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TECHNOLOGY ENHANCED LEARNING

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Organometallic
Chemistry-I
Prof. Debabrata Maiti
Department of Chemistry, IIT Bombay

Module No. 3

Lecture No. 15

EXTERNAL ATTACK BY LIGANDS & REDUCTIVE COUPLING

Welcome everyone, in today's class we will discuss two final topics of the fundamentals of organometallic chemistry and specifically for their reaction mechanism and their type of reaction that we would like to discuss further in later classes. Today we will discuss external attack by ligands and subsequently we will discuss the reductive coupling reactions. So external attack by ligand is the first topic.

As you know the organometallic complexes promotes a number of unusual reactions without the organometallic complexes such reactions will have been impossible to happen. For example, if you have simply olefin you would like to get it attack by any external nucleophile and you do that, the simple answer will be most often you cannot, but what is that olefin is attached with a metal complex then perhaps you can get a cationic intermediate as where a nucleophile encourage attack on the olefin.

So organometallic intermediate or metal centered in particular is promoting such an atmosphere that the olefin which is otherwise and reacting towards a certain nucleophile becomes reactive and therefore and wide variety of reaction can be promoted by utilizing this static, let us look at external attack by ligand. So first of all as I was trying to tell you it is acting as an of ligand towards attack by external nuclephile.

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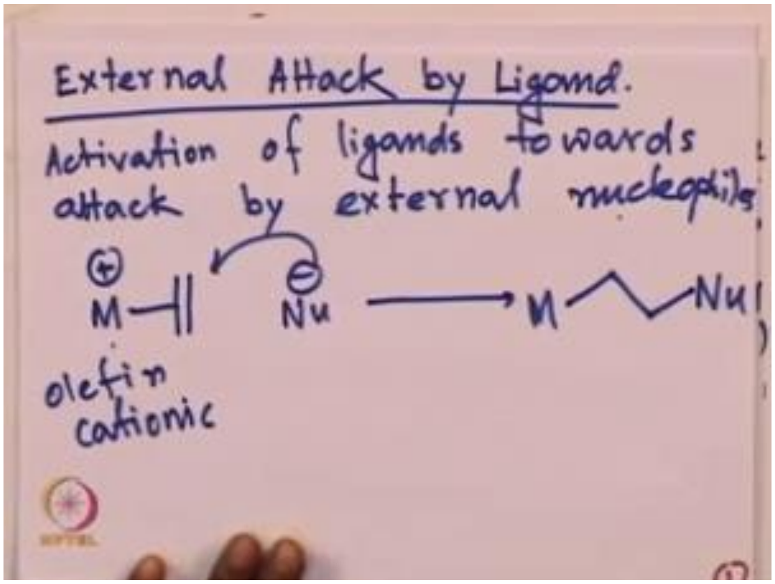

External Attack by Ligand.

Activation of ligands towards attack by external nucleophile

So from an outside source in nuclephile will attack on the ligand then the olefin and that ligand is associated with the metal center, without association of the metal center this attack cannot be feasible. So let us say you have a metal olefinic intermediate you take that olefin cationic show over here, you feel that olefin will be cationic in nature and then external nucleophile will come and attack to give you the overall product and that is in this metal nucleophile intermediate.

Is this metal center was not there simple attack of nucleophile on this olefin would not have been possible in a normal scenario. Of course, this type of there are variety of reaction that can be of this type mostly we will discuss by the few example over here and try to say wow this metal olefin or metal ligand interaction is helping you to get the nucleophile on to that particular ligand okay and example if the iron complex okay.

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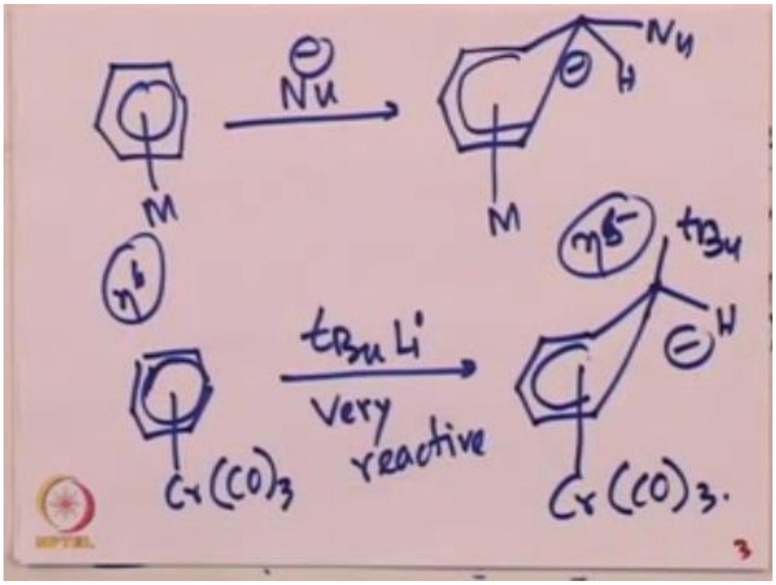

The first example will be one where you have a iron complex associated with carbon monoxide so to this and this CP + where you have olefin coordinated with it this is an 18 election species now this is a intermediate over here meth oxide for example will attack and given iron meth oxide complex with a co and Co to be there cyclopentadieny with so this is one of the clear example of a nucleophile attack on ethylene for example in this case where did oxide is a nucleophile and you get this alkyl metal alkyl intermediate from there okay other type of reaction that can be promoted is the metal you have metal cyclopentadieny or been in complex.

For example metal benign complex it has 6 metal benign complex which then can be attacked while external nucleophile so let us take a look at one of those example metal alkyl or that is metal benign or metal benzene intermediate it has 6 benzene intermediated is associated with the metal and then those metals in the it prompting an atmosphere to those benzene it has 6 benzene rings so that one of the carbon center of the benzene ring now can be attacked by an external nuclephine okay.

Let us try to look at that so you have η benzene and there is a nuclephine associated with it and over carbon reaction you are going to get a nuclephine getting attacked with the this particular center to give you an η 5 metal center okay. So this is an η^6 metal center over all now you have η5 metal center if particular example of this type could be the chromium complex so you have η^6 chromium 3c carbonyl complex tertiary butyl lithium for example one of the nuclephine which is very, very reactive intimidate now over all can be the this product where your terbutaline is attractive on W wave overall to deviate this η 5 intermediate and this chromium $Cr(CO)_3$ complex.

Of course as you can see in this cases in both the prototype and the example chromium complex I will try to discuss, both these cases we have seen that aromaticity is getting lost and in the form of course that is going to be one of the very difficult process one should yeah once can be imagine that have been using the aromaticity is going to be very difficult.

So perhaps this nutrition attack is not be feasible in the what happening in these cases is some something like carbon monoxide to draw the ligand draw the negative charge so that overall this you know that anemic intermediate that is getting generated over there can be stabilized through a metal center, so it is essential or it is important to have the carbonyl is to stabiles the intermediate.

Therefore the nuclear fuel attack can be possible so overall what we have seen so far in the iodine complex the olefin, edge fin encourage to be attack by an external nucleophile i think it talks like in this we have seen terbutaline lithium is attacking the η6 benzene which is coordinated with the metal center such as chromium, pres- carbonyl species, since it is a pres-carbonyl species such an attack or become feasible.

Using aromaticity still is possible because the generated intermediate will be dense stabilized by this 3 carbonyl inter species, okay let us try to look at related some other example of course we are coming here with the Pie ally chemistry, right.

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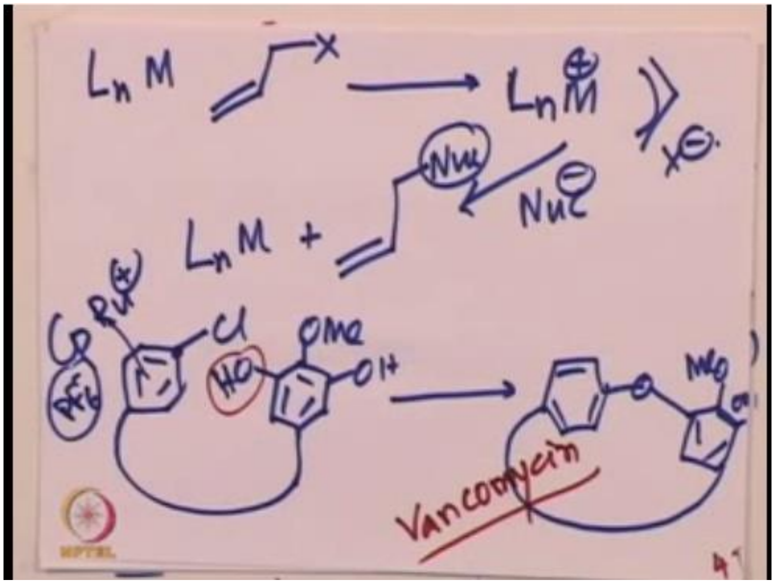

So in the last case we seem that attack is happening by an external ligand you can have let us say this ally halide or any ally intermediate overall you can get this organometallic intermediate where you have this ally this is generated from there, now from there if a nucleophile is attacking we are going to get L_nM plus this nucleophile over here, this is also an example of a nucleophile attack by an external attack by a ligand.

Here any nucleophile you can attack on these intermediate metal or organometallic intermediate that we clearly see that the ally halide for example, if the starting material on that this intermediate that involve with the Pie ally intermediate where Pie ally now is getting encourage to add the attack by a nucleophile from outside and we see that overall this is a allelic, allelic nuclear intermediate.

That is getting generated this sort of reaction that also be applicable for even bigger molecules such a methodyl products is this is one might will be familiar with the Bankomicen as a you know Bankomicen is the one of the last we sort for the antibiotic and you know this first centrists of the Bankomicen was done by actually by this technique we will just give you an example where they maintain step or the key step in all the attack by the external ligand so it is 9.42 complex for example.

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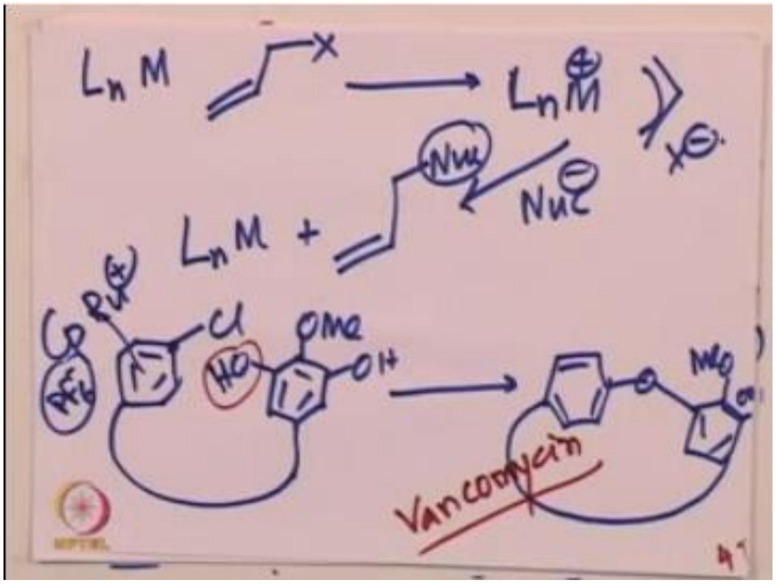

The nutro complex first so this is, this is the complex you have it huge attachment I am not going to draw the all of it because it is really gigantic attachment and overall you have methoxide over there hydroxyl over there right and the product that one is going to get from this complexes is you know the overall this hydroxyl is that attack at this carbon center did you do the final product as I was saying this is a gigantic molecular and you know draw it so you have this final product in the form of 4Me and hydroxyl over here.

Right but you know in these complex of course if you are looking at this reaction this is the starting material where you have the halobenzyme and in one hand and you have the phenol in the other hand so you have two counter path way in one part you have the halobenyzme and in another part you have the nuclear file that is hydroxyl you want to replace the halogen with these hydroxyl group in general such reaction is not going to happen if you have a chloro benzyme for example and if you have a phenol.

This if you want to displace the chloro with the phenolic oxygen you are not going to get this reaction that very easily without the help of organometallic intermediate or organometallic spaces now in this particular case what scientist has done it that chloro benzyme continuing rate they have interacted it with a metal center therefore this benzyme ring feels encouraged or benzyme ring can be then attacked by an external nuclophy in this case it is an internal one.

Because you have a intra molecular setting and overall then if you look back again with this complex it is a ruthenium complex catatonia complex you generate with the PF6 counter an iron over there so this species without the ruthenium this reaction does not occur with Cp ruthenium and PF6 – once you form a complex or institute to you form a complex and then this hydroxyl group can attack or at this ring this hydroxyl group can attack on this ring to give you the overall product and this is the synthesis of one of the key step of early vanconmycin synthesis, okay. So what we have learn so far in this part external attack by ligand is one of the very powerful technique but it has to be utilized quite efficiently for the reaction propose.

It is even possible to synthesis a variety of natural products by utilizing this technique where organo metallic intermediate will make a positive charge or partial positive charge on the electro file or show to speak let us say on olefin or on the benchin ring where it has expense in more it was attached with the metal center and therefore those partial positive charge which is created by the metal center now can be utilized by an external or a intermolecular substance to give you the very interesting example of such category of the reactions, okay.

So in this topic what we have learned is if variety of reaction can be promoted by an external ligand file but this reaction needs the help of the metal center without the metal center such a reaction may not be or most likely will not be possible. The next topic will see the reductive coupling reaction where we will try to see that alkyne and olefin putting hands together and to form a jaigantic molecule or a heterocycle or a metal cycle reaction which can be of real great example for the organo metallic chemistry, so next topic we are going to see is reductive coupling.

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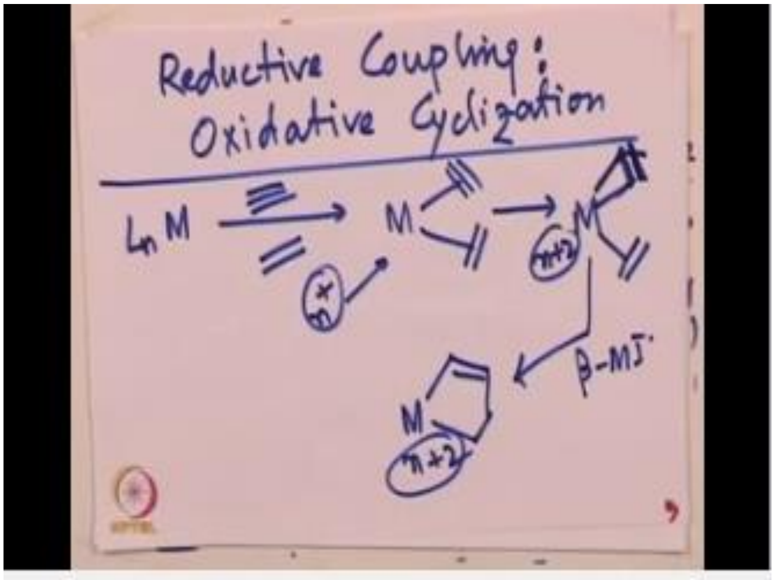

This is almost the last topic going to be on this series of reactions where we were discussing various techniques to do the reaction, right. The reaction mechanism show to speak it is the oxidative cyclization process, now this is again one of the other type of reaction which sometime we see of course say we have a d electron space in this metal center ligand metal center alkynyl and alkaline we take let us say for example alkaline and olefin both what we have is metal alkaline interaction as metal olefin interacts of course let us say this is n class oxidation state over here.

Subsequently what we can happen what we can see is this metal alkaline can interact with the metal center in a three member fashion and can give you this bond where one of the alkaline is getting bond inserted in to there, and of course you have steal the olefin, interacting with it, so beta migratory insertion occurs further with this show from this intermediate where you have this double bond and to double bond with coordination with the metal centre, then you have metal n+2 oxidation state of course this will be also n+2 oxidation state.

Over all you have an intermediate which is pi member in nature and therefore from there on we can get the reductive limitation to get a Varity of rod, so this is an example of reductive coupling, where oxidative cycles, occurring we have a metal centre, and metal centre is having an alkaline and olefin interaction in the first step, alkaline with associated with the meta centre further to give a 3 centered or three member meta cycle, intermediate with the olefin double bond.

That intermediate is going to be very worth reactive, and then over all that 3 member meta cycle intermediate will react, with the olefin, and there by forming a over and final five member meta cyclic intermediate to give you the product, and of course this five member meta cyclic intermediate you can react with different, let say halogen, its bromine, chlorine, iodine, to give the carbon halogen formation, at those metal carbon centers, okay. Let us look at other examples of this category. And which is by neighed actually, and here we have.

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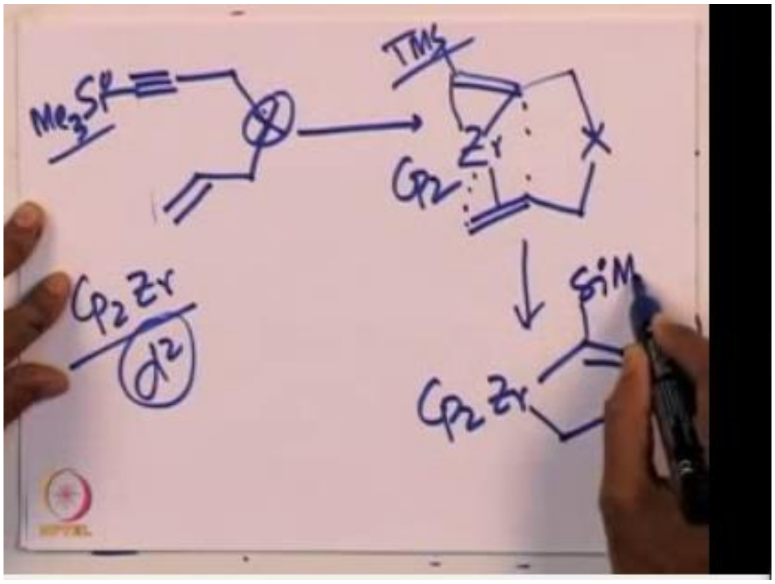

N alkaline intra molecular substance in this case, alkaline is there, so it is an intermolecular alkaline olefin to gather, of course you can have for here let say , you can have x over here, you can have NBN, benzyl oxygen over here, or some other even carbon you can have, over all what you can have is a CP$_2$ zirconium species reacting with them to give this is a d$_2$ species of course, and first you form an intermediate zirconium is associated, with this is tri methyl CL.

Sylile is also known as, TMS usually we write down as an d then from there on, we can get an intermediate, where let this X comes in to the picture, and the olefin, attach it is with it to give the further intermediate, so over all what we are having is, an alkaline and olefin together, attach, intermolecular substance this alkaline is interacting with this zirconium ship cyclo penta dyne zirconium species.

To give you a three member medulla cyclic intermediate from there on, this oxidative cycle ij's and happens and those are subsequently, you will get a, of course Cp2 is over there, cyclopentadine zirconium and you get intermediate, where these two bond formation happens, and the metal gets attached within over there and five membered cycle, five membered, the cyclic intermediate cyclic formation happens and then polyphine or Tms membered.

So what is happening over here is metal is interacting over here and forming a three member intermediate and this 2 carbon centered then subsequently bond and of course it is between the two centers and it goes on to form five member cycle there and further five member cycles there over there. If you want you can treat it with x2 x both the x can join over there to give you the final product. So in today's class we have learned so for that external attack by ligand is a, is a process where metal spread ft or metal, in courageous the external gang attack on the unsaturated part of the molecule or polyphines specifically and subsequently have seen oxidant in cyclosation reaction.

Where of core by detective coupling, where we have seen that alkaline and oliphine can be stitched together to give you the five member medulla cycle or even the two different five membered ring depending on the nature of the external substance. Now these are different type of reaction so far we have discussed, we have seen trying from the very beginning we have seen oxidative addition, reductive addition subsequently α insertion, α elimination β extraction, β elimination and all different types of migratory.

Insertion we have seen and very recently as you allow 4 centered reaction mechanism followed by 2+2 reaction, external attack by ligand and very recently we have seen the oxidative cyclation process. So thee, all these methods are going to very useful if we are going to apply this methods for synthetic setter, if we are going to see reaction mechanism, is going to be very huge full technique to you. In a moment, in the next class we will be discussing how these very fundamental processes are almost invariably there in every reaction.

All these fundamental steps that we have discussed o far will be utilized for so called different name, we accept or more famous reaction which we have seen all over in the organ metallic chemistry. We will take all the understanding to effect for discussing those simple reactions. In the next class specifically w will be discussing the hydrogenous reaction and how thee hydrogenous reaction are utilizing these basic principle to come up with the hydrogenous and see of different unsaturated molecule, okay. Till then, se you so, keep studying and next class will be on the hydrogen nous. Thank you very much.

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

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Project Attendant

Ravi Paswan

Vinayak Raut

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