NPTEL

NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

IIT BOMBAY

CDEEP
IIT BOMBAY

Organometallic Chemistry-I

Prof. Debabrata Maiti
Department of Chemistry, IIT Bombay

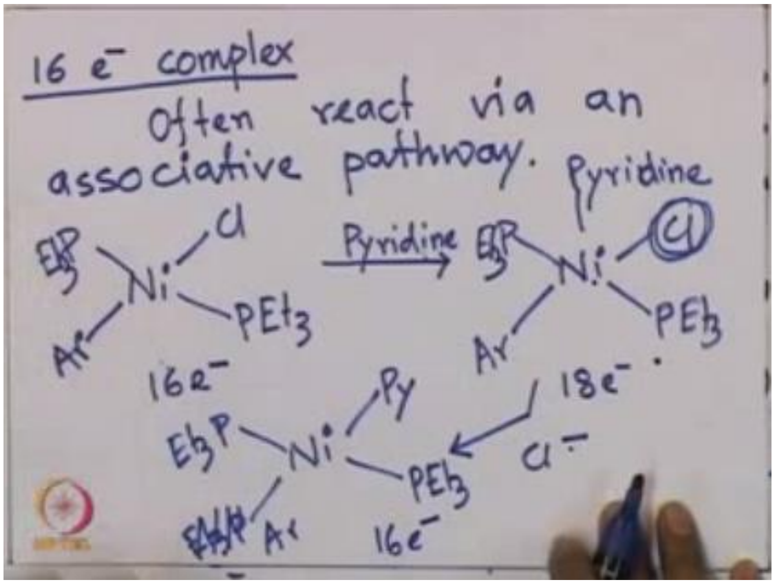
Module No. 1

Lecture No. 3

LIGAND SUBSTITUTION REACTIONS

Hello every one welcome to today's class in the last class we have discussed how to count electrons for given Organometallic complex so we have seen usually the complexes are having 16 electrons or 18 electrons now in today's class we will discuss how this 16 and 18 electron complex reacts preferentially with respect to each other specially let us try to discuss 16 electron complex of course by now I am sure you can given example of 16 electron complex before going into that let us discuss you know 16 electron complex.

(Refer Slide Time: 01:02)



16 e⁻ complex

Often react via an associative pathway.

Reactivity pattern that they often react via and associative path way so there are two ways of reactions one is associative path way another is dissociative path way I will come shortly to that so 16 electron complex what you will often see is they are reacting higher and associative path way let us try to discuss with an example we have one of this complex which is again a organometallic complex nickel complex rather this nickel are chloro and then trith and Phosphine complex.

Now if you quickly do the electron count you will find that this is just 16 electron complex right now if you want to react this 16 electron complex with Pyridine rather you are try to a ligand exchange you will find that the first step will be the Pyridine association with the complex okay so the whole complex remains exactly same pyridine binds with the nickel center to give a pyridine nickel complex now since pyridine is a two electron donor you will find that the total electron count has gone up to 18 so it is now 18 electron complex.

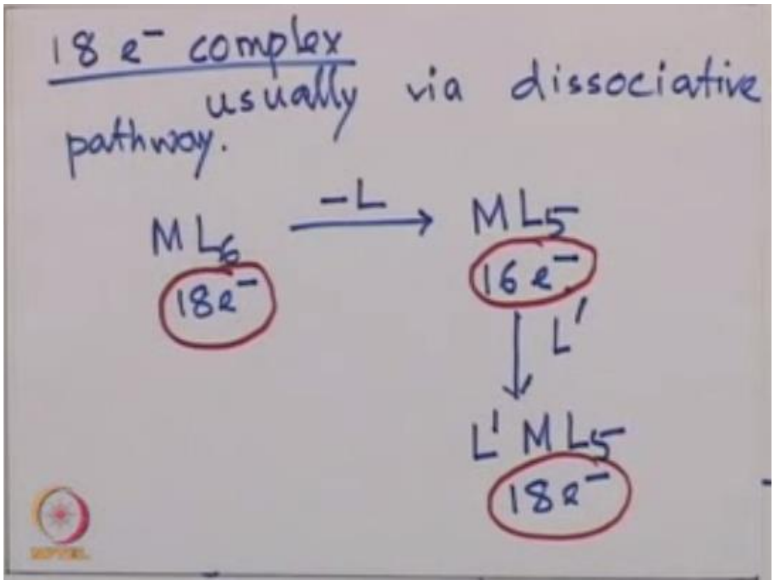
Subsequently what you will see that one of the chloride or the chloride where here will come off and eventually you will have again a square planar complex starting from a square planar complex finial complex is the one where chloride comes out and pyridine take that place to give you sorry this one should be argon to give you the nickel complex so what you see here is nickel which is a square planar complex to start with it is a 16 electron complex reacting with pyridine or pyridine is getting associated.

That is why we are calling it has an associative path way pyridine is getting associated with nickel center 16 electron complex as now transformed to 18 electron complex from which 1 chloride goes out is chloride over here to give rise to a square planar complex which is essentially again a 16 electron complex so what have we learnt that is starting 16 electron complex in this case it is square planar complex reacting with pyridine by an associative path way to give an initial complex which is an 18 electron complex subsequently the chloride comes out to give you the square planar finial complex that is gain 16 electron complex.

So 16 electron complex starting material gives another 16 electron complex in between there is a complex that is 18 electron this associated path way is usually true if you have it starting material or a organometallic complex with 16 electron then usually the ligand exchange in this case pyridine is exchanging with chloride this ligand exchange is happening where an associative path way okay.

So the example you will remember hopefully in case just you want to try you can try with other 16 electron complex to see how things are going whether it is 16 to 18 to 16 or not okay now let us take an example with 18 electron complex how the 18 electron compels will react we have seen right now how 16 electron complex is reacting now 18 electron complex.

(Refer Slide Time: 05:58)



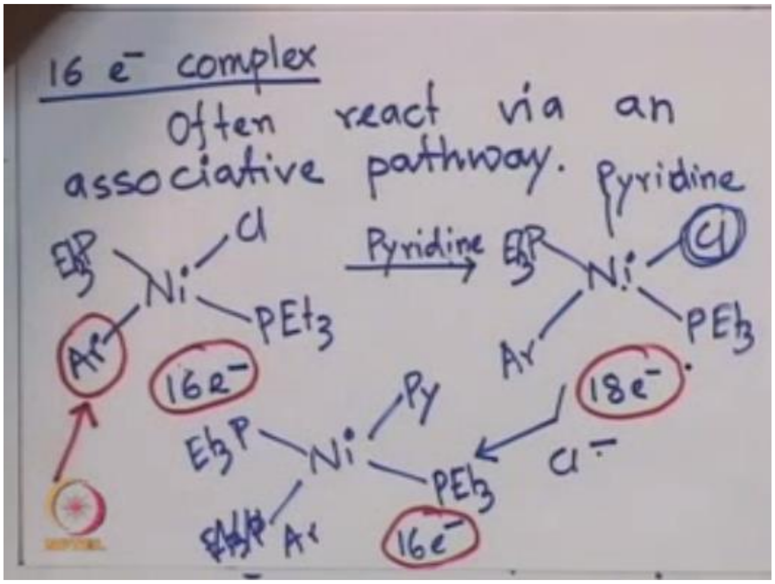
$18\,e^-$ complex usually via dissociative pathway.

These usually react so again usually not hollow is the case but most often you will find that, that is the case usually via A dissociative path way, 16 electron complex recast via associative path way 18 electron complex reacts usually via and via dissociative pathway right, now this 8 for example over here if you have a complex ML_6 that is an 18 electron complex and if you try to do the dissociation of the ligand this ligand dissociation will give you ML_5.

18 electron complex will go to a 16 electron complex subsequently you will see another new ligand L’ can get associated with it to give to L’ ML_5 once again this is an 18 electron complex, so what have we learn here, that 18 electron complex that immaterial will give rise to 16 electron complex, now this 16 electron complex will react with an exogenous ligand like whatever you are using let us say L’ to give to an 18 electron complex, okay.

I will come to this 18 electron complex very soon; let us discuss briefly one more time about the 16 electron complex now as we where discussion.

(Refer Slide Time: 08:02)



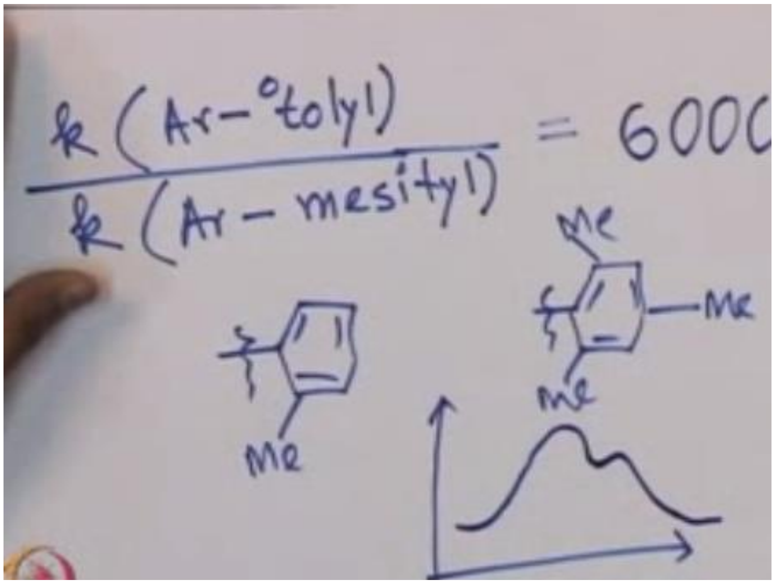
16 e⁻ complex

Often react via an associative pathway.

This 16 electron complex that example we were trying to give is this nickel complex right a 16 electron complex giving 18 electron complex and coming back to 16 electron complex, now of course you might will ask me how to prove such mechanism, can we gather some information or evidences in support of such mechanism, in order to do that what scientists has come up with is very simply.

They have tried to vary this arrived right, how can you vary the aril group, aril group is nothing but avenging ring continuous fragment, right. Now if you substitute this Aril group with different spherically demanding group, for example if you have you know.

(Refer Slide Time: 09:00)



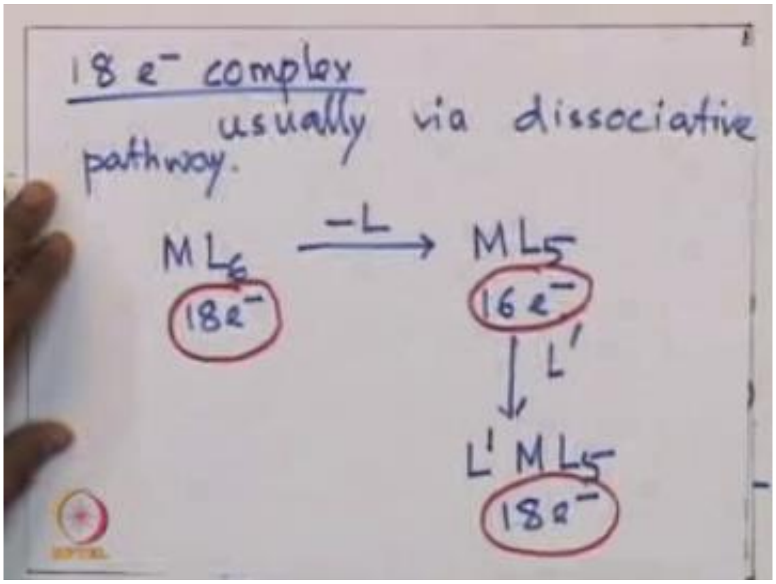
That aril group edge towline means Ortho physician will be having methyl group, the rate of that reaction compared to when aril group is mesityl that means 2, 4, 6 try-methyl complex okay, since it is a associative mechanism you will see that steric hindrance for this mesityl group with higher or huge and thereby the reaction is very fast for the tolyl compared to mesityl, so an exogenous ligand.

For example in that case towards iridium is coming to react with your organometallic complex therefore mesityl due the bulkier one will have much difficulty in reacting with pyridine tolyl is comparatively less bulky, therefore the reaction rate will be faster for tolyl and slower for mesityl if you really do the experiment if you will find that tolyl reacts 6000 times faster compared to mesityl, right.

But in tolyl once again this is going to be your tolyl with Ortho methyl group this is your tolyl and the mesityl will be 2, 4, 6 try-methyl complex, now if you try to do the reaction co-ordinates for this reaction it will be the first step which is the slow one that is the pyridine co-ordination and the second step will be the first or one and that how the reaction coordinate look like.

So this is the period in coordination and this is the one which is to your that disassociation of chlorine okay, that is we are now let us go back to the 18 electron complex we are trying to tell you that 18 electron complex will usually react by a dissociative path way.

(Refer Slide Time: 11:32)



18 e⁻ complex usually via dissociative pathway.

$$ML_6 \xrightarrow{-L} ML_5 \xrightarrow{L'} L'ML_5$$

ML_6: 18e⁻

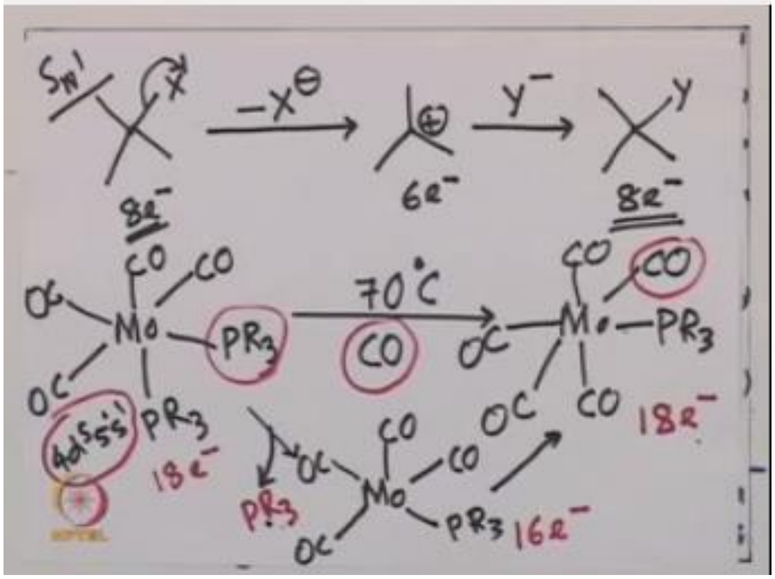
ML_5: 16e⁻

$L'ML_5$: 18e⁻

They are by ML_6 which is then 18 electron complex will be the dissociating one of the ligand to give you the 16 electron complex and this 16 electron complex then will react with the outside or exosonious ligand L' in this case to give you L' ML_5 complex.

Which is again 18 electron complex in the last case also in the 16 electron case also you have seen 16 electron complex is the starting material it gives 16 electron complex at the end in this case also 18 electron complex is the starting material 18 electron complex is the final material but in between there is a 2 electron difference of the into mediate complex all a before that I think it is better if we try to give you an real life example or more familiar example for the 16 and 18 electron complex now.

(Refer Slide Time: 12:35)



All of you are familiar with 8 electron spaces right so if you are talking about SN1 reaction this is 8 electrons species organic compound lives the X – so you are leaving X- and you get a 6 electron complex which is subsequently go for nuclear folic attack to give you substituted Y and again 18 electron complex even in S_n1 reaction you see that exactly 8 electron complex or 8 electron species is giving you 8 electron spaces similarly for organometallic reactions it is 18 electron complex that will give you 18 electrons, 18 electron final product okay.

Now I will give you one real example with an organometallic species this is a molybdenum complex molybdenum do wonderful complexes with carbon monoxide for example one is shown in over here this an Octahedral complex molybdenum is having 4d5 5s1 right can you do the electron count for this, this molybdenum complex Octahedral complex do you will find that so molybdenum in 64d55s1 total 6 electrons 1 2 3 4 5 6, 6 ligand each of them are giving two electron so six times two 12 electrons and 6 for the molybdenum.

One second this is an 18 electron complex so I am writing that this is an 18 electron complex now this 18 electron complex if you hit it at 70°C you will get the final product and in presence of CO one of that first ligand will come out to give you a Penta carbonyl species the starting material as Tetra carbonyl now you will see that it is a Penta carbonyl species so one of the carbon one of slide is getting in one second without counting electron you will be able to tell that this is an 18 electron complex 18 electron complex.

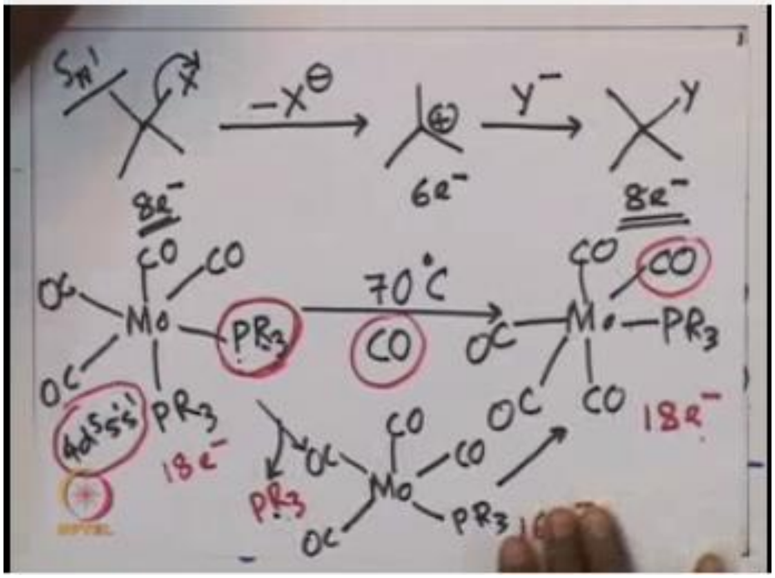
Giving you 18 electron complex but in between what happens is the intermediate you get in these cases is the one where one of the fasting ligand let say this one, one of this first in ligand is coming out this PR_3 is coming out from a Octahedral complex you will get a Penta coordinated intermediate and thereby you will have a 16 electron complex and shown in here the starting material losses one of the first field and now you have from 18 electron complex you have 16 electron complex.

Okay it is clear now can you do the electron count for these cases, this monlybdenum case that we have shown just right now is an 18 electron complex starting material undergoing a dissociation of ligand in this case for spin ligand to give you penta-coordinated intermediate which is 16 electron complex.

And thereby CO reacts with that five coordinated compound you finally once again to give you the 18 electron complex and the final complex will have one of the ligand exchange that is one of the first spin ligand exchanged with carbon monoxide, so tetracarbonyl species gives you penta carbonyl species allow with that we see the intermediate formation and that is a 16 electron complex, just to summarize again an 18 electron complex will undergo dissociative path way to give you 16 electron complex and finally comes back to 18 electron complex again.

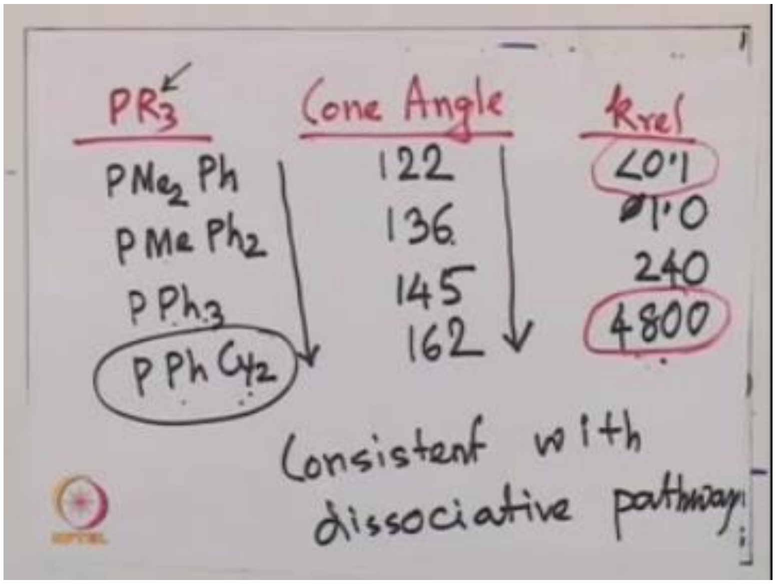
On the other hand a 16 electron complex will undergo associative pathway to give you the 18 electron complex and after that these 18 electron complex will undergo one of the ligand dissociation to finally give you the 16 electron complex. The starting material and the final product it means exactly same in electron count, but it will go electron count change to the intermediates spaces, now for this monlybdenum M complex.

(Refer Slide Time: 18:24)



The one we were trying to discuss, how can you get some information that this 18 electron complex is undergoing a dissociative path way to give you the final complex. Once again what we can try to do is in laboratory we can try to run the experiment where your this first in R substituent can be changed now this substituent R would be your alkali airalie and whatever you want, right this tri R_3 or triR alkali complex. Now what scientist have done previously is this PR_3 when this PR_3.

(Refer Slide Time: 19:14)



PR_3	Cone Angle	k_{rel}
PMe_2Ph	122	<0.1
$PMePh_2$	136	1.0
PPh_3	145	240
$PPhCy_2$	162	4800

Consistent with dissociative pathway

Is taken by different substituent we find that for example, if we have PMe_2 Ph and $PMePh_2$ again this R is varying this R is varying and let us say triphenylphosphine or dicyclohexylphosphine so in all these cases PR are there or would be this R could be different two methyl one phenol, one methyl two phenol, three phenol, one phenol two cyclohexylamine in all these cases PR_3 is the general formula, the cone angle, cone is something you need to know you do it at your, as your homework cone angle actually defines how bulky the ligand is compared to each other, right.

Now this cone angle will vary depending on the bulk of the substituent on the R group, so these cases for the first cases, case it is 122, for the second case it is 136 because the substituent is getting bigger and bigger so one phenol to two phenol angle increases so it becomes construable bulky PPh_3 you would expect that it is in a bulkier 145, one of the phenol or two of the phenol are getting replaced by two of the cyclohexyl which is again a compare bigger compare to phenyl and they are by you will see that the cone angle increases to 162.

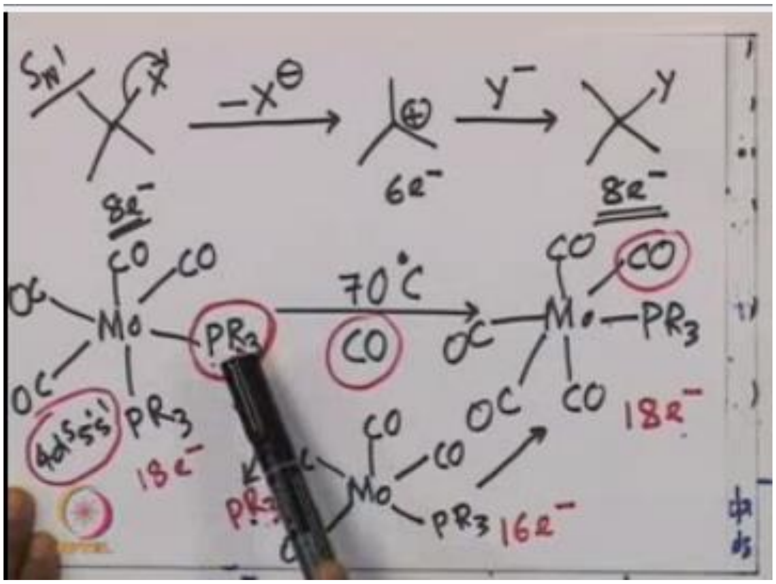
So from this serious as you see the elegant size is increasing the cone angle is also increasing. Now if you look at that 18 electron complex where PR3 was there the relative rate of this complex when you are wearing different fast fin lagan you will find that the dissociation is faster if the lagan PR3 is bulk here.

So bulky lagan gives raise to streak entrants and therefore dissociation of the fast bin becomes much easier, right the relative rate will weary in the order this is the first one is the lowest and then you have relative rate of 1 240 these are not absolute value it is relative to each other and 4800. You see the difference in the reaction rate this is the fasted and this is very fast compare to that the first is very, very slow.

So as the lagan size is increasing you see the cone angle is increasing and therefore streak entrants is quite high and dissociation of the lagan began much more easier that is the first step of the reaction so that will be the faster in case of this mono phenyl dicyclohexyl complex it is actually 4800 times faster compare to this mono methyl di phenyl of that okay, now such an observation will be consistent with dissociative mechanism this observation is consistent with dissociative path way right if it is not dissociative you will not see such observation.

Since that streak walk is controlling the reaction rate or the streak ball first at the reaction so the reaction that be your discussing earlier that is your molybdenum complex this molybdenum complex.

(Refer Slide Time: 23:50)

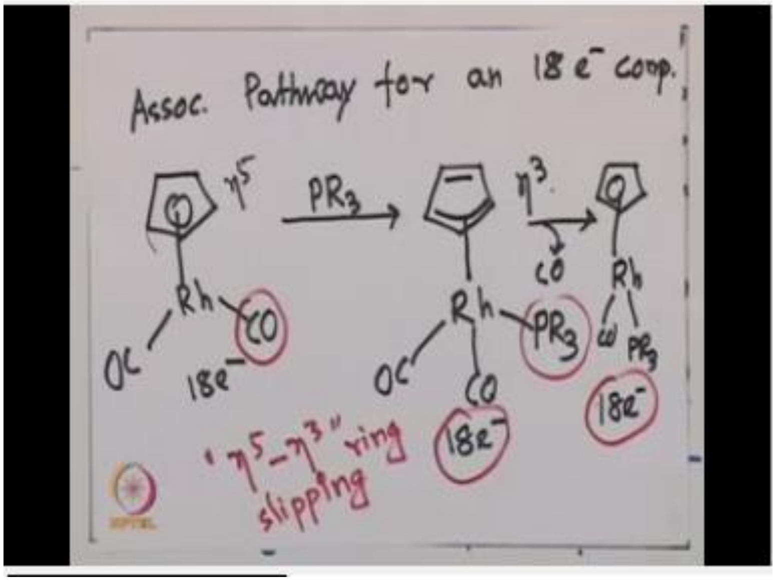


High bigger the PR3 this two Pr3 you have bigger this R groups are one of the PR3 will dissociate faster to give you 16 electron complex that is again it experimentally shows that when you have 18 electron complex the inter mediate form for this reaction is a 16 electron one, which will undergo lagan exchange within exogenous lagan to give you 18 electron complex, that is the reaction truant that is the truant we see for 16 electron and 18 electron complex is it universal that is definitely one of the question might will be having is it allow it is true all the time are going to see 16 electron complex will undergo associating mechanism.

Or 18 electron complex will undergo dissociative mechanism the insert for that question is no it is not allow it is true but most often let us say 99% cases you will see such a you know presidents but there are few cases which you will need to know at 18 electron complex for example can undergo even a dissociative not a dissociative path way but rather and associative path way or we have seen in 18 electron complex going by a dissociative path way.

It is possible in some rare cases that 18 electron complex will undergo associative path way let us try to take one of the example, well this is once.

(Refer Slide Time: 25:45)



It is not a norm it is a special case associative path way for an 18 electron complex but we have learn so far 18 electron complex should undergo dissociative path way but here you will see associative path, what could be the example? Let's take this rhodium complex, okay. Let say cyclopenta Dyane, di- carbonyl complex of rhodium, if you do the electron count once again it is the 18 e^-, now if you try to react this with a ligand, what we expect? You would expect one of the CO should come of, to give you 18 e^- to 16e^- complex.

But in this case it doesn't happen in that way, PR_3 rather under go, association, so PR_3 will add to the rhodium spaces, is unusual, then you might be thinking that 18 e^-complex should be undergoing 20 e^- complex for this, that is not true, what option have in this case is, it is a η 5 complex, right? This is what is known as ring slip.

One of this η 5 complex, are this η 5 complex will undergo ring slip, from η 5 to an η 3 mode, an you will see, $PR_3$is coordinating with the rhodium complex, now you do the electron count from a η5 you have η 3, over all you see agail18 e^- complex formation in this case as well,.

So this process you can call it is a η 5, η 3ring slipping right. giving rise to the 18 e^- complex, 18 e^- complex is not undergoing a 16e^- complex, formation, rather a ring slippage is going on mode of co ordination of one of the ligand, is varying from η 5 to η 3, that lives out an option for ligand exogenous legandPR_3, to co-ordinate with the radium associative fashion alright! Of course this is the intermediate final step would be where this CO comes out, and the η 5 mode of binding of CP gets back to rhodium, and you have a rhodium carbonyl PR_3 spaces.

At that experience of CO, so CO comes out, this CO comes out and η 3 now goes back to η 5, over all again you have an 18 e^- complex, so what have you seen in these example, in this particular example, is 18 e^- complex undergoing a ring slippage, so without any dissociation from the mηl complex we will see that exogenous ligand, in this case phospane is getting associated with the metal complex

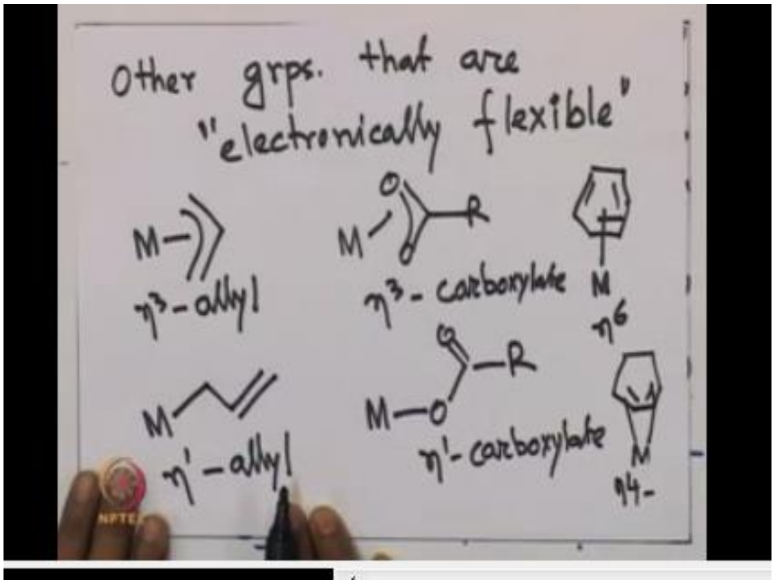
18 e^- complex is very Uncommonly undergoing an associative mechanism, to give you another 18e^- complex, finally one of the ligand that is in this case sure comes out, to give you the final complex and that is the one where we see that, cyclo penta dyne rind η 3 to η 5 mode, gets back to give you rhodium co phospane complex.

Finally once again e once again 18e^- complex, so eaten electron complex starting material, gives you eaten electron complex intermediate, and gives finally the eaten electron complex product which is rather uncommon, and thereby, this is an example uncommon example, that an eaten electron complex is undergoing associative mechanism.

To give you the ligand exchange, well once you know that, that cyclopentadiene can do the ring slipping or flipping is possible, is there other mode of reaction? Is there other example where we can expect such, such ring slipping or such mode of electron flexibility? Okay, next we can discuss briefly other groups that are electronically flexible. What we have seen? Cyclopentadiene is electronically flexible at their other example, indeed they are for example, you can have η3 allyl complex.

And this allyl complex can undergo again similar to ring slippage, it is now η1 allyl, so η3 to η1 slipping, you can have similarly, carboxylate linkage where you can have η3 carboxylate undergoing similar ring slippage to give you η1, so this will be η1 carboxylate or other immerse examples include the metal coordination with benzene by η6 mode, now the slippage can be possible to give you an η4 mode of coordination.

(Refer Slide Time: 33:07)



Other grps. that are "electronically flexible"

So they are some example, of course there are lot of other phase you can see, electronic flexibility η3 allyl giving rise to η1 allyl or vice versa, you can have Librium between these two things. You can have η3 carboxylate giving rise to η1 carboxylate; also η6 benzene can give you η4 benzene, so what so far in the last part we have understood is, although there is a general reactivity pattern for 18 electron complex going to 16 electron complex as an associative path way and then 18 electron complex finally forms.

There could be some example, there could be some cases where ring slippage is possible from starting with a 18n electron complex, we can get intermediate 18 electron complex, in these cases as you seen right now, an allyl or the carboxylate or a η6 benzene complex, can give rise to such 18 electron intermediate with slippage, are not happening usually, each complexes are very rare, not all the complexes with these ligand will undergo the ring slippage as we discussed.

But in some case, w can expect that this ring slippage is happening, okay. Once again it's not a common phenomenon, it happen only in rare cases, so with this today’s session, I would like to conclude that I hope you learned the reactivity pattern of 16 electron complex and 18 electron complex, as well as there are few examples, where 18 electron complex not follow the text book rules, and those are the warns directly, those art thee warns quit interesting and those are the warn which research are found quit attractive for carrying out lot of unusual reactions. Okay will e you again in the next class, till then bye, bye.

NPTEL
Principal Investigator
IIT Bombay

Prof. R.K Shevgaonkar

Head CDEEP

Prof. V.M Gadre

Producer

Arun Kalwankar

Digital Video Cameraman

&Graphics Designer

Amin B Shaikh

Online Editor

&Digital Video Editor

Tushar Deshpande

Jr. Technical Assistant

Vijay Kedare

Teaching Assistants

Arijit Roy

G Kamalakshi

Sr. Web Designer

Bharati Sakpal

Research Assistant

Riya Surange

Sr. Web Designer

Bharati M. Sarang

Web Designer

Nisha Thakur

Project Attendant

Ravi Paswan

Vinayak Raut

NATIONAL PROGRAMME ON TECHNOLOGY

ENHANCED LEARNING

(NPTEL)