Introduction to Organometallic Chemistry
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Lecture - 15
Migratory Insertion reaction with alkynes

Today, we will consider some reaction mechanisms in organo metallic chemistry especially with respect to insertion of neutral ligands. We had already seen that carbon monoxide can be inserted between a metal carbon bond, we will continue with this discussion first. And subsequently we will look at some other neutral ligands which can participate in this reaction.

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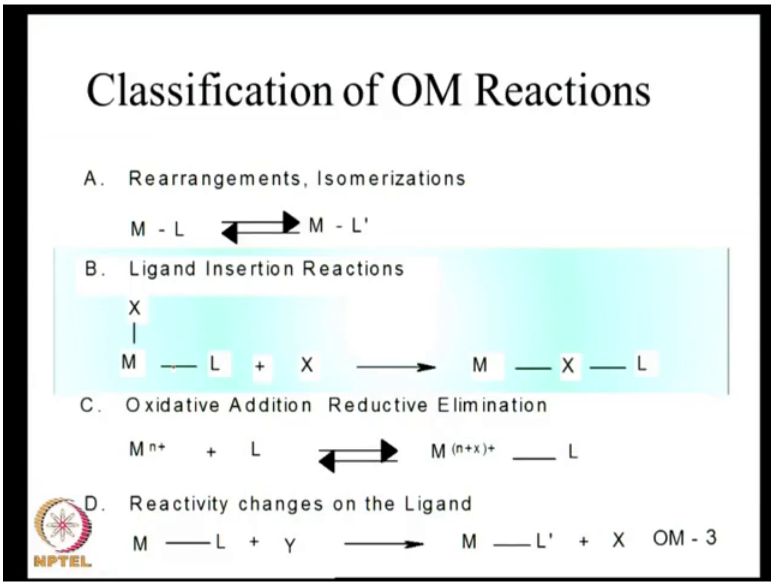

Classification of OM Reactions

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

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

OM - 3

So, we have classified the type of reactions that can happen in organo metallic chemistry broadly into these four categories. The first category comprises of rearrangement and a simple isomerization reaction, where the position of the ligand or type of ligand that is involved in these complexes undergoes a change. In the second group, we talk about ligand insertion reactions, and that is what we are going to be concern with today in this lecture. Basically, what we have is the insertion of a neutral ligand apparently into the M X bond. In this particular case the way we have written it, M L is the bond that is broken and then X group is inserted in between. So, let us take a look at the type of reactions that can happen and what are the pathways by which these reactions happen.

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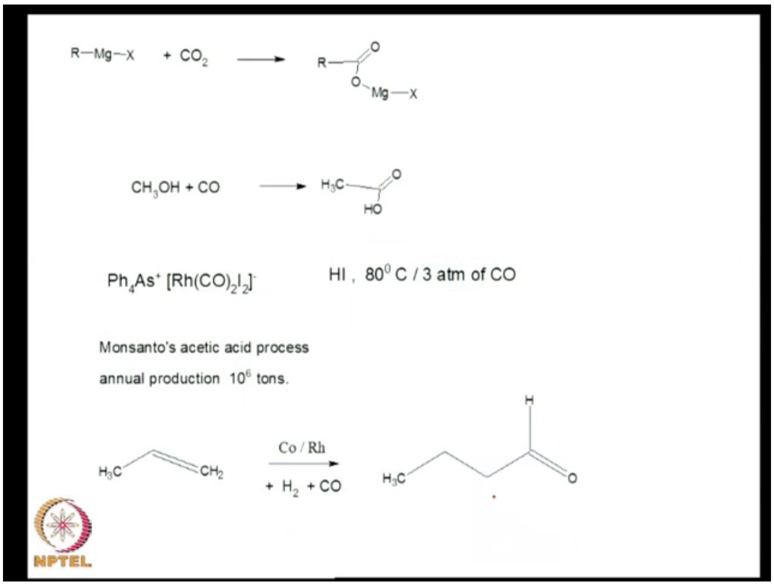
$R{-}Mg{-}X + CO_2 \longrightarrow$

$CH_3OH + CO \longrightarrow$

$Ph_4As^+ [Rh(CO)_2I_2]^-$ HI , 80^0 C / 3 atm of CO

Monsanto's acetic acid process

annual production 10^6 tons.

$\xrightarrow[+ H_2 + CO]{Co / Rh}$

We first note that in the case of organo metallic reactions involving transition metals, the reagents that are involved. The type of insertions that can take place are distinctly different from what can happen in main group, organo metallic chemistry main group organo metallic chemistry is characterized by very polar substrates. In this particular instance, I have shown carbon dioxide. Here, carbon dioxide is undergoing insertion between an R M g bond and in R convention we know that carbon dioxide is polarized as C plus and O minus R is also polarized as R minus and M g plus. So, it is very easy to understand an insertion reaction where you have insertion of carbon dioxide in such a fashion that the oxygen, now bonds to the magnesium atom. However, we notice that in the case of organo transition metal chemistry, it is possible to insert a neutral molecule like carbon monoxide which has a very small dipole moment.

This neutral molecule is able to insert between a metal carbon bond and this is the basis. The insertion of carbon monoxide into methanol is actually the basis for formation of acetic acid and this particular process is used by the company Monsanto to produce a very large amount of acetic acid. So, it is an extremely useful process and it is also modified to generate a variety of small molecules, which are useful in synthetic organic chemistry. Especially, in the pharmaceutical industry and so this reaction is an extremely valuable reaction.

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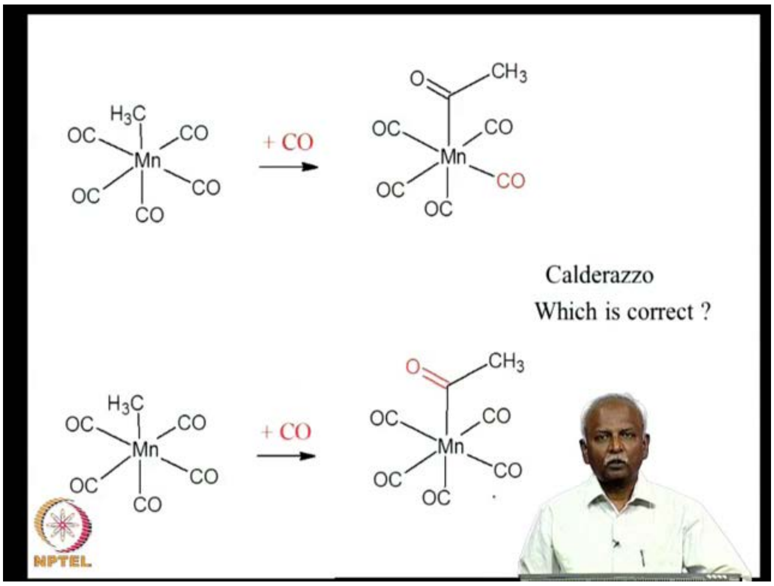

Calderazzo
Which is correct ?

Now, some time back Calderazzo figured out that there are two possibilities for having this reaction take place. In the first instance, we insert a molecule of carbon monoxide between the metal carbon bonds to do that we will have to break. For example, if you want to insert carbon monoxide in this bond we break this carbon bond and then the carbon monoxide can be inserted. I have color coded the carbon monoxide, so that you can recognize what we are doing here we are inserting carbon monoxide between the metal methyl bond and in there is another possibility.

In this possibility what we are doing is, inserting carbon monoxide into a vacant site in the coordination sphere of the metal first the methyl migrates first. The methyl group actually migrates on to carbon monoxide and a vacant site is generated. On this vacant site, carbon monoxide is capping the vacant site and as a result we have octahedral complex again. So, Calderazzo is trying to answer this question and through isotopically labeling experiments. He showed clearly that the methyl group is migrating to a carbon monoxide and generating an acetyl group.

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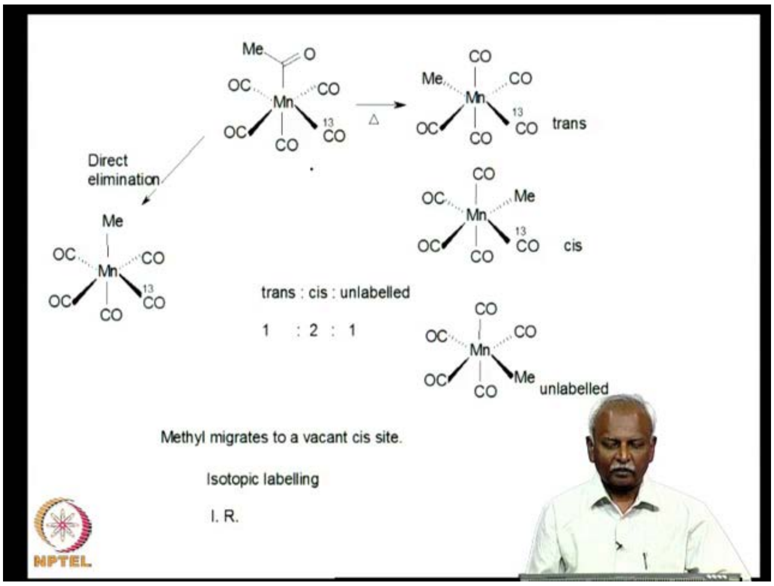

trans : cis : unlabelled

1 : 2 : 1

Methyl migrates to a vacant cis site.

Isotopic labelling

I. R.

The incoming carbon monoxide is merely filling up a vacant coordination site. He found out that it is possible for the carbon monoxide to migrate or the methyl group to migrate. He showed very clearly that, it is a methyl group which is migrating and he did this by utilizing an isotopically labeled compound which had the carbon 13 label in the Cis position of the acetyl group.

Looking at the reverse reaction, most of these reactions are reversible. He heated this compound to slightly higher temperature till it lost the carbon monoxide. The reverse of this insertion reaction, I wish we could call it D insertion reaction, but we have to call it abstraction reaction or an extrusion and that is what happening here carbon monoxide leaves. He showed any one of these carbon monoxides which are Cis to the acetyl group any of them can leave.

So, you get a ratio of Trans to Cis to unlabel as 1 is to 2 is to 1. This is exactly the ratio in which you have the four carbon monoxides which can leave the coordination sphere of the metal. So, very clearly he demonstrated that it is the anionic group or the formally anionic group, the methyl group here that is the one which migrates to a vacant coordination site. So, he did this isotopic labeling and through infrared spectroscopy.

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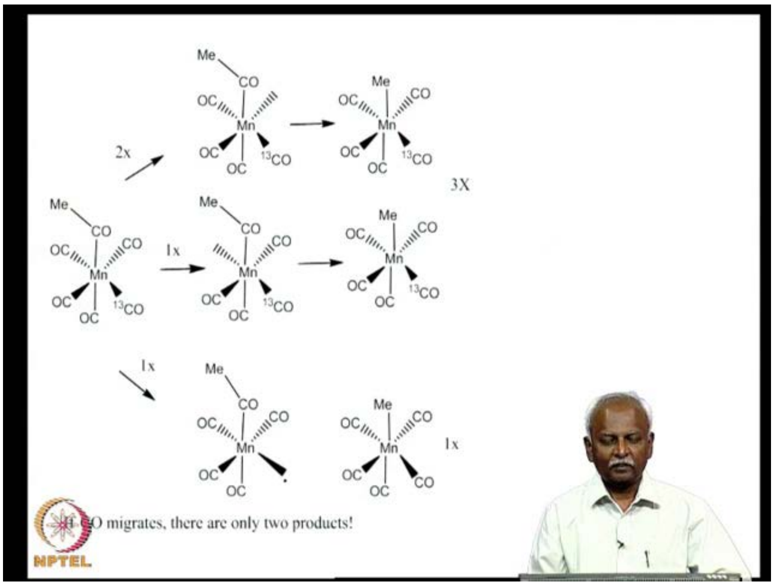

O migrates, there are only two products!

So, if the C O had migrated, a different ratio of compounds would have been formed and there were clearly it was indicated that the methyl group was migrating.

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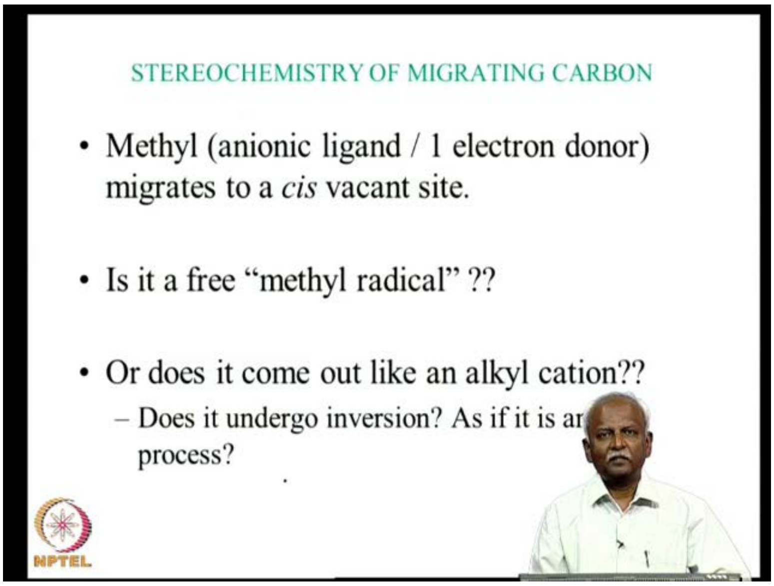

STEREOCHEMISTRY OF MIGRATING CARBON

- Methyl (anionic ligand / 1 electron donor) migrates to a *cis* vacant site.
- Is it a free "methyl radical" ??
- Or does it come out like an alkyl cation??
  - Does it undergo inversion? As if it is ar process?

So, we have answered about some questions about the migration reaction. Now, in today's topic, we are going to talk about the stereochemistry of the migrating carbon you remember it is the methyl group which is migrating. Now, a methyl group can migrate to a carbon monoxide as an anionic ligand and if it does, so it would migrate with a pair of electrons in the neutral method of electron counting. We consider that as a one electron donor, but if we consider that as a two electron donor it is an anionic ligand that seems to be more appropriate method to count electrons in this particular talk.

So, we will use the anionic method if it migrates to a Cis weaken site then, we can ask this question what will happen to the stereochemistry. If it migrates as a free methyl radical then what would happen to the stereochemistry. Now, it is also known that the methyl group can migrate as an alkyl cation especially, when it is substituted. So, we can think of it as if there has been a nucleophilic substitution carried out on the methyl groupl, in which case it will have to undergo inversion during the process.

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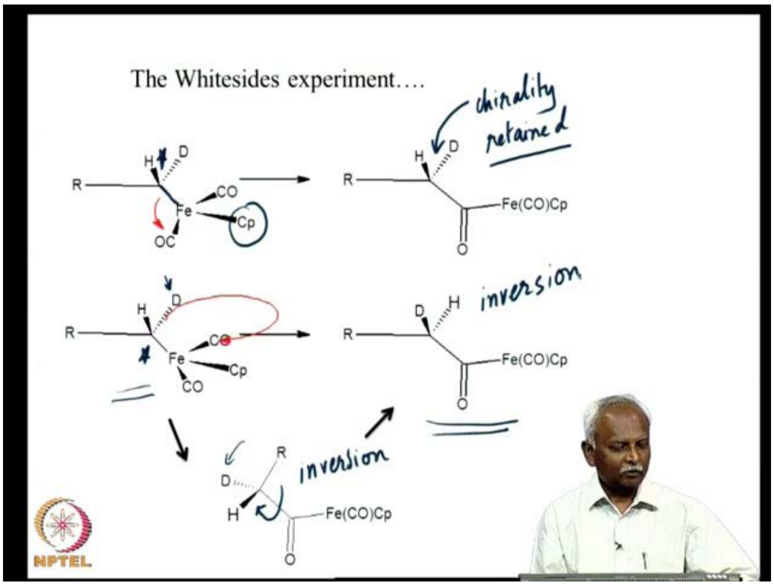

The Whitesides experiment....

So, let us proceed further. There was this experiment out carried by Whitesides which is an extremely useful experiment and very creative experiment. Where he carried out an insertion reaction by taking a molecule which had stereochemistry marked out by hydrogen and deuterium. So, if you have an R group, a hydrogen and deuterium, you can see that this carbon center is actually chiral, so let us mark this chiral carbon center. This is the carbon center which is chiral, this is the chiral carbon center. This is the one which is undergoing migration and it is migrating to a carbon monoxide which is on the iron C P is in fact, a cyclo pentadienyl group.

But, for the purposes of today’s discussion, we can just keep it as one of the three groups which are present on the iron atom. Now, after migration we can look at the chirality of this center and try to understand what the geometry of the carbon is after migration. So, as I mentioned to you before, there are two possibilities, one is to undergo migration with retention of stereochemistry. That is what is pictured on the top half of the slide if the carbon just migrates.

Let us say this is the bond that is migrating, if that migrates with retention of stereochemistry, the product that we would get is this particular product which I have on the top slide, top part of the slide. It should be mentioned that this is, now chirality is retained, so here chirality is retained in doing this process of this migration. So, an acyl group was formed by migration of the alkyl group on to the carbon monoxide. The same thing could have happened with an inversion of stereochemistry, in which case you would have this carbon undergoing an inversion.

So, let us try to understand what will happen in during a Walden inversion. What you have is inversion of this particular carbon which we have put a star on and so the deuterium atom which was pointing upward, this is the deuterium atom which is pointing upward. That will have to go down and that is what has happened it has come down and so has the hydrogen. So, the hydrogen and the deuterium atoms which we are pointing up in this molecular structure the hydrogen and deuterium were pointing upwards. Now, they are pointing downwards and the R group has come up on the other side as well, so here an inversion has taken place in this case.

Now, because we want to compare in a similar fashion I have rotated this chiral center with respect to this carbon C O bond and when I do that, I get this molecule which is pictured here. You will notice the chirality of the carbon which has undergone migration, here it is undergone inversion. So, it is very clear that in one case you will retain the chirality. In other case, if you have inversion if you undergo Walden inversion, the chirality would be exactly the opposite chirality of what we started out with. Now, how will you figure out whether the molecule has undergone inversion or not and that is where the ingenuity of the experimental in this case the White sides comes into play?

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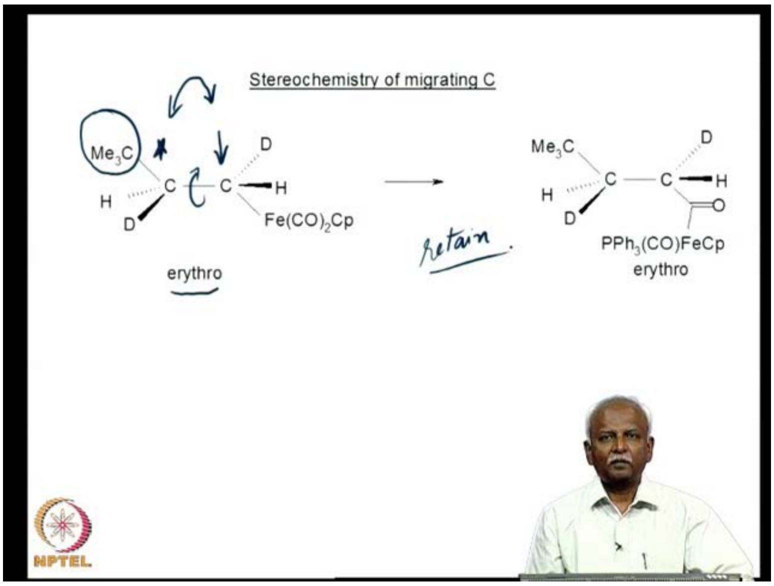

Stereochemistry of migrating C

What he did was to attach another chiral center next to the carbon undergoing migration. So, the carbon undergoing migration was here and he put second chiral center next to the carbon undergoing migration. So, what he did was to compare the chirality of one carbon center with respect to the other carbon center before and after migration. In this experiment, he attached in a fairly large group this is a tertiary butyl group. Here, a very large group on the carbon, so that rotation about the carbon carbon bond would not be facile.

If the carbon carbon bond cannot be rotated then the relationship between the two deuterium and two hydrogens is forced to be the same before and after migration. So, let us see what happens in this particular reaction. He took an erythro compound which means the hydrogens were on the same side. So, he took the erythro compound and you can see that they are on the same side because you have put the large groups Trans to each other.

If you rotate around this carbon carbon bond, you can see that the two hydrogens are on the same side. So, this is the erythro compound and after migration you can see that the chirality was still retained and the two hydrogens are still on the same side with respect to each other. So, he started with an erythro compound and ended with an erythro compound showing that the stereochemistry of the migrating carbon that is retained.

So, retained the stereochemistry after migration this seems to indicate that the migrating group is actually migrating like an anionic group which would have a lesser propensity to undergo inversion. Suppose to the methyl radical which will undergo inversion fairly rapidly or as a methyl cation, where also a planar structure would be involved.

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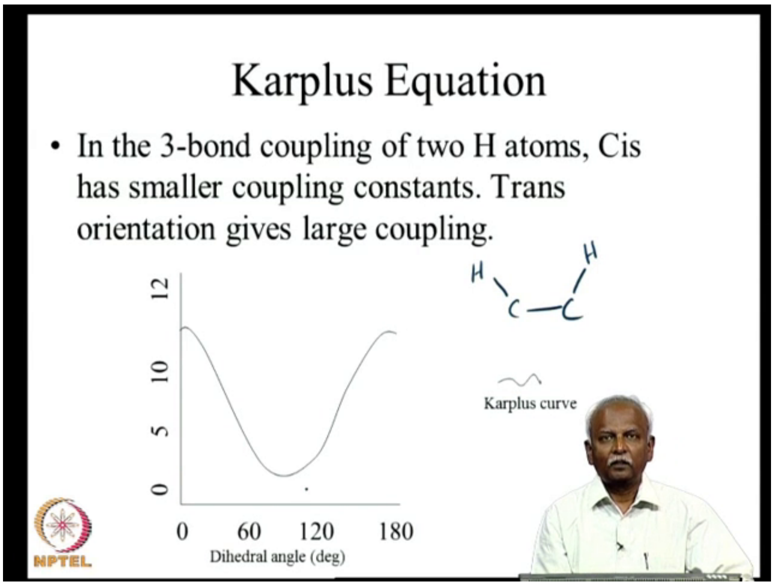

Karplus Equation

- In the 3-bond coupling of two H atoms, Cis has smaller coupling constants. Trans orientation gives large coupling.

So, how did he measure this inversion or retention in chirality, here we have to use what is called a Karplus equation. The Karplus equation merely connects the hydrogen hydrogen coupling constant the coupling constant of the two hydrogens which were connected to the two carbons and as we said it was in an erythro position. So, the coupling constant was the Cis, has a smaller coupling constant, the Trans orientation gives a larger coupling constant. As I showed you, because of the two large groups that are present on the two carbons, the hydrogens will rotate in such a fashion that they will maintain a 180 degree angle, so this angle was close to 9 to 12 Hertz.

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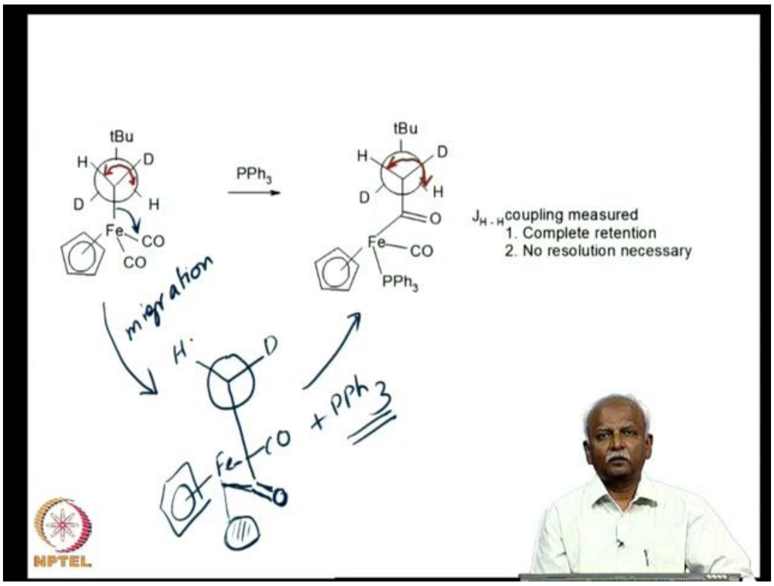

J_{H-H} coupling measured
1. Complete retention
2. No resolution necessary

That clearly indicated that, the coupling constant between the two hydrogens was in fact Trans, both in the starting material and in the product. So, in order to visualize this, we have shown here a Newman projection of the two molecules before and after migration. So, before migration what you notice is that, this is the compound before migration. The migration happens on to a carbon monoxide group and there is a vacant coordination site which is generated. So, you would have the same molecule with hydrogen deuterium and iron and with one C O, so you have, this is the carbon monoxide which is undergone migration.

So, you would have a vacant coordination site on, so here is the vacant site on the iron which has been formed because the alkyl group has migrated on to the C O group. So, this is the C O, on to which the alkyl group is migrated. We can see that, we can picture that, here by moving this bond here, and this is what you would get and a vacant site would be there on the iron which is now occupied with P P h 3 if you react that with P P h 3, this is the product that you would get.

So, this is a two step reaction where you have the migration and subsequently you have the reaction of, subsequently you have the reaction or the addition of a P P h 3 molecule on to the vacant site and you will get the final product. But, you notice that the migration has happened without affecting the trans relationship between the two, you can see that we have not affected the trans relationship here between the two carbons.

So, this relationship is maintained before the reaction it was in a Trans position and after the reaction it is still in a Trans position. So, this allows you to only measure the coupling constant. Because the coupling constant you have is very different at 60 degrees, when you come close to 60 degrees, the coupling constant becomes close to 0 to 5 Hertz. If you have Cis geometry where you have 0 degrees or 180 degrees, the coupling constant is close to 9 to 12 hertz in this particular instance this was close to11 hertz. So, you can without measuring the stereochemistry using optical activity or any other method x-ray method you can just conclude that the stereochemistry has been retained in the migrating carbon.

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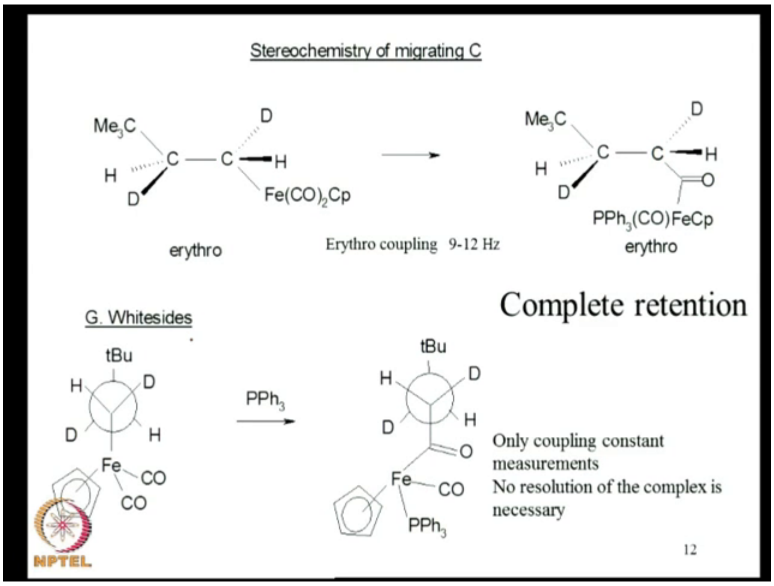

Stereochemistry of migrating C

erythro

Erythro coupling 9-12 Hz

erythro

Complete retention

G. Whitesides

PPh$_3$

Only coupling constant measurements

No resolution of the complex is necessary

So, this brings out a very interesting possibility that is, the migrating group can jump from one center. That is, from the iron center on to the carbon monoxide molecule, carbon monoxide group without losing the stereo chemical identity and complete retention was observed in this particular case. So, no resolution was necessary and Whites have performed this excellent experiment in order to show the stereo chemistry of the migrating carbon.

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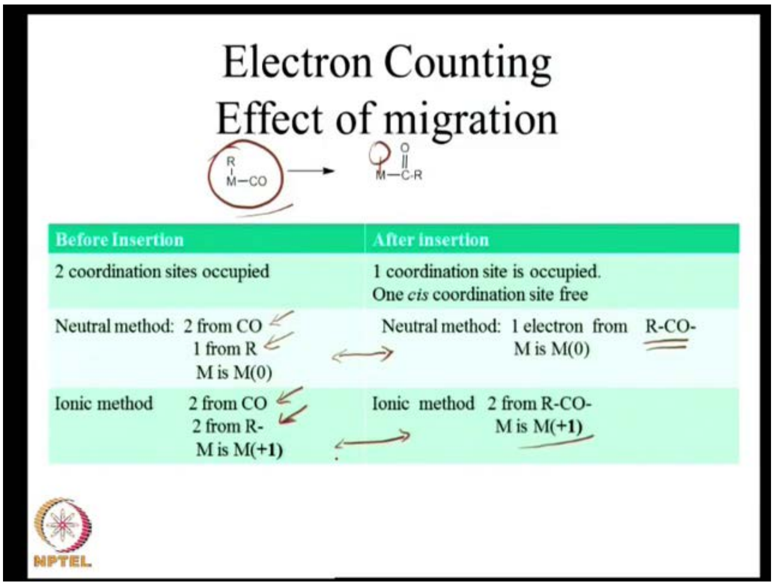

Electron Counting
Effect of migration

Before Insertion	After insertion
2 coordination sites occupied	1 coordination site is occupied. One *cis* coordination site free
Neutral method: 2 from CO 1 from R M is M(0)	Neutral method: 1 electron from R-CO- M is M(0)
Ionic method 2 from CO 2 from R- M is M(+1)	Ionic method 2 from R-CO- M is M(+1)

Let us, now take a look at what is happening at the metal center, the metal center before it undergoes an insertion reaction it has two coordination sites occupied I have indicated this by, before the reaction you have this fragment. Here, there are other groups on the metal, but we would not concern ourselves at the reaction site, we have an R group which will, in the neutral method it will donate one electron and the carbon monoxide. That will give you two electrons and two coordination sites are occupied and methyl, the formal oxidation state of the metal in this particular fragment is M as zero in the neutral method.

In the ionic method, on the other hand we have an R group which is an R minus and that will give you two electrons. That is what we have pictured here, two electrons from carbon monoxide because we have an R minus the metal has been oxidized to plus one oxidation state. So, for this fragment alone one can see, for this fragment before insertion you have the electron counts as indicated here.

Let us take a look at what happens after the insertion. We will notice that after the insertion, one coordination site is occupied and one coordination site is free and that is the site here, that site is in fact free. So, you have a free coordinate site on the metal and as far as electron count goes, you have one electron from R C O. So, you have a coordinatively unsaturated system when you undergo insertion reaction.

In the ionic method if you had two electrons from R minus initially you, now have two electrons from R C O and the oxidation state is plus one. So, basically what you are doing is generating vacant coordination site on the metal, you are generating a vacant coordination site on the metal. But, you are not changing the oxidation state on the metal atom itself, so this is fairly important. We have to remember that during an insertion reaction whether you use the neutral method.

If you use the neutral method M remains as M 0, and if you use the ionic method M remains as M plus whichever way you count you are not changing the oxidation state of the metal. Whereas, the electron count on the metal undergoes a two electron gloss, so if you started with an eighteen electron complex you will end up with sixteen electron complex. Similarly, one coordination site is vacant at the end of the reaction.

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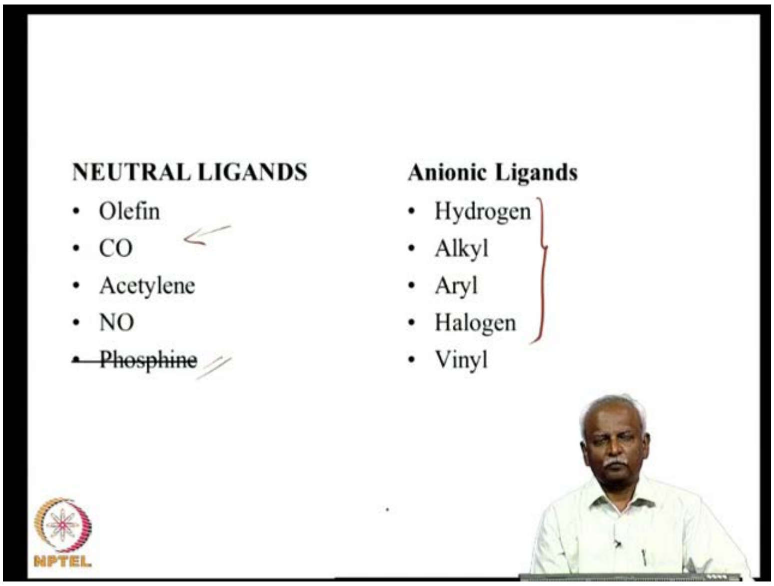

NEUTRAL LIGANDS

- Olefin
- CO
- Acetylene
- NO
- ~~Phosphine~~

Anionic Ligands

- Hydrogen
- Alkyl
- Aryl
- Halogen
- Vinyl

So, let us take a look at what are the species which can undergo insertion reactions. Because of the explanation that we just gave regarding the migration which keeps the stereochemistry of the migrating carbon carbon, we will look at them as anionic ligands. So, there are two species which are undergoing a reaction, the anionic ligand migrates to the neutral ligand in the case of its R C O, R is an anionic ligand. It migrated to a carbon monoxide that is a neutral ligand. Similarly, we can have various other combinations of anionic ligands migrating to neutral ligands. Here, are on my right I have a group of ligand which are anionic ligands, which can migrate on to neutral ligands. So, the neutral ligands that are most often studied are species like carbon monoxide which we just considered.

Today, we will continue with some reactions where you can have migration of an anionic alkyl or hydrogen on to olefin as well and acetylene as well. So, these are the anionic ligands and these are the neutral ligands which can undergo insertion reactions. In general species like phosphine are not capable of undergoing insertion reactions and the reasons for these will be obvious as we proceed further.

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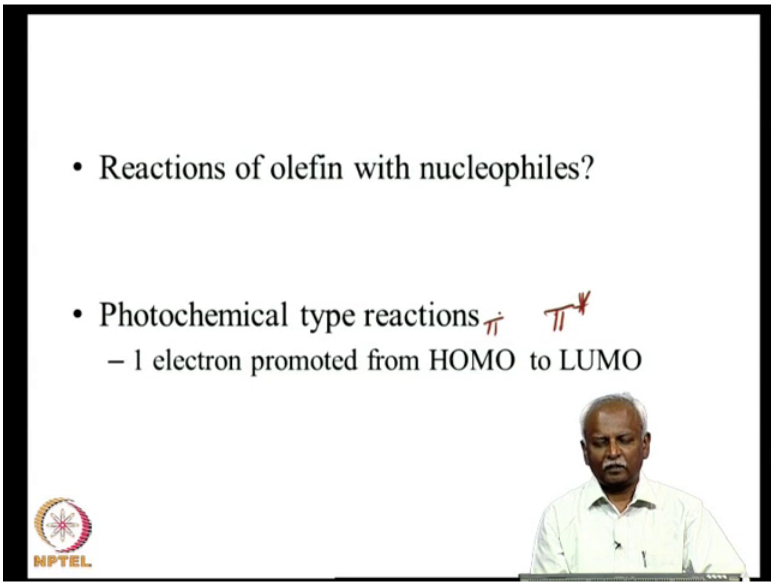

- Reactions of olefin with nucleophiles?
- Photochemical type reactions π π^*
  - 1 electron promoted from HOMO to LUMO

So, let us take a look at the insertion reactions further. Now, based on the discussion that we had we can in fact, think of this whole insertion reaction as if a nucleophilic attack has taken place on the neutral ligand. So, in the precious instance we had carbon monoxide as a neutral ligand and an anionic group was attacking it. So, if you have an olefin can we have an attack of a nucleophile is not it true that the olefin is electron rich. It will prevent a nucleophilic attack that is in general true. But, if you remember after coordination to a metal the electron density on the olefin has been reduced, electron density has been moved from the olefin to the metal center. It undergoes typically photochemical type of reaction, because you are populating the LUMO which is the lowest unoccupied pi star orbital. The LUMO is in fact, the pi star orbital and the HOMO is in fact, the pi orbital. So, you move electron density from the pi to the pi star, just as you would do when you photo excite an olefin.

So, these reactions are cases where you are pumping in electron density in to the LUMO where nucleophile attacks the LUMO it pumps in electron density into the unoccupied orbital. So, turns out that when an olefin is coordinated to a metal center, you can still have attack of a nucleophile, because it is the one which is less populated with electron density and the HOMO has been depleted. So, it is ready to accept electrons as well.

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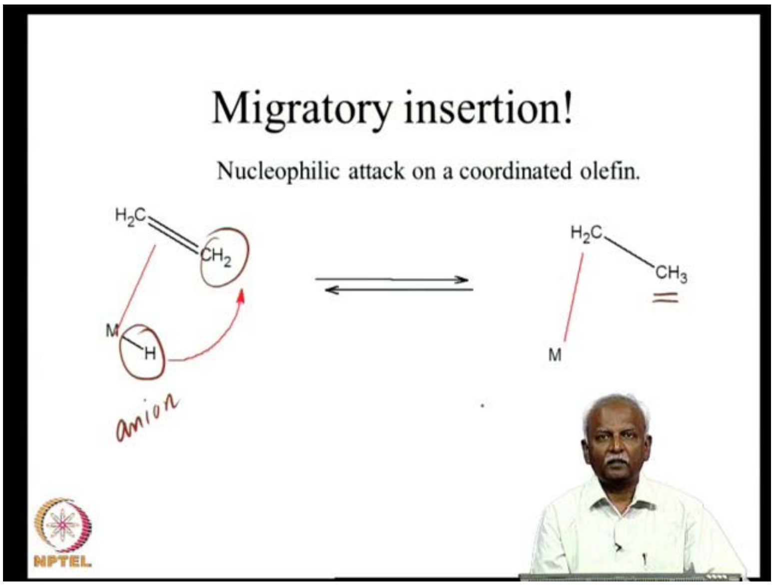

Migratory insertion!

Nucleophilic attack on a coordinated olefin.

So, the migratory insertion can in fact, be though about as if it is a nucleophilic attack on a coordinated olefin, I have shown here a coordination of an ethylene to a metal hydride species. So, this is the anionic group that we are talking about, this is the anionic group and that is attacking an olefin, which is coordinated to the metal and when it does, so this hydrogen has migrated here. So, this C H 2 group becomes C H 3 and a C H 2 this double bond is, now instead of a coordinative bond. You, now have a sigma bond formed between the metal and the C H 2 group.

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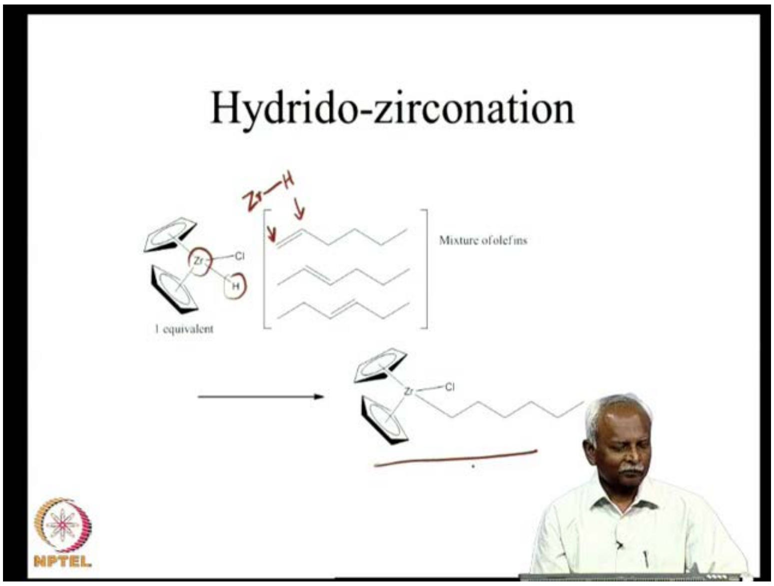

Hydrido-zirconation

So, let us take a look at a simple example of a hydro zirconation reaction. Now, this reaction simply involves the insertion of a hydride on the zirconium and the addition of this hydrogen to this olefin which is pictured here a mixture of olefins is shown. But, any one of them is sufficient, but let us take a look at what happens when you have a mixture of olefins. If you add the hydrogen and the zirconium across the nucleophile, if you add the hydrogen and the metal across the olefin what you end up with, is addition of hydrogen and one side of the olefin and the metal on the other side of the olefin.

So, we have added M H into the unsaturated olefin, now this is exactly what we are going to do. Here, we are going to add this hydrogen and we are going to add zirconium to either side of the double bond. So, what we have pictured here, as a product is addition of zirconium to the terminal position zirconium here, and hydrogen here, so this is where zirconium has added and hydrogen has added.

The product would be this notice that even if we use a mixture of olefins, there was only one product isolated at the end of the reaction. So, this was a puzzle which people solved and it was understood that it was the sequence of addition of hydrogen and abstraction of hydrogen, which means it is a insertion of hydrogen and it is a deinsertion or rather abstraction of hydrogen from the olefin, from the alkyl group.

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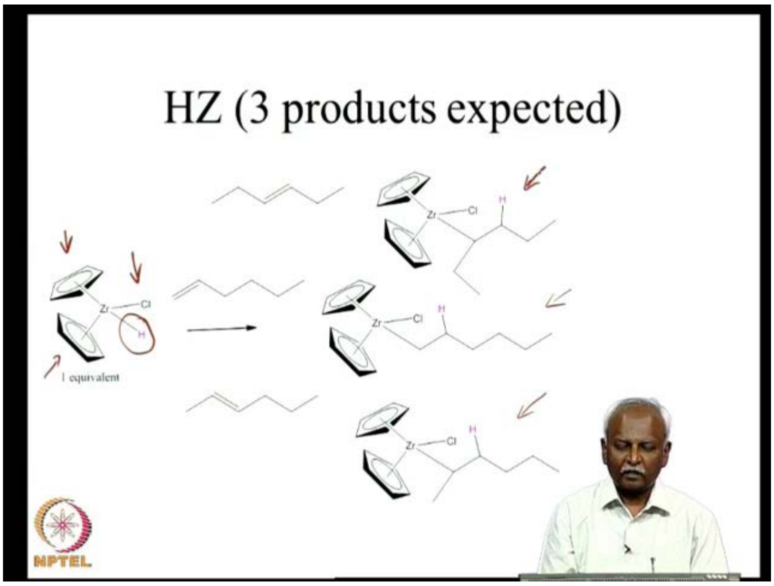
HZ (3 products expected)

So, let us take a look at what we expect what we would have expected from a simple hydro zirconation reaction that means addition of hydrogen and zirconium on to the three olefins. Now, I have color coded the hydrogen on the zirconium, so that we can see where it is ending up at the end of the reaction. So, let us assume that the pink hydrogen is coming from the zirconium if you add it to the three olefins you would end up with three different products as pictured here. So, notice that the addition reaction is performed in such a way that zirconium is adding to the least hindered position on the olefin.

This is understandable because zirconium seems to be baring three large groups, two cyclopentadienyl units, which are pictured here and one chlorine. So, all of them have to be attached to the methyl group. So, invariably an anti Markovnikov's addition happens and the product is as shown. Here, from the one substituted olefin, you would end up with the product here which is the product which we had shown earlier.

If you take the two substituted product, you would end up with product from here and with the three substituted olefin, you would end up with this hydro zirconation product. But, surprisingly at the end of the reaction what they found was it there was only one hydro zirconation product, so that is what we are trying to explain this was expected.

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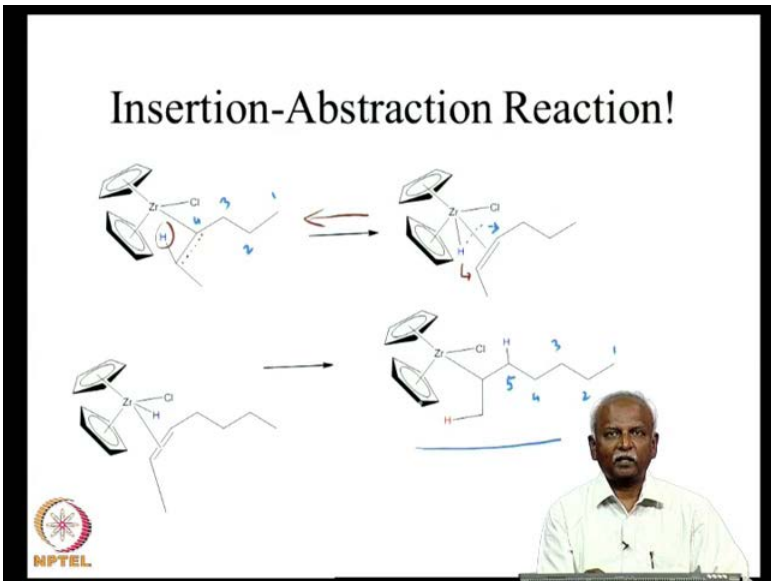

Insertion-Abstraction Reaction!

Due to a series of insertion and abstraction reactions in this leads to isomerization. So, let us take a look at what happens let us mark the hydrogens, which are undergoing reactions with different colors, so that we will be able to follow where the abstractions taking place.

So, in the case of the hydro zirconation which has happened in such a way that the middle carbon is, now baring the zirconium you can easily see that the zirconium is quite crowded. So, it abstracts hydrogen and it keeps shuttling between these two sites. So, what is happening is that, this hydrogen is abstracted and an olefin bond is forming in this case. So, what you end up with is a hydro hydrogen abstraction or beta hydrogen abstraction reaction which is very simply reverses of the migratory insertion.

So, if this hydrogen goes back here you would have ended up with this product, but instead of going back into this position what happens is the hydrogen goes into this position which we will mark in a different color. Let us mark in a blue color, so the preferred attack of hydrogen. Now, is in this position, so what you end up with is if hydrogen attacks the internal part then you end up with the zirconium migrating from the carbon which we can label as 1 2 3 and 4. It is migrated to this position here from the 4 positions we have we have added the hydrogen to the 5positions here. So, let us take a look at what will happen here when if you keep doing this migration, you can see very easily that the zirconium can migrate from one carbon center to other carbon center.

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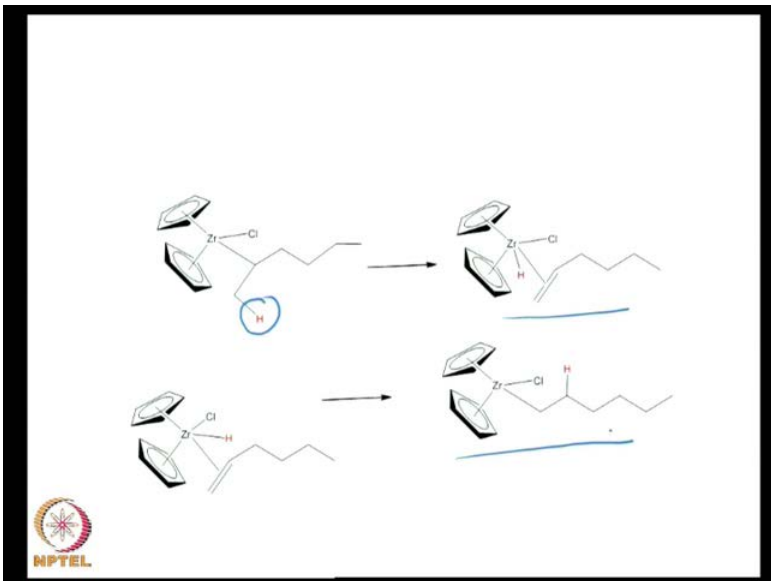

So, in the second step we can do the same thing again once more, but now we will have a terminal olefin generated as a result of hydrogen abstraction. This time the hydrogen that is abstracted is from the carbon atom number one and if you do that then you end up with hydrido zirconium species which can. Now, transfer the hydrogen to the second place, this is the second position on the carbon. So, you end up with the compound which was only product which was isolated at the end of this reaction. So, in other words what we are doing is that we are allowing the metal to walk along the alkyl chain by a series of hydrogen insertion and hydrogen abstraction reactions.

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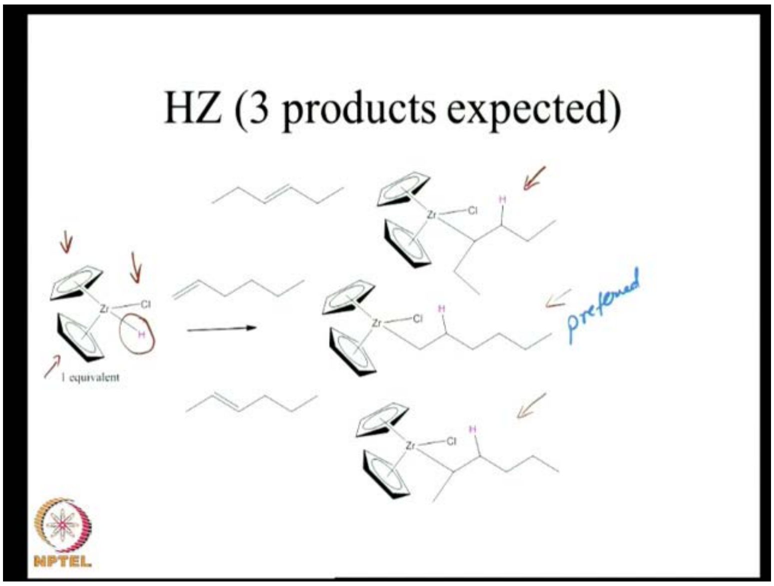

HZ (3 products expected)

So, you can in fact use a mixture of olefins, but all of them will walk around in such a way that only this one product, the preferred product is, this is the preferred product. That is the only product that is formed at the end of a reaction.

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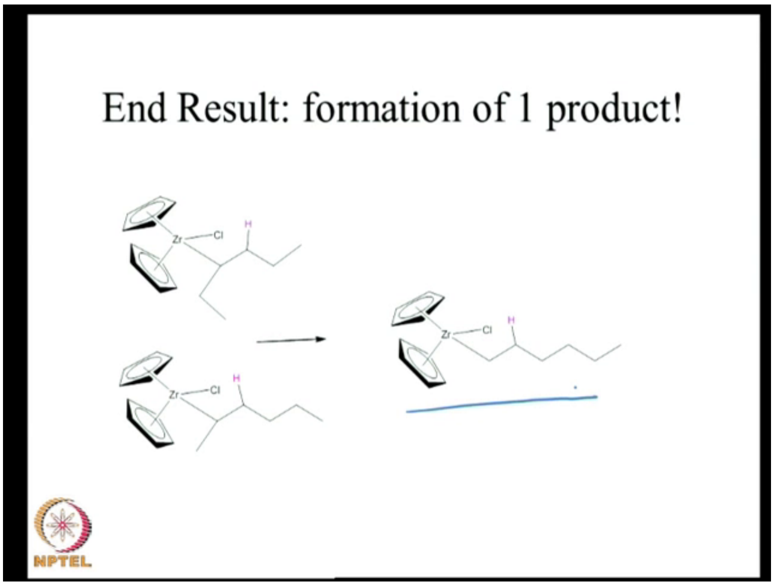
End Result: formation of 1 product!

So, this end result is a formation of a single product whichever product is taken whichever hydro zirconation occurs, the walking of the metal along the alkyl chain results in the formation of a single product.

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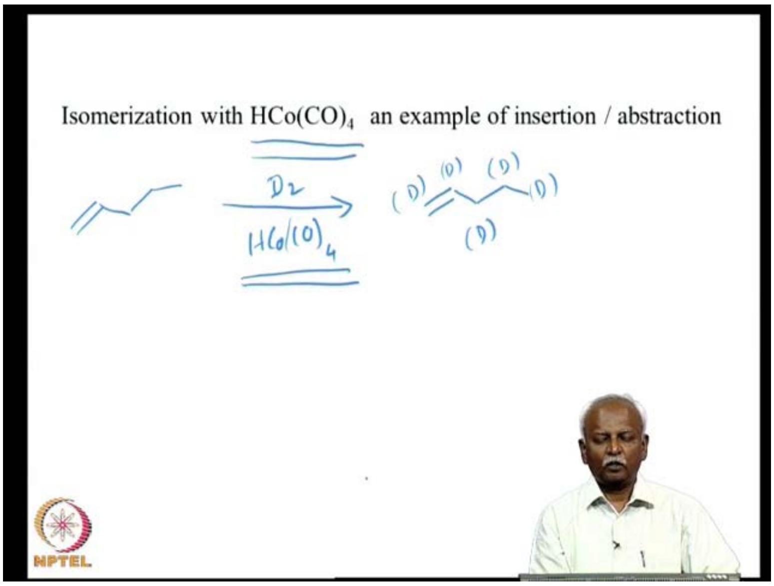
Isomerization with $HCo(CO)_4$ an example of insertion / abstraction

So, this gives us a very clear example of how the metal can add abstract hydrogen from an alkyl group had hydrogen to an olefin. So, lead to isomerization it is very common to observe this kind of an insertion and abstraction reaction with H C O, C O 4. So, a similar situation was encountered when deuterium, in the presence of deuterium it was found that H C O, C O 4 will in fact, isomerize a series of olefins even if you take a terminal olefin you end up with a terminal olefin.

But, now you have deuterium in all the positions at this olefin, so in other words the amount of olefin that you add and abstract keeps increasing as time progresses. If you have deuterium gas, you can in fact, populate all of these sites with deuterium because you are adding and abstracting hydrogen with H C O, C O 4. So, this can be a useful exercise that you can attempt in the presence of deuterium how you can add and abstract a hydrogen atom from an olefin.

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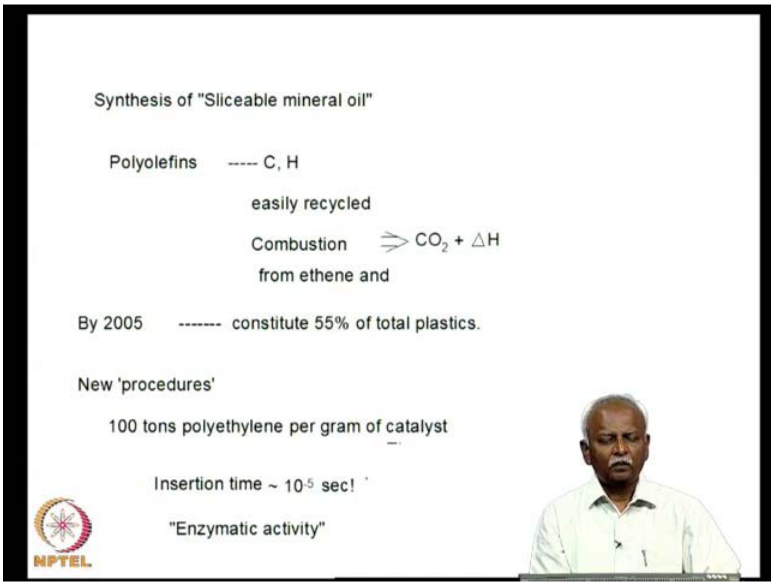

Synthesis of "Sliceable mineral oil"

Polyolefins ----- C, H

easily recycled

Combustion $\Rightarrow CO_2 + \Delta H$

from ethene and

By 2005 ------- constitute 55% of total plastics.

New 'procedures'

100 tons polyethylene per gram of catalyst

Insertion time ~ 10^{-5} sec!

"Enzymatic activity"

So, this is also the insertion reaction, is also the basis for the famous Ziegler Natta process. In fact, it is possible to make large amount of olefins using simple olefins and this is a basis for the generation of a large amount of easily useable plastics. It is estimated that more than 55 percent of a plastic products are generated using this particular insertion process.

It is very interesting that, polyethylene, you can take ethylene, and polymerizes it using this particular process, which involves a simple insertion reaction and as much as hundred tons of polyethylenes are generated using just one gram of catalyst. So, that means the insertion is happening very efficiently and the insertion time for this particular process has been estimated to be 10 power minus 5 seconds. That is close to how fast enzymes carry out reactions and so this has been labeled as enzymatic activity of metal complexes for olefin polymerization. So, olefin polymerization also involves the simple insertion reaction. It has been extensively studied the basic process just involves the migration of an alkyl group into the olefin.

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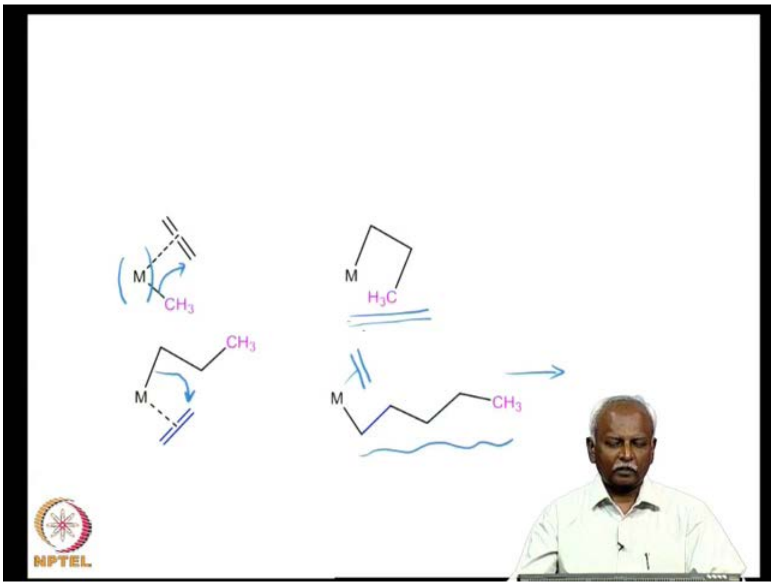

Let us take a look at the two steps, the key steps that are involved, without concerning ourselves with what else is present on the metal. Very often in the industrial setup and industrially, relevant complexes a large amount of methyl alumoxane is used. It is not clear what is the group that is present on the metal, so let us just mark it as M, there are two groups one is an alkyl group and the other is an olefin. The group that migrates is the alkyl group and the alkyl group migrates to the olefin in such a way that it generates a new alkyl group. This is marked here, we have for simplicity we are starting with a methyl group.

But, it could be a butyl or any group that can be added because we have color coded we can now see that the entering carbon had a double bond. Now, you have all single bonds and the vacant site that was generated on the metal, so that metal is, now capped with an olefin. So, the initial olefin is shown in black and the second olefin is shown in blue.

Now, what happens is that you have a migration of this alkyl group onto this olefin and remember the anionic group is the one which migrates onto the neutral moiety. If it does that, then once again you have the formation of a metal carbon covalent bond and you have the formation of a longer alkyl chain. Now, this process is repeated several times you have, now the coordination of an olefin in this position and subsequent migration you will have the formation of a very large alkyl chain and this is a process that is essentially at the back of the Ziegler Natta process. So, earlier we had discussed the reaction with hydro zirconation and zirconium and titanium are probably some of the most common elements which are used for the Ziegler Natta polymerization reaction.

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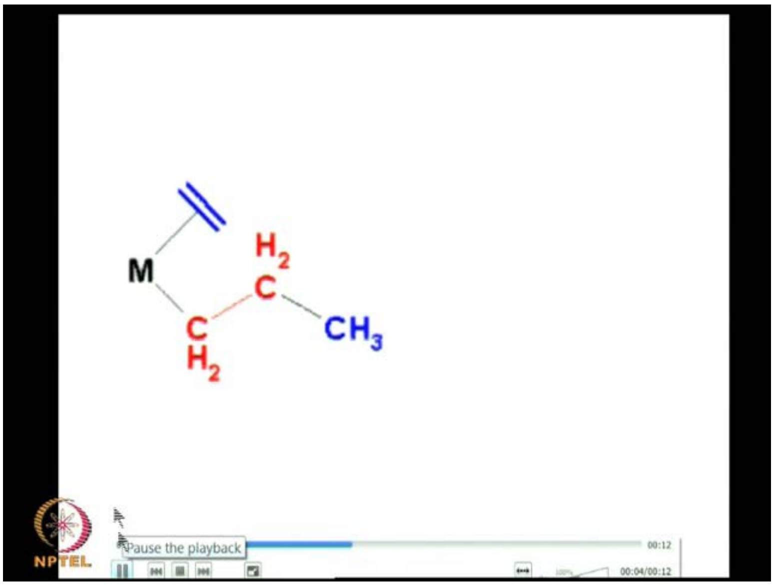

Let us take a small look at, so here I have the olefin coming in.

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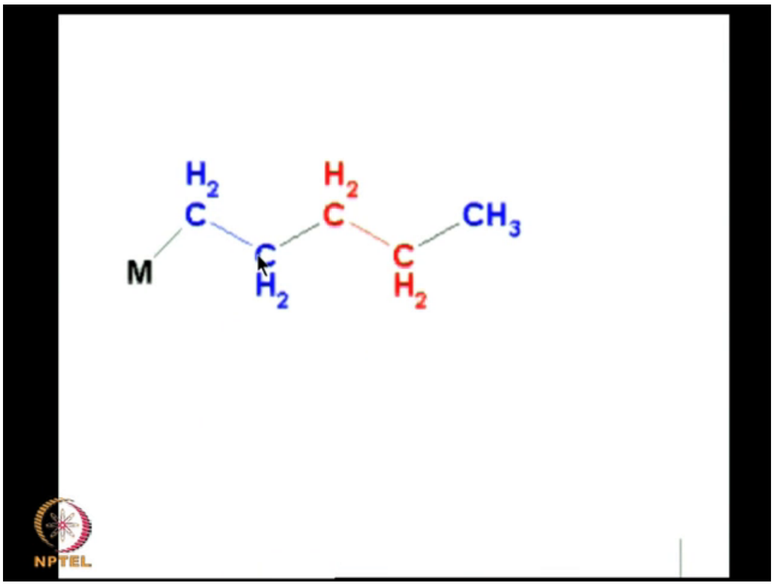

Then it inserts the second olefin that is pictured in red again and then again it inserts and gives you the olefin.

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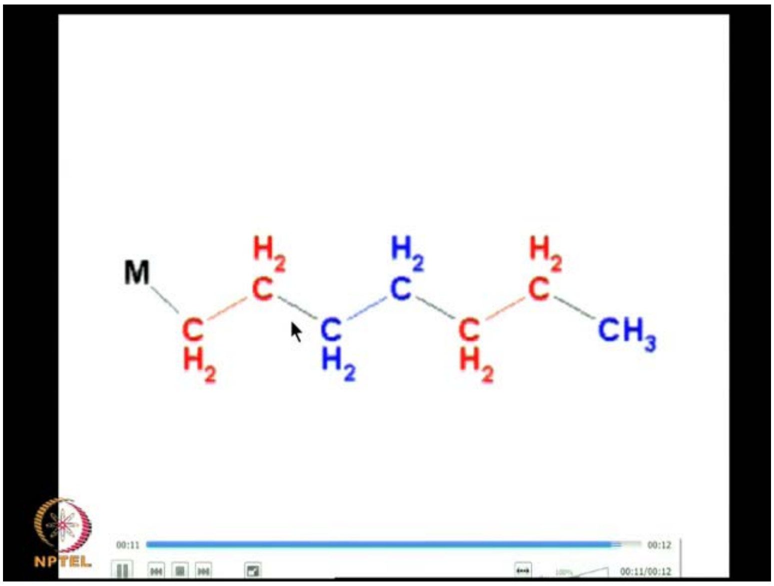

So, we can see that each insertion leads to lengthening of the chain and the second group is added sequentially.

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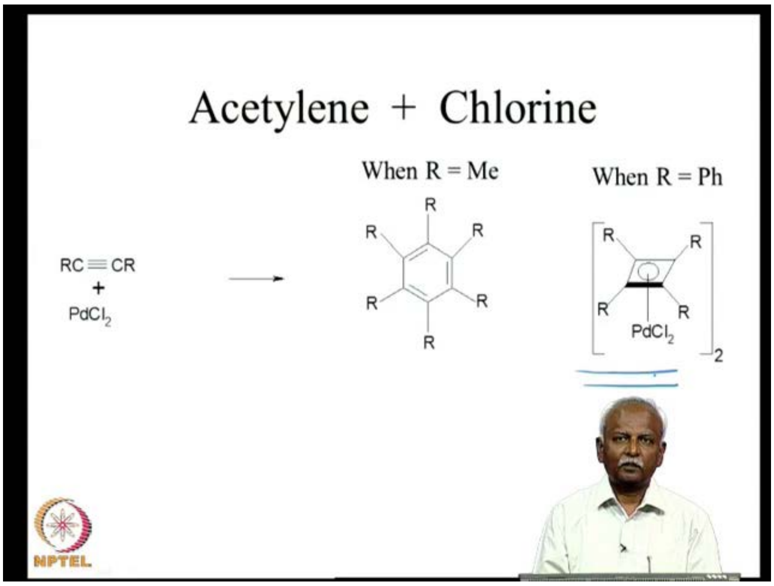

Acetylene + Chlorine

When R = Me

When R = Ph

$RC \equiv CR$ + $PdCl_2$

So, apart from olefins one can also introduce acetylenes and the last part of this lecture we will look at how acetylenes can undergo insertion reactions. So, I have given here a simple reaction where an acetylene molecule is polymerized in the presence of palladium chloride. Surprisingly, this involves an insertion of chlorine and surprisingly it involves an addition of the P d C l bond across the acetylene molecule. Although the final product is completely, an organic moiety in many instances it could be the simple formation of hexa methyl benzene if you use dimethyl benzene.

So, if dimethyl benzene, dimethyl acetylene is a starting material, then hexa methyl benzene is a product. However, when you use a bulky group as a phenyl group on the acetylene, so if we use diphenyl acetylene then the product is different it is usually the cyclo butadiene complex of palladium chloride. So, this particular reaction was studied extensively and it was shown by experimentation that in fact, it is going through a sequential addition reaction. Let us take a look at this reaction and see how the addition reaction is capable of carrying out these cyclisation.

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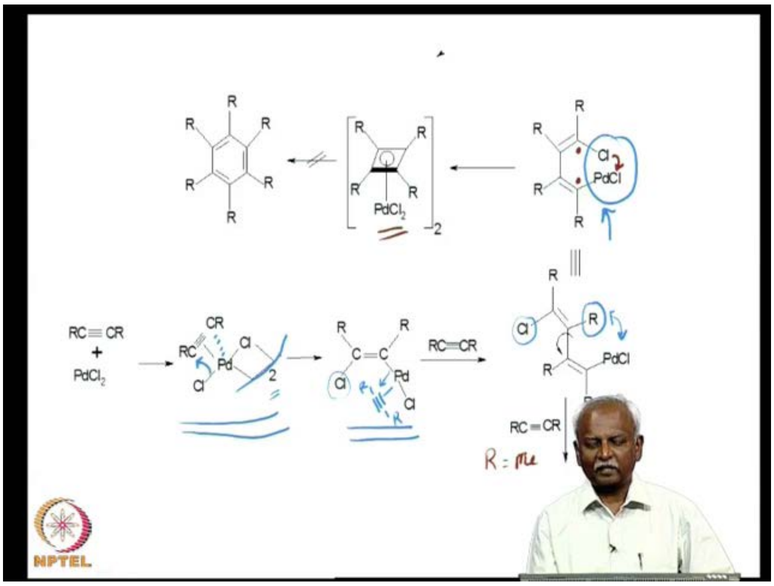

So, first step we have the coordination of palladium chloride to acetylene. What you have pictured here, is a complex which is a dimer and very often organo metallic chemist or coordination chemist will only draw half of the molecule. So, half of the molecule is drawn and a 2 is indicated to show that it is in fact, part of the molecule and the other half is the mirror image of what is pictured here. So, this dimer could be undergoing the reaction in a sequential addition fashion, addition of another molecule of acetylene.

So, from this point onwards we will draw only part of the molecule. So, let us take a look at this species, you have chlorine which is undergoing insertion into the C triple bond C and a carbon palladium bond is formed. As a result, a carbon palladium bond is formed and this is a product that you have, now this product which could be a dimer, as I told you earlier could, now reacts with another molecule of acetylene. Notice that what you have ended up creating is another anionic group, a vinyl group attached to the palladium.

Now, if acetylene is coordinated to it, what you would end up with is a neutral molecule coordinated to the palladium and this vinyl group migrating onto the R group. So, the product would be once again, it would be a group where you have this chlorine which originally came from palladium is, now sitting at the end of this vinyl moiety. The vinyl moiety is, now attached to another alkyne which has been inserted between the carbon and the palladium group. So, this carbon palladium bond is broken and another carbon

carbon bond is formed as a result of which you end up with a molecule where there are two vinyl moieties stitched together.

Now, notice that in this molecule you have this R group which is sitting here and it is quite close to the palladium and if this R group is very large, it would impose some steric interaction and as a result, it rotates around this carbon-carbon single bond. So, rotation of this carbon-carbon single bond leads to the formation of this molecule. This molecule which I have pictured here and here the chlorine which was originally on the palladium is brought close to the P d C l bond again. So, these two groups which were originally together are found close together.

Now, if you can do an abstraction reaction or a deinsertion reaction in such a way that you move the chlorine back from the carbon chlorine bond, if you can move it back onto the palladium. So, let us change the color of the ink here, so if I move this, if I move this chlorine back onto the palladium then what I would end up with is a P d C l 2 moiety which will again be a dimer. So, I have indicated that as a dimer, but then the carbon-carbon, there is a carbon-carbon bond being formed between these two centers which I am indicating with two dots. So, these two centers will form a carbon-carbon bond and a palladium chloride is extruded from this reaction.

So, an abstraction of the anionic C l minus back to the P d C l results in an abstraction reaction which gives you a cyclo butadiene, now coordinated to a palladium. So, notice how this reaction can either stop here because you have a large group. This steric repulsion resulted in turning around of this moiety in such a fashion, the vinyl group in such a fashion with the two chlorines are brought together. Now, the alternative is especially when the R group is small as in the case of R equals methyl, then the reaction proceeds further and undergoes a second insertion, third insertion.

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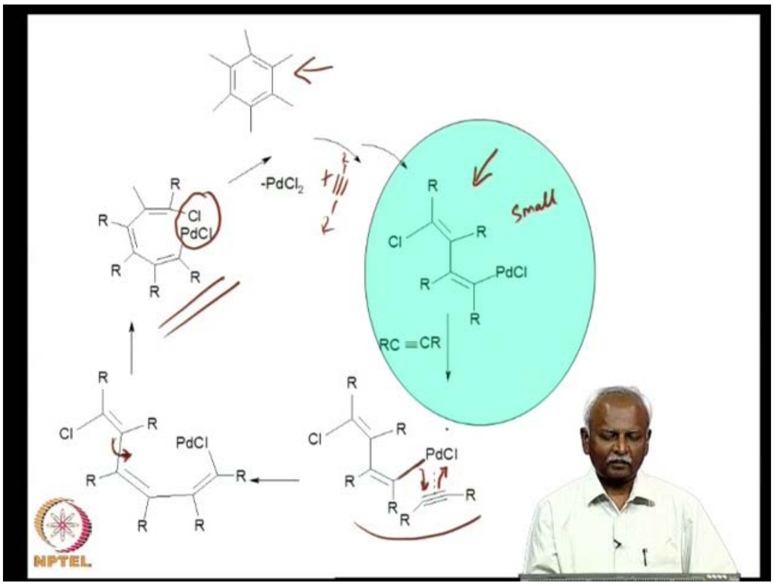

So, let us take a look at this is the case where the R group is only a methyl group. So, I have indicated it in this fashion, in this slide first the moiety that we start out with is the species which we said, which we showed in the previous transparency. This is the species that we showed if R group is small, R is small then we can end up with a second insertion. A second insertion of this vinyl moiety this is the vinyl group and this vinyl group can migrate here and a carbon palladium bond can be formed. So, what you have here is three alkynes stitched together. The three alkynes stitching can happen only if you have a reasonably small alkyl group. Otherwise, the reaction will not proceed in this direction it will not proceed in this direction. But, it will in fact proceed towards the cyclisation of the initial group.

So, if you have three alkyl groups alkynes moiety stitched together you now have once again you have the rotation of the carbon carbon single bond. Here, you have the carbon carbon single bond rotating and so you end up with palladium and chlorine close together. An extrusion reaction or an abstraction reaction follows these two groups are reacted with each other in such a fashion that the chlorine migrates back to the palladium and it is exactly the reverse of the migratory insertion.

So, the chlorine migrates to the palladium and you have the formation of a hexa methyl benzene moiety and this hexa methyl benzene moiety is more, has got more number of electrons and what the palladium would like. So, the molecule falls off the coordination sphere and it prefers to coordinate to another molecule of the acetylene. So, you end up with after two insertions you end up with this moiety which I have colored in green color and that is your key intermediate which keeps in inserting one more molecule of an acetylene to give you a catalytic cycle. So, a simple insertion reaction that we have pictured here is capable of generating two different molecules one is a cyclo butadiene.

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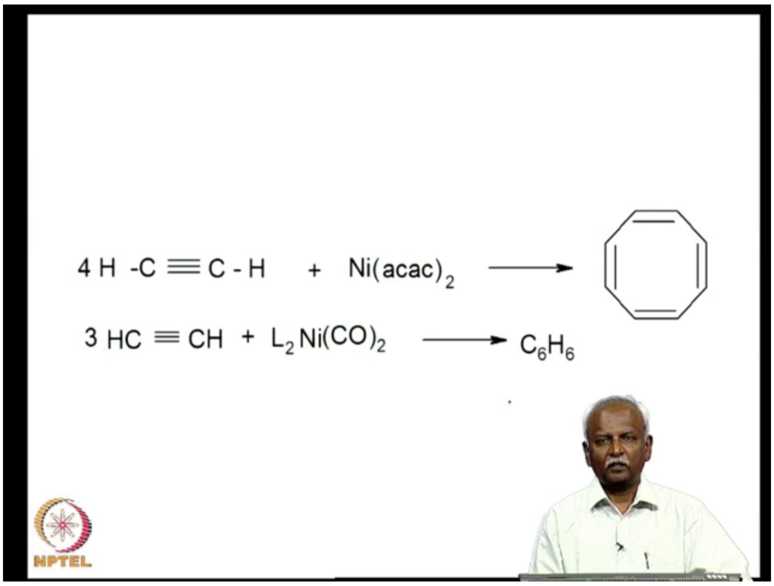

$4\ H\text{-}C \equiv C\text{-}H + Ni(acac)_2 \longrightarrow$

$3\ HC \equiv CH + L_2Ni(CO)_2 \longrightarrow C_6H_6$

If the R group is large and the other is an aromatic ring benzene moiety, if the R group is small surprisingly, the previous reaction was carried out with palladium. The same reaction was carried out with nickel and there are two nickel species that are pictured here. The use of nickel a c a c results in the formation of cyclo octatetraene what that means is that four molecules of acetylene are stitched together in order to make this acetylene tetramerise to give you cyclo octatetraene.

On the other hand surprisingly, if we use nickel zero as a catalyst, you also end up with a benzene moiety, so this is an interesting variation. In fact, this reaction was not understood for a long time and the formation of cyclo octatetraene was solved only in 1980s. Although the reaction was known for a very long time for more than 100 years and still the reaction was studied only recently.

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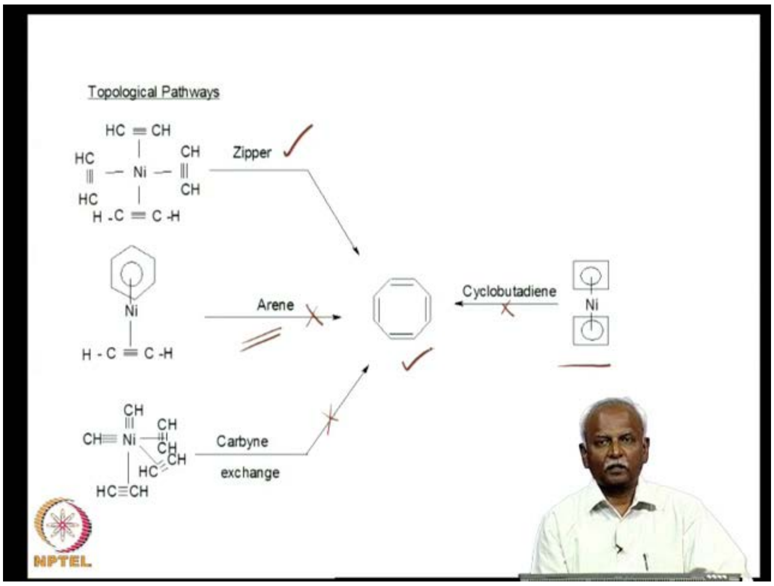
Topological Pathways

What they showed was through some isotopic labeling experiments, they showed that it was only the zipper reaction, the zipper reaction which was happening and four acetylene molecules are stitched together sequentially. They showed through the isotopic labeling that cyclo butadiene is not involved as an intermediate nor is an aromatic ring involved as an intermediate. So, these two are not happening and it is the zipper mechanism which is happening as the possible, as a best possible mechanism to explain the formation of cyclo octatetraene.

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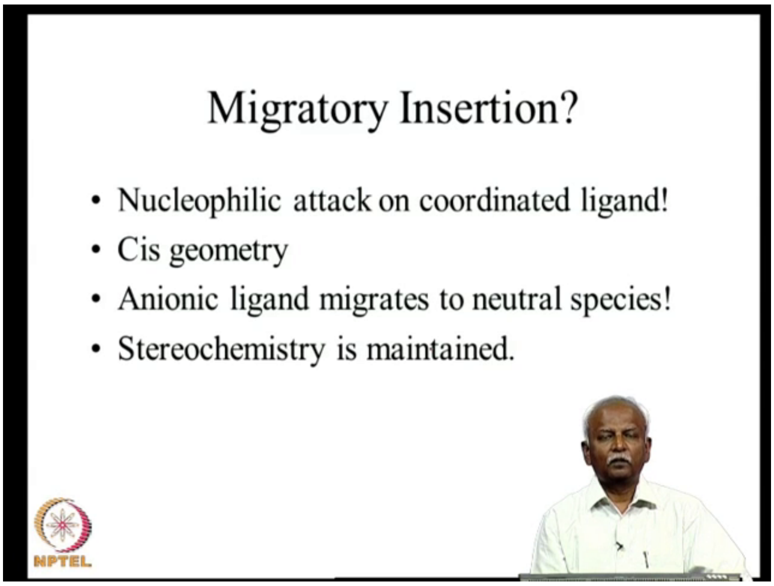
Migratory Insertion?

- Nucleophilic attack on coordinated ligand!
- Cis geometry
- Anionic ligand migrates to neutral species!
- Stereochemistry is maintained.

So, I will conclude by saying that the migratory insertion is an extremely important reaction, but one must now ask the question, is it really necessary to call it a migratory insertion. It seems to be a simple nucleophilic attack of an anionic group attached to the metal atom on to a coordinated ligand. The coordinated ligand, as I mentioned earlier could be any neutral molecule like carbon monoxide or it could be an acetylene molecule.

The anionic group of course, could be a hydride or an alkyl group or it could be some other groups which are quite easily obtained in organo metallic molecules. Usually, the migration happens only in the Cis position. So, the Cis geometry is universally accepted as a place where the migration will take place or the insertion will take place and the anionic ligand is the one which migrates on to the neutral species. This is again, something that has been shown repeatedly in several instances. Finally, we should remember that the stereo chemistries of these molecules are maintained. Especially, when the migrating carbon is stereo chemically labeled and then one can see that it is retention of stereochemistry rather than inversion of stereochemistry.