Introduction to Organometallic Chemistry
Prof. A. G Samuelson
Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore

Lecture - 30
Fluxional Properties of Organometallics

Molecules are dynamic and organometallic compounds are quite dynamic and flux, that is the meaning of the term fluxionality.

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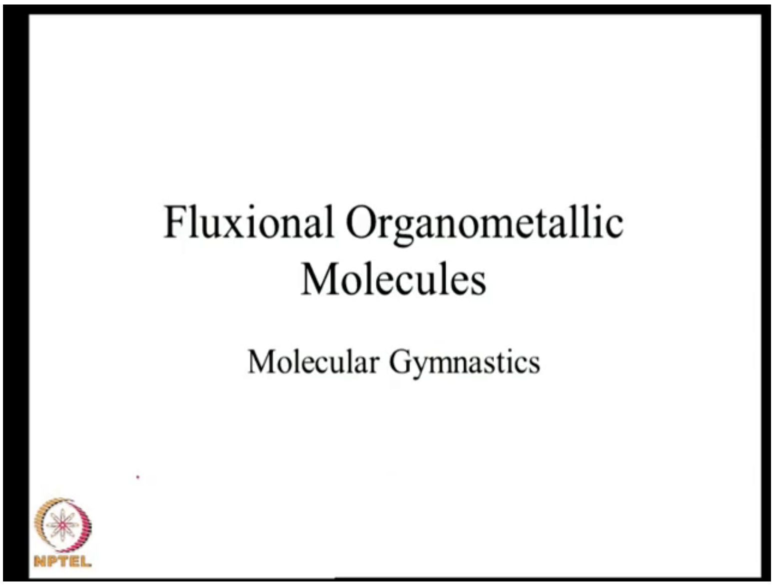

Fluxional Organometallic Molecules

Molecular Gymnastics

In fact, there are several instances where the molecules behave almost like gymnast. So, today we will talk about some molecular gymnastics.

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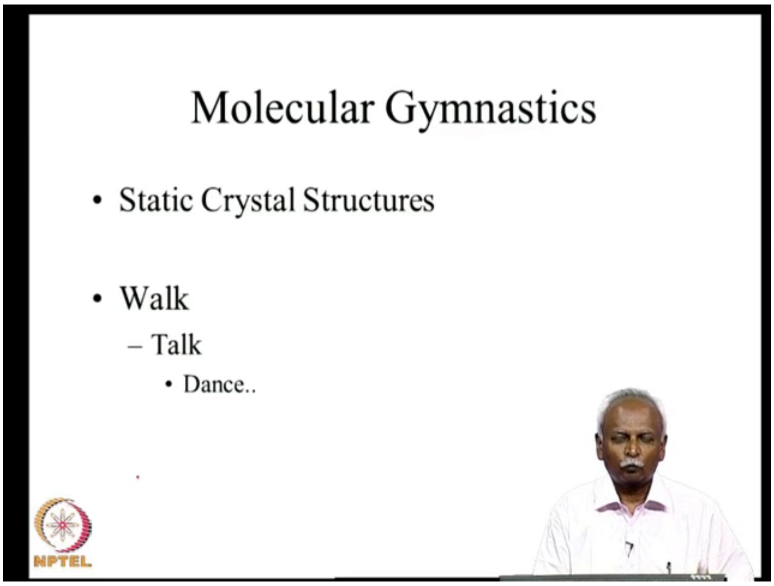

Molecular Gymnastics

- Static Crystal Structures
- Walk
  - Talk
    - Dance..

We are very often accustomed to looking at static crystal structures, but molecules are not static and they keep walking, they can sometimes talk and many times they are dancing all the time. So, if you want to think of a molecule as a static picture, you are missing out on what it can really do and what it is really doing.

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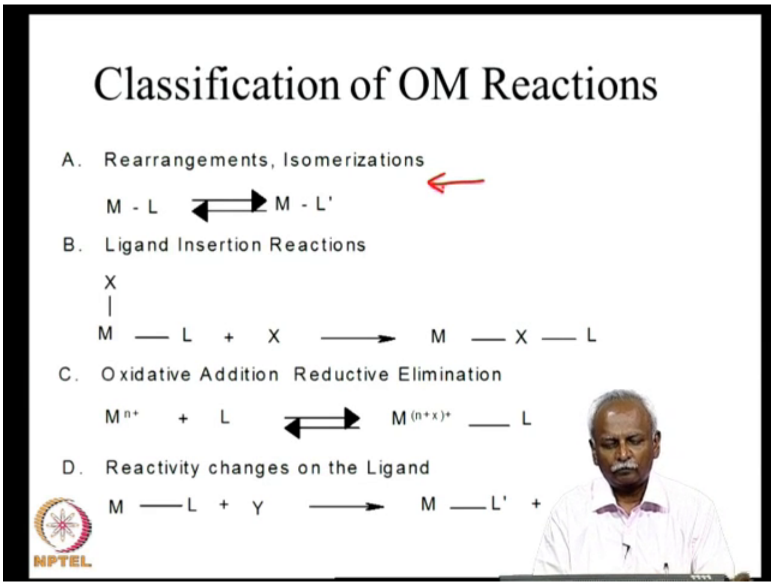

Classification of OM Reactions

A. Rearrangements, Isomerizations

$$M - L \rightleftarrows M - L'$$

B. Ligand Insertion Reactions

$$\overset{X}{\overset{|}{M}} — L + X \longrightarrow M — X — L$$

C. Oxidative Addition Reductive Elimination

$$M^{n+} + L \rightleftarrows M^{(n+x)+} — L$$

D. Reactivity changes on the Ligand

$$M — L + Y \longrightarrow M — L' +$$

Let us look at the overall picture of reactivity in organometallic chemistry before we look at fluxionality in particular. The first section that we have in the list of organometallic reactions is rearrangements and isomerizations and fluxionality falls in this particular group of reactions. It is in this group of reactions that we can talk about the fluxional behavior.

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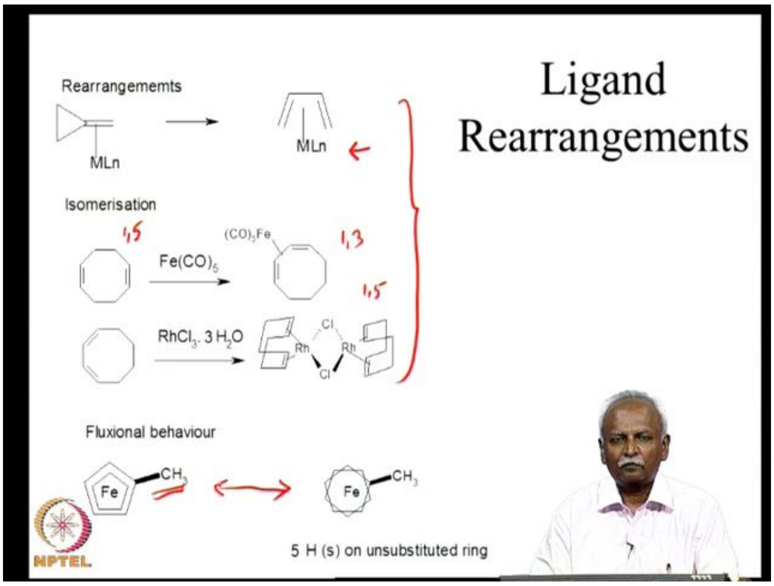

Ligand Rearrangements

Rearrangememts

Isomerisation

Fluxional behaviour

5 H (s) on unsubstituted ring

Both rearrangements and fluxionality come into this group and by rearrangement, I wish to talk about systems where there are rearrangements of the size of the ring. For example here there is a methylene cyclopropane that is rearranged to a butadiene complex or you have a 1, 5 cyclooctodiene, which is rearranged to a 1, 3 cyclooctodiene. Similarly 1, 3 cyclooctodiene which is rearranged to 1, 5 system.

So, these are rearrangements whereas fluxional behavior is distinguished from rearrangements by the fact that the ring system or the carbon framework that is attached to the metal is not changed. It is only the arrangement of the ring with respect to the metal or with respect to another part of the organometallic molecule which is changing. So, here for example, I have shown for you ferrocene, which is eclipsed and one ring is substituted with a methyl group. This position of the methyl group if the ferrocene is in an eclipse form would be looking like this where the hydrogens of one ring are on top of the other.

So, one methyl group will be on top of another hydrogen atom here and this would be energetically unfavorable situation, and it would like to move over to a system where you have the metals staggered with respect to the other hydrogens. However, the energy difference between these two forms is very small, so you have rapid exchange between these two structural reforms and that is what we are talking about as fluxional behavior.

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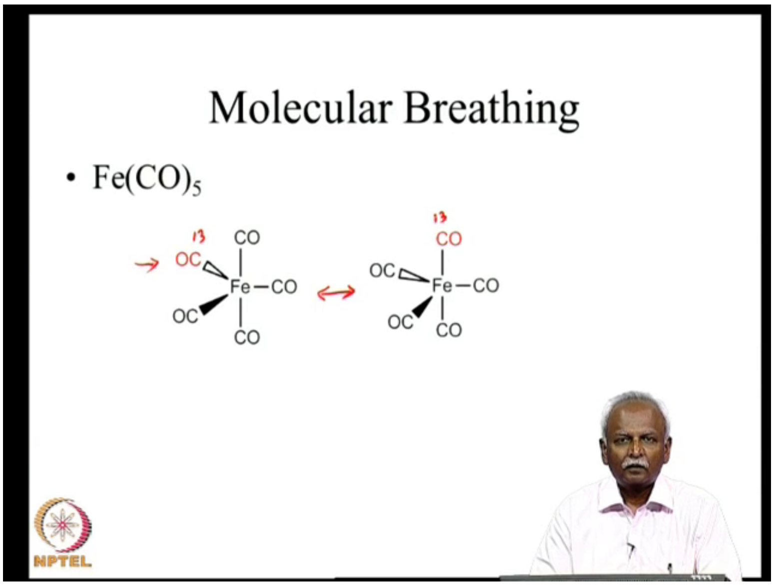

Molecular Breathing

- $Fe(CO)_5$

The first example that I want to talk about, is an example of molecular breathing. So, here I have shown for you a mononuclear metal carbonyl and pentacarbonyl and you will notice that I have marked one of the carbon monoxide molecules in red color. That is present in the equatorial position of the iron pentacarbonyl and this rapidly exchanges with another form where the carbon monoxide is in an apical position in the same FeCO5 molecule. Now, this type of an isomerization cannot be noticed unless we have, let us say the thirteen clabeled carbon monoxide, in which case the carbon monoxide stretching frequency in the two positions will be different.

This inter conversion can be measured or quantified or noticed. Unfortunately, in the case of iron penta-carbonyl, this rate is extremely fast and it is so fast that it is difficult to observe this type of inter conversion very easily. One often measures these using N M R spectroscopy carbon 13 N M R spectroscopy and it is not possible to arrest the inter conversions easily. That is because just like any living system that reads the breathing is essential for the molecule and it is done at a very fast rate, so fast that you cannot notice it when normal spectroscopic means.

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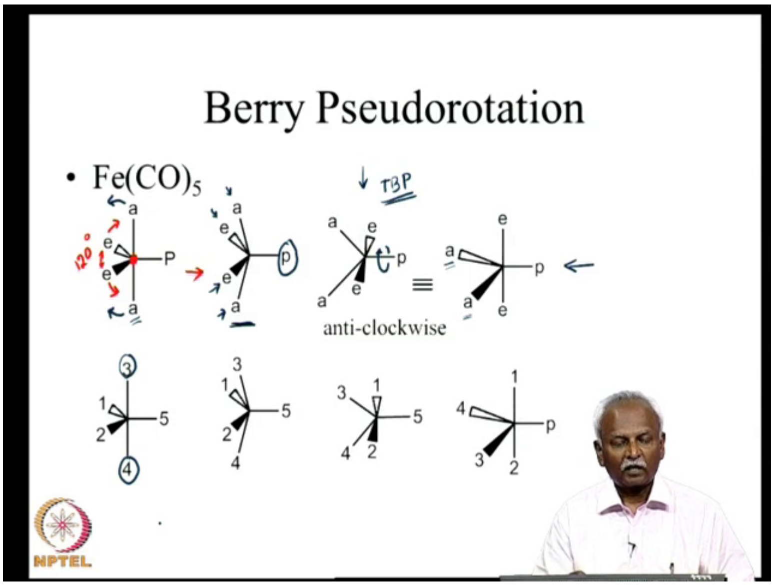

Berry Pseudorotation

- $Fe(CO)_5$

So, how exactly does it do it in the case you have learnt very pseudo rotation, which is quite popular and known in inorganic systems then you already know how this equatorial carbon monoxide can move to the axial position very rapidly. So, here I have pictured for you trigonal biopyramidal molecule where the five, where there are five ligands in the molecule in which the center is the metal atom.

Now, the groups that are labeled can move in a particular direction, so if the equatorial ligands which are labeled here as e and one is labeled as a P and that will become the obvious why I have done that in a few minutes. If these equatorial ligands are moved in the direction in which the shown here, so that the angle between the two increase beyond 120 degrees. Then you would move over to a system where the angle is widened and at the same time, let us move the axial ligands simultaneously in such a fashion that you have this geometry which I have indicated here.

So, this geometry is in fact the result of two movements, one is a widening of this equatorial metal atom, equatorial angle, equatorial ligand metal atom, equatorial ligand angle, and at the same time decrease of this axial metal, axial ligand angle. So, if one is decreased and the other is increased then you end up with a molecule which is distorted. It is almost like a square pyramid in which these four ligands, which I am marking here with an arrow form the basal plane and what is marked as P, is in fact in the apical position of the square pyramid.

Now, let us continue this motion further and then you end up with a molecule in which these two axial ligands have an angle of 120 degrees. The equatorial ligands have an angle of 180 degrees and this brings us to another trigonal bipyramidal geometry. This trigonal bipyramidal geometry can be rotated along this p metal bond in an anticlockwise fashion to achieve this geometry which I have labeled on the right side.

Now, let us see what has happened, you started with two ligands which are labeled as a, because they were on the axial position, but after this pseudo rotation, the ligands are in the equitorial position. So, this particular motion which is called the very pseudo rotation transforms an axial to equatorial bond and this rapid inter conversion is at the rate of femto seconds occurs at very fast rate in terms of femto seconds.

As a result, it is possible to have very pseudo rotation in iron pentacarbonyl, such that all the carbon monoxide can be interchanged can be moved from the axial to the equatorial and back to the axial positions. Notice that one atom was labeled as P because that was the pivot around, which the axial and the equitorial ligands interchanged. Now, this apical P could be in any one of the three equatorial positions, so it is possible to interchange all the carbonyls with one another.

So, let us label them as 1 2 3 4 and 5 and you will notice that at the carbonyls 3 and 4 were interchanged with carbonyls 1 and 5. So, it is possible as long as you have trigonal bipyramidal geometry revealed to have this very pseudo rotation happening at an extremely fast rate and. So, iron pentacarbonyl has got no axial or equatorial carbonyls in a distinct fashion.

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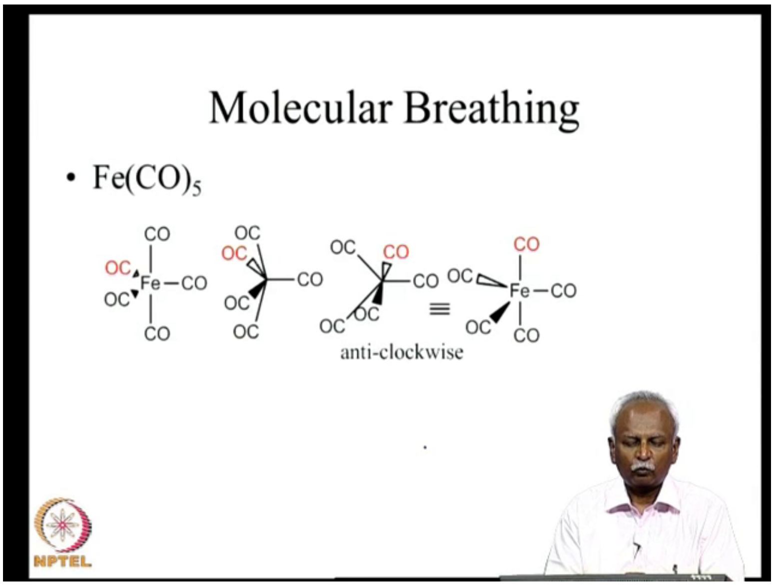

Molecular Breathing

- $Fe(CO)_5$

So, that is the reason why you been able to interchange this carbon monoxide which were labeled in the first place.

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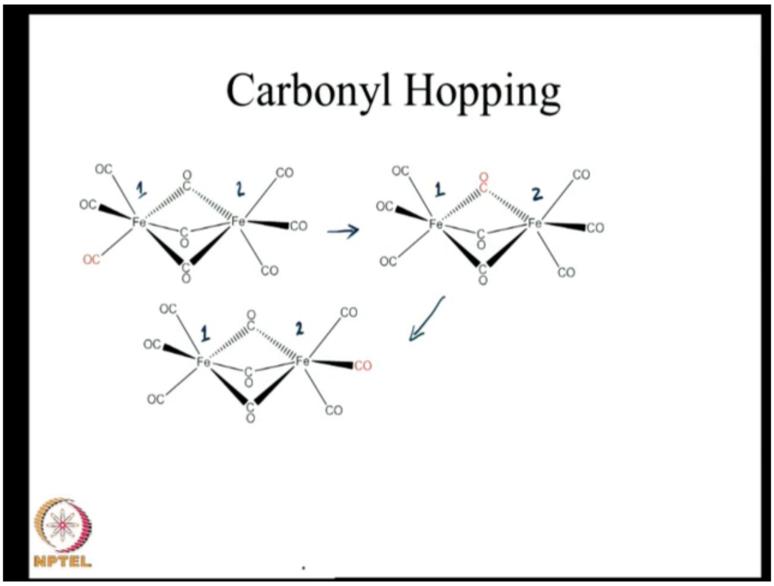

Carbonyl Hopping

This carbonyl hopping becomes even faster and more fissile when you move from mono nuclear systems to poly nuclear systems. Here, I have shown for you iron pentacarbonyl and in iron pentacarbonyl, there are three bridging carbonyls and six terminal carbonyls and these carbonyls keep interchanging at a very fast rate. I have shown again for the sake of convenience one carbon monoxide, which is labeled in the red color and you will notice that it first goes on to the bridging position and from the bridging position it moves onto iron atom number 2.

If this was the first position where the carbon monoxide was atom number 1, it moves over to the bridging position between atom numbers 1 and 2 and then finally, it moves over to atom number 2 and again to the terminal position. So, this kind of carbonyl hopping happens because the molecule again has a breathing motion and this breathing motion is involved with opening up of the bridge to form a terminal carbonyl and then again to form a bridging position if it is possible.

So, it is easy to move from a terminal to bridging and then again from a bridging to a terminal position and in the case of clusters it happens at an extremely fast rate. In fact even in the solid state, it has been shown that tri nuclear carbonyls, metal carbonyls have the capacity to move from one position, from one metal atom to the other. This is the reason why people have even supposed that there is in the case of metal clusters with carbonyls on the surface, it has been supposed that there is a sphere on which the carbonyls are moving. The metal cluster is in fact embedded inside the sphere and is able to freely rotate, so this type offered dynamic behavior is extremely well-known in metal clusters especially with carbonyls.

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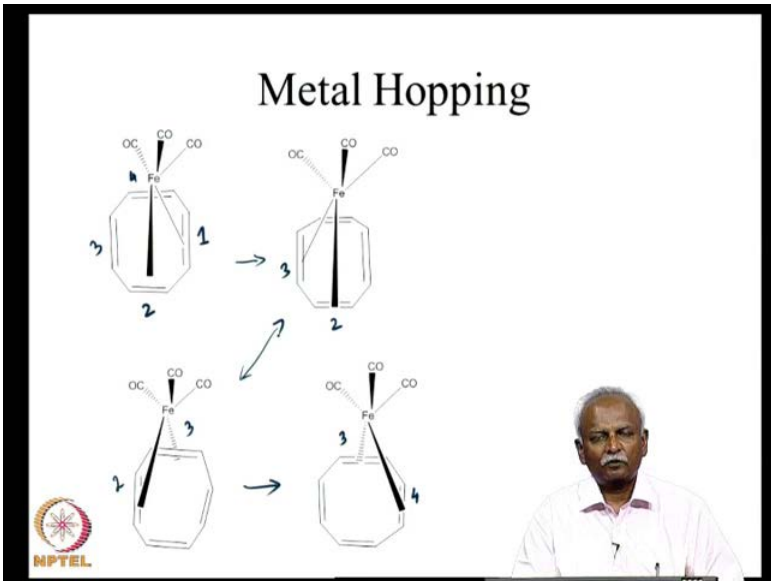

Metal Hopping

So, it is also possible for metal carbonyls to move from one position to the other position in a ligand system where more than the necessary numbers of pi bonds are available. A typical example is metal hopping which happens in cyclooctatetraene complexes, where only two pi systems can be coordinated to the metal system. So, here I have an iron tricarbonyl, which requires another four electrons in order to achieve the 18 electron magic number, and you can see that it is moving from position number.

If you label this as 1 2 3 and 4, if the first pi bond and the second pi bond are interacting with an iron atom in the second step the second and the third pi bonds are interacting with the metal atom and in another movement you can move the metal from position number 1 to position number 3, so that you have 2 and 3. Now, this could happen by a rotational cum sliding movement and this type of interesting fluxional behaviors in the metal carbonyl systems have fascinated organometallic cameras for a long time.

So, you can move from 1 to 2, 2 to 3 and 3 to 4 and this can go on endlessly in a very easy fashion and leading to the same type of structures. So, we can distinguish the carbonyl hopping from the metal hopping because, here it is very obvious that the ligand system appears to be stationary and the metal is the one which is moving from one pi system to the other.

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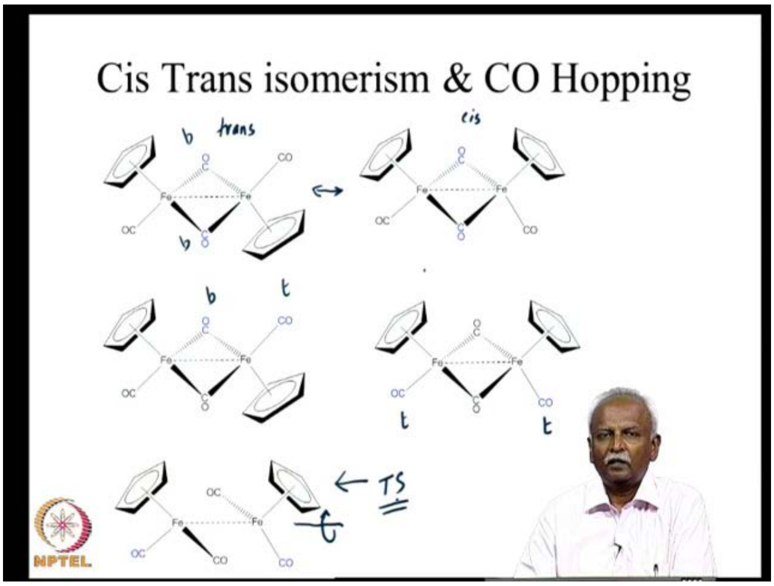
Cis Trans isomerism & CO Hopping

In the case of some metal carbonyls like the molecule that is shown, here it is possible to have Cis trans isomerization where the Cis and the Trans are distinguished by the position of the cyclopentadienyl groups. So, here is an example where a cyclopentadienyl group is Trans to the other cyclopentadienyl group. The number of carbonyl molecules, one is bridging and the other is terminal in each metal atom and this becomes, now a Cis molecule because a cyclopentadienyl groups are separated, well separated they do not bump into each other and do not cause steady condition.

So, as a result the energy of these two forms is quite close and energy required for moving from one to the other is also not very high. Notice that at the same time you can also have carbonyl hopping, so I have labeled for you the bridging carbonyls in blue and these carbonyls can shift from the bridging position to a bridging and the terminal position.So, here I have blue carbonyls and bridging and terminal positions and, here I have blue carbonyls in two terminal positions, so I can do both carbonyls hopping over carbonyl shifting as well as Cis Trans isomerization.

So, this type of a dynamic behavior can be explained very easily, if the iron cyclopentadienyl complex moves in such a way that it generates a single iron, iron bonded system which I have pictured for you here without any bridges. Rotation around this iron, iron axis can lead to isomerization. The Cis trans isomerization and it can also equivalence the two carbon monoxide, which are attached to the iron. So, the bridging and the terminal carbon monoxide can be interchanged when the molecule is in this transition state which is pictured here. So, this type of Cis trans isomerization and CO Hopping can lead to a fairly interesting n m r patterns in the proton of the carbon 13 n m r spectroscopy.

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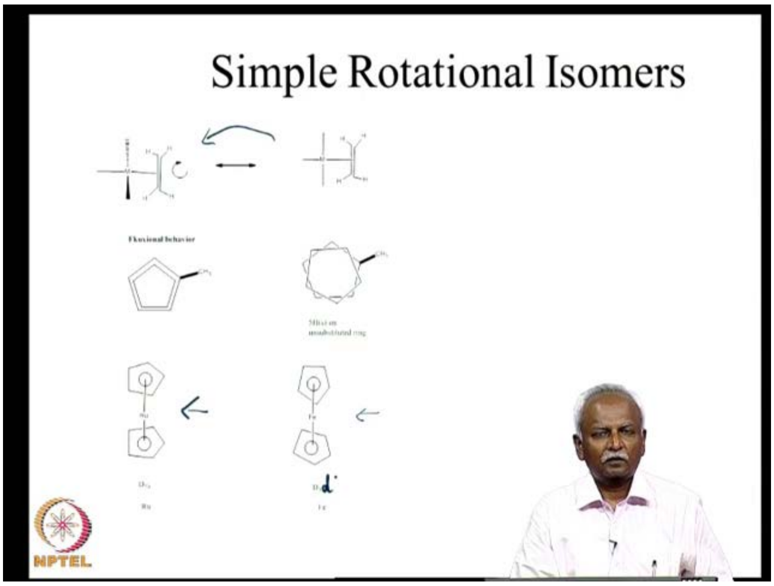

Simple Rotational Isomers

Now, after we can have considered the carbonyl isomerizations, let us move onto simple double bonded systems and to cyclopentadienyl systems. Simple double bonded systems can undergo a variety of interesting fluxional behavior because you can have rotation of the metal with respect to the olefin.

In a square planar system like precise complex where the olefin is perpendicular to the plane of the metal ligands system, you can have isomerization, so that all atoms come into the same plane. So, you can have that as a high energy intermediate and then it can go back on to the ground state which is the olefin in the perpendicular direction to the rest of the ligand systems. So, you can have olefin rotation, you can also have cyclopentadienyl rotation, which I explained to you awhile ago and you can have rotation of one ring with respect to the other.

Notice that this type of isomerization or fluxional behavior requires very little energy and, so there can be slight changes in the size of the metal atom for example, which can favor one form over the other. Typical example is the case of ferocene and with ruthinocene, ruthenium prefers the D 5 H structure which means the two cyclopentadienyls are eclipsed, whereas ferocene refers the D 5 D form and that is the standard form of the complex. This is explained by the larger size of ruthenium which allows for the complete eclipsing of two cyclopentadienyl links.

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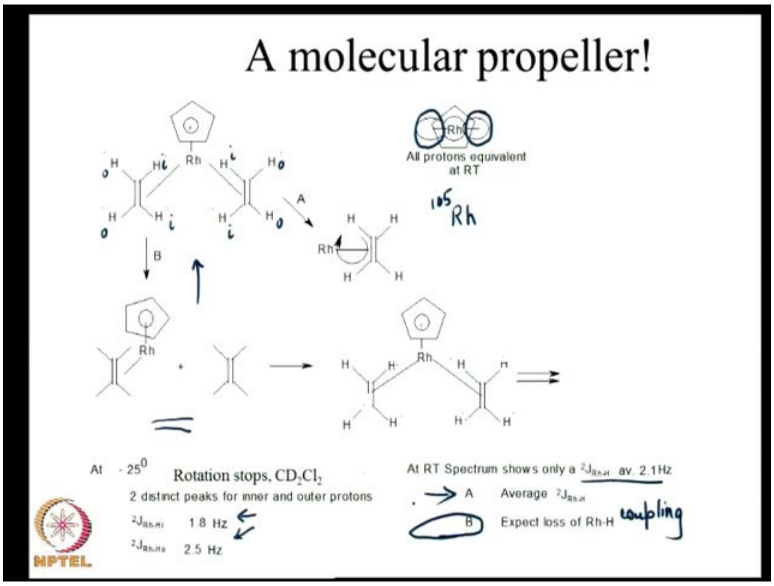

A molecular propeller!

All protons equivalent at RT

At - 25^0 Rotation stops, CD_2Cl_2

2 distinct peaks for inner and outer protons

$^2J_{Rh\text{-}Hi}$ 1.8 Hz

$^2J_{Rh\text{-}Ho}$ 2.5 Hz

At RT Spectrum shows only a $^2J_{Rh\text{-}H}$ av. 2.1Hz

→ A Average $^2J_{Rh\text{-}H}$

B Expect loss of Rh-H coupling

Let us move on a little further and combine cyclopentadienyl and olefins in this light. Here is an example of rhodium complex, rhodium olefin complex where two ethelenes are coordinated to a rhodium cyclopentadienyl unit. This turns out to be an extremely interesting system because the two olefins, if they are ((Refer Time: 21:31)), you would end up with protons which are facing each other and we will call them the inner protons. So, there are four inner protons and four outer protons. So, these outer protons are away from each other and they are pointing outside.

If the molecule can allow for rotation of the olefin with respect to the rhodium, you will notice that this will almost look like a propeller. So, the end on view of this molecule would look somewhat like this, where I have two propellers going round and round on either side of the rhodium. If these olefins can rotate very fast and indeed they can and this has been observed in proton n m r spectroscopy and this has been studied in detail. In fact, the exchange of the inner and outer protons can take place by an alternate mechanism without rotation and that can happen if the molecule rapidly dissociates an olefin.

Then the inner and the outer protons do not have any meaning and they can recombine and when they recombine the outer can become the inner and the inner can become the outer. So, the dissociation mechanism has to be distinguished from a simple rotation mechanism and this was done fairly easily because rhodium as an N M R active nucleus rhodium 1 0 5 is N M R active. As a result, you can observe rhodium hydrogen coupling and this rhodium hydrogen coupling for the inner protons is 1.8 Hertz and for the outer protons it is 2.5 Hertz.

At minus 25 degrees, if you cool the reaction or solution containing this complex and you can do that very easily in C D 2 C L 2 duteraded dichloromethane and the rotation stops. You can observe these two distinct coupling constants and what is interesting is that, at room temperature, when you warm the solution you have a system where there is only one coupling constant and that is 2.1 Hertz, which is the average of the two coupling constants.

Now, if the molecule were to dissociate, then the connection between the rhodium nucleus and the hydrogen nucleus would be lost. If the mechanism of interchange of the inner protons and the outer protons was happening through a dissociation mechanism that is mechanism B, then you would expect laws of the rhodium hydrogen coupling.

So, this coupling would be lost if you have dissociation and you would have an average coupling constant if this involved only rotation of the olefin with respect to the metal olefin bond. In fact, you do observe the 2.1 Hertz rotational coupling constant which suggest that, the mechanism of interchange for the inner and outer protons is actually through a simple rotation mechanism.

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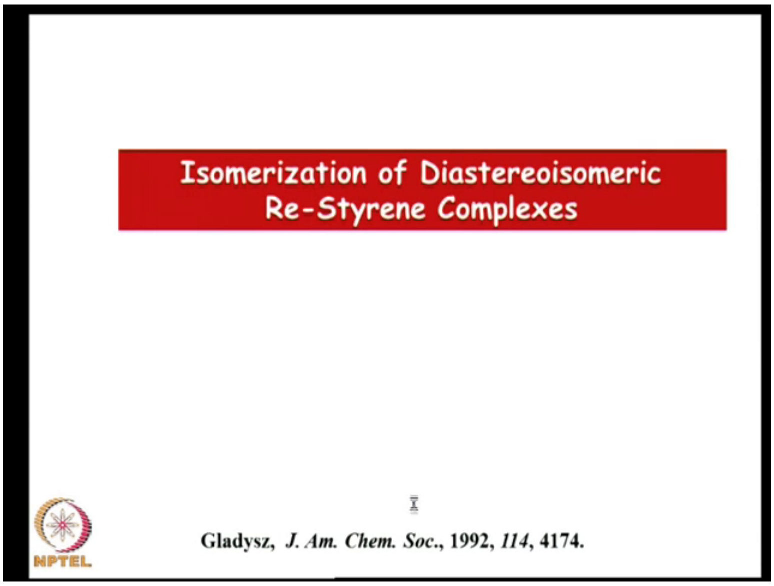

Isomerization of Diastereoisomeric Re-Styrene Complexes

Gladysz, *J. Am. Chem. Soc.*, 1992, *114*, 4174.

I will briefly discuss for you another interesting system that was discovered by Gladysz and this involves.

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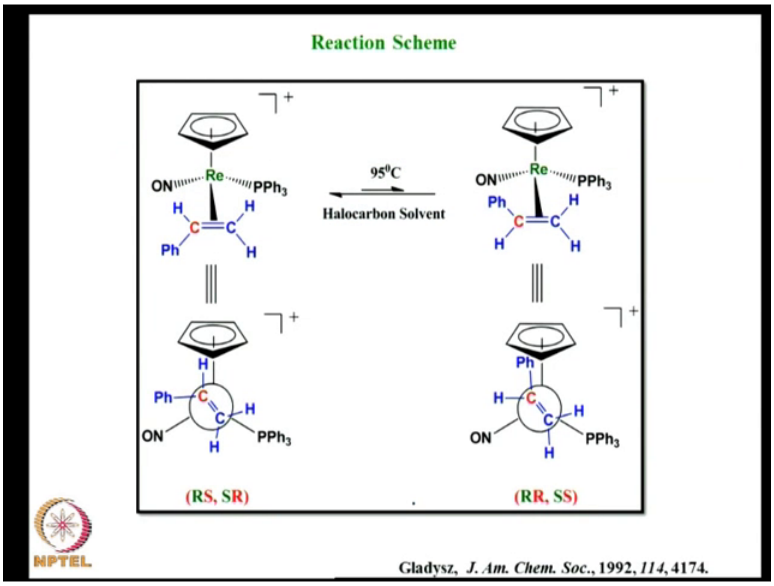
Reaction Scheme

Gladysz, *J. Am. Chem. Soc.*, 1992, *114*, 4174.

A rotation of an olefin in a very strange fashion because the olefin has got pi system and the nodal plane, in the nodal plane which contains the atom which are attached to the carbons which are bonded in a pi fashion. One normally thinks that, the metal cannot move from one side of the olefin to the other. Surprisingly Gladysz and co workers synthesize this molecule which has got two different chiral centers, one is a rhenium center which is chiral and the other is a carbon center which is chiral.

Rhenium center is marked in green and the carbon center is marked in red and, so you can either take this molecule which is R S R on the rhenium and S on the carbon, the other isomer will be equi energetic and that will be the S R isomer. But, if you take either one of them and keep them in a chloroform or a dichloromethane solvent in a halocarbon solvent, usually you would have to take as C D C L 2 tetrachloro ethane solvent. If you want to do that reaction at high temperature and that is what these researchers did, you can isomerizeonly the carbon center is isomerized, in other words it goes to the mirror image.

This is equivalent to saying that, the rhenium has moved from one phase of the olefin to the other phase and this is shown here, in the Neumann projection which is given in the lower half for you. You can see that the olefin has moved has flipped over and formed the R R isomer starting from the R S isomer if you take the S R isomer that would become the SS isomer. So, this was an extremely interesting discovery was made by Gladysz.

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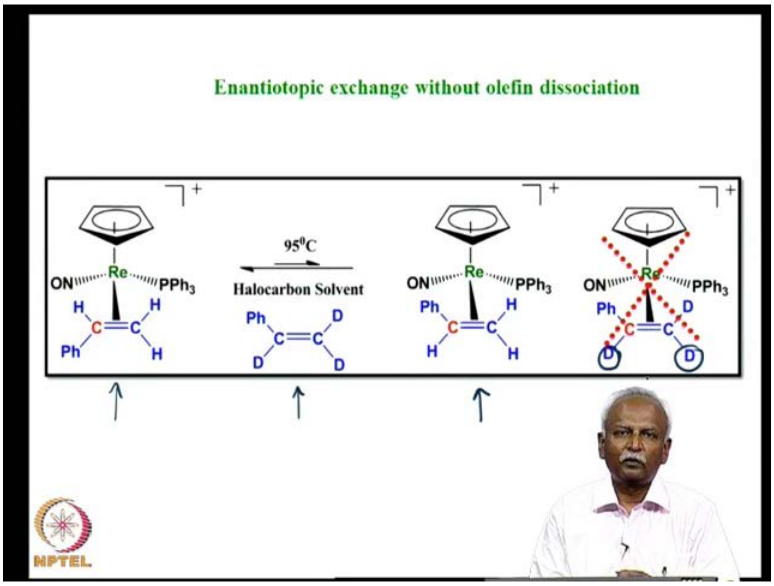

Enantiotopic exchange without olefin dissociation

He showed by a series of isotopic labeling experiments that, in fact it is not possible for the enantiotopic exchange to happen with olefin dissociation. So, one possibility is that olefin comes out from the metals coordination sphere, flips over and bonds to the metal again. So, he did the reaction with a labeled olefin and he also had an unlabeled olefin coordinated to the metal center.

And then after heating it for some time he observed diastereomerisation. But, the diastereomarised olefin was not the one which had the labeledolefin. So, in other words the labeled olefin which is available in solution and plenty could not exchange with a coordinated olefin and clearly tells you that olefin dissociation requires a lot more energy than, what is required for the simple flipping of the olefin.

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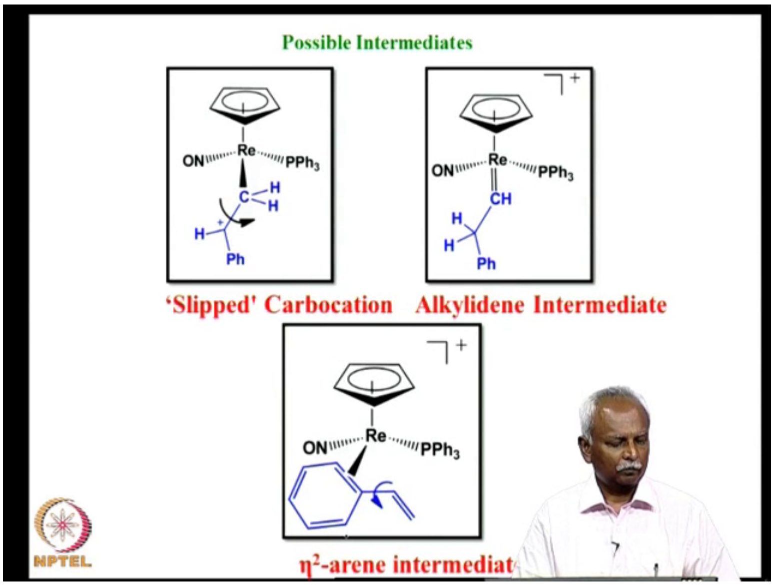
Possible Intermediates

'Slipped' Carbocation

Alkylidene Intermediate

η²-arene intermediate

So, he in fact looked at three different mechanisms and all of them very carefully and the first one involved a slipped carbocation. So, if you want to flip the olefin over you could in fact move the metal to one of the carbon centers and then you will form a carbocation which can lose the chirality at the carbon center. So, he looked at the slipped carbocation and alkylidene intermediate and also because he looked at the styrene complex, heinvestigated the possibility of moving over the metal to the aromatic ring and then moving it back again after rotating it at about the vinyl aromatic ring bond.

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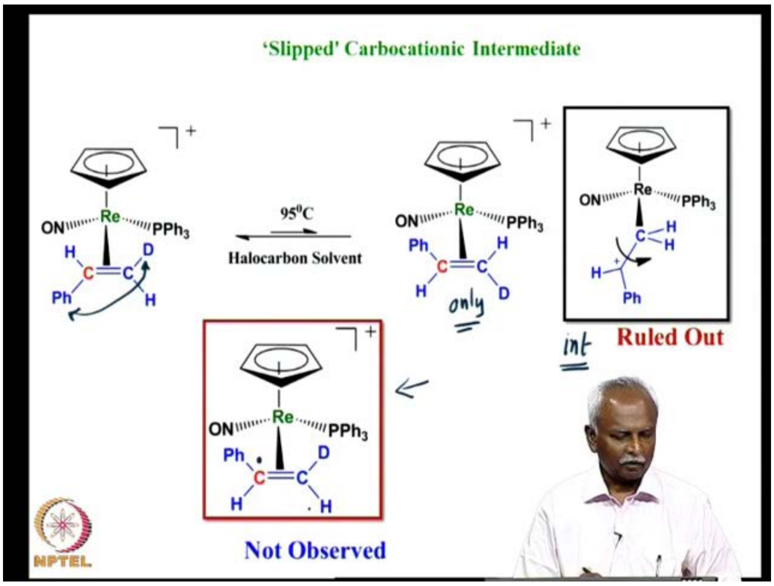
'Slipped' Carbocationic Intermediate

95⁰C

Halocarbon Solvent

Ruled Out

Not Observed

So, let me look at the slipped carbo cationic intermediate, the slipped carbo cationic intermediate requires that you move over to one of the carbon centers and then rotate the carbon carbon bond in such a way that you obtain the isomer. So, if you want to distinguish these two options, the option where the metal flips over to the opposite side and metal passing through a carbo cationic intermediate you need to label the two carbons and look at the stereochemistry before and after the flipping.

So, if it goes through carbo cationic intermediate you would expect this product to be formed, where the carbon center would have undergone isomerization. The fennel would, now be Cis to the deuterium whereas in the previous instance it was Trans to the deuterium, so it is this relationship which would get affected if indeed this was an intermediate. So, they ruled out this intermediate by observing the fact, by noticing that the fennel deuterium relationship was maintained. This was the only product that was observed and this product was not observed indicating clearly that it was not for proceeding through a slipped carbo cationic intermediate.

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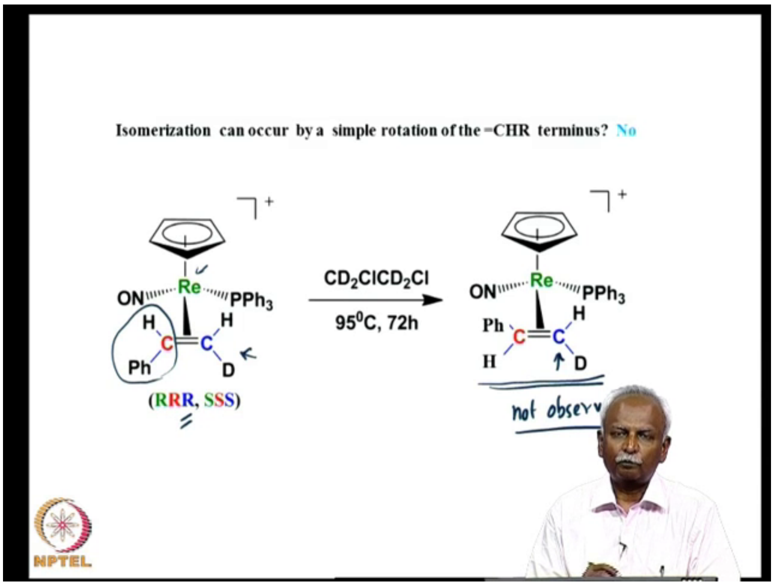

Isomerization can occur by a simple rotation of the =CHR terminus? No

Another isomerization is the rotation of the C H R terminus and you can do that if you want to turn around only the center and keep the center the second carbon intact. Then also you would have a different mechanism for moving from one face of the olefin apparently moving from one face of the olefin to the other whereas, you only flipped the carbon-carbon bond. So, Gladysz actually synthesized another deuterium labeled compound where the second carbon had a chirality also this time he had R R and R, R which is green at the rhenium R red at the carbon and R blue at the second carbon.

After the isomerization he found that both centers were flipped, in other words the metal was in fact going from one side to the other completely. So, he ruled out several different mechanisms, so he actually showed that this product where you, this product where you would retain the chirality at this carbon are not observed. So, this is not observed and it is not possible to flip the carbon independent of the other carbon. So, he showed that the complete rotation of the metal from one face of the olefin to the other was happening.

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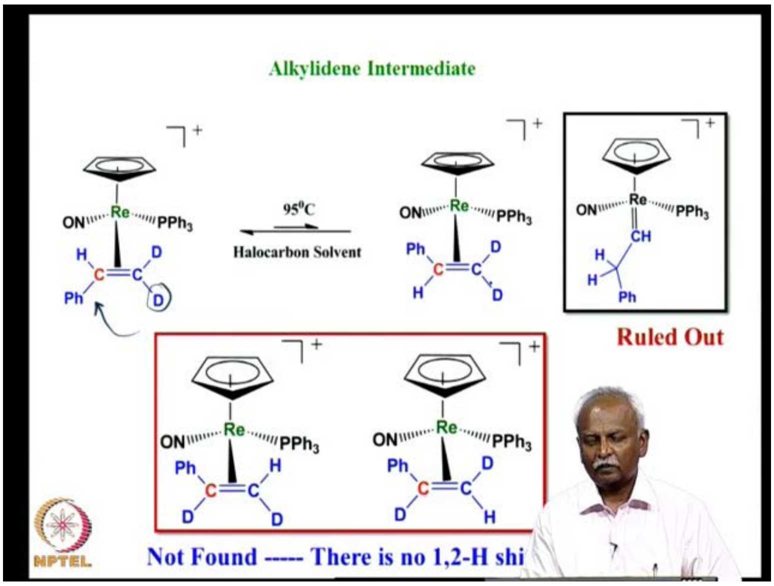
Alkylidene Intermediate

Ruled Out

Not Found ----- There is no 1,2-H shi

So, he also looked at an alkylidene intermediate to form alkylidene, you would have to transfer one of the atoms attached to the carbon from one position to be other position. If you did that, you would if you had a labeled a carbon with deuterium labeled carbon you would be able to distinguish these two mechanisms. So, indeed he did the reaction again and he found that the diastereomerisation could be carried out exclusively with no deuterium scrambling with suggested that there is no one-two hydrogen shift and alkylidene was not involved.

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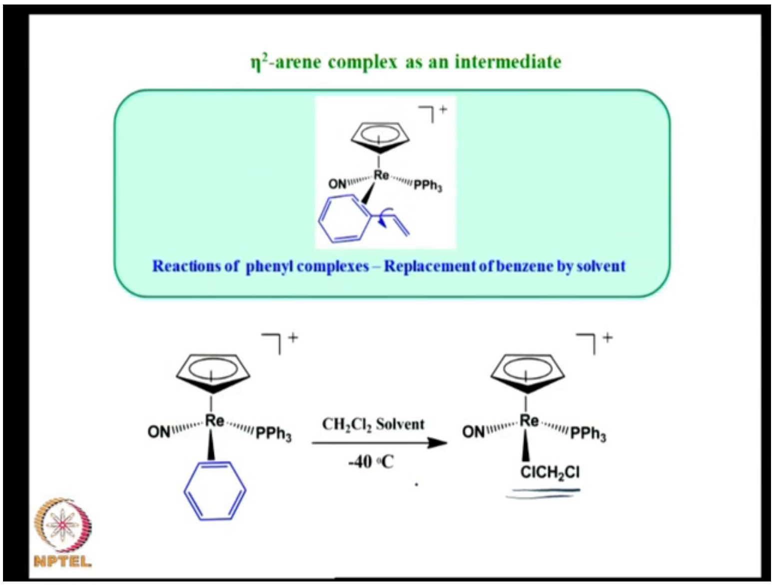

η^2-arene complex as an intermediate

Reactions of phenyl complexes – Replacement of benzene by solvent

So, the pi in intermediate was ruled out in an indirect fashion and he also carried out a labeling study where he labeled their C H of the styrene and looked at the rates at which the isomerizations were happening. So, the first result was an indirect result which he looked at the benzene complex and showed with the benzene complex was in fact an extremely unstable complex. Even at 40 degrees, minus 40 degrees it was the exchanging with a dichloromethane solvent molecule coordinated to the rhenium. So, he suggested that would be highly improbable situations to have the styrene isomerized by moving rhenium to the benzene ring.

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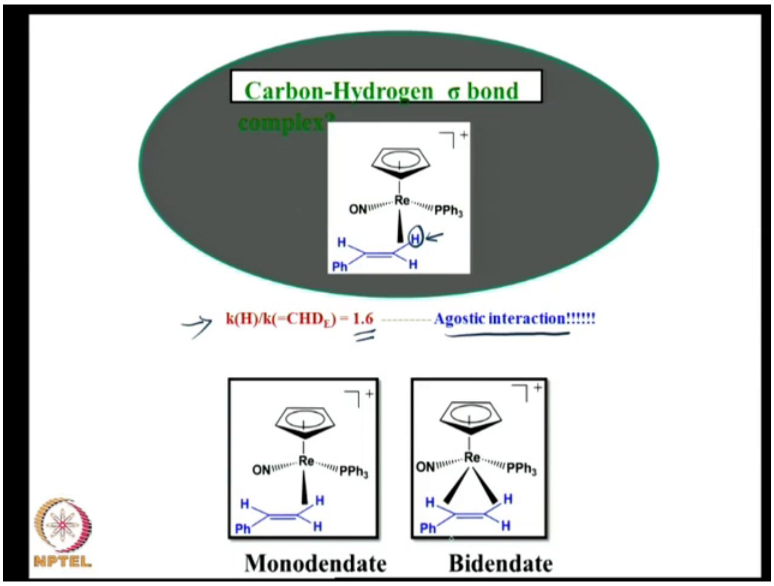

Carbon-Hydrogen σ bond complex?

$k(H)/k(=CHD_E) = 1.6$ ---------- Agostic interaction!!!!!!

So, what he suggests is that the carbon hydrogen sigma bond is in fact interacting with the rhenium center and then because it is a sigma interaction, Agostic Interaction is a sigma interaction is possible to move the rhenium from one face of the olefin to the other. In this case he observed when you replace any one of these hydrogens with a deuterium you look at the rate at which the diastereomerisation takes place the K H by K D turns out to be 1.6 for the hydrogen which is Trans, which is in the Trans position.

So, in other words it is the Trans C H bond, which is interacting with the metal center during the inter-conversion from one side to the other. Now, if you break a C H bond you would have a kinetic isotopic effect, which is indicated here or if you have a weak interaction in the transition state which inter converts the two isomers. Then also you would expect a K H by K D which is greater or lesser than one, so there are two possibilities. Now, it is possible that it is interacting through the C H and moving over to the other phase of the olefin and it is also possible that it is interacting in a bi dentate fashion through two hydrogens, which are attached to the metal which are interacting with a metal.

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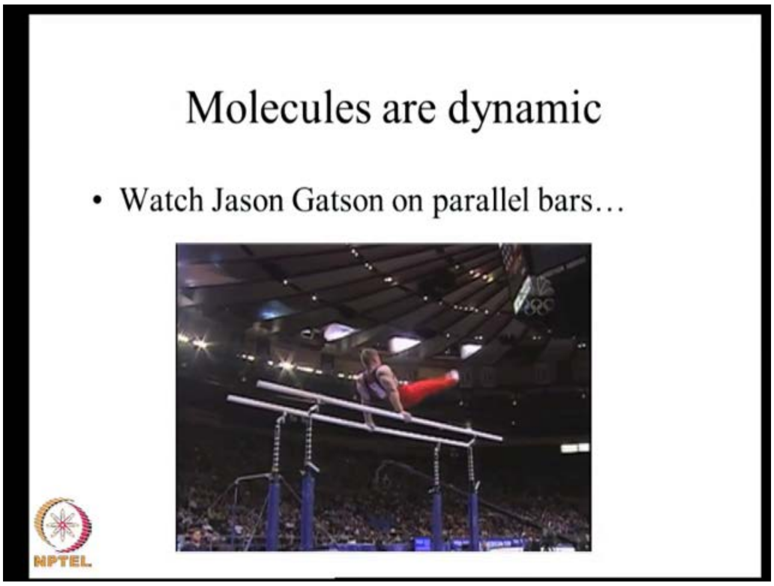

Molecules are dynamic

- Watch Jason Gatson on parallel bars…

So, at this point I just want you to look at a movie which is the short clipping of Jason Gatson, who is a gymnast working on the parallel bars. You can see the facility with which he moves from one side of the parallel bar which can be considered as olefin to the other side. If Jason Gatson is a metal center, then you can see the facility with which you can move the metal center from one side of the double bond to the other.

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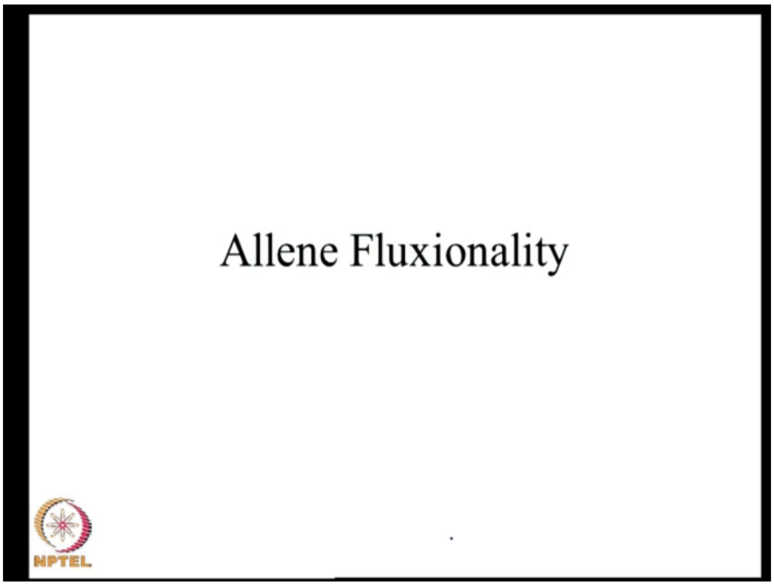

Allene Fluxionality

Let us now take a brief look at allene fuxionality; allene fuxionality is another strange phenomenon because you have two double bonds.

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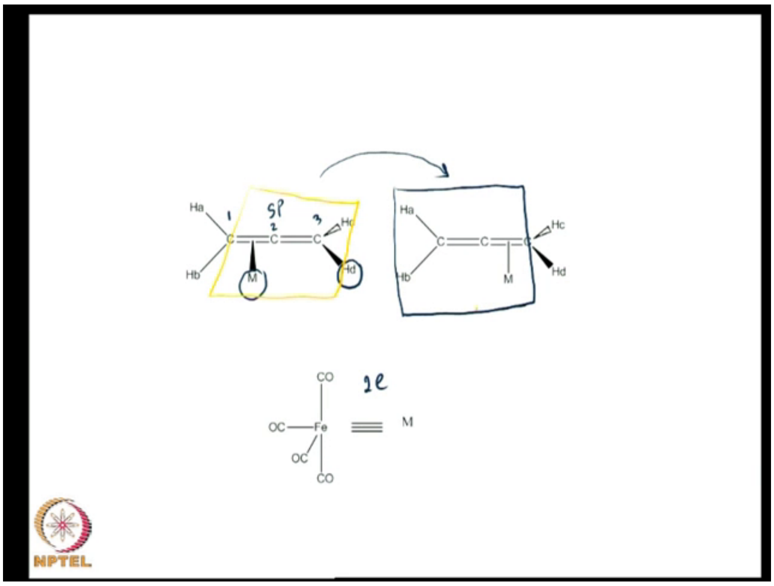

The two double bonds are in fact perpendicular to one another because you have a central carbon which is S P hybridized. You will have a double bond on between carbon atoms 1 and 2 perpendicular to the double bond which is between carbon atoms 2 and 3.

Allene itself as you might want recall has got four hydrogens with these four hydrogens have two hydrogens perpendicular to the other two. So, if I draw the allene metal complex and allene forms interesting metal complexes with FeCO4 which requires only two electrons this fragment requires two electrons to achieve the 18 electron rule.

So, F e C O 4 with a name that can be considered as the M and the M is coordinated in such a fashion that if the two hydrogens H a and H b are in the plane of the allene molecule then the H c and H d are going in and out of the screen or in and out of the plane of the board. So, the metal atom is coordinated such that it is coming towards you, away from the towards the viewer away from the screen and into just like this atom H d.

So, both H d and M a coming towards the viewer, so this is the geometry of the allene F e C O 4 molecule, now turns out that this position is not unique and the metal rapidly moves over to the other double bond and since the two double bonds are perpendicular to one another. It would be difficult to understand, it is difficult to understand how the metal moves so easily from one side to the other. Now, when the metal moves from carbon from the pi bond between carbon atoms 1 and 2 to the one between 2 and 3.

You will notice that a metal now moves in a position that is below the plane in which these four atoms present C 2, C 3, H c and H d and the metal, now comes down below the allene. It is on the same plane as the metal atom iron is in the same plane as the three carbon atoms and H a and H b, so in other words all these atoms, now become planer. So, let me draw plain now, so all these atoms are in the same plane and earlier these four atoms or rather these six atoms were in the same plane. So, you can see that the metal has moved from one plain to the other and since the pi bonds are perpendicular to one another, it is difficult to understand how this movement is taking place.

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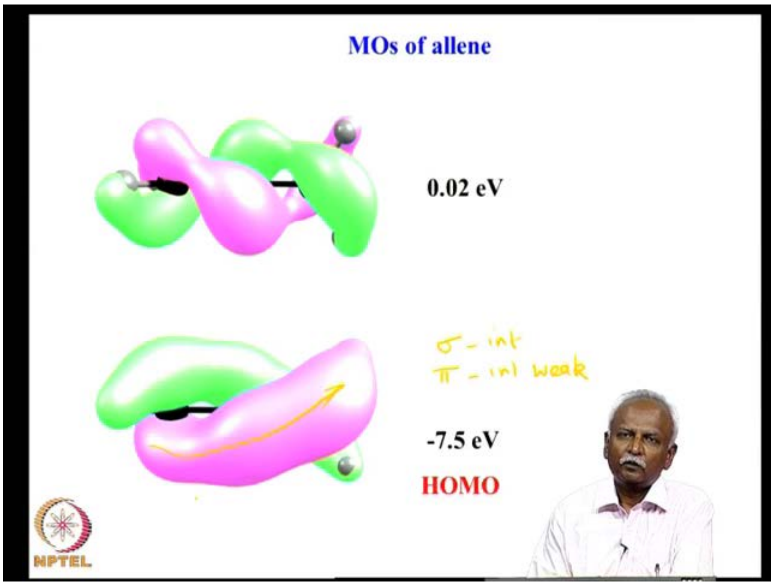

MOs of allene

0.02 eV

σ - int

π - int weak

-7.5 eV

HOMO

However, if you do a computational study of the molecular orbital of allele, you notice that the highest occupied molecular orbital allene is in fact of pi system which has a donor, which is the donor orbital for the F e C O 4 which is wrapping around the allene. In such a fashion that it moves from one side or from one end of the allene to the other end, so it is very easy to understand. Now, if you look at this molecular orbital how the metal atom is moving from one side to the other side, from one side of the allene, one end of the allene to the other end of the allene because there is a smooth pi system along which it can travel.

Of course, if you remember any olefin metal bond involves two components, the sigma component and the pi component. The sigma component would not be disturbed when the metal moves like this, but the pi component would be disturbed. So, if the sigma component is very strong interaction and if the pi interaction is weak, then there is no difficulty in understanding how the metal is able to move from one end of the allene to the other end.

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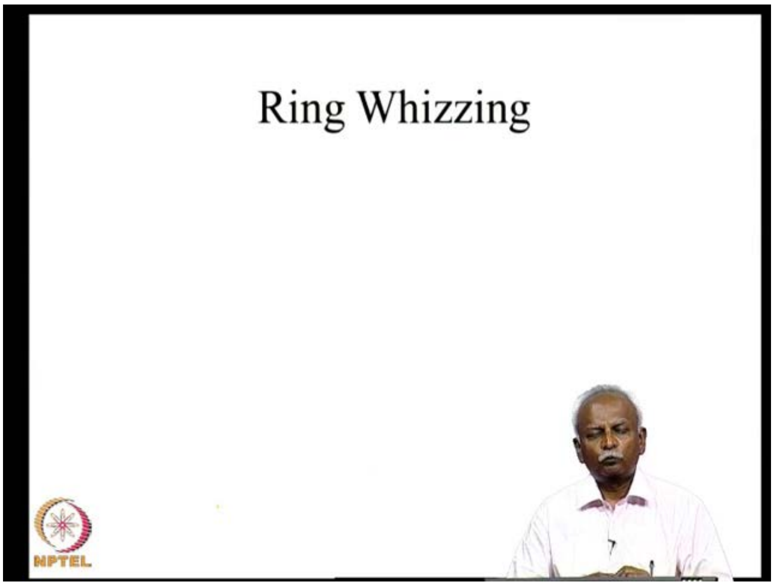

Ring Whizzing

Now, let us move onto a system which is called Ring Whizzing.

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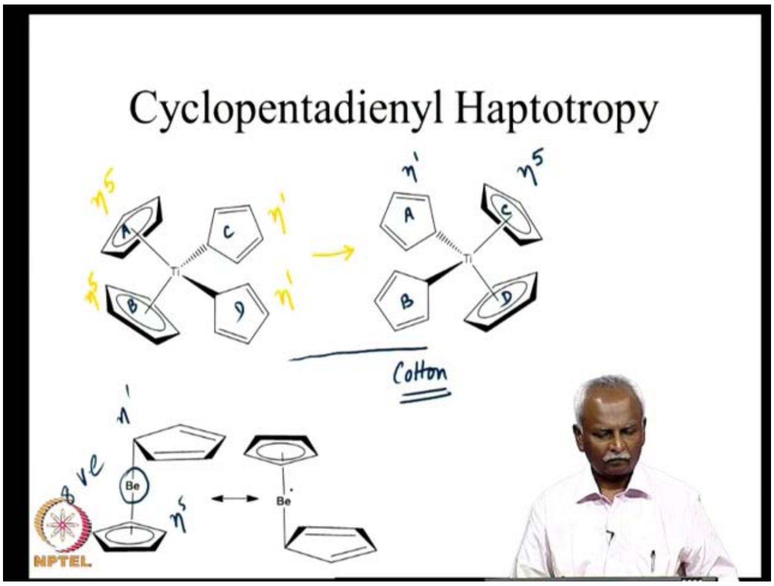

Cyclopentadienyl Haptotropy

Ring whizzing again is a very common in the case of cyclopentadienyl complexes and it is required sometimes by the electron count on metal. So, in the case of titanium where you have titanium 4, where four cyclopentadienyl anions are interacting with titanium. You cannot afford to have 20 electrons around the metal, so the metal compensates or rather corrects for this difficulty by having two cyclopentadienyl atoms as eta 1. So, these are eta 1 atoms and these ligands, these are eta 1 ligands and these are eta 5 ligands.

So, you can understand or you can then envisage a situation where the eta 5 ligands become eta 1 and the eta 1 ligands become eta 5. So, let us mark this in a different color, now these rings are labeled as A B C and D and in this molecule, the A B has interchanged with C D in terms of hapticity. So, the hapticity of A and B were eta 5 the hapticity of A and B on the molecule on my right is actually eta 1. So, these are eta 1 and these are eta 5.

Now, we have written as if both A and B change simultaneously this may not be the case. You can have a flip where C becomes eta 1 also and then there is an interchange of the ring and such a fashion that at no point in time the electron count around the titanium exceeds 16. So, here is one example where cyclopentadienyl haptotropy leads to very fast ring exchange, this was studied by cotton. This was very interesting system which was studied using Carbon 13 N M R spectroscopy and proton N M R spectroscopy.

Now, this type of situation is very common in main group chemistry also where both due to the size of the metal atom and due to the electron count which cannot exceed 8, now the balance electrons cannot exceed 8. So, you tend to have systems where you have less than 5 atoms of the carbon coordinated to the metal atom. Here we have shown a beryllium which is eta 5 on one end and eta 1 on the other and because it is B e 2 plus, it can support to cyclopentadienyls.

But, at the same time it cannot support two eta 5 cyclopentadienyls and, so it is with decides to have eta 5 and eta 1 and because it cannot distinguish between the two cyclopentadienyls. There is a rapid exchange between a structure where the top ring is eta 5 and the bottom ring is eta 1 and on my left side I have eta 5 on the bottom and eta 1 on the top.

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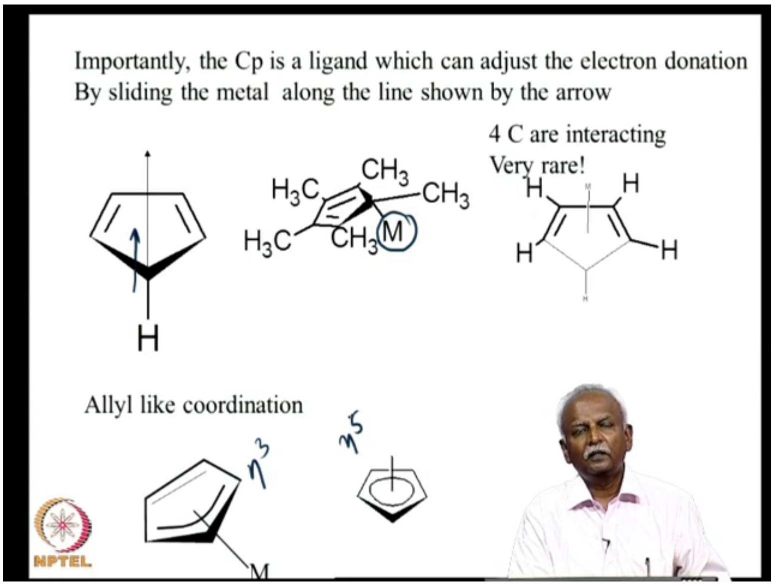
Importantly, the Cp is a ligand which can adjust the electron donation By sliding the metal along the line shown by the arrow

4 C are interacting
Very rare!

Allyl like coordination

So, this is called cyclopentadienyl haptotropyand this haptotropy was studied at various levels of theory and experiment. It can be simply understood as elegantly explained by Hoffman by a sliding of the metal along the cyclopentadienyl bisecting plain. So, if you would draw a cyclopentadienyl system where the two double bonds are fixed. Then you notice that, there is a plain which is dividing the two and if the metal moves from one end of this arrow to the other you go all the way from eta 1 to eta 3 to eta 5.

So, here I have shown for you with a system where metal is bonded to only carbon atom number 1 and as it moves towards the center along this arrow, as it moves along this arrow you have an allyl like coordination where three carbons will start interacting. This will be eta 3 and if it moves further then it moves to the center of the ring and then it is eta 5. It is very rare to have four carbon atoms interacting with the metal in an eta 4 fashion and that means the anion has to be supported only by the carbon and that rarely happens.

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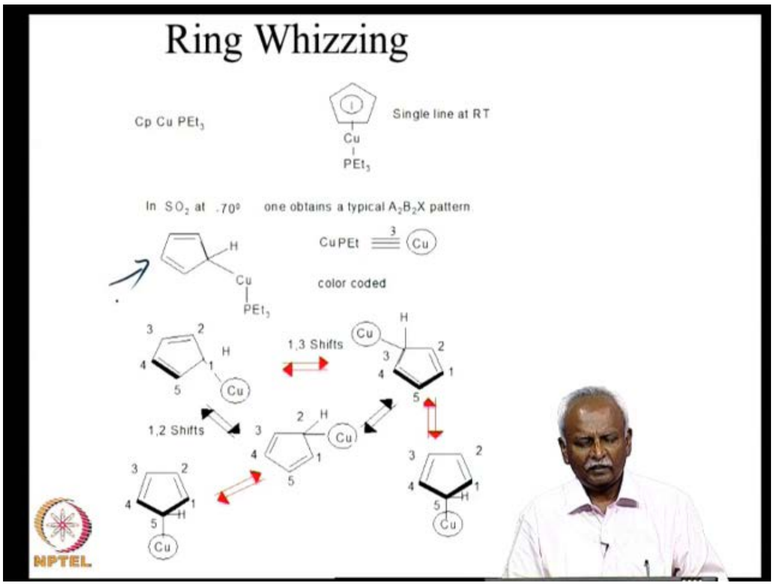

Ring Whizzing

Cp Cu PEt_3

Single line at RT

In SO_2 at -70° one obtains a typical A_2B_2X pattern

$CuPEt_3 \equiv$ Cu

color coded

1,3 Shifts

1,2 Shifts

So, Ring Whizzing was also studied extensively with copper complex where because of electron count you would like to have a system which is less than eta 5. So, in liquid sulphur dioxide at minus 70 degrees, one obtains a structure where copper is in fact coordinated only to one carbon atom and this is indicated by the structure which is given here. But, in the N M R spectrum even at minus 70 degrees it is obvious that the copper atom is not stationary, it is moving from carbon atom 1 to 2 to 3 to 4 to 5.

You will notice that the movement of the copper from 1 to 3 is actually like an allyl group which is shifting. If it shifts from 1 to 2 or 1 to 5, then it can also act as it is doing a 1 5 shift. So, because of these shifts which are metallotropic shifts, now instead of proto-tropic which you have observed in organic chemistry.

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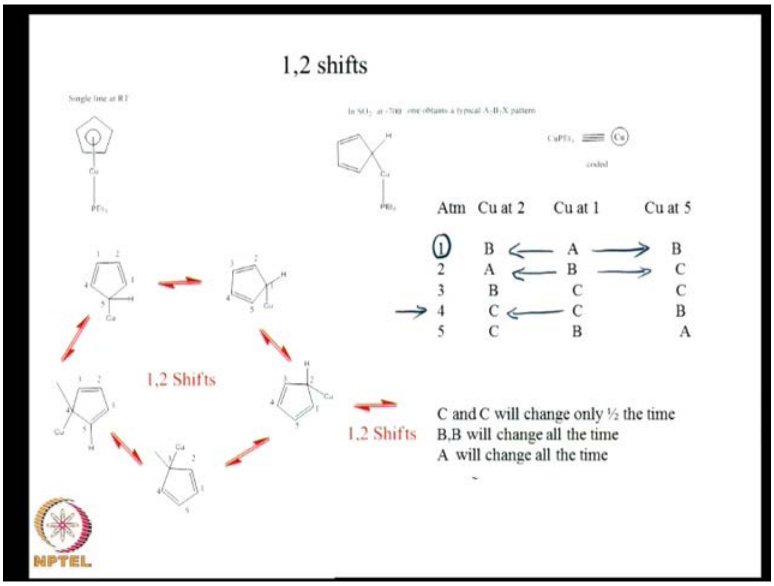

1,2 shifts

Atm	Cu at 2	Cu at 1	Cu at 5
1	B	A	B
2	A	B	C
3	B	C	C
4	C	C	B
5	C	B	A

1,2 Shifts

C and C will change only ½ the time
B,B will change all the time
A will change all the time

You can have very easy shifts which can be studied at low temperature, now when you shift from 1 to 2 and this is the result of a 1 2 shift. If you have only 1 2 shifts, then you will notice that the carbon atom which if it is initially carbon atom number, atom number 1 is labeled as B then it becomes A when it moves to C u at. When the copper moves from atom number 1 to atom number 2, it changes from A to B and if it moves to atom number 5 it changes again to B. Whereas in a similar fashion and copper is at atom number 1.

The B what is labeled as B becomes A and what is labeled as B becomes C when copper moves to atom number 5 both of these are 1 2 shifts. So, you cannot distinguish between the left and right between moving to copper atom 2 or copper moving to atom number 5. So, what you notice is that A changes all the time B also changes, B will also change all the time. Whereas atom number C moves to atom type C when you have 1 2 shifts in this which is labeled as 4.

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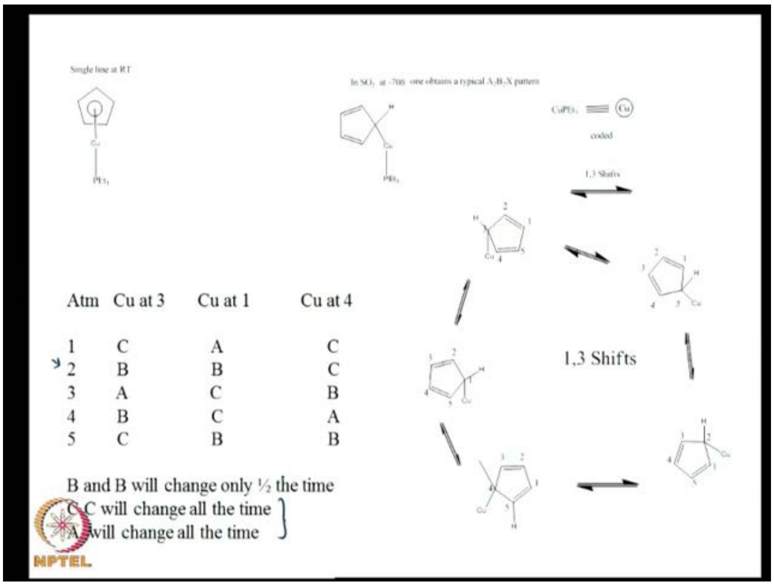

Single line at RT

In SO$_2$ at -70 one obtains a typical A_2B_2X pattern

Atm	Cu at 3	Cu at 1	Cu at 4
1	C	A	C
2	B	B	C
3	A	C	B
4	B	C	A
5	C	B	B

B and B will change only ½ the time

C C will change all the time

A will change all the time

So, what you have is a situation which can distinguish between 1 2 shifts and 1 3 shifts because in 1 3 shifts you have atom numbers B, which is changing only half the time and C and A end up changing all the time. So, this type of a change is shift which is happening either in a 1 2 fashion or in a 1 3 fashion ends up changing the type of carbons in an unsymmetrical fashion.

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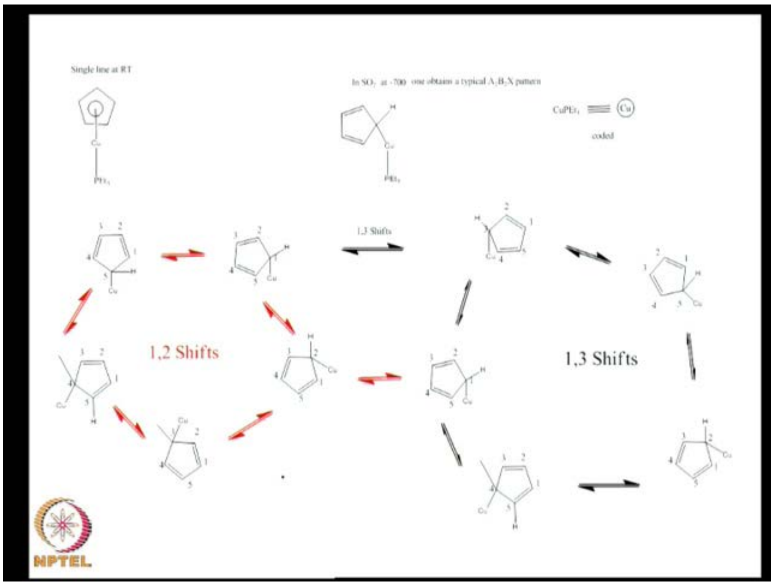

Single line at RT

In SO$_2$ at -70 one obtains a typical A_2B_2X pattern

Let us take a look at what will happen if it is completely random, if it is completely random and both 1 2 shifts and 1 3 shifts can happen and that is pictured here on this slide for you. Then all the carbon atoms will become, will change in the line widths of all the carbon atoms will be the same.

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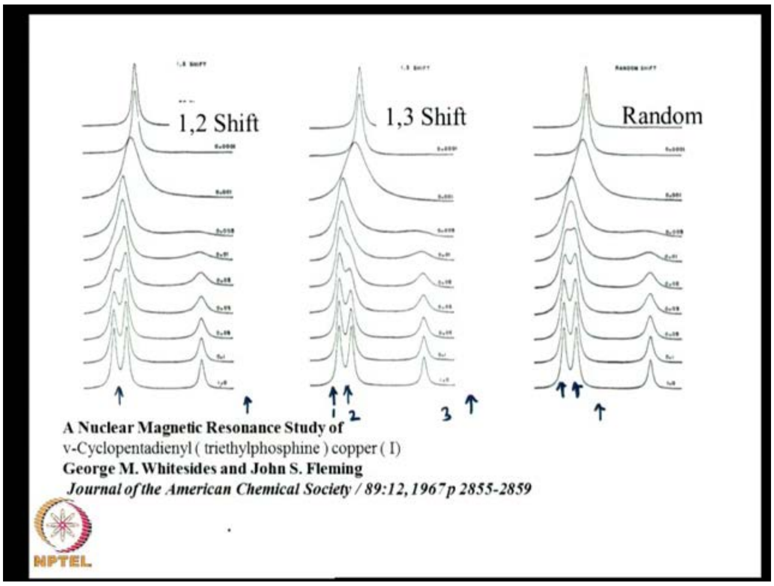

A Nuclear Magnetic Resonance Study of
v-Cyclopentadienyl (triethylphosphine) copper (I)
George M. Whitesides and John S. Fleming
Journal of the American Chemical Society / 89:12, 1967 p 2855-2859

It was assimilation study that was done by George Whitesides and he showed that a 1 2 shift will have a change in the type that I have shown you here where as a pure 1 3 shift will have a change which is shown here. A completely random shift will have a change which is the same for the two resonances which are marked by this blue arrow, so in these two cases if you have a pure 1 2 or a pure 1 3 shift, the line shape would be in a skewed fashion.

So, you can see on the 1 3 shift, the second resonance is the 1, if this is 1 this is 2 and this is 3, the second resonance is decreasing faster than the first resonance. So, this kind of a skewed change will happen if you have only 1 2 shift or only 1 3 shift, a random shift would lead to a uniform change of these two peaks.

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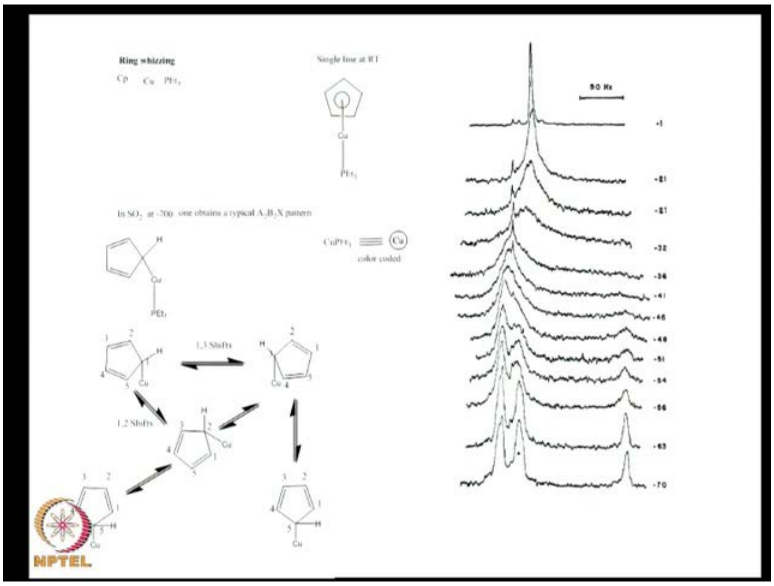

Ring whizzing

Cp Cu PEt$_3$

Single line at RT

In SO$_2$ at -70 one obtains a typical A$_2$B$_2$X pattern

CuPEt$_3$ ≡ (Cu) color coded

In fact, in the experiment it was found that it was only a skewed shift that was happening and as a result he concluded that either it has to be 1 2 shift or a 1 3 shift.

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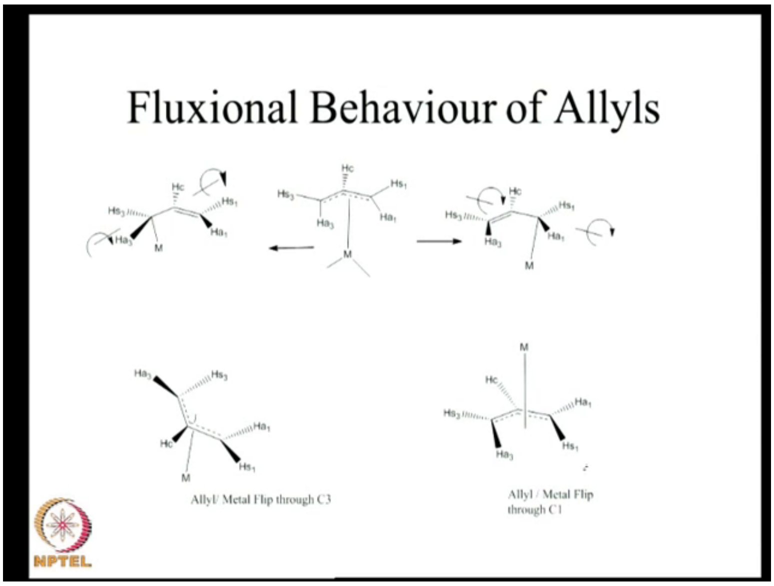

Fluxional Behaviour of Allyls

Allyl/ Metal Flip through C3

Allyl / Metal Flip through C1

Now, you have already looked at fluxional behavior of allyls and here the car metal moves from carbon atom 1 to carbon atom 3, if it is eta 1 bound or it can move from one face to rather face if it is a metal flip.

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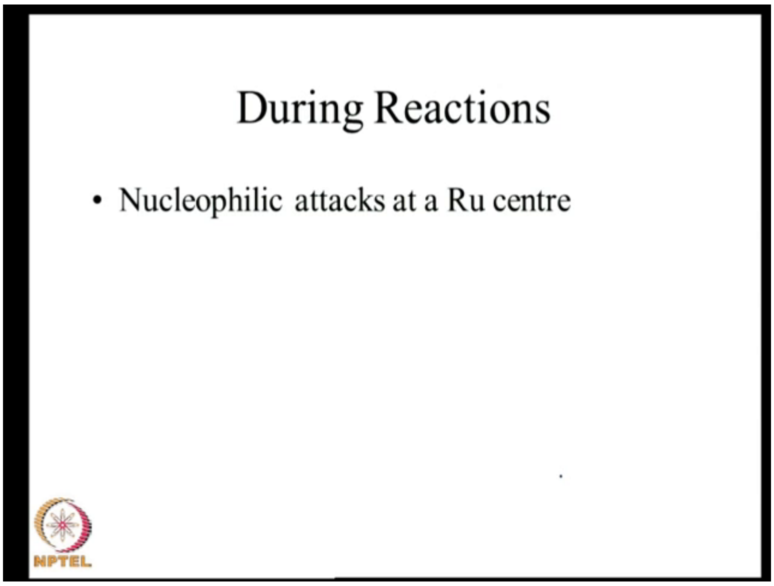

During Reactions

- Nucleophilic attacks at a Ru centre

So, this is something which we have looked at earlier, we can also have changes during a reaction.

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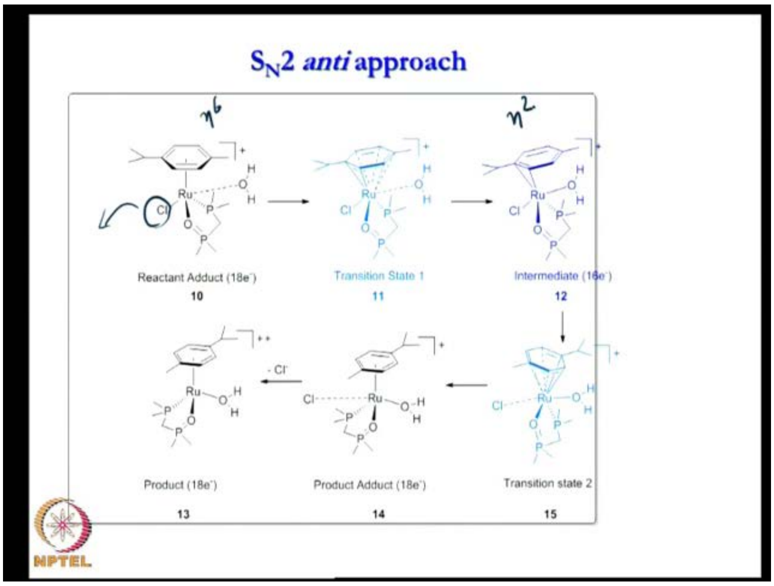

S_N2 *anti* approach

For example, this change that needs to happen when you have a nucleophilic attack on a metal center, and a let us say a chloride is attacked by a water molecule or rather a chloride is replaced by a water molecule. In the intermediate, both chloride and water are bound and the total electron count increases and so the metal instead of increasing the electron count the metal goes from eta 6 to eta 2. So, this type of a movement is also possible in during the course of reaction and it may not happen in a static molecule.

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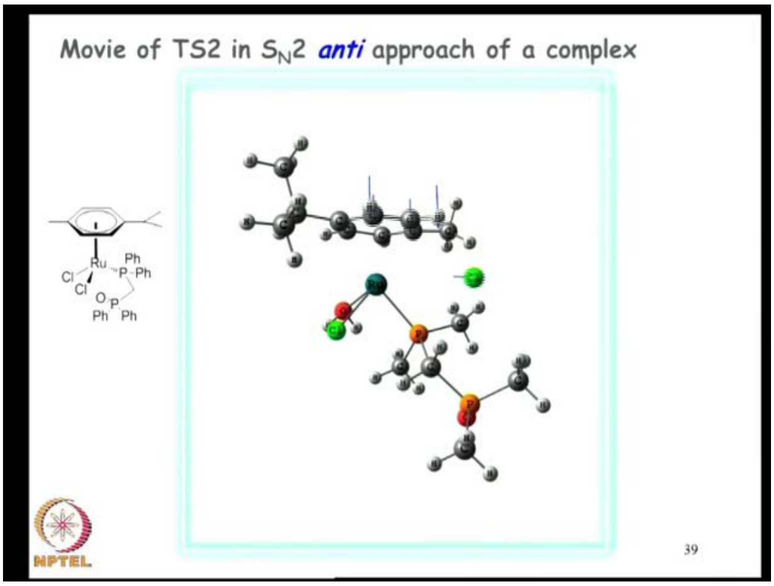

Movie of TS2 in S_N2 *anti* approach of a complex

Here, I have for you pictured a transition state which is being simulated and you can see that the six member arene ring, which is you can see with the six member arene ring which I have here which is shown here the six member arene ring keeps changing as the chloride comes in and goes out. So, this type of a dynamic behavior is something which can be noticed only during the course of the reaction.

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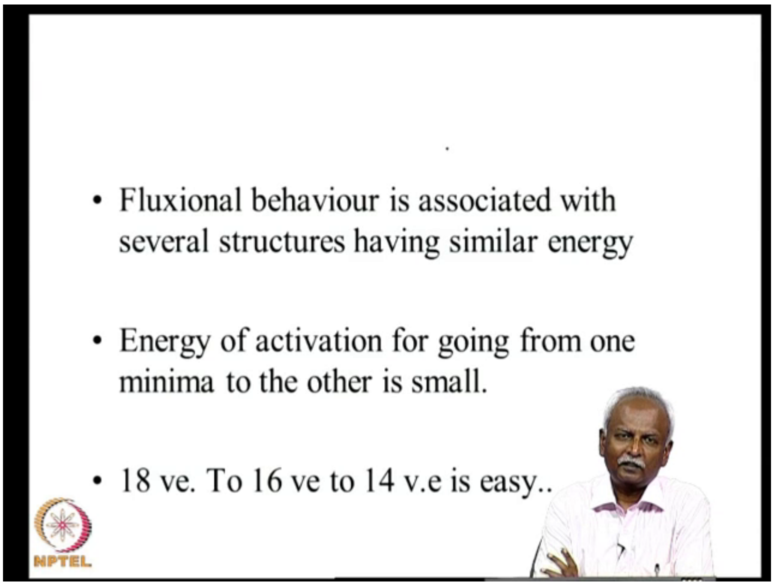

- Fluxional behaviour is associated with several structures having similar energy
- Energy of activation for going from one minima to the other is small.
- 18 ve. To 16 ve to 14 v.e is easy..

So, to conclude this discussion about fluxional behavior, one must note that the fluxional behavior is associated with a fairly flat potential energy surface. When you have a flat potential energy surface and you have several structures having similar energy. Then you can have very good fluxional behavior and one also needs to have a small energy gap for moving the metal, or moving the organic fragment from one position to the other.

In other words it is energy activation for going from one of these minima to the other minima should also be small. In general 18 electron count holds the key to fluxional behavior you have several structures, which are having a maximum of 18 electrons. Preferably 16 and during the movement also the number of electrons are maintained at 18 or less.