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Organometallic
Chemistry-I
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Module No. 2

Lecture No. 9

MIGRATION & INSERTION

Hello everyone today we will continue on discussing the last topic which were which we were having that is α migratory insertion α migratory elimination or then β migratory insertion and β elimination in the last class we were discussing mainly the α migratory insertion and you have seen few examples with that but of course all of us get confused about the fact that whether it is you know migration or insertion α migration or α insertion that is a really difficult or tricky question to answer because both the migration and insertion seemingly can lead to the same product.

Therefore it was essential for researcher to come up with a method come up with an experiment that can distinguish perhaps between these migration and insertion reaction one such example will try to discuss right now subsequently we will try to discuss the stereochemistry related issue what happens when the insertion happens and with that stereochemistry gets changed or not let us first try to take an example where we perhaps we will be able to understand whether an insertion or an migration is going on the query is again the same.

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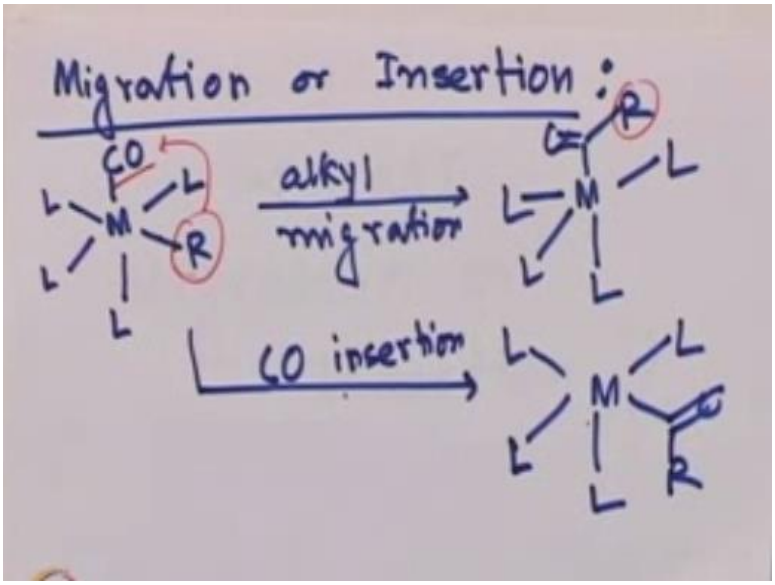

Whether it is a migration or insertion remember it is a tricky experiments to do but you know scientist has done it anyway where they have taken let us say a you know the metal complex with CO now first before getting into the exact experiment let us try to discuss what will be possible if it is alkyl migration if the alkyl group is migrating that means you know we have the R group our group migrating over here if alkyl group is migrating then the product that you should expect in this case is this one right where R group is getting migrated to the CO.

Now if the CO insertion is happening okay from the starting from the same compound if we see the CO insertion it is you know just exactly the same compound but written in a different way of course you know it is again a Penta coordinated compound and in this case CO is getting inserted into the RCO this CO group is getting inserted into the R, so in the first case R is migrating that is what alkyl migration is about.

In the second case we were telling that CO is getting inserted into the into the R bond now it is again it is a very tricky experiments to do it is a very difficult thing to find out which exact thing is going on in this particular case or in any case because the product is again in this case as you

have seen from a six coordinated one we get the five coordinated one the product is exactly same in the both the cases.

Now of course there is a subtle difference or there is some experiment perhaps that can prove that exact nature of this transformation whether it is migration or insertion, let us say let us try to discuss a specific example which perhaps can shed light into this you know tricky problem.

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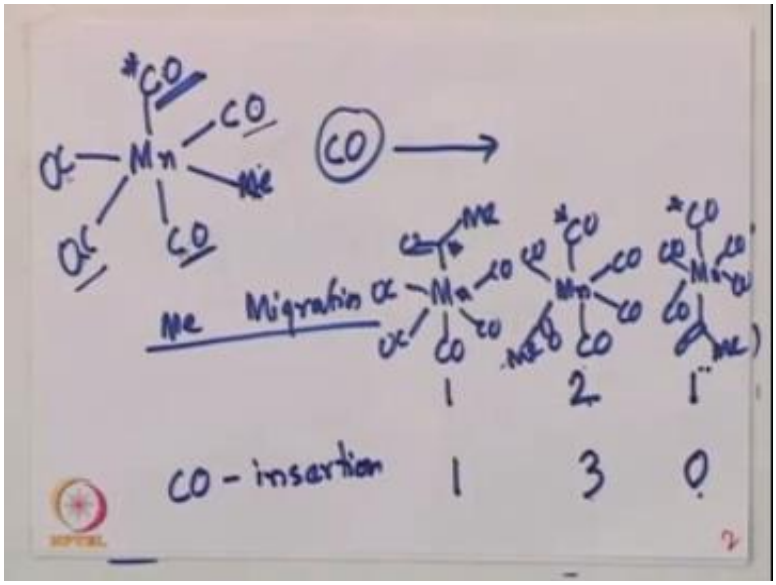

The scientist has come up with a complex or a strategy a manganese complex and one of the CO is leveled in this case one can you know selectively do these experiments and very efficiently this reaction can occur, now if we were doing this experiment with CO that means in presence of CO effectively you will be able to effectively you will be able to maintain the six coordinates and anyway right.

So in this particular case you are expecting to form a series of compound okay, first of all there is a level CO, right. So if it is a methyl migration okay if it is a methyl migration then the product you are going to get is this is a manganese one anyway CO Me with a star in there since we are doing the reaction in presence of in presence of the CO atmosphere of course one can understand

that it will be it will be six coordinated one, right. And you get these products and of course you can get another product where CO M_e is in the axial position Co.

So these are the three different product formation you can expect if methyl is migrating over CO now if methyl is migrating over the co you can have methyl migration as you know cysts should be ceased to each other so one position is possible and this is another position that is this product so an another position is this one so this methane is seized to this carbonyl this carbonyl that will give you the product the second one if method is migrating these two this one.

That will lead to this product formation and if the methyl is migrating to this CO that will lead to the first product formation so if methyl migration is happening all possible product formation include methyl migrating here methyl migrating there methanol migrating here methyl can migrate over there but methyl should not migrate great over here because this CO is trans to methyl and such migration is not allowed only the sis migration is allowed right now the product formation pattern should be 1 : 2 : 1 and why is that because this methyl can migrate over here and here both these mode will give you the same product.

That is why this is twice this one is onetime that is here and this one from hereto here it is going to be another time so 1 : 2 : 1 product formation you would expect if ridge a methyl migration now the other case is the CO insertion right, what the product formation will be if CO is getting inserted is it going to be the same let us look at the compound very carefully and try to analyze in case of CO insertion what is the product formation that one can expect let us go back to the compound again the same compound now imagine methyl is not migrating but CO is inserting if CO is inserting right.

Show all these this CO and this these three CO all these three CO can we will give you the exactly same product that is CO M_e CO M_e will be in the equatorial position right CO M_e will be that in the equatorial position of course there is a CO M_e will be in the equatorial position now yes that is going to be the case then you are going to get three of these CO this CO is traversing here or the CO is inserting here this you is inserting here and the CO is inserting here so three of them, right. Of course you know another thing that will be possible is CO, Co will be in the axial

position as well in this particular case this is the leveling one you will get one, but this product you will not be able to get at all because there is no way you can get the axial CO leveled if CO is getting inserted.

So the product formation pattern for CO insertion is going to be 1:3:0 that means this product formation thus where CO is in the axial position the level CO is in axial position and the COMe is opposite to it, it is not going to be feasible if this CO insertion is happening. But when the chemist has done this experiment they have found that only the 1:2:1 product formation is happening that means methyl migration is happening but not the CO insertion.

This is a once again very tricky experiments to do and we can have only 1:2:1 product formation let us look back at it again.

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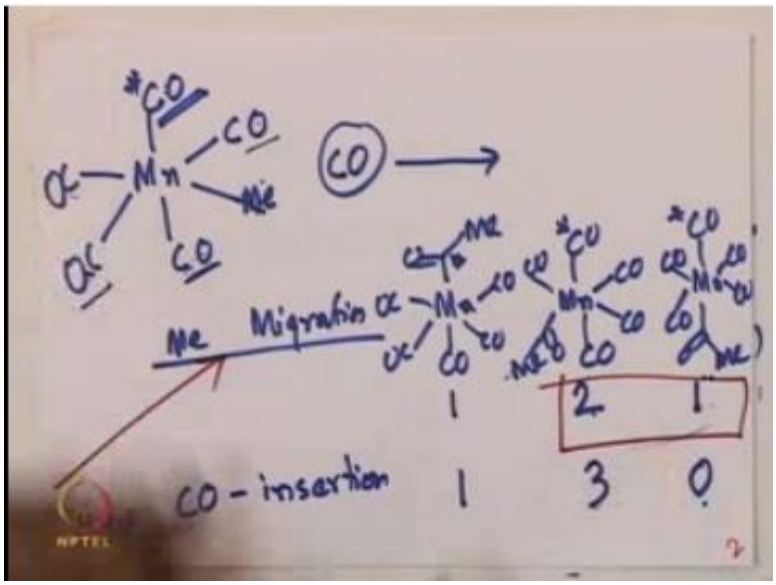

We are having we are having these manganese complex and three different product formations are likely and for methyl migration we end up getting 1to 2 to 1 for CO insertion if it is the case we are going to get 1 to 3 to 0 and experimentally what we see is these 2 to 1 product formation this is not observed at all, so this kind of suggests or you know as maybe strongly you can say

that these perhaps proves but of course you know it is nothing in you know chemistry can be proved 100% guaranteed away but you know this is an elegant experiment that suggests that the methyl migration is likely since this is the pattern observed 1:2:1 this specifically this ratio is observed, okay.

We will then move to the next topic okay, that would be the stereochemistry, what will be the stereochemistry we have discussed briefly the stereochemistry in all other previous cases as we were coming along oxidative addition reductive elimination so in this case also if we are having alpha migratory insertion and in these cases at least one component is having the stereochemistry what will be the outcome or what will be the fit of the reaction in this particular case let us try to look at the one of the example particularly in this case so the experiment we are going to look at is stereochemistry of the migratory group.

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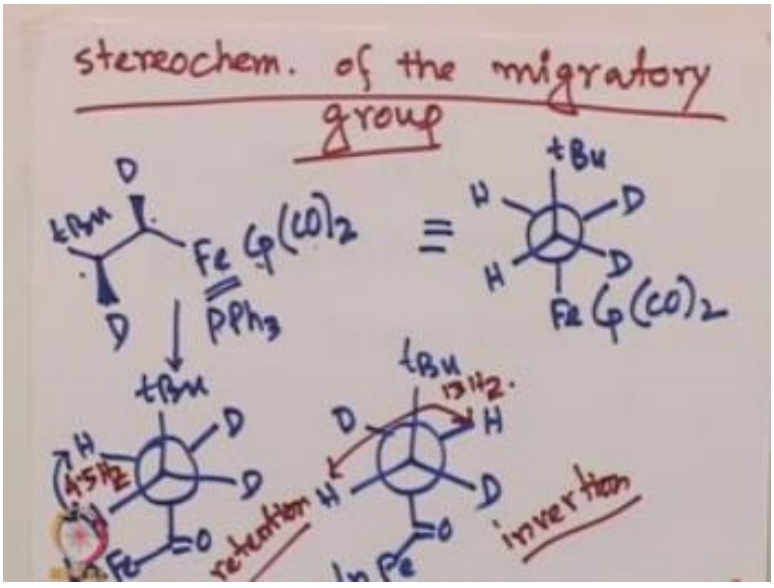

Stereochemistry of the migratory group right now again this is an experiment one has to design very carefully and you know it is not that it is going to be always very easy to do but in UF scientist has managed to you know design a perfect experiment at least in this case to send some light into the problem of the stereochemistry and to get to know what could be happening in this

case okay this is an iron complex as you can see it is a cyclopentadiene oil and di-carbonyl species and one of the alkyl group the R group over here that is having to stereo centers as you can see over here right.

If you want to put it in new man projection you would get simply the tertiary butyl group over here let us say if it is in this pass and you want to write and if you want to put the deuterium so it should be on the right hand side since it's it is the above the plane and then you have Fe CPC0_2 this is the Newman projection anyway now if you are reacting this within presence of tri phenyl Phosphine okay.

Then what you would see is that do product formation is likely okay now what are those two product formation we would like to have the fact that it can you can have of course the you know the alkyl group will migrate to co and tri phenyl Phosphine will come and coordinate with iron so we are not going to write down what are going to be the ligand on iron it will be one pph 3 and1 C 0 and 1 CP and the R group will migrate into one of the co.

We just simply will write this where we will put that co is getting you know alkyl group is migrating and iron Ln, this ligand we are not writing that would be 1C_P, 1C_O, and 1triphenylphosphine, and two type of product formation is possible this is one of them, and another one would be similar but stereochemistry will be different, as you can imagine.

So two possibilities are there, retention of configuration or inversion of configuration right In this case also we will put iron Ln. now as you can see; you can see among these two products among these two products the first product. The first product is having the retention of configuration right, and the second product is having inversion of configuration.

See the starting material is having D over here, to DS over here if it is a retention of configuration, this is the one, so I would like to name this as retention, this is the retention of configuration, this is inversion, now scientist has done this experiment okay, and this particular compound being synthesized, and then triphenyl Phosphine being added, and treated under suitable reaction condition.

What they were able to find is? of course you know getting a crystal structure will be great, but NMR can be of help, if this product is forming you would get from NMR this coupling constant should be 4.5 H right, if this is forming this to proton, this coupling constant would be13 H, now it's a very simple at this point if you if you try to look at.

So two product formations are likely one would lead to the retention of configuration view, the second one will give you the inversion of configuration, the retention of configuration geometry these two proton as I was highlighting, should have a four point five Hertz coupling, constant whereas for the inversion of configuration the second compound should give us a coupling constant value of 13Hertz.

This is something excremental immeasurable, and by synthesizing this complex scientist was, able to scientists were able to do these NMR experiment, by simple NMR experiment they were able to determine that indeed the first product is forming, that means retention of configuration is happening, that means that four point five Hertz coupling constant is the one they are getting, the other one which is the 13H one they are not getting.

This again suggests that the retention of configuration, in this case I would say very strongly the retention of configuration is happening during the Alpha migratory insertion reaction, it is insertion or I know insertion or migration, you have seen that you know the alkyl group is migrating, it is not, you know it is it is not that co is inserting but then again on top of that we have seen that the stereochemistry is retained during the process okay.

Next try to move on to the next topic and that is related whatever we are discussing and in this particular case we will be discussing, we will be discussing that how these migratory insertion is happening in the carbine species so, far we have mainly focused on the car metal carbonyl species, will now look at the similar variation of the α migratory insertion that is, that is the α migratory at the metal carbon species.

Let us try to take one of the example in this particular case once again, okay so the, we are looking for a case where a transition metal carbine is there, transition metal carbine is there. Now

the transition metal carbine as you may be aware of this sort of complex okay where metal and this double bond they are with a carbon in there here you can have some substituent or without it in this particular case you have two hydrogen atoms.

Now this is the double bond between metal and carbon so this is the metal and carbon bond this is a double bond this, this is what it is called carbine species and let us say on the metal another our group is also present. In this case, of course metal carbon usually means this is the species right? It can have different substituent on that. Now what was what was interesting that similar to what we have seen in the Co carbon monoxide case.

We can have α migratory insertion and α elimination in this case that after α migratory insertion we can get the product MR; if it is the reverse of it we will get α elimination right. Now of course there is a way to figure out what is happening in these cases, what is migrating in these cases as well whether it is migration or insertion that is one of the question, another question that we would like to discuss in the next class is whether the migratory aptitude that means which groups migrates faster if you have the competition between two different groups.

such as let's say hydride migration versus alkyl group migration, H migration versus alkyl group migration what will be the fit which one migrates faster, the migratory aptitude can be measured by experimental path, pathway will try to look at in that in the next class. So today's class once again we will conclude over here and in today's class we mainly try to focus on the discussion of whether it is a migration or insertion and then the stereo chemistry of the processes and then we have introduced the transition metal carbine as a component as a topic where again a migratory α migratory insertion is possible and in the next class we, will discuss again α migrated inserts an α elimination, β migratory insertion and β elimination. Till then see you, bye, bye.

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