Introduction to Organic Chemistry
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Lecture - 11
Ligand Insertion Reactions

In this lecture, we will look at some reaction mechanisms in organometallic chemistry. So far, we have looked only at substitution reactions which are simple replacement of one ligand by another ligand.

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Reaction Mechanisms
in
Organometallic Chemistry

Today we will look at how some more complicated reactions take place in organometallic chemistry.

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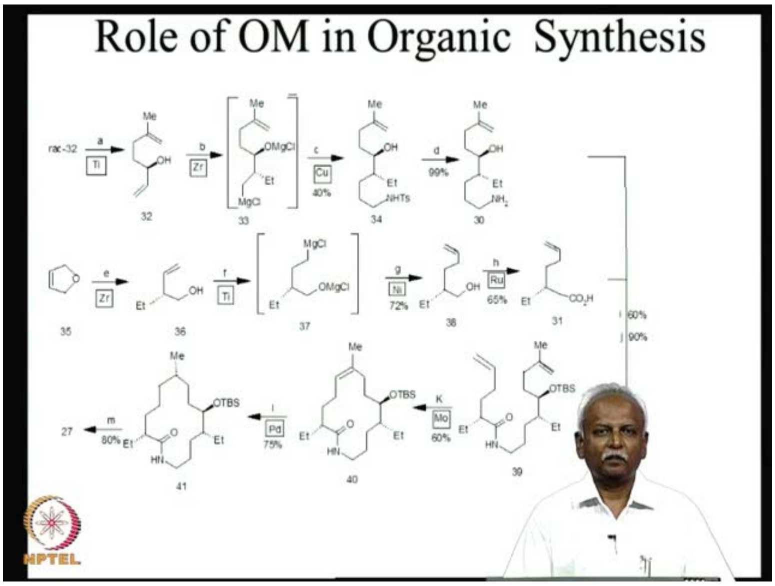

Role of OM in Organic Synthesis

Actually organometallic chemistry has become an essential part of organic synthesis and they show this set of equations very often. Because it illustrates how in a total synthesis at several points in the synthetic methodology, the researchers have used repeatedly organometallic and organic reactions inter changeably. And it is indeed important for us to realize that organometallic chemistry cannot be divorced from organic chemistry, or organic synthesis any more.

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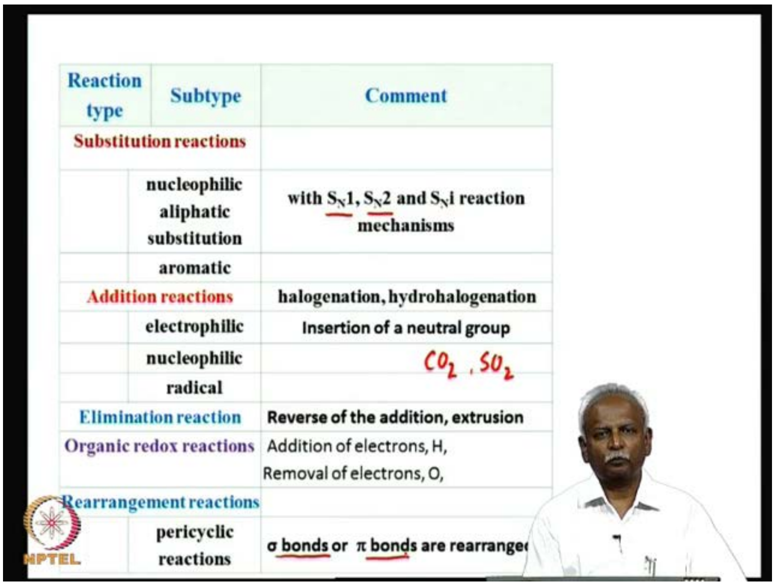

Reaction type	Subtype	Comment
Substitution reactions		
	nucleophilic aliphatic substitution	with S_N1, S_N2 and S_Ni reaction mechanisms
	aromatic	
Addition reactions		halogenation, hydrohalogenation
	electrophilic	Insertion of a neutral group
	nucleophilic	CO_2 , SO_2
	radical	
Elimination reaction		Reverse of the addition, extrusion
Organic redox reactions		Addition of electrons, H, Removal of electrons, O,
Rearrangement reactions		
	pericyclic reactions	σ bonds or π bonds are rearrange

If you look at organic synthesis, it is a well developed field and the classification of organic reactions has been done long ago. And very often it is easy to substitute one reagent with another reagent, or one reaction by another reaction in organic chemistry. It would be useful if you could have a similar classification of organic reactions, or organometallic reactions. And today we will look at the possible way of classifying organometallic reactions.

First let us just look at how organic reactions are classified. This is broad. This is one way in which we can classify organic reactions and this is found in many text books. We have first of all substitution reactions, where you can substitute one group in an organic molecule either by a nucleophilic substitution. If it is an alkyl moiety which where the substitution is happening in which case also the reaction might happen either as an SN 1 reaction, where the substitution is nucleophilic. And it goes in a first order fashion or in a second order fashion. And then we call it an SN 2 reaction.

So, these are mostly nucleophilic reactions when it happens in an aliphatic chain. But if it happens in an aromatic chain very often it is in electrophilic mechanism. So, substitution reactions can either be a nucleophilic reaction or an electrophilic reaction. And these are grouped as one class of reactions. And then come addition reaction where an unsaturated molecule is converted to a saturated molecule by addition of a group. It could very often be in the case, as in the case of halogenation two X groups are added across a double bond.

So, halogenation hydro halogenation where H and the C L are added or an H and a B R are added. And then they are called hydro halogenation in all these groups. Of all these reactions we add a molecule which is split in two fashion in a heterolytic fashion very often and added to the unsaturated molecule so that it becomes saturated molecule in a few instances.

We do have addition of a neutral group like a carbon dioxide or a sulphur dioxide. These groups might be added to an unsaturated molecule in such a fashion that the whole molecule becomes saturated or more saturated. These reactions also proceed in electrophilic nucleophilic or a radical fashion, that depends on how the reaction is carried out. And one can in fact tune reactions for that. The reaction proceeds in a particular fashion.

Now, the third group of reactions are elimination reactions, which are essentially a reverse of the previous group of reactions. So, instead of going from an unsaturated molecule to the saturated molecule, in this case one is going from a saturated molecule or a more saturated molecule to less saturated, unsaturated molecule when you extrude a neutral molecule. In these instances you could extrude a carbon dioxide or sulphur dioxide.

And then you end up with a reaction which is the reverse of the insertion of the neutral group. The fourth group I would call it as the organic redox reactions, where you have addition of electrons. These are very rare. But addition of hydrogen is also called addition of electrons. Because you are adding a group which is less electro negative than carbon to the unsaturated molecule. So, addition of hydrogen or addition of electrons is classified as a organic reduction reaction. And similarly, if you oxidize the species on organic molecule you could do it either by removal of electrons or removal of a more electro negative group. If you add a chlorine or an oxygen then it becomes an oxidation reaction of an organic moiety.

So, in the final group you have what is called the rearrangement reactions. The rearrangement reaction could either involve purely sigma bonds or purely pie bonds or a combination of both. And many of these reactions are called pericyclic reactions there are mostly orbital controlled. And this bases or this a topic or a famous rule, the Woodward Hoffmann rules, which drawn these reactions.

Now, rearrangements reactions need not always be pericyclic. You can also have rearrangement of complicated skeletons like nobelium and adamantine skeletons. These large ring system can also rearrange depending on the ring size requirements and the strain that is involved. One can have rearrangement of a molecule where only sigma bonds are involved. Either sigma bonds or sigma and pie bonds or pie bonds can be involved in this rearrangement reactions. Now, the reasons for going through this classification of organic reactions is that, I just want to draw parallel to the organometallic reactions and show how these can also be classified.

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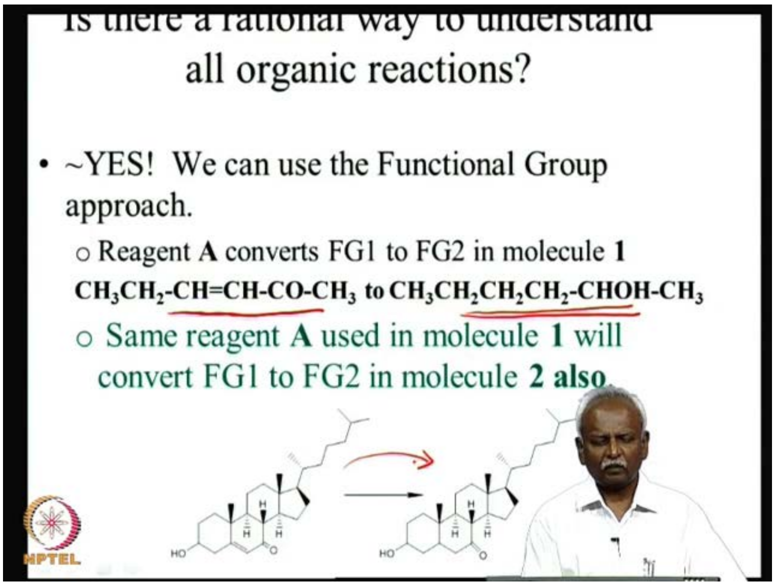

Is there a rational way to understand all organic reactions?

- ~YES! We can use the Functional Group approach.
  - Reagent **A** converts FG1 to FG2 in molecule **1** $CH_3CH_2\text{-}CH{=}CH\text{-}CO\text{-}CH_3$ to $CH_3CH_2CH_2CH_2\text{-}CHOH\text{-}CH_3$
  - Same reagent **A** used in molecule **1** will convert FG1 to FG2 in molecule **2 also**.

Let us ask this question. Is there a way in which we can classify? Or is there a way in which we can use a functional group approach in which we can substitute one reagent by another reagent? Now, in organic chemistry if you want to convert one functional group to another functional group you can have a group of reagents which will do this. So, if I want to convert for example, here an unsaturated molecule.

I have shown here an unsaturated molecule which is unsaturated at two places. One is a carbon carbon double bond. Another is a carbon carbonyl group. I only want to reduce one of them or I want to reduce both of them. In this case I have reduce both of them. I can use a particular reagent. In the same way we can take another more complicated molecule and ask the question. Can I carry out the same reaction? Can I carry out one of these reductions? Or can I carry out both reductions simultaneously? Which reagent would I use if one has the knowledge of converting this molecule? This unsaturated molecule to the second unsaturated molecule, that we have shown here a similar transformation can be carried with this. More complicated molecule using the same reagent. This type of transferability give organic chemistry an excellent way of extending the chemistry and also helping the student understand many complicated reactions.

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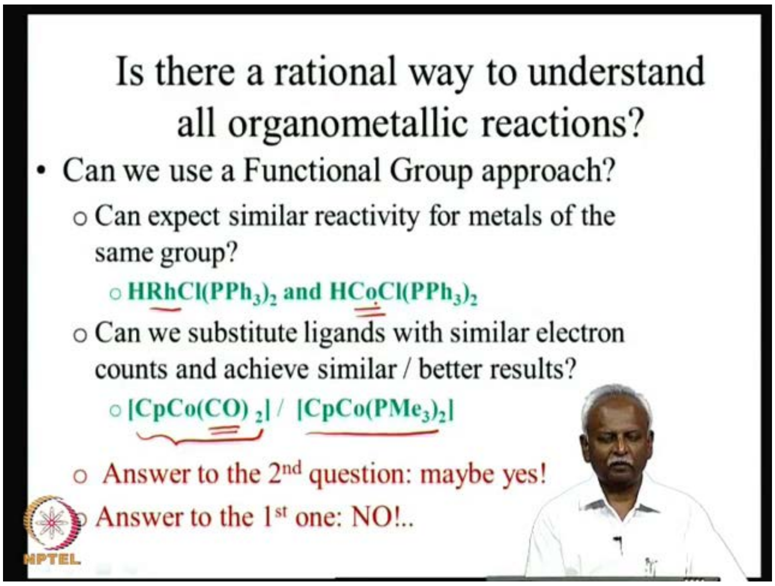

Is there a rational way to understand all organometallic reactions?

- Can we use a Functional Group approach?
  - Can expect similar reactivity for metals of the same group?
    - $HRhCl(PPh_3)_2$ and $HCoCl(PPh_3)_2$
  - Can we substitute ligands with similar electron counts and achieve similar / better results?
    - $[CpCo(CO)_2]$ / $[CpCo(PMe_3)_2]$
  - Answer to the 2nd question: maybe yes!
  - Answer to the 1st one: NO!..

So, it is important that we also have some kind of transferability in organometallic reactions. Also is there a way to do this? Let us take a look at a few examples. Now, here are two reagents which you might be familiar with. One is a rhodium complex which is a Wilkinsons catalyst. And other is a cobalt analog. And here are two other examples. We have the same cobalt complex, but now, I have substituted the two ligands. The answer to the second question may be yes. If you substitute the ligand on the metal complex one can very often transfer the reaction capabilities.

So, the reaction that is carried out by this particular complex might be carried out by this complex. It might be possible. But on the other hand the answer to the first question is, actually on the reaction that is carried by rhodium is not carried out by the cobalt complex. This transform to be a reasonably well established fact. Because the chemistry of the three D and the four D are very different. And the four D and the five D are reasonably similar.

So, very often the transferability might be possible between four D elements and four D complex and a five D complex. But it is very difficult to transfer the reaction which is happening on a four D element to a three D element.

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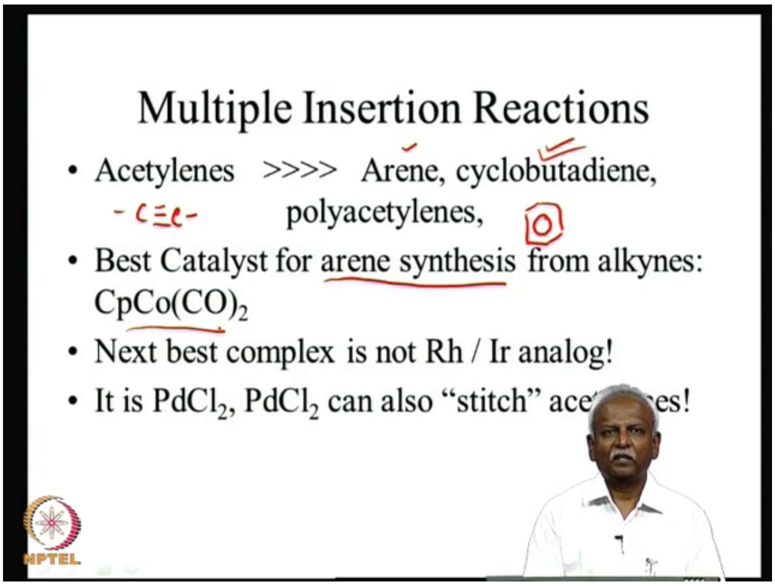

Multiple Insertion Reactions

- Acetylenes >>>> Arene, cyclobutadiene, polyacetylenes,
  $-C\equiv C-$
- Best Catalyst for arene synthesis from alkynes: $CpCo(CO)_2$
- Next best complex is not Rh / Ir analog!
- It is $PdCl_2$, $PdCl_2$ can also "stitch" ace es!

So, let me give this example where we have multiple insertion reactions. Now, I will talk about these insertion reactions in more detail. And I have chosen this example where we can use acetylenes and convert them to arenes. That means you are taking 3 C triple bond C molecules. This acetylene molecule, acetylene molecules, three acetylene molecules converting them to a arene moiety.

So, you can see that we have stitched together three acetylenes. One metal complexes can be chosen in such a way that one can get exclusively arenes or one can get only cyclobutadiene molecules or even poly acetylenes. And the best catalyst for carrying out this reaction so that you can get mostly the arene. So, you to synthesize only aromatic molecules from alkynes and the best molecule for this particular reaction turns out to be the cobalt complex.

So, one can ask this question is the same analog capable of carrying out the synthesis of arenes. If cobalt is replaced by rhodium. If the cobalt complexes carries out the synthesis of arenes can we also use it for, can we also use the rhodium complex for carrying out the same reaction. It turns out that for synthesizing arenes it is more easy to use a palladium complex. Not the rhodium or the radium analog. So, in some in some ways it is very difficult to have transferability in organometallic chemistry. We classify the reactions on the basis of the transformation organic transformations they carry out. And we will show this in a few slides later.

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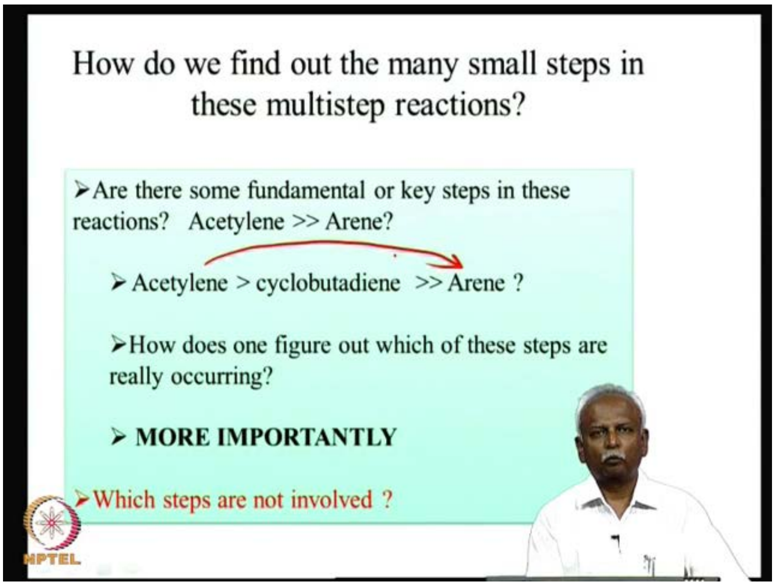

How do we find out the many small steps in these multistep reactions?

- Are there some fundamental or key steps in these reactions? Acetylene >> Arene?
  - Acetylene > cyclobutadiene >> Arene ?
  - How does one figure out which of these steps are really occurring?
  - **MORE IMPORTANTLY**
- Which steps are not involved ?

When we classify these reactions it is important for us to understand the fundamental or the key steps involved in these reactions. When we change an acetylene, when we stitch together acetylene to form an arene, is it going through the cyclobutadiene? Or is it directly converting from an acetylene to an arene?

So, are we going directly from the acetylene to the arene? Or are we going through an intermediate? How does one figure out which of these steps are really happening? Or more importantly we have to ask, which steps are not involved? This will help us to design better catalyst. It will help us to understand this reactions better. And probably even promote the same type of transferability that we have in organic chemistry to organometallic chemistry.

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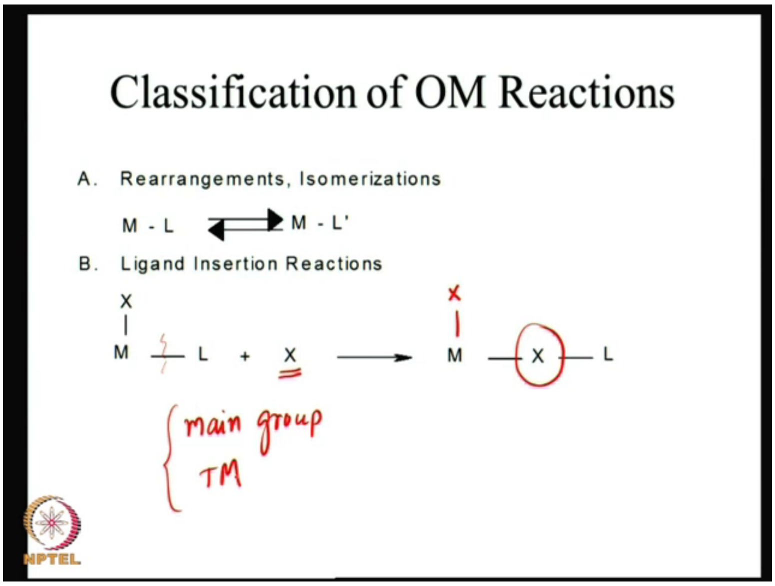

Classification of OM Reactions

A. Rearrangements, Isomerizations

$M - L \rightleftharpoons M - L'$

B. Ligand Insertion Reactions

$\overset{X \atop |}{M} - L + \underline{\underline{X}} \longrightarrow \overset{X \atop |}{M} - X - L$

main group
TM

So, I have classified the organometallic reactions into four broad classes. And probably we will have to extend it to five. But we can for initial lecture use only four broad classification of reactions. First of all I would like to talk about rearrangements of isomerization. These are situations where the ligand rearranges from one position on the metal to another position. So, you can have transits isomerizations and so on. These are rearrangement reactions.

And these can probably happen in both main group and organometallic reactions. And then come ligand insertion reactions. In these cases if you have a ligand that is pictured here as X. It can be neutral molecule. If it can add between the metal and the ligand then one can have such a transformation, that is you can have the insertion of this X group in between the metal ligand bond. So, it looks as if this metal ligand bond is broken and you have insertion of the X group.

So, we have the same group. Here X group which is plus at this particular place. So, M X is converted is left unchanged and M X is there. And you have this transformation of M L to X L. Now, these reactions are very often possible in both main group chemistry and transition metal. So, I would write it as main groups and transition metal chemistry. Both main group and transition metals are capable of carrying out these reactions.

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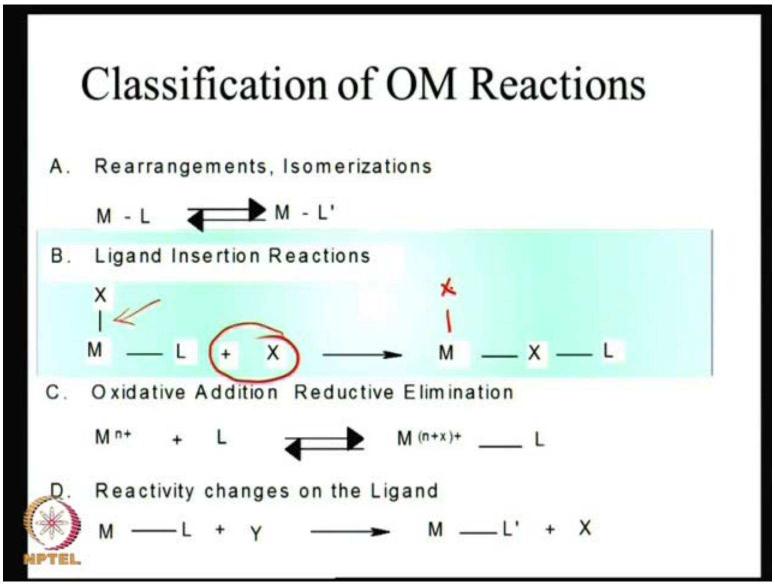

Classification of OM Reactions

A. Rearrangements, Isomerizations

$M - L \rightleftharpoons M - L'$

B. Ligand Insertion Reactions

$M — L + X \longrightarrow M — X — L$

C. Oxidative Addition Reductive Elimination

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

D. Reactivity changes on the Ligand

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

Now, there is another group of reactions. Here we are oregano transition metal reactions. Exclusively these are situations where you have oxidative addition and reductive elimination. I have pictured here the oxidative addition where the metal undergoes an oxidation state change. And this change can be anywhere between one oxidation state change or a two oxidation state change. And we will look at these situations as we go along. The second set is a reactivity change on the ligand. This is again a reaction which is exclusively or mostly in domain of transition metal compounds.

So, transition metal organometallic compounds have this capability of carrying out oxidative addition and reductive elimination. Because transition metals have got capability of changing the oxidation state. Main group elements are very often species which will not change the oxidation state. So, if you look at all the reactions together organo transition metal chemistry comprises of these four major groups. And in these four major groups we have the last two which is oxidative addition and reductive elimination. And reactivity changes on the ligand mostly restricted to organo transition metal chemistry.

Now, today we are going to look primarily at ligand insertion reactions. These are reactions where the X that is added on is added on to M L group in such a fashion that we have a M X L complex being formed. It turns out that the X group can count from outside as we have pictured here. It can be added externally or it can be added internally.

So, if it is added internally you have the formation of M X L. If it is added externally then we can have this X group intact. So, we will look at these reactions in fairly great detail today as we go through this lecture.

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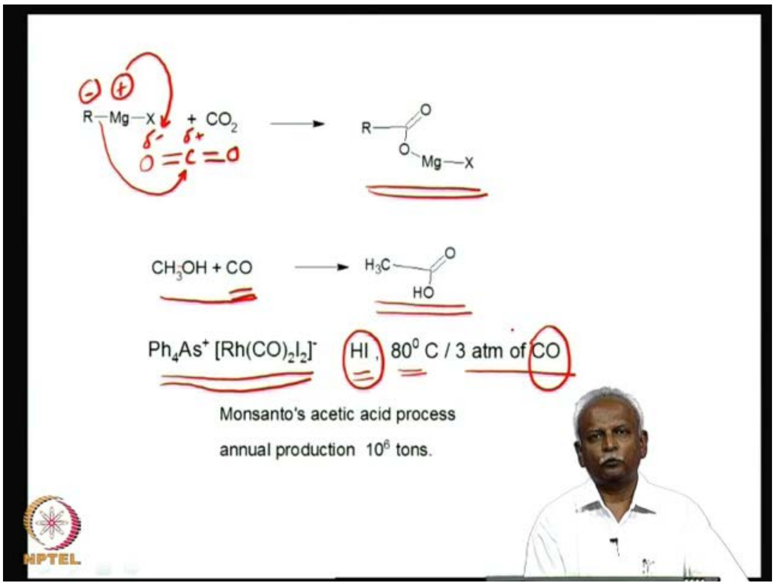

$CH_3OH + CO \longrightarrow H_3C\text{—}COOH$

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

Monsanto's acetic acid process

annual production 10^6 tons.

Let us take a look now at the main group insertion reaction. If you have a simple grenade reagent where you have R and G X. You have a simple grenade reagent. It is highly polarized as R minus and Mg plus. This is the polarization of R, the grenade reagent. So, if a molecule like carbon dioxide is allowed to react with it, carbon dioxide is also polarized and the polarization is quite obvious. This is a delta minus.

And this is a delta plus because of this polarization, a very easy addition of the R minus group, very easy addition of the R minus group occurs on the carbon. And so, you have the formation of an R C O O Mg X, the magnesium. Because it is positively charged or positively progressed when it adds on to the oxygen group. So, we have a R C O O Mg X formed.

Now, this is a very favorable reaction and this happens very readily. On the other hand, let us take a look at an insertion reaction that is common in organometallic chemistry. And that is the insertion of carbon monoxide. Carbon monoxide has got a very very small dipole movement. And carbon surprisingly is a negative end.

So, even though it is polarized but because the dipole moment is very small if you mix methanol and carbon monoxide. At even very high pressures of carbon monoxide, at very high temperatures this reaction is unlikely to happen. You would not have the formation of acetic acid starting with methanol and carbon monoxide. On the other hand, if we had small amount of this catalyst which is an organometallic species.

This organometallic species has the capability of transforming methanol to acetic acid in the presence of hydro iodic acid at 80 degrees. Just a mild heating of 80 degrees and three atmospheres pressure of carbon monoxide is sufficient to bring about this remarkable transformation, where we have added a neutral carbon monoxide molecule. We have added a neutral carbon monoxide molecule to methanol to form acetic acid.

So, this is almost looks like magic as far as transformation is concerned. We have added a molecule of carbon monoxide between the metal and the carbon C H 3 O bond has been broken. And a carbon monoxide molecule has been inserted. Now, this is the basis for the famous Mansanto's acetic acid process and more than a million tons of acetic acid have made annually every year. You make more than a million tons of acetic acid using this particular process. This is very surprising considering the fact that hydro iodic acid is a very corrosive molecule and you have to pump hydro iodic acid in.

In presence carbon monoxide which is a toxic gas of course, but you add hydro iodic acid and carbon monoxide. You pump in using heavy duty pumps which will easily get corroded because of of this hydro iodic acid. And still this process turns out to be a violable process and it turns out to be a profitable process. They have to change the pumps often, but inspite of that, this is a best way of making acetic acid and that is why we have a million tons of acetic acid produced using this method.

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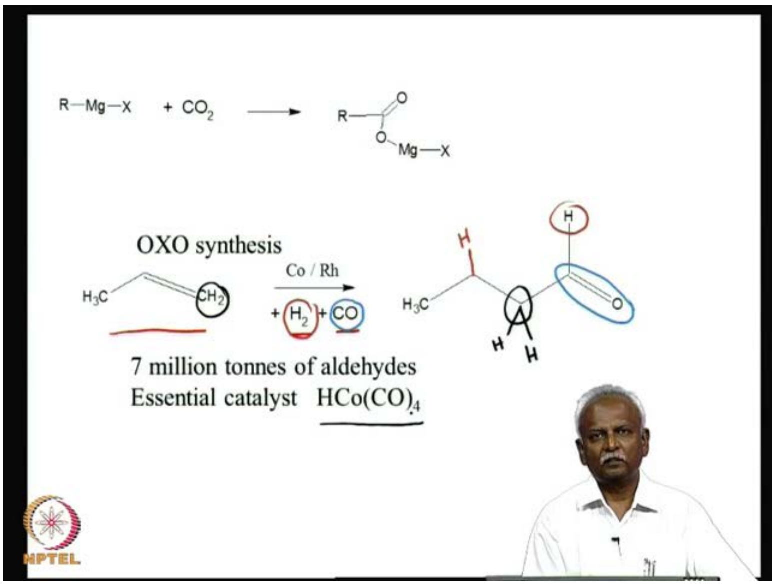

OXO synthesis

7 million tonnes of aldehydes

Essential catalyst $HCo(CO)_4$

So, here is another method where seven million tons of aldehydes are generated. And this is the conversion of propane to butra aldehyde. And what we have added in this reaction is a molecule of hydrogen. A molecule of hydrogen and a molecule of carbon monoxide. So, we have added these two species to a molecule of propane. Here once again we see that all the three species they are involved in this reaction are almost neutral or hardly polarized. They do not have strong polarization of the bonds. Inspite of that you have managed to insert carbon monoxide, which we will indicate in different colors so that it is easy for us to follow.

So, here is the carbon monoxide and we have inserted it here. This is a carbon monoxide which has been inserted and here is the hydrogen. We will indicate the hydrogen using a dark red color. So, this is the hydrogen which has been added. And this hydrogen one of them has been added here. And the other hydrogen has in fact ended up in this position. So, this the original the C H 2 that we had here. The C H 2 that we had here has remained intact in this particular position so that the two hydrogens are in this position and they are unchanged.

So, you can see that you have transformation of one unsaturated molecule to another molecule, which has added hydrogen as well as added a carbon monoxide molecule and the essential catalyst or the catalyst that is involved in this process. This simple carbonyl species, this hydrido carbonyl species. We have not talked about hydrido carbonyl species, but I would like to give this example that you will see the value of a such transformation.

So, this insertion reaction is involved in several of the industrial process. And here I have pictured for you another transformation which is extremely useful, which has been carried out using cobalt and rhodium catalyst and you transform aryl alcohol. This is aryl alcohol, right? Here aryl alcohol is converted once again in addition of a hydrogen and a carbon monoxide has been carried out.

And we can see that it is essentially the same reaction that we talked about in the previous case. Here also we have added a hydrogen and a carbon monoxide, that is exactly what we have done here. But in the industrial process the product that is formed, the aldehyde is converted to an alcohol by a reduction reaction by using hydrogen raney nickel, which is a heterogeneous process. But in the course of this transformation aryl alcohol is converted to one fourth butanol.

And this is an extremely useful molecule because it can be converted to tetrahydrofuran which is T H F. A very popular and a common solvent and a very useful molecule. So, this is a simple way of converting aryl alcohol using hydrogen carbon monoxide. And elimination of a water molecule after hydrogenation to produce T H F. And this is again carried out in very large quantities because one fourth butanol is an extremely useful molecule, and is an intermediate in the formation of several organic molecules as well other than T H F.

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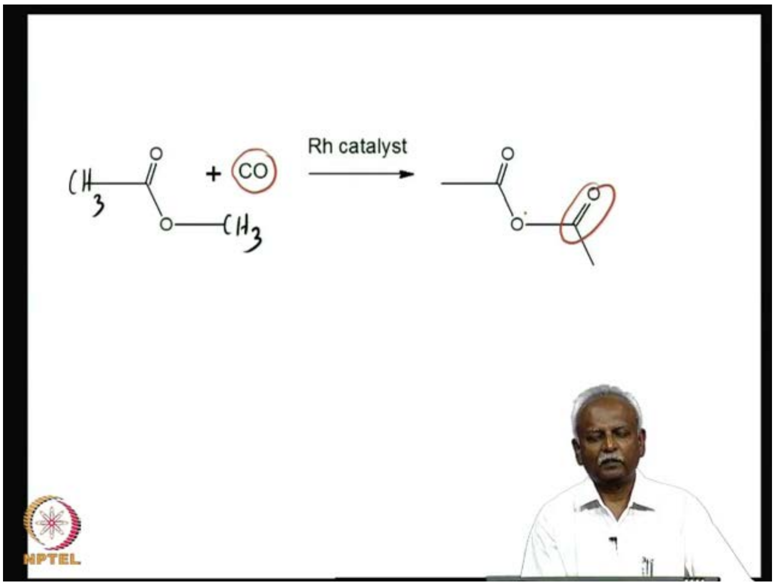

So, here is one last example where an insertion reaction is involved. In this particular case we add a simple addition of carbon monoxide. This involves methyl acetate. So, these are methyl groups. So, you have a methyl group here and you have a methyl group here. This is methyl acetate and you convert it into acetic anhydride. This again sounds like magic. You just added a molecule of carbon monoxide.

We will indicate this by showing the molecule of carbon monoxide that is coming in. And here is the molecule of carbon monoxide that you have added. So, it is a same molecule of methyl acetate except that you have one C O added in between. And this is the best way of making acetic anhydride starting with rhodium. And no organic catalyst will actually bring about this transformation.

The chemistry is completely organo transition metal chemistry. So, it is very important for us to understand such insertion reactions where there is hardly any polarity change that is bringing above the transformation. It is primarily the ability of the metal which is able to bring about the insertion of a neutral organic moiety.

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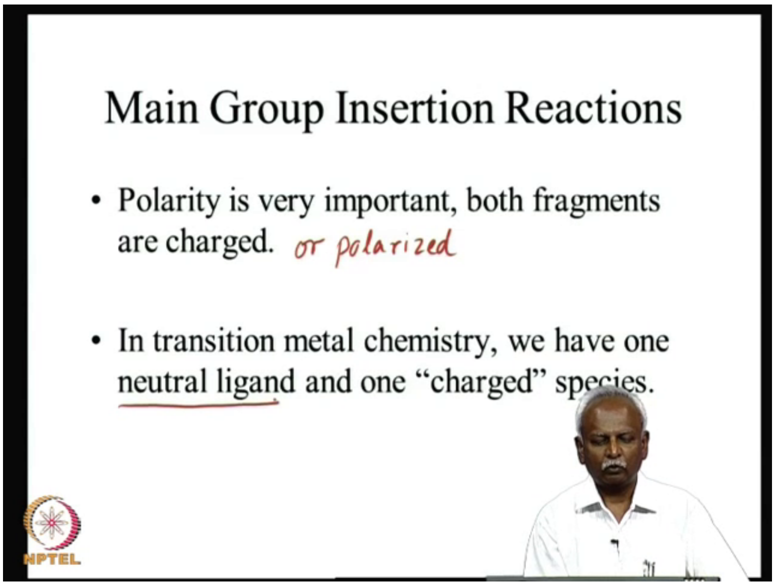

Main Group Insertion Reactions

- Polarity is very important, both fragments are charged. or polarized
- In transition metal chemistry, we have one neutral ligand and one "charged" species.

So, main group insertion reactions polarity is very important. Both fragments have to be charged or polarized. And this is very important. Whereas, in transition metal chemistry very often you have a neutral ligand that is undergoing insertion reaction. So, neutral species can be added using organo transition metal chemistry where as polar compounds can be added using main group organometallic chemistry.

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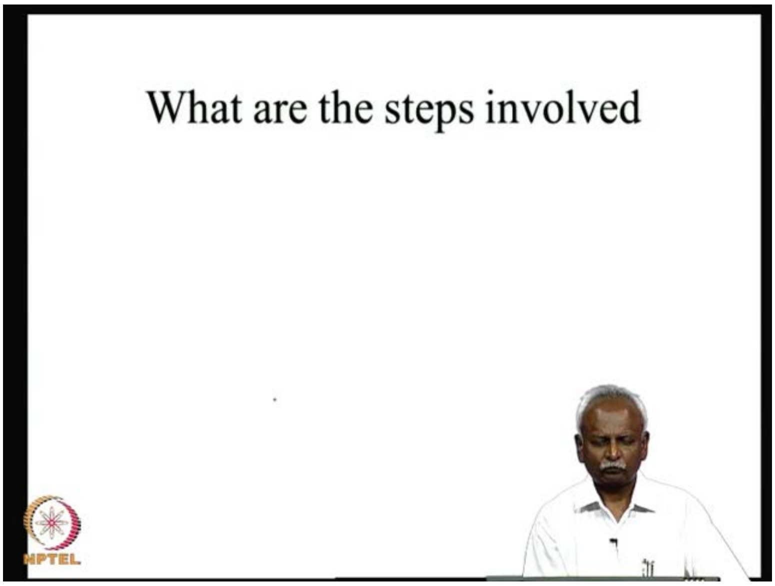

What are the steps involved

So, let us take a look at what are the steps involved in this insertion process because this is a well studied reaction and many examples are known.

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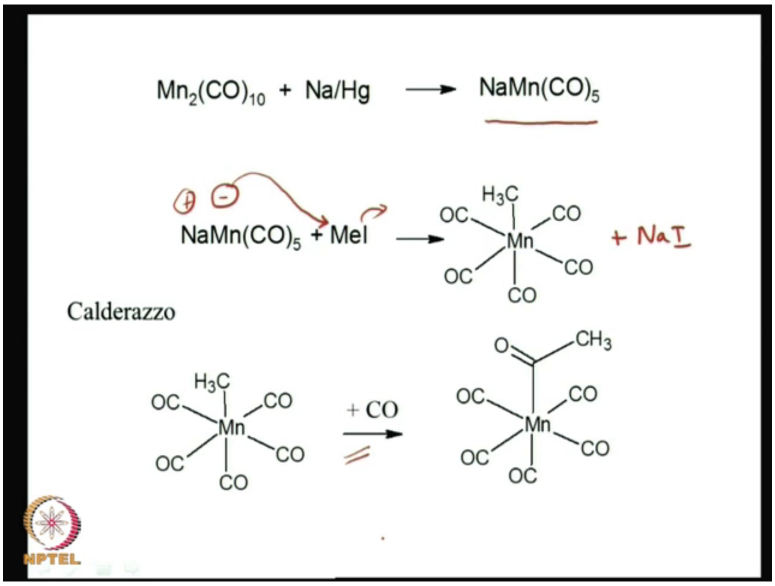

$Mn_2(CO)_{10}$ + Na/Hg → $NaMn(CO)_5$

$NaMn(CO)_5$ + MeI → $CH_3Mn(CO)_5$ + NaI

Calderazzo

And we will take a look at one example that has been an extremely useful because of some kinetic reasons which I will explain as we go along. If we take Mn 2 C O 10 or this di nuclear manganese carbonyl complex, and if you reduce it with sodium and mercury, if you reduce it with sodium and mercury and then you end up with a sodium salt of manganese penta carbon anion M n C O 5 minus. And this sodium salt can undergo further reaction with a methyl iodide. And this will give us a C H 3 M n C O 5 species.

So, basically it as if you have a M n minus species and a sodium plus species. And a M n minus species has made a nucleophilic attack on methyl. That is exactly what is happening. And the iodine goes off goes away as I minus. And as a result we will have in the net reaction. We will have sodium iodide being left out and the methyl compound of M n C O 5 being formed. Now, it turns out that if you add a molecule of carbon monoxide, if you add a molecule of carbon monoxide then you form an acetyl complex of M n C O 5. So, this a classic example where you have this. A classic example where you have, you added neutral carbon monoxide molecule and carried out an insertion reaction.

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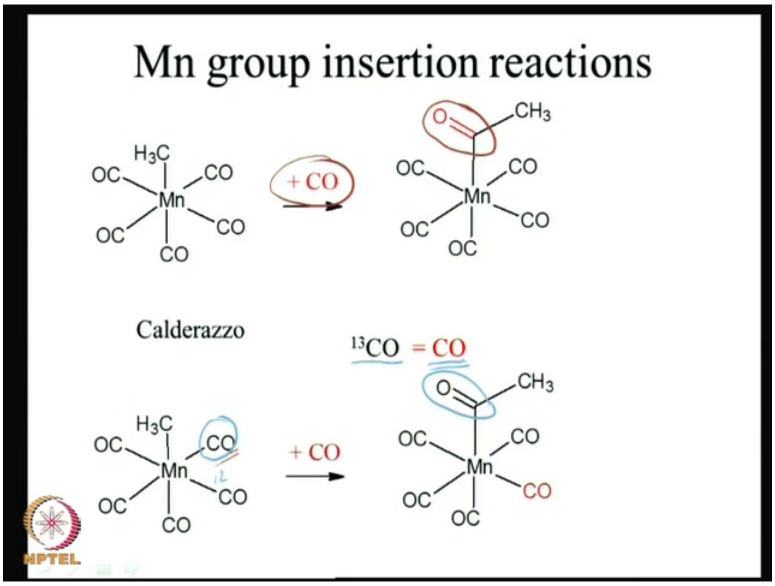

Mn group insertion reactions

Calderazzo

Now, this reaction which was studied by Calderazzo grid detail turns out that the carbon monoxide that you add, the carbon monoxide that you have in the molecule cannot be distinguished. So, he wondered whether it is indeed an external carbon monoxide which is inserted itself between the methyl group and the manganese. So, this is one possible scenario. The other possible scenario is that one of these carbon monoxide groups has in fact fact been utilized.

And it is this carbon monoxide, it is this carbon monoxide which has now transferred to this second position and the entering carbon monoxide is occupying a vacant side on the molecule on the manganese. So, there are two possibilities and he realized that he used labeled carbon monoxide, which means you cannot color the carbon monoxides in real life using a color code. You can add a isotope.

You can use a isotope which is different from the naturally occurring isotope. So, usually 12 C, most of the carbon monoxides will be isotopically will be having the isotope carbon 12. And instead if you have isotopically enriched carbon monoxide then we can use it as if it is concluded. And then we can look at where the isotopically labeled carbon monoxide as a redox. This is exactly what he did.

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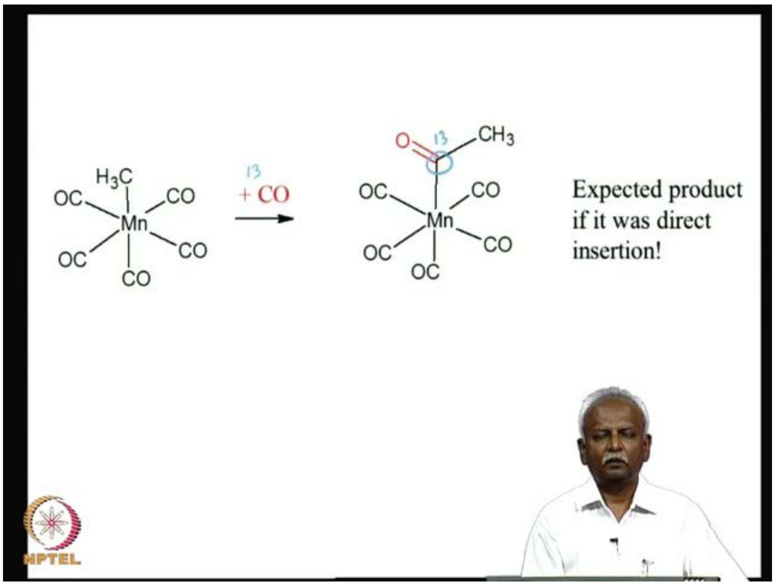

Expected product if it was direct insertion!

So, if you add carbon monoxide and here he has added labeled carbon monoxide and that what we mentioned in the previous slide. So, we have 13 C labeled carbon monoxide coming in and a expected product. If it was direct insertion of carbon monoxide we will have the 13 C labeled in this position. So, this would be labeled with carbon thirteen and you can easily monitor this using carbon thirteen N M R. One can distinguish the position at which the carbon monoxide is coming.

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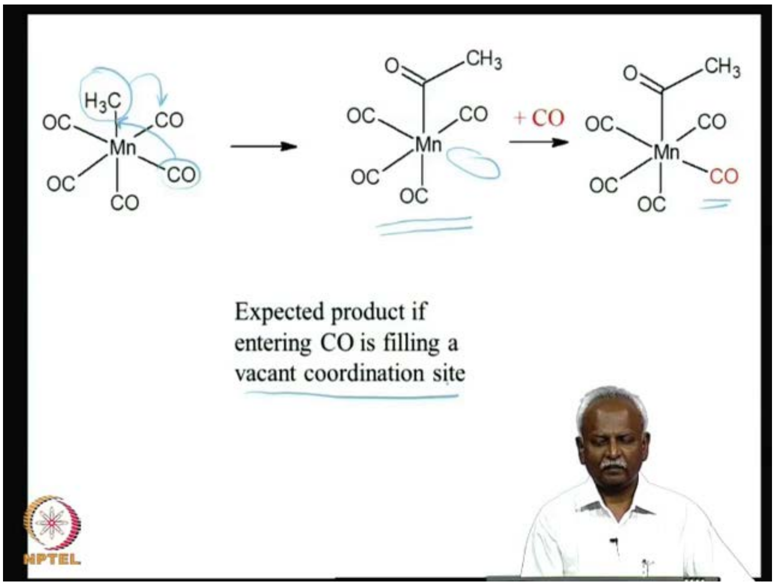

Expected product if entering CO is filling a vacant coordination site

The other option is that you initially have a conversion of the existing carbon monoxide molecule on the manganese to an acetyl group. So, this could have happened in two ways. We could had have the migration of a methyl group ways could had have the migration of a methyl group to a carbon monoxide. Or you could have had the carbon monoxide in the molecule going in between the methyl and the manganese.

So, in both instances you would have got an acetyl manganese complex which has now a vacant coordination sight. This coordination sight has now become vacant and the carbon monoxide which is labeled would come in and occupy this position. So, this is other alternative and this the product if the entry carbon monoxide is merely filling in a vacancy on the manganese.

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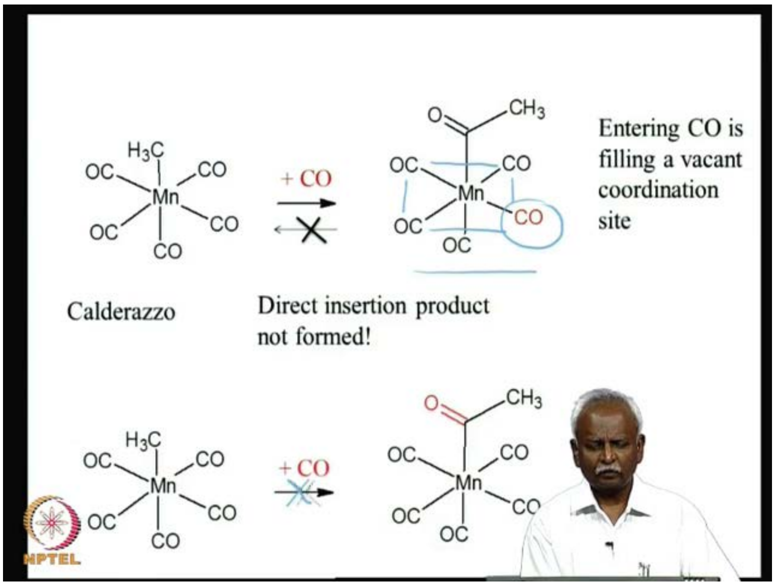
Entering CO is filling a vacant coordination site

Calderazzo

Direct insertion product not formed!

So, that was when the reaction was carried out what he found was the direct insertion product which is pictured here below. That is not happening, it is not the direct insertion product and what he had was the formation of carbon monoxide in this position where it was not found as the acetyl. So, the entering carbon monoxide was merely filling in at a vacant coordination side on the manganese. Now, he used infra red spectroscopy extensively to figure out where the carbon monoxide was placed in the final molecule.

So, one other interesting aspect of this molecule is that if indeed the carbon monoxide what is entering a vacant coordination side if the reaction was under equilibrium. If the reaction was under equilibrium then you would have lost the positional identity of this molecule of this entering carbon monoxide. If the carbon monoxide was going out and coming in then the position would have been lost. Because once you found this molecule you will notice that all four carbon monoxides are identical with respect to this acetyl group.

So, any one of them if the reverse reaction was possible, any one of them could have been lost. And the entering carbon monoxide would have mixed with the available carbon monoxide on the molecule. And so, the positional identity would have been lost. But on the other hand the positional identity was not in this reaction was under what is called kinetic control. Once the carbon monoxide was inserted the product remained as an acetyl moiety and no reverse reaction was happening.

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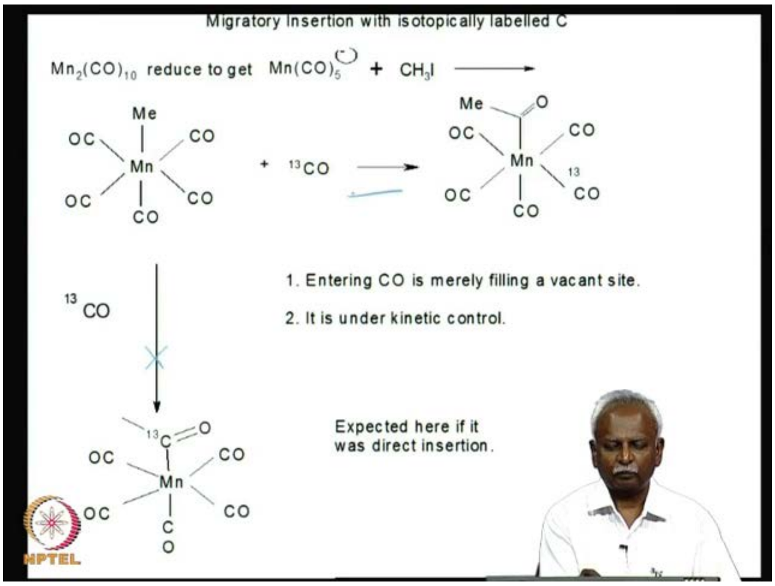

Migratory Insertion with isotopically labelled C

$Mn_2(CO)_{10}$ reduce to get $Mn(CO)_5^{(-)}$ + CH_3I ⟶

1. Entering CO is merely filling a vacant site.
2. It is under kinetic control.

Expected here if it was direct insertion.

So, two thing were discovered in the process. In this course of this study one is the fact that carbon monoxide that is coming in is not inserting itself in between the manganese and the methyl group. And secondly that fact is that it is under kinetic control. And the reaction was not going was not under equilibrium with a non inserted product. And so, the reactions not going back at fourth. So, this is a reaction which was not happening that is, it was not a direct insertion. And secondly the reverse reaction was also not happening in this reaction.

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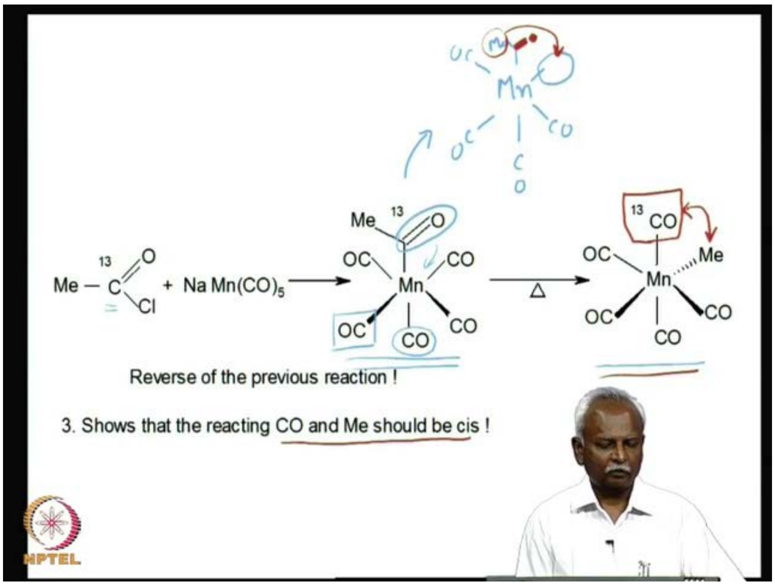

Reverse of the previous reaction !

3. Shows that the reacting CO and Me should be cis !

So, let us take a look now how he confirmed whatever he had studied in this first case. What he did was a clever experiment between the sodium manganese salt that is talked to you about earlier. He treated that with labeled acetyl chloride, labeled acetyl chloride is what pictured here. So, you take acetyl chloride which has got a carbon 13 label at the acetyl group. And now, if you treat it with the manganese salt you end up with a product that you had prepared by insertion of carbon monoxide into the methyl complex. So, once this labeled complexes were made he was able to study the reverse reaction.

Now I told you that under the conditions of adding carbon monoxide you did not have the reverse reaction. But if you heat it, if you supply sufficient heat it was possible to convert the labeled acetyl group into the methyl complex by exclusion of carbon monoxide. Now, it turns out that this is the exact reverse of the reaction. And usually in chemistry we know that there is a principle of microscopic reversibility, which means that the forward reaction is mirrored in the backward reaction, just retraces the way by which the complex or the product was formed.

So, when he heated this molecule of acetyl group and then you know that the carbon monoxide on the metal. One of them should have left. And here in this particular instance you have carbon monoxide which is transferred to the acetyl group. This could have left and then you could have had movement of the carbon monoxide which is in this acetyl group. You could have moved this carbonyl group back on to the metal. So, it could have been one of these carbon monoxides.

It could have been either one which is stitched to the acetyl group which I have, which I am marking as a square, or it could be the one which I have marked as the circle. And exclusively the product that was formed turned out to be the one, where you had a loss of a carbon monoxide which is on the cis position to the acetyl group. So, one of them which I have labeled as a square is one of the carbon monoxides who are left and the methyl group must have migrate to the manganese. So, you have migration of let us just write this off.

So, you have a intermediate where you have a vacant coordination sight. So, you have this acetyl group and then you have a vacant sight generated because one carbon monoxide has left the coordination sphere. And now, the methyl group migrates to that vacant coordination sight. So, because we had this carbon monoxide which is labeled. This carbon monoxide was labeled. So, we have the label in that position. The label is still in that position and the methyl group, the methyl group has in fact migrated to this vacant sight. And that is what we have here.

So, we have a reaction which suggest that the reacting carbon mono acetyl group and the vacant C should be in cis position with respect to each other. In other words the C O and the methyl group should be cis to each other. And that is exactly what have here. They are cis related. So, that is the only way in which you can have a migration. So, this cis migration was proved by Calderazzo by using this isotopic limbered subtract.

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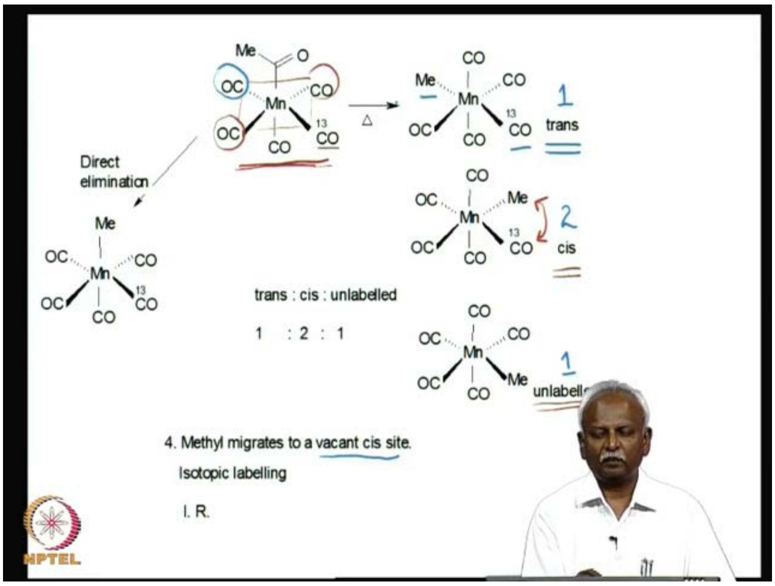

trans : cis : unlabelled

1 : 2 : 1

4. Methyl migrates to a vacant cis site.

Isotopic labelling

I. R.

Now, the third react that Calderazzo did was to check if you can use this product where which was formed in the first reaction. In the first reaction he added labeled carbon monoxide to a methyl manganese complex. And he heated this product which was formed in the first reaction. He heated this product and he got both trans and cis labeled molecules. How is that possible? Because you have four carbon monoxides in the cis position.

Now, to the acetyl group you have four carbon monoxides which are equitant one of them. Of course, is labeled because that is the carbon monoxide which came in the external addition of carbon monoxide. Now, if you heat it its possible that this 13 C labeled carbon monoxide leaves. If that labeled carbon monoxide leaves then you would have the migration of the methyl group to that position. And then you would get an unlabelled product. If you had loss of this carbon monoxide when you heat it. If you have lose of one of these carbon monoxides which is cis to the labeled carbon monoxide then you would end up with this product.

So, I am labeling this as a cis product because there are two of them. Two of the carbon monoxides are there which is possible that one of them leaves and both of them are cis to the acetyl group. Any one of them can leave and then you would get a cis product here. The methyl group is cis to the labeled isomer, labeled carbon monoxide.

Now, it is also possible that this carbon monoxide which we will mark with a different color. So, it is also possible that this carbon monoxide leaves and if this carbon monoxide leaves then you would get a trans isomer. And labeling this is trans with respect to the, I am identifying this as a trans isomer because the labeled carbon monoxide and the methyl group are trans related.

Similarly, the methyl group and the 13 C are cis related here. So, depending on which carbon monoxide will lose in this reaction, depending on which carbon monoxide will lose you will end up with one of these three isomers. If the labeled carbon monoxide leaves, you get the unlabelled isomer. The probability with which these carbon monoxides leave are about one fourth. In the case of the unlabelled isomer because there are four carbon monoxides and each one of them can equal have a equal probability, leaving when you heat his molecule and there only one carbon monoxide, which is trans to the labeled carbon monoxide.

So, this will be formed in the same ratio as ratio in which the unlabelled molecule is formed. However you have two carbon monoxides which are cis related to the labeled carbon monoxide and they are also cis related to the acetyl group. Remember the carbon monoxides which have to leave in order for the reverse reaction to take place are the ones which are cis to the acetyl group. So, the acetyl group is present here and there are two cis related carbon monoxides which are also cis related to the labeled carbon monoxide. So, these two have a twice the probability of leaving the molecule.

And so, you will end up with two equivalents of the cis product with respect to the trans product and with respect to the unlabelled product. This is exactly what he found. He found that there was no formation of the, there was no direct elimination possible. It was only these molecules which were formed and they were formed in 1:2:1 ratio. Now, if this the ration in which the three products are formed, it is very clear indication that the cis elimination path way or the cis insertion path way is the one that is been followed by this molecule.

Methyl migrates to vacancy sight and to vacant cis sight. If carbon monoxide had migrated inside and it was not a methyl migration, you would have obtained a very different result. So, let us just take a look at that. If carbon monoxide migrates what would happen in the previous instance. We assumed that the carbon monoxide leaves the coordination sphere and the methyl migrate to a vacant side.

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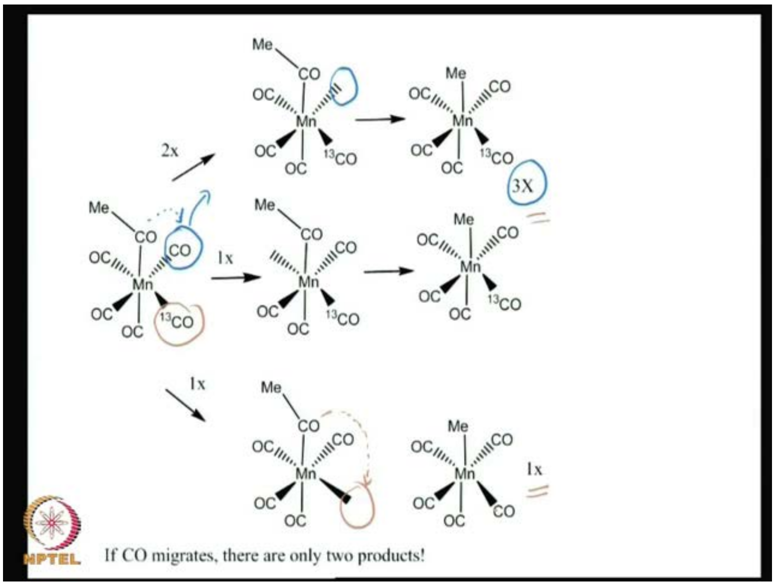

If CO migrates, there are only two products!

So, here we are going to check what would have happened if indeed the carbon monoxide migrates. If carbon monoxide migrates then of course, you would have got the probability of forming this molecule. Let us take the first one the carbon monoxide. If the C O leaves and first we are assuming that this carbon monoxide leaves and so you would have a vacant site here. And then the carbon monoxide migrates to the cis position. So, let us just mark that here in this fashion.

So, the carbon monoxide migrates here, then in that case you would form exclusively this product. This product here which I have marked as 3 x. And we will explain why 3 x is possible? Because there are three carbon monoxides like that. And each one of them could have then, all of them would end up with formation of this product. On the other hand if one looses this monoxide. Let us mark that with a different color. If this carbon monoxide leaves you would end with a vacancy in this cis position.

Also but you would have if C O migrates then it is this C O that is migrating and then you would end up with this product. So, the possibility of this species being formed from one of these carbon monoxides migrating. And one of these carbon labeled carbon monoxides migrating the ratio would have been 1:3 and there would have been only two products. And because we have the formation of a set of three products the labeled, the unlabelled one, the trans found and the found we suggest that the reaction is happening only by methyl migration and not by C O migration.

So, here we have assumed that it is the C O migration is happening. And we have shown clearly that the ratio of these two products would have been 3:1. You would have got three times the labeled and once you would have got the labeled product and that is not happening. And so, in fact we say that it is the methyl migration to a vacant site which has happening. So, let us just proceed further. Now, let us take a look at what happens when you move from this methyl migration.

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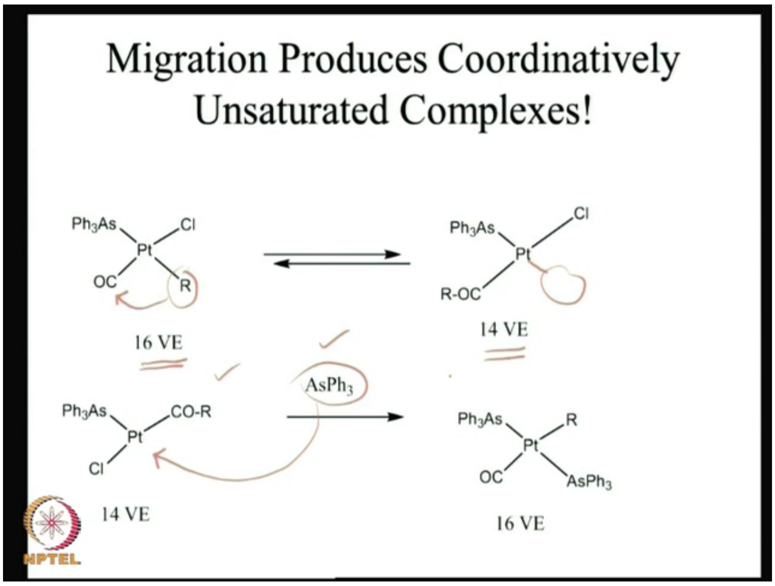

Migration Produces Coordinatively Unsaturated Complexes!

Let us take a look at what happens when you have methyl migration. I have used a different complex here. What we are doing is that we are generating a coordinative unsaturated complex. And because you can have both sixteen valance electron species and eighteen valance electron species, one should think about the fact that what will happen if you have a migration first and then coordination sides being filled in the previous example?

We had eighteen electron complexes but we have pictured here this example, a sixteen valance electron complex. If have sixteen valance electron complex, one has to go through the intermediate where you would end up with a fourteen valance electron species. If this species is if this reaction is reversible then you would end up with rate dependence which is not dependent on the added triphenylarsane. As we have pictured here the second step, the triphenylarsane is coming in and blocking the vacant coordination site on the platinum. First it is the migration of the R group. First it is the migration of the R group and then in the second step the vacant site on the platinum is blocked, the triphenylarsane.

So, here is what is happening. We have the conversion of a sixteen valance electron complex to a fourteen valance electron complex. And then the fourteen valance electron complex is now converted back to the sixteen valance electron complex by the addition of the ligand. So, one can check these reactions using kinetics depending on whether the first step is determining or the second step is very determining.

We would have a first order dependence on first order reaction or a second order reaction. If the second step is re determined clearly it would depend on the concentrations of both of these species. And so, you would have a second order reap constant. Now, here the generation of a fourteen valance electron intermediate is postulated and in general the reactions go through either a sixteen or eighteen electron intermediate.

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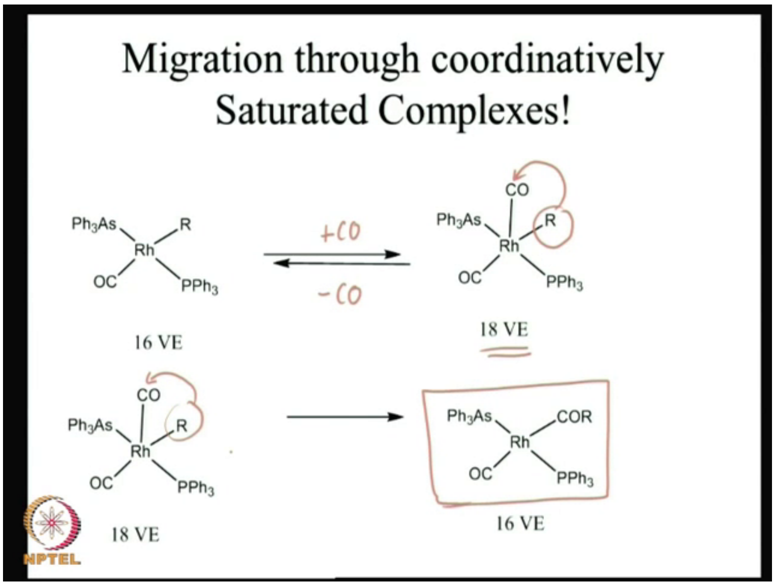

Migration through coordinatively Saturated Complexes!

Now, how will how can one go through sixteen electron intermediate in the case of complexes which start with a sixteen electron complex. So, here is a example. In this case also we have the migration of a carbon monoxide or migration of an R group onto a carbon monoxide and if we add carbon monoxide here in this reaction. Let us add plus C O and you have minus C O, then we can prove the equilibrium with an eighteen electron species. So, sixteen valance electron species add on a molecule of carbon monoxide becomes an eighteen valance electron species. And now, we have the migration of an R group onto the carbon monoxide.

In the cis position remember the two groups have to be cis related. So, the C O group the resource is the one onto which the R group migrates. So, if you have the migration of this R group. Now, on to the cis position you will end up with a sixteen electron species again. So, you go from a sixteen to a eighteen to a sixteen. It is generally agreed that most catalytic cycles or most reactions would like to go through a sixteen electron eighteen electron cycle rather than a sixteen electron fourteen electron cycle. So, it is generally understood that this is the reaction you can assume.

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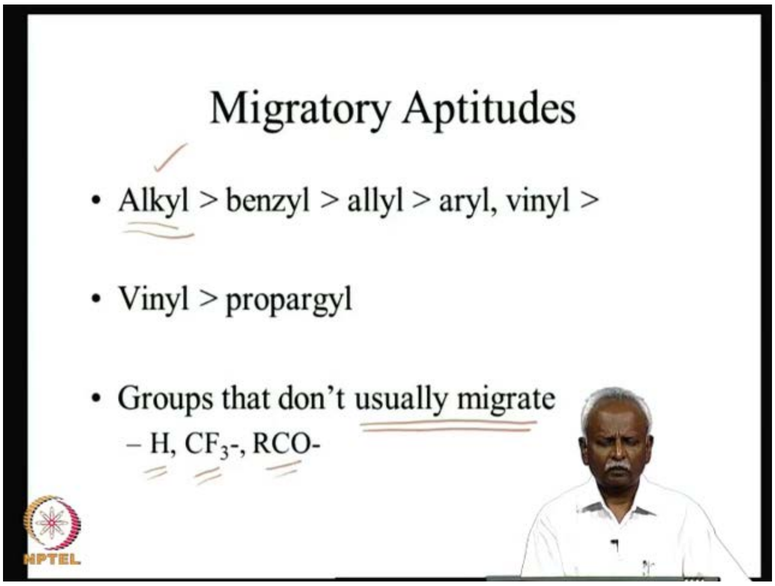

Migratory Aptitudes

- Alkyl > benzyl > allyl > aryl, vinyl >
- Vinyl > propargyl
- Groups that don't usually migrate
  - H, CF_3-, RCO-

Lastly one can also look at the migratory aptitudes. By migratory aptitudes we want to look at either reaction rates, mostly reaction rates. If you have a set of complexes where you have alkyl, benzyl, allyl and vinyl species. Then these groups will migrate much faster than vinyl or propargyl. Propargyl group does not migrate easily compared to the vinyl. On the other hand the alkyl group has the greatest tendency to migrate and it is the one which will undergo migration fastest. If you have a molecule in which two different alkyl groups are there, say an alkyl and a benzyl. It is the alkyl group which migrates and not the benzyl group. Similarly, benzyl migrates faster than allyl.

Now, this could be because of their electron nature of the R group which is attracted to the metal and this is something which has to be studied further. Now, some groups have a very little propensity to migrate and these are groups like hydrogen, trifluromethyl. So, this a methyl group where all the hydrogens are been replace by fluorine or an aryl group.

So, if an aryl group migrates it would end up with double carbonization. So, you already have an R C O group. If it migrates on to another carbonyl group then you end up with a bi carbonyl species. Now, this usually does not happen and so a single carbonyl migration is what you observe in many cases. And you have no double carbonyl ration reactions, very few double carbonyl ration reactions are known.

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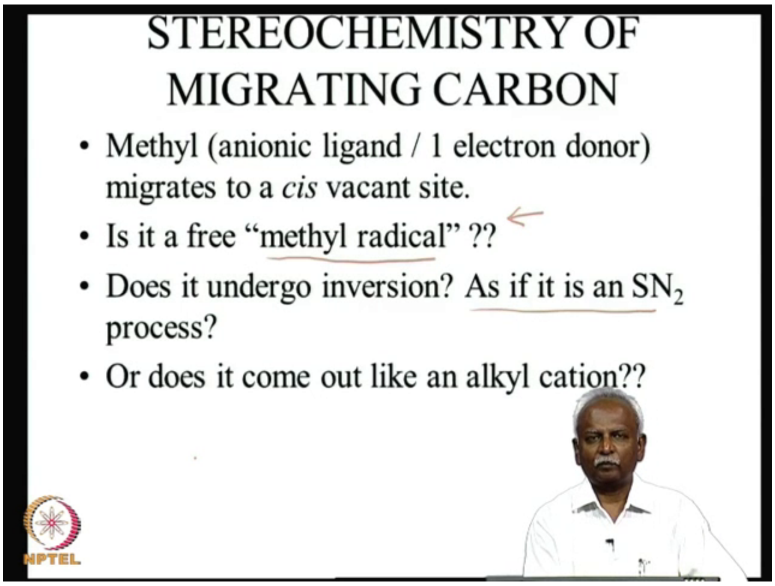

STEREOCHEMISTRY OF MIGRATING CARBON

- Methyl (anionic ligand / 1 electron donor) migrates to a *cis* vacant site.
- Is it a free "methyl radical" ??
- Does it undergo inversion? As if it is an SN_2 process?
- Or does it come out like an alkyl cation??

Finally, I would like to look at the stereochemistry of the migrating carbon. The migrating carbon could be migrating as an anionic species or it could be migrating as a radical species. If it migrate as an radical then the radical species would lose the stereo chemical on the R group. If it undergoes inversion as in the case of a SN 2 process then the stereo chemistry of the migrating group would be changed, but never the less it would the stereo chemical information is retained.

In other words if you start with a optically active product, you would end up with an optically active. If you start with an optically active substrate, we will end up with a optically product. So, if we use the neutral method of electron counting we would think of it as a radical species. I have mentioned it as a methyl radical. But it could also be an alkyl radical that is migrating. Now, if you use it as an anionic species then we would imagine that it is undergoing SN 2 type of reaction.

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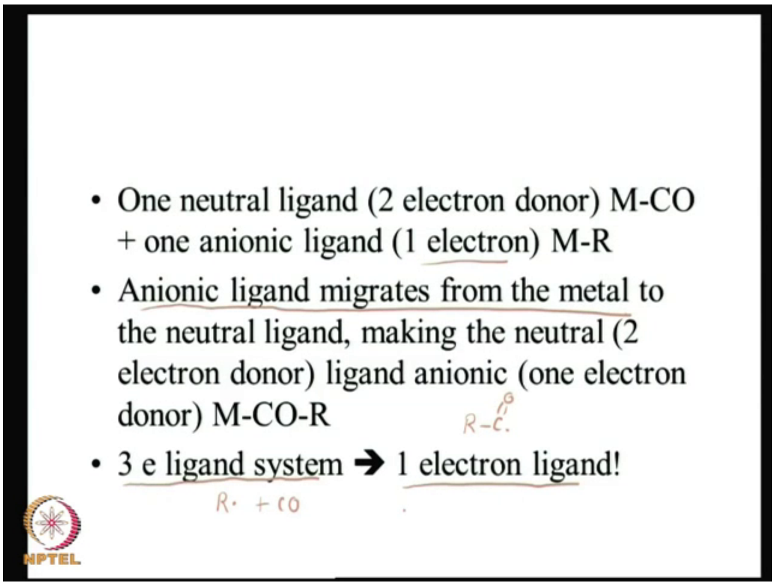

- One neutral ligand (2 electron donor) M-CO + one anionic ligand (1 electron) M-R
- Anionic ligand migrates from the metal to the neutral ligand, making the neutral (2 electron donor) ligand anionic (one electron donor) M-CO-R
- 3 e ligand system ➔ 1 electron ligand!

$R-\overset{O}{C}\cdot$

$R\cdot + CO$

Let us look at some other features of this migration reaction. If you have a neutral ligand a two electron donor like carbon monoxide, you have an anionic ligand. Or if you use a neutral method then you talk about as if it is a one electron donor. Then the principle is that the anionic ligand migrates from the metal on to the neutral species. So, carbon monoxide is a neutral species and anionic ligand is migrating onto the carbon monoxide. Initially, we have a total of three electrons on the ligand which is been donated to the metal. At the end of the reaction on the ligand counting neutral electron counting procedure, we end up with a one electro ligand that is the R C O group.

So, the R C O group is a one electron donor and the R group is a one electron donor. And then the C O group is a two electron donor. So, total of three electrons are present on the metal. And finally, you end up with a one electron donor on the metal. So, this turns out to a loss in the number of electrons around a metal and this is something that we have to bear in mind.

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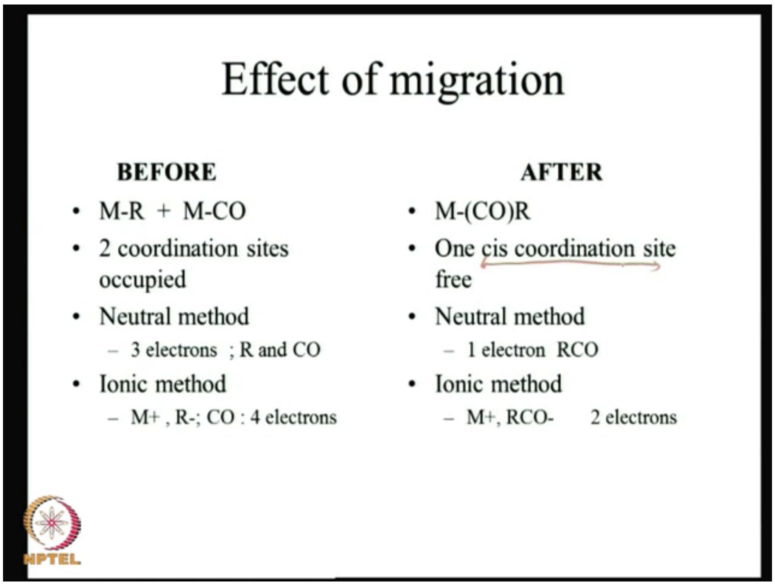

Effect of migration

BEFORE

- M-R + M-CO
- 2 coordination sites occupied
- Neutral method
  - 3 electrons ; R and CO
- Ionic method
  - M+ , R-; CO : 4 electrons

AFTER

- M-(CO)R
- One cis coordination site free
- Neutral method
  - 1 electron RCO
- Ionic method
  - M+, RCO- 2 electrons

And if we look at the net effect on the metal we realize that after the insertion reaction we also lose one coordination site, becomes one coordination site on the metal becomes free. So, based on whatever electron count procedure he might use, you end up with a loss of two electrons on the metal. And we also end up with a loss of one coordination site on the metal being free at the end of the reaction. So, these are the effects of migration and we will discuss the reaction in a greater detail in a future lecture.