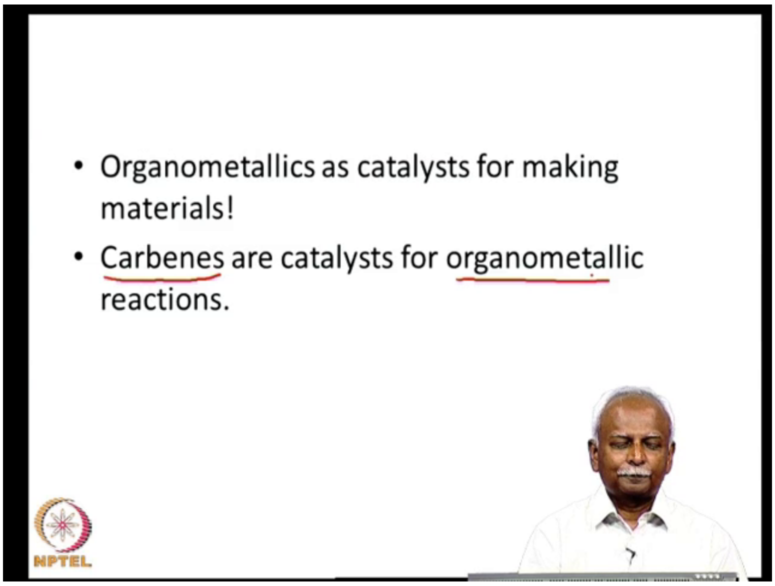

- Organometallics as catalysts for making materials!
- Carbenes are catalysts for organometallic reactions.

In most of these cases, that we have talked about today organometallic compounds are used as materials. And in some instances in recent times, it has been used as a catalyst for making a material. In other words the organometallic itself, is not part of the material that is formed, but it is used in very small amounts. So that, the material is generated in a pure form and a useful material is generated and there is another example where a carbene has been used as a catalyst.

This is an organic compound, this organic compound has been used as a catalyst for an organometallic reaction. So this is, the inverse of what we have been seen so far. We have been using organometallic catalyst, for carrying out organic reactions. Now, we are going to talk about two examples where organometallic compounds are used as catalyst in very unique ways.

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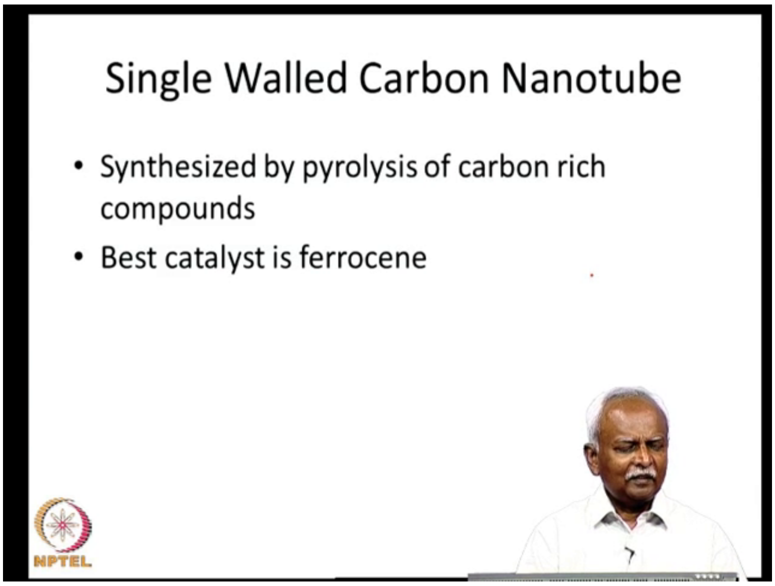

Single Walled Carbon Nanotube

- Synthesized by pyrolysis of carbon rich compounds
- Best catalyst is ferrocene

The first instance that I want to talk about is, single walled carbon nanotube. Single walled carbon nanotube is often formed by something very close to the chemical vapour deposition that I talked about. It is conducted by pyrolysis of carbon rich compounds, When you pyrolise the carbon rich compound, you lose hydrogen and generate carbon network which is like a tube. So, this is a carbon nanotube and multiple tubes are formed. What is interesting is that the best catalyst that is available for making this carbon nanotube. Especially, single walled carbon nanotube is ferrocene which is this organometallic molecule.

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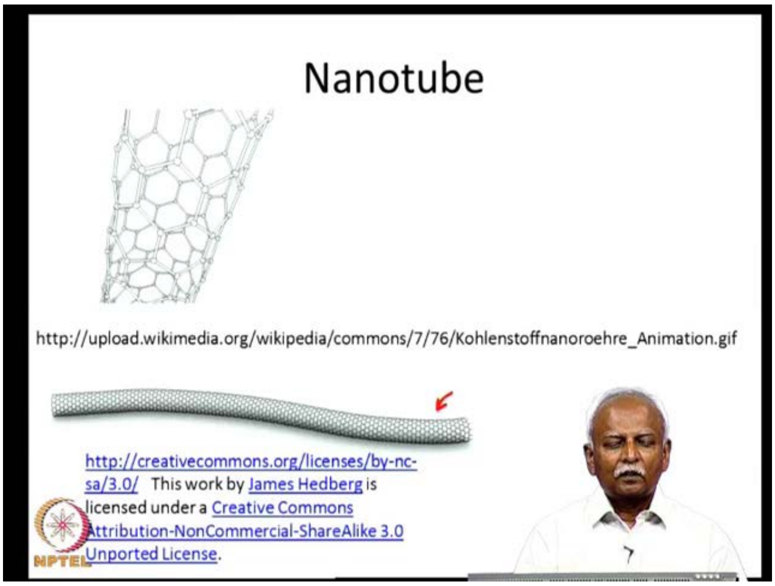

Nanotube

http://upload.wikimedia.org/wikipedia/commons/7/76/Kohlenstoffnanoroehre_Animation.gif

Let us see why this is the case. If you look at piece of a carbon nanotube, very often it is indicated as a series of hexagons, which are connected with each other. Here is a long, picture of a long carbon nanotube, single walled carbon nanotube that is shown for you here. Here is another picture which is dynamic, but you can see that the carbon nanotube is primarily made up of hexagons, which are connected with each other.

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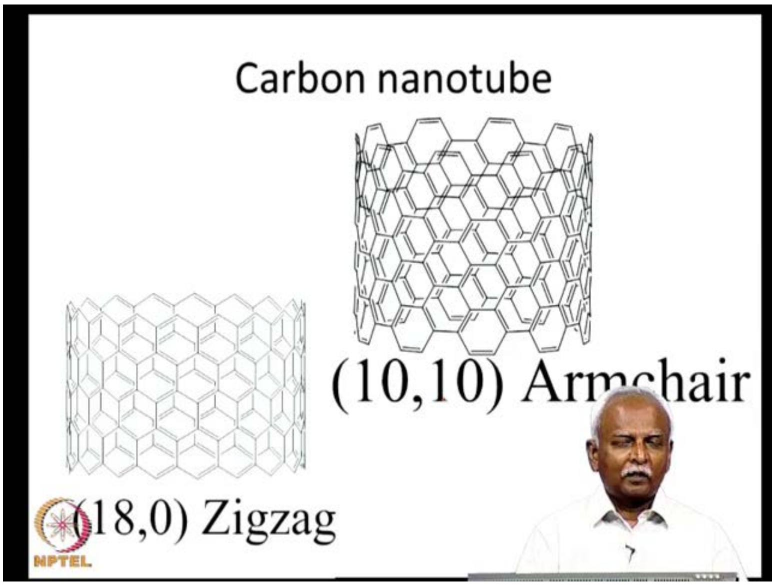

Carbon nanotube

(10,10) Armchair

(18,0) Zigzag

Now, there are different types of carbon nanotubes and these nanotubes have got different conducting properties, different properties which have been utilised for different applications. But in most of the nanotubes you will notice that it is the six memebered ring, which is being linked to one another.

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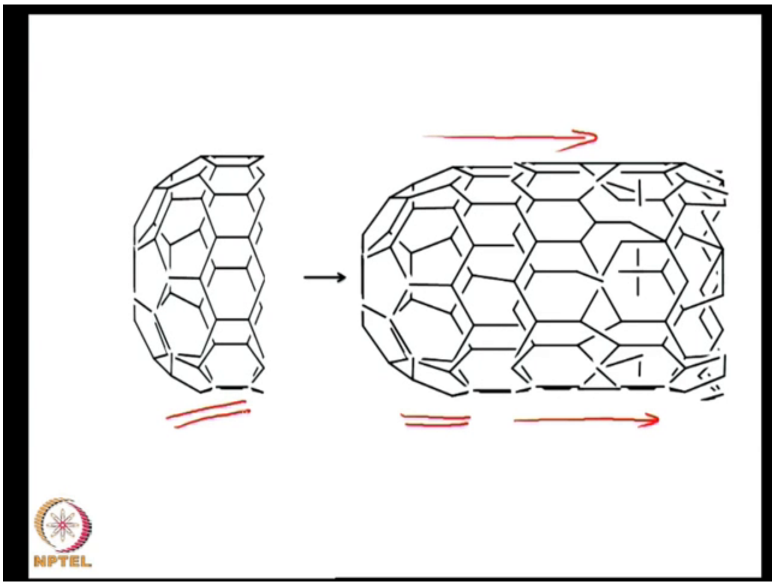

So, how are these carbon nanotubes attached to or how are these hexagons attached to each other and how are they formed in the first place. Although we indicate, carbon nanotubes, the middle part of the nanotubes, what we do not realise is that the end of the nanotube. There is in fact a cup that is attached and it is this cup that is responsible for the formation of this nanotubes. In other words, the cup is formed first and then the nanotube propagates along this direction growing along this direction. So, the cup is of great importance, if it cannot make the cup, then you cannot make the nanotube. So let us take a closer look at this cup that we are talking about.

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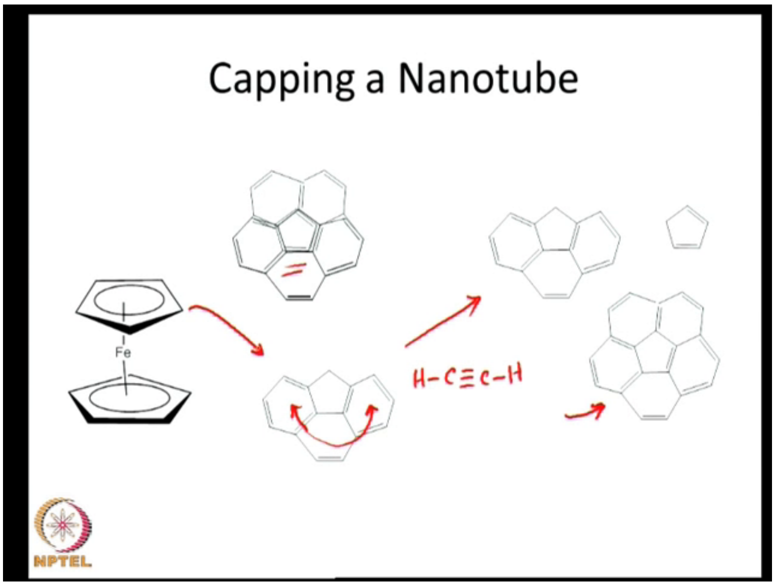

Capping a Nanotube

It is often called a capped further nanotube and here is how one thinks about making the carbon nanotube. If you have acetylene as, the source for the carbon required for making the require carbon nanotube. You can think of capping or attaching three benzene rings around a cyclopentadienyl rings. If you use only benzene rings, it would not be possible to make the curved cup formed at the end of the nanotube. So if you have a cyclopentadienyl ring however, you can attach three C6 units around it to form this curved molecule. Although we have drawn it in a flat two dimensional form, you can see how this molecule will be curved. We think of the fact, that it is not possible to keep all five carbon atoms in a plane, when you have only a single double bond inside the ring. So, let us take a look at what would happen if you, attach some more cyclopentadienylrings to this final structure and you will now understand why one need ferrocene.

Because ferrocene supplies this five member ring which is not accessible, when you use only as a source for the carbon. So, ferrocene turns out to be an excellent catalyst because to form this initial curved structure, that we have indicated here, it is important to have a nucleating center. And that nucleating centre comes from this cyclopentadienyl ring of the ferrocene. Once it is formed of course, it keeps growing.

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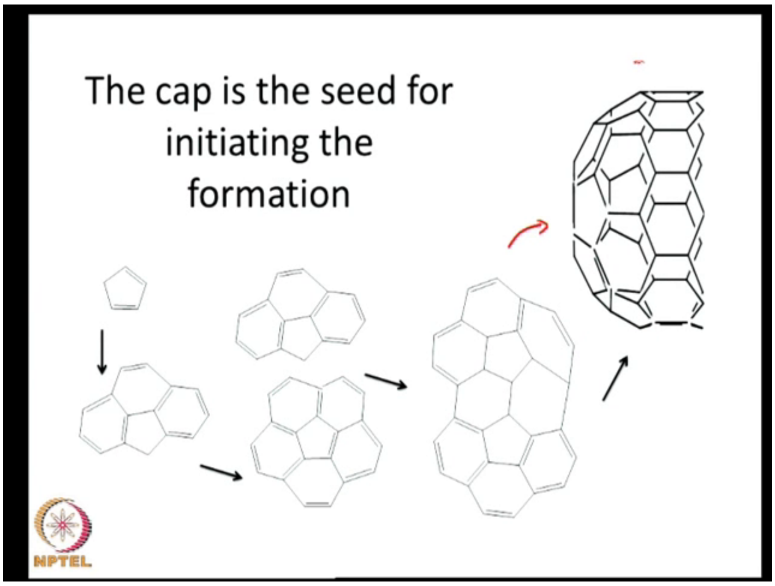

The cap is the seed for initiating the formation

And that is what is showed here schematically, first the formation of the cup is indicated. And that happens by combining 2 or 3 units of this cyclopentadienyl, containing a ring structure, which are surrounded by C6H6 units and then the hydrogen are lost. And then again you end up with a curved structure, which can now propagate in a linear fashion.

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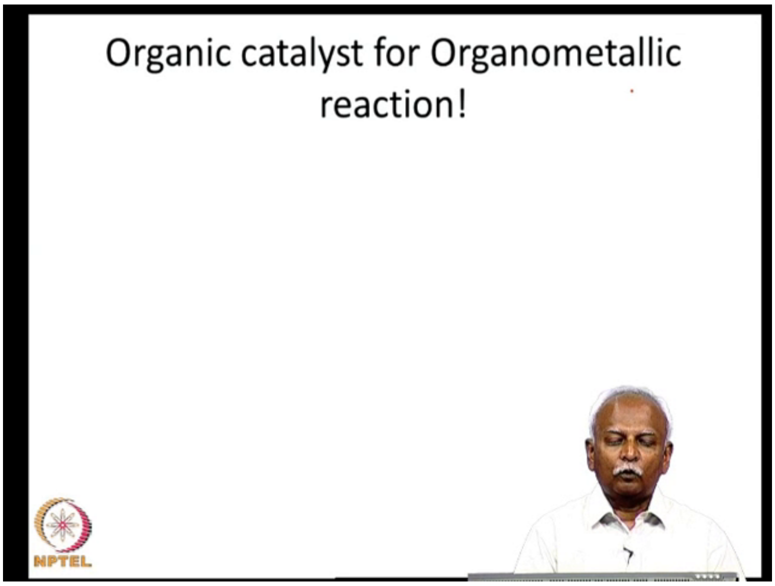

Organic catalyst for Organometallic reaction!

So, the cap is all essential for forming the nanotube and so that is why carbon nanotube are mostly formed using ferrocene as a catalyst. Now, I will come to one other example where an organic catalyst has been discovered for organometallic reaction, although this is a novelty at the moment.

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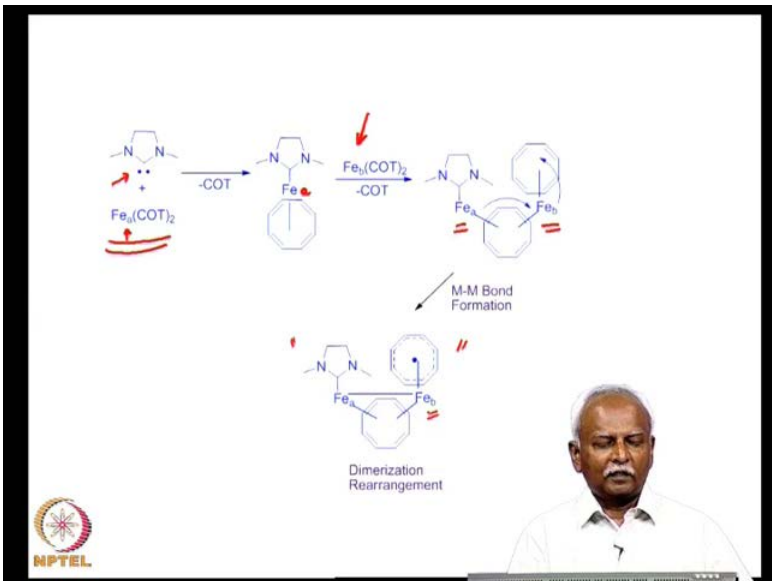

The principle behind this whole discovery is very important and that is, if you have a molecule which can both give and take electrons, give and take protons then that molecule will be a good catalyst. Now, organometallic molecules were good catalyst because they could both accept electrons into vacant orbitals and give electrons into the anti-bonding orbitals of the organic molecule. By doing so they facilitated many electron, electronic structure changes on the molecule, or in other words reactions. Now, if you look at a carbene, a carbene has got if it is a carbene such as what shown here then it has got, a pair of electrons which it can donate.

But at the same time perpendicular to the pair of electrons you have a vacant orbital, which can accept electrons density. So, as a result carbene can function very similar to organometallic molecule then they can be catalyst. And in this example it so happen that, they are catalysing an organometallic reaction. An organometallic reaction that has happened is a conversion of this cyclooctatetraene ion, which is basically ion coordinated to 2 cyclooctatetraene units. In one case, it will be three double bonds coordinated to it, in the other case the ring is different only 2 of the double bonds will becoordinated to it.

Now, we have indicated an a here to show that, there are two different ion atoms that are going to react. So, initially you have Fe a. And then a second molecule of the cyclooctatetraene complex comes in and that is labelled as Fe b. So, there are two sources for the ion in the dinuclear complex and a di-nuclear intermediate is formed. This molecule in which there is a carbene attached to an ion. And two cyclooctatetraene units attached to the second ion atom, is an intermediate and also been isolated and characterised.

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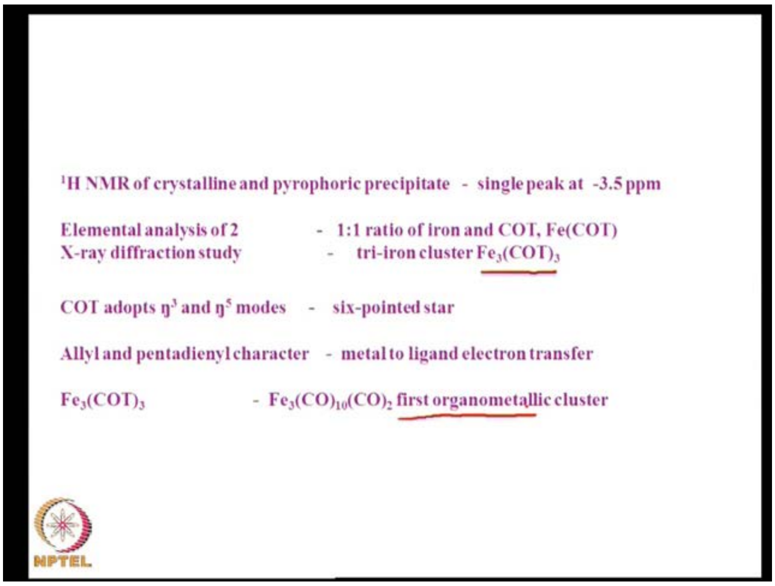

^{1}H NMR of crystalline and pyrophoric precipitate - single peak at -3.5 ppm

Elemental analysis of 2 - 1:1 ratio of iron and COT, Fe(COT)
X-ray diffraction study - tri-iron cluster $Fe_3(COT)_3$

COT adopts η^3 and η^5 modes - six-pointed star

Allyl and pentadienyl character - metal to ligand electron transfer

$Fe_3(COT)_3$ - $Fe_3(CO)_{10}(CO)_2$ first organometallic cluster

The beauty of this study was that, in most cases it was possible for them to show the NMR of the compound. And also characterise, some of the intermediates using X-ray crystallography. And the compound they finally isolated as the most stable or the majority of the species was tri-iron triscyclooctanetetron compound. And this molecule is got a beautiful structure, where it adopts a six pointed star kind of a structure and you have a first organometallic cluster, which does not have carbon monoxide.

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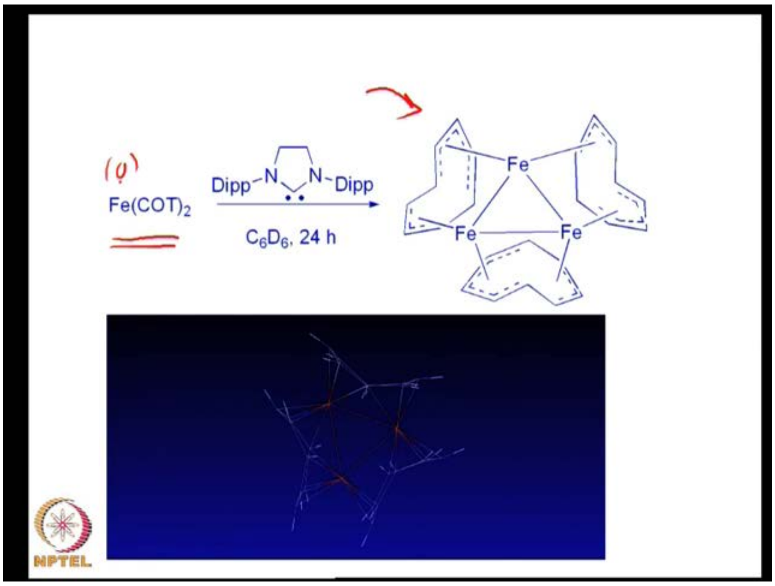

So, here is a molecule shown for you, it is a simple reaction where this cyclooctatetraene ion molecule is transferred, as converted into tri-iron triscyclooctanetetron compound. This compound has got a unusual oxidation state, you can see that the ion is in fact attached, each ion is attached to a 5 carbon unit and a 3 carbon unit. You start a doubt with a neutral species, but by oxidating coupling you have infact oxidised the ion and coupled 3 cyclooctatetraene units. In such a way that ion now has astate of plus 2. So, let us take a look at this 6 pointed star here, it is 6 pointed star that I was telling you about. It is a very beautiful structure.

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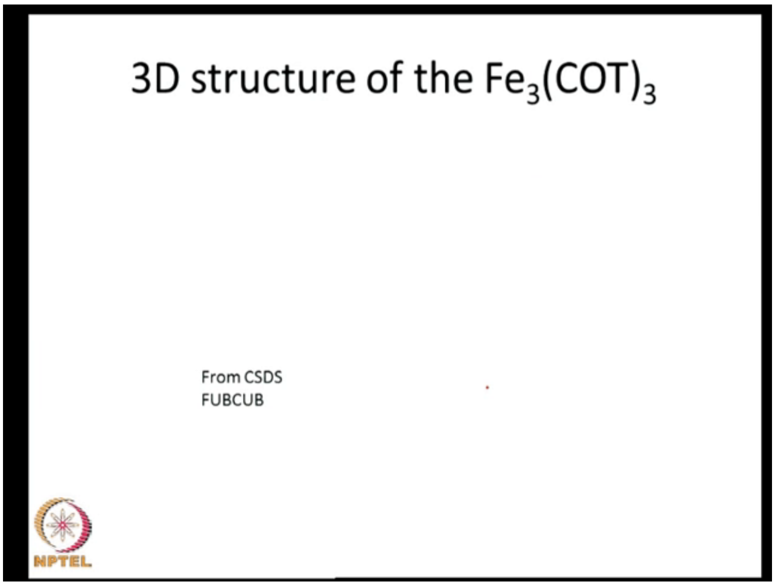

3D structure of the $Fe_3(COT)_3$

From CSDS
FUBCUB

That we will look at in a three dimensional fashion.

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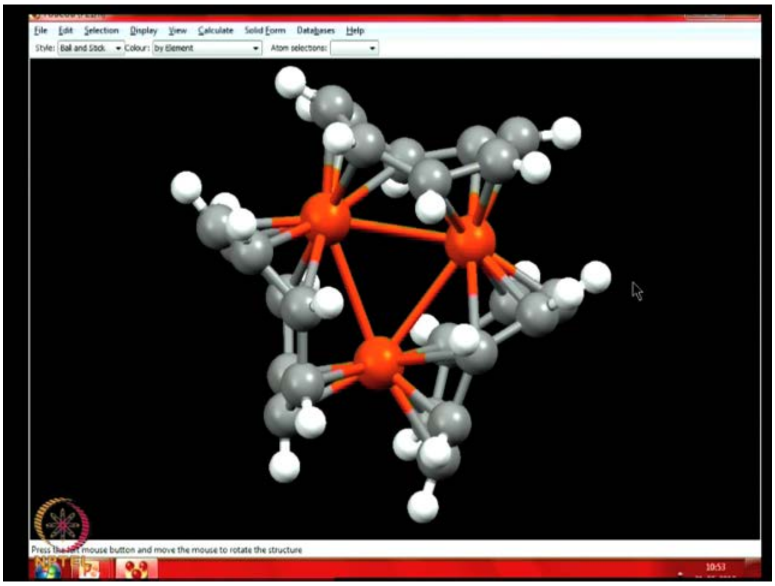

Press the left mouse button and move the mouse to rotate the structure

To appreciate the beauty of this molecule, here it a molecule in a three dimensions and you can see that, each ion atom is coordinated to either 5 carbons on one side, here are the 5 carbons that are interacting with the ion. And on the lower side, you will see that the same ion atom in interacting with all the 3 carbon atoms. So, on one side it has got three and on the other side it has got 5 carbons. And if you look at it and through this axis, you will notice that it forms a 6 pointed star structure. So, this beautiful molecule is in fact formed by, interacting an organic molecule with an organometallic species and it is the organic catalyst, which generates this molecule very efficiently.

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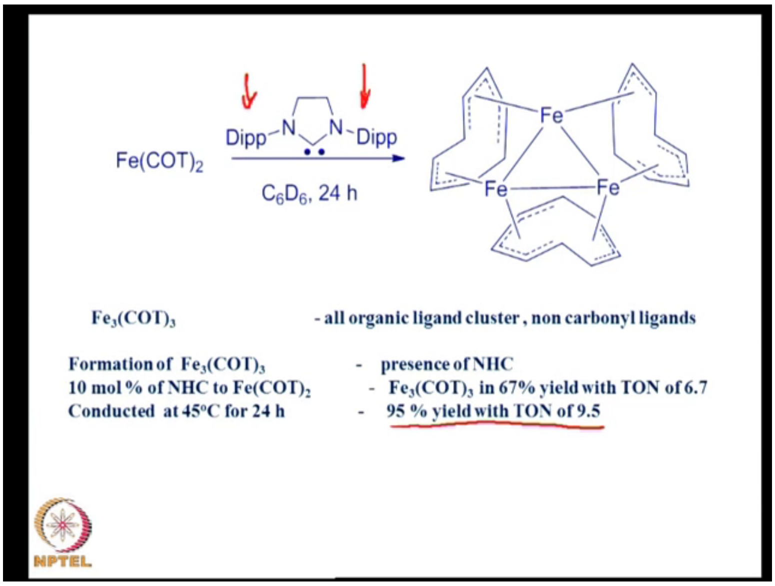

Fe$_3$(COT)$_3$ - all organic ligand cluster, non carbonyl ligands

Formation of Fe$_3$(COT)$_3$
10 mol % of NHC to Fe(COT)$_2$
Conducted at 45°C for 24 h

- presence of NHC
  - Fe$_3$(COT)$_3$ in 67% yield with TON of 6.7
- 95 % yield with TON of 9.5

In fact, this whole reaction can be carried out in 95 percent yield, with a turnover number of 9.5 with this inhydrocyclene carbene. What is interesting is that, this, all the intermediates, several of the intermediates have been characterised using, variations in the structure of the alkyl groups which are attached to the nitrogen.

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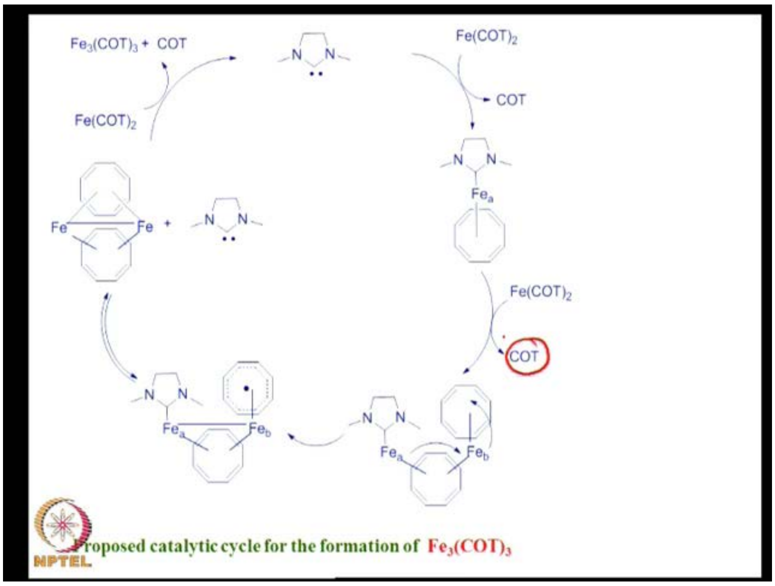

Proposed catalytic cycle for the formation of $Fe_3(COT)_3$

So, here is the proposed catalytic cycle which just involves loss of cyclooctatetraene in a sequential fashion. Formation of an ion and a bond and the formation of a tri nuclear intermediate.

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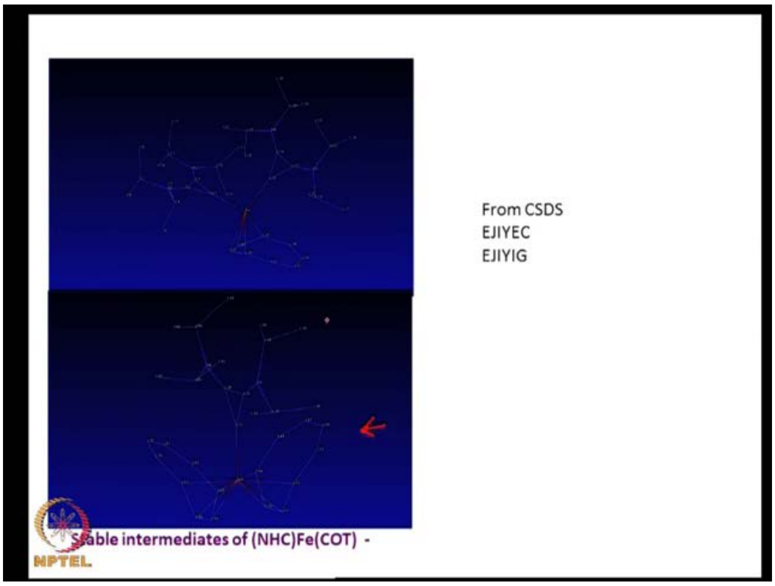

From CSDS
EJIYEC
EJIYIG

Stable intermediates of (NHC)Fe(COT) -

So, here are two intermediates, which have been isolated and these are available in the cambridge structure database. And in one case you have, ion atom which is coordinated to a carbene and 2 cyclooctatetraene and that is this molecule. And in other case you have a molecule, which is coordinated to two of these carbene units at the same time. So that is this molecule which is shown here.

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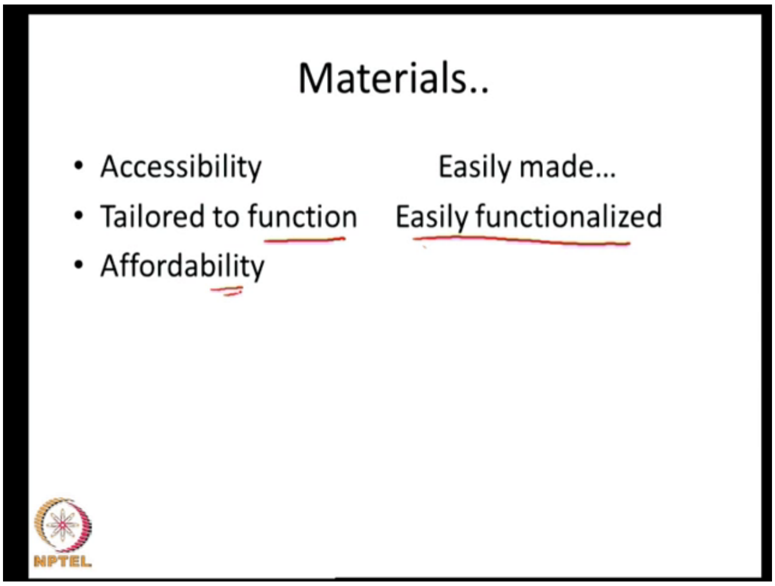

Materials..

- Accessibility
- Tailored to function
- Affordability

Easily made...
Easily functionalized

So, with this let me conclude that by saying that materials for making new organometallic materials, can be used in a variety of ways. Very organometallic compounds be used as materials and also for generating new materials. The advantage of organometallic compounds is that, they areaccessible, easily accessible, easily made and they can be tailor made to function in a particular way. And this is because they can be easily functionalised, any of these organic ligands can be converted to new ligands and new molecules can be generated. And to top it all, they are extremely affordable, which is also important for any thinking or making new materials.

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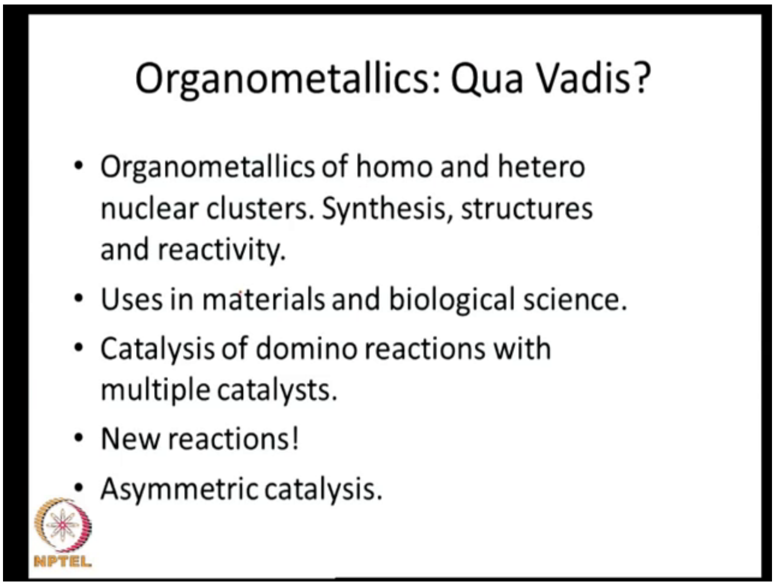

Organometallics: Qua Vadis?

- Organometallics of homo and hetero nuclear clusters. Synthesis, structures and reactivity.
- Uses in materials and biological science.
- Catalysis of domino reactions with multiple catalysts.
- New reactions!
- Asymmetric catalysis.

Finally, let me conclude by talking about organometallics in general. We have talked about a variety of systems where, organometallic has been used for organic synthesis. They are useful for, making new molecules, new drugs, new moleculesfor materials and in the biological science, also for both for diagnosis and for therapy. But in all these cases the advantages of organometallic compounds make them fairly unique. You have the redox properties of metal atoms, which you can play around with. You also have organic structure which you can change very readily.

Where are we going, well it is now possible to have systems where, you can have domino reactions, which means you combine two different organometallic catalyst in such a way that, you can carry out a reaction in a single pot. You can carry out two different reactions sequentially so these are called domino reactions and these domino reactions are possible because of organometallic compounds, which are behaving as catalyst. And this also leads to new reactions which are not been known earlier.

And in this series of lectures, we have considered some of the very basic and simple lecture, simple reaction that are possible organometallic compound. Finally, of course, asymmetric catalyst is extremely important project, that is ahead of the organometallic chemist. In order to make cyromolecules very efficiently, it is important to use cyral ligands. And asymmetric catalysis will play a very important role in organometallic chemistry, in the future also.