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Organometallic Chemistry-I

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Module No. 3

Lecture No. 14

FOUR-CENTER REACTIONS
[2+2]REACTIONS

Welcome back so today we will discuss I think you know one of the most important reaction mechanism and that is σ bond metathesis of course related to that or subsequent to that we will be discussing 2+2 reactions. So today is topic is going to be four center reaction mechanism also known as σ bond metathesis and 2+2 reactions. Let us look at that so first we will discuss four center reactions.

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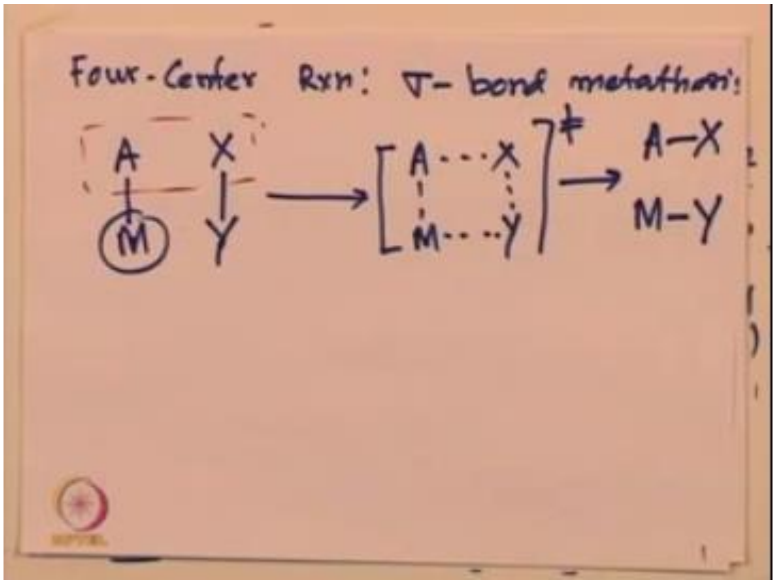

Four-Center Rxn: σ- bond metathesis

All for four center reactions you need of course four centers right, that is that is the beauty of it you have to have four centers what are there, you have you can have a metal center let us say you have attached A with it and you have X along with that you have Y. Now this is the four center 1,2,3,4 the transition state that involves for these reactions are of course going to be the interaction among all these centers and the net result will be the exchange of partners so now you have X with A and M with Y.

So essentially what you have seen in this particular case is these two guys go together and other two guys going together so this is a four center reaction also known as σ bond metathesis you have the organometallic intermediate which is crucial for this reaction anything you can take you cannot expect a four center reaction organometallic intermediate with a substituent and an external substrate which can come and interact with the organometallic intermediate.

Therefore, four centers can come together to give you the exchange of partners and effectively then you we are going to get a σ bond metathesis four centered σ bond metathesis reaction. Most importantly if you try to look back at these reactions again the very first thing one should note is there is no change in oxidation state.

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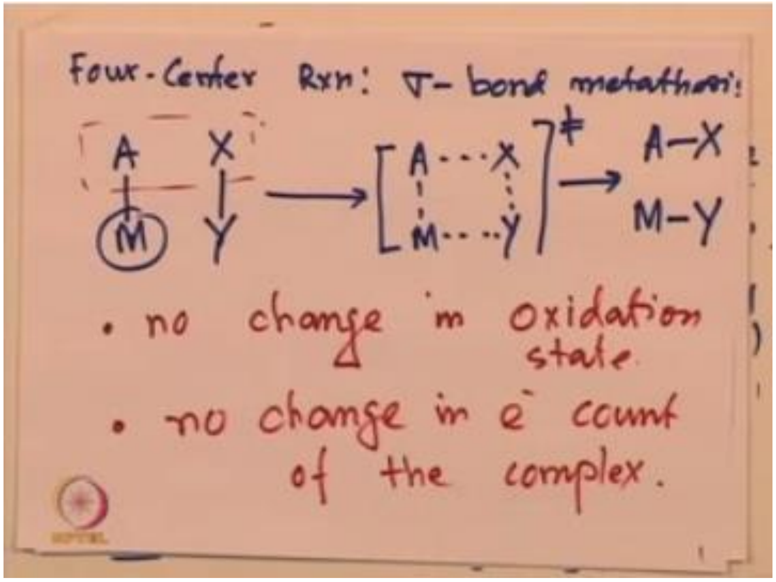

Four-Center Rxn: σ- bond metathesis

$$\begin{matrix} A & X \\ | & | \\ M & Y \end{matrix} \longrightarrow \left[\begin{matrix} A \cdots X \\ \vdots \quad \vdots \\ M \cdots Y \end{matrix}\right]^{\ddagger} \longrightarrow \begin{matrix} A{-}X \\ M{-}Y \end{matrix}$$

- no change in oxidation state
  Δ
- no change in e^- count of the complex.

No change in oxidation state, oxidation step that is most important and of course there is no change in electron count, count of the complex. So these are the two most important feature of these reactions that four center reactions usually are usually are undergoing absolutely no electron change or no electron count change at the metal centre it is virtually the exchange of partners without having any trouble and without having much of an barrier.

It is a very, very simple reaction okay, one partner was there just a partner exchange happen at the metal center and resulting or of course the organic compound also changes the partner. Now this is a σ bond metathesis right, now how are we going to know that σ bond metathesis is going to be any different compared to the one or the more famous one or the more early one such as only known one such as oxidative addition and reductive elimination.

Essentially if you have the oxidative addition and reductive elimination you can exactly get the same product. Now most important to understand how oxidative addition reductive elimination sequence is different from σ bond metathesis and in which particular case the σ bond metathesis is occurring oxidative addition reductive elimination is not occurring. Essentially they can give the same product oxidative addition plus reductive elimination can give you the same product exactly same project as that of your σ bond metathesis. Let us look back and that alternate mechanism one time.

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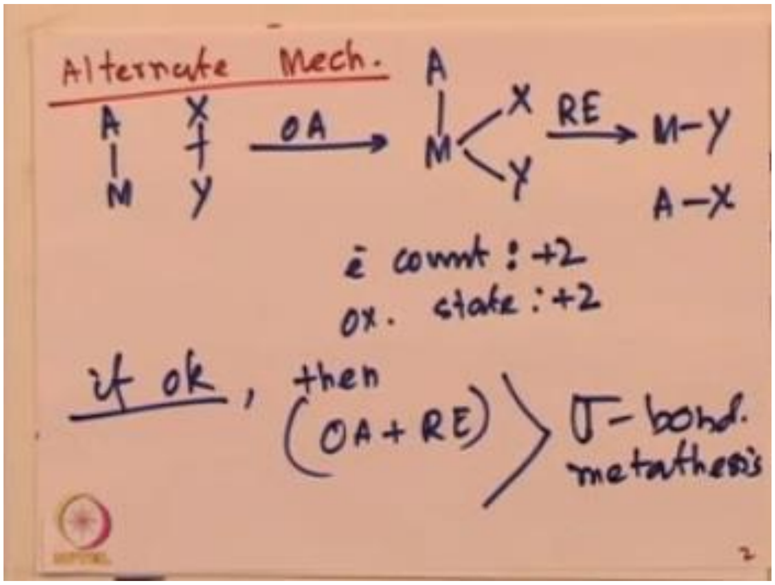

Alternate Mech.

$$\underset{M}{\overset{A}{|}} + \underset{Y}{\overset{X}{|}} \xrightarrow{OA} \overset{A}{\underset{|}{}}M\langle^{X}_{Y} \xrightarrow{RE} M-Y \quad A-X$$

ē count : +2

ox. state : +2

if ok, then (OA + RE) > σ- bond. metathesis

So the alternate mechanism that is oxidative addition and reductive elimination for the same product formation, so the alternate mechanism involves your intermediate MA and XY as you are saying in that place these who are going together and this one was coming together but if you imagine oxidative addition it is going to be all the way you know oxidative addition into this so overall you are going to get x and y and subsequently you are going to get reductive elimination to get m y and a x of course electron count electron count for electron count if you have for this one it is going to be plus two oxidation state is going to be also plus two also if okay.

If possible if okay then oxidative addition plus reductive elimination are going to be more preferred than Sigma bond metathesis and that is what is most important thing to understand that most often we see oxidize sequence of oxidative additions and reductive elimination of course both of them oxidative addition and reductive elimination and Sigma bond metathesis can give you the give you the exactly same compound and most often oxidative addition and reductive elimination is energetically favorable or the preferred pathway compared to Sigma bond metathesis.

But there are situation where oxidative addition reductive elimination sequence is not likely and therefore Sigma bond metathesis is the only pathway the same way we have seen alpha elimination versus alpha instruction where alpha obstruction is only pathway only remaining pathway for the product formation and alpha elimination is ruled out then only we are going to get the Alpha obstruction same is for β elimination versus β abstraction we have seen β obstruction is happening only if alpha elimination is not going to happen due to electronic factor okay.

Similarly if oxidative addition and reductive elimination this combination is not going to happen because of certain electronic requirement we are going to get Sigma bond metathesis let us try to take one example of Sigma bond metathesis of course there are some example very well known famous examples are there will take just one example to discuss sigma bond metathesis and then we will try to approach in that scenario we will try to discuss why oxidative addition is not favorable.

And therefore that sequence of oxidative addition and reductive elimination is not going to happen okay.

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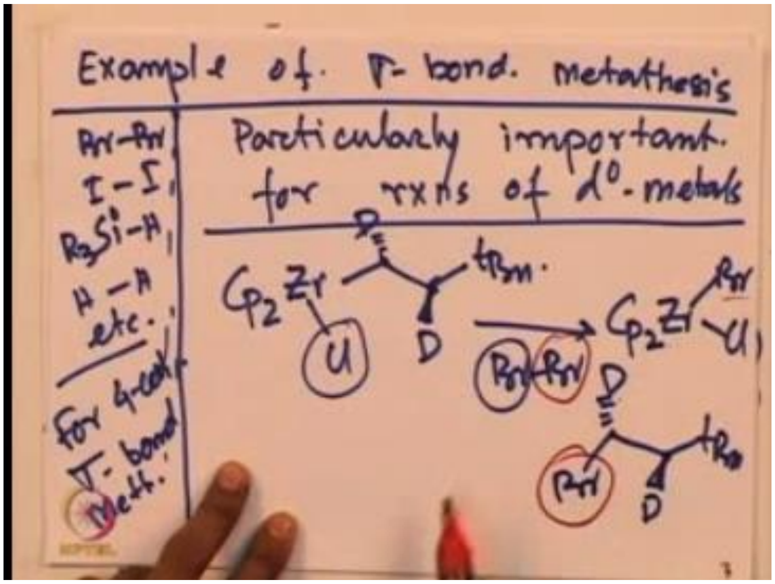

Example of σ- bond. metathesis

Br–Br, I–I, $R_3Si–H$, H–H etc.,

For 4-cent. σ- bond Meth.

Particularly important for rxns of d^0-metals

Now example of σ bond metathesis of example of σ bond metathesis of course that XY group we can have a number of XY group such as bromine we can have the bond which can undergo this σ bond metathesis and a series of things we can have and you know this is for 4 centered σ bond metathesis σ bond metathesis we can have this all these different things bromine as you can see bromine iodine silayl hydride hydrogen etcetera if you can undergo σ bond metathesis.

Now this is particularly important for d 0 metal center particularly important for reactions of d0 metals this is what one of the most important thing to remember this is particularly important for d 0 metal for example d0 metal center you have seen a lot we will discuss one over here and with a stereo center let us say you have deuterium over there and this is a dash trim to pick molecule and you have the zirconium alkyl species with two stereo center okay, and you want to do a abomination reaction with this right.

Now if you want to do huge bromine of course this one of them so these are the one which can undergo sigma bond metathesis readily so the product you are going to get is CP to zirconium brome and chloral the other this is the one which is this one and one of this one is going to be with zirconium and this centered over all over here you can you can get a very good product formation and where this bromine is coming and getting into the product.

So what you have seen so far here is you have two bromine centers one bromine over here and bromine is going over here. So the exchange of alkyl group okay with this one of the bromine is happening and then other bromine is coming with this alkyl group to give you the product. Of course, this is in this case particularly if you look at the example we try to discuss with is zirconium 4+ zirconium having 4+ oxidation state 2 cyclopentadiene ringing is there and one alkyl group is there and one halide is there.

Zirconium 4+ it is a d0 metal centre and therefore it cannot undergo oxidative addition with bromine, oxidative addition will require a +2 oxidation state from their own since it is already a d0 center it cannot undergo oxidative addition. Therefore, if you see the product formation in this particular case we have seen the exchange of partners there is only one way left for this the conium d0 metal centre to give this product and that sigma bond metathesis not oxidative addition reductive elimination.

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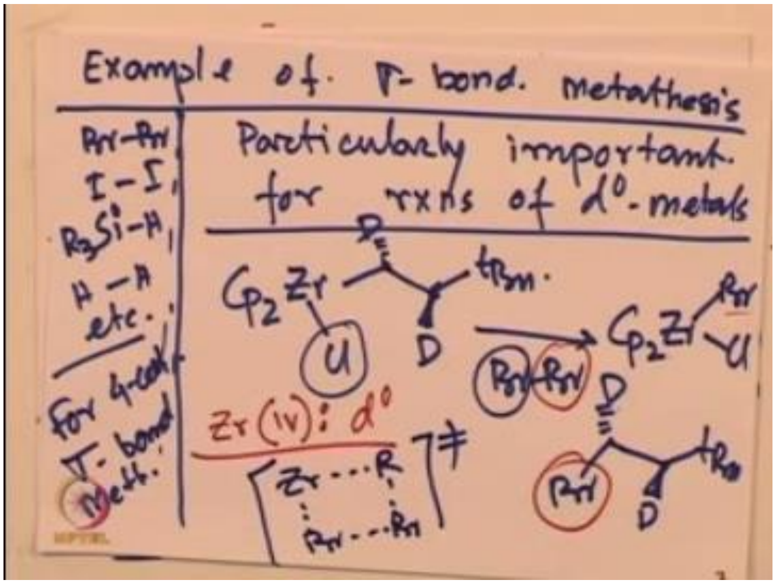

So what we see here is a specialized case very special case with zirconium 4 d0 metal center and we have also seen that it is going to give you this sigma bond metathesis that we were discussing over here. So this is the sigma bond metathesis reaction. Also another thing is more important to notice we have taken a center which is optically active, well if you look at the product formation you will see that retention of configuration that is another you know strong take-home message is for sigma bond metathesis reaction it is a 4 center reaction mechanism which undergoes a retention reaction with retention of configuration.

If you look back at the product formation once again the product formation in that organic fraction this molecule is retaining the configuration. So retention of configuration is one of the most you know preferred pathway or most important thing for the sigma bond metathesis reaction there is no change in formal oxidation state of the metal. Of course, it is a d0 metal center, zirconium 4+ there is no formal change oxidation state change of this metal center.

Since this oxidation state change is not possible therefore oxidative addition and reductive elimination sequence is not likely in this case only option left once again is sigma bond metathesis okay. But one must remember that oxidative addition and reductive elimination is combined this process is a preferred pathway almost always invariably you see such pathway oxidative addition and reductive elimination.

Sigma bond metathesis is a very highly engineered pathway only some few cases, but those are very important cases which expect that sigma bond metathesis may happen okay. Now what we next try to understand or will understand is 2+2 reactions right, 2+2 reaction actually one of the I think most importantly, one of the most important reaction and its rich the beauty and the type of product formation type of flexibility it gives I think it is unparalleled.

And it is loved by many and practiced by many and it is one of the powerful technique for even very complex very, very complex molecule synthesis shows such as natural product synthesis and natural product synthesis particularly these 2+2 reactions are widely used but it is important therefore for organometallic chemist or people either doing organic organometallic or inorganic side of organometallic I think both the people should both the areas of people should understand the sigma bond metathesis is very simply and in the mechanism underlying principle is really simple and that is what makes it so important. So 2+2 reactions next topic if we are going to discuss is 2+2 reactions.

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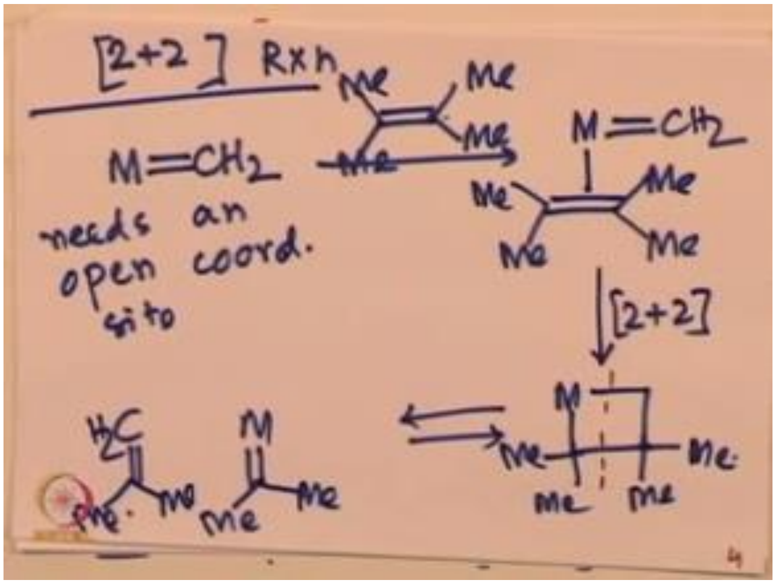

Of course for 2+2 reaction one could imagine that there is a necessity of having a PI bond in both the coupling partner right now one of the most common or very simple way of writing this example is metal this have being intermediate of course it needs an open coordination site for this reaction to happen and an olefin likely these okay let us say for example you have this olefin it is very easy to track that is why we took this olefin what first step would be your coordination you have to coordinate your two center so you have 1, 2 so 2 1, 2 these are the 2 centers where 2+2 reaction will undergo and you have this olefin over there.

So it is coordinating first is an open coordination site which is let us say it is happening now next step is the actual this is the olefin binding then is the 2+2 reaction where you see the intermediate is going to have your methyl, methyl, methyl, methyl, methyl so overall you can get then the exchange of partners okay and then over here you will get this partner exchange gives you the product formation which looks like this.

So what we have seen over here it is a it is a 2 + 2 reactions right and this 2+2 reaction you have to olefin center so to speak one is metal carbine another is simple olefin you have first interacted the olefin is the metal center and therefore these two centers the is ready to undergo a 2+2 reaction you have a 4 - member metal a cycle intermediate wherein you have an opportunity to exchange the partner.

So the metal carbon partner the carbon part or the CH2 part in this particular case is now exchanged with the olefinic carbon center so one of the olefinic carbon Center is now attached with the metal center after the 2+2 reaction and the metal carbon centers carbon is associated with the olefin center so it is a perfect example of the of the exchange of partners okay and this is how actually a lot of transformations are done where you start with something.

And then let us say metal carbon intermediate and then you bring in another olefin another fragment olefin or even alkyl or other unsaturated part of the molecule and then simply you are able to swap the position you are able to exchange the carbon center and or un saturation Center and thereby giving rise to an wide variety of complex which perhaps could be an think of any other methodology.

And it has been popularized it has been industrialized it is one of the most preferred reaction I think people look at specially the natural product synthesis or the complex molecule synthesis people and the efficiency is quite good for this reaction and this is one of the most famous reaction one can look at let us try to look at one of the example and few more features of these 2+ 2 reaction’s.

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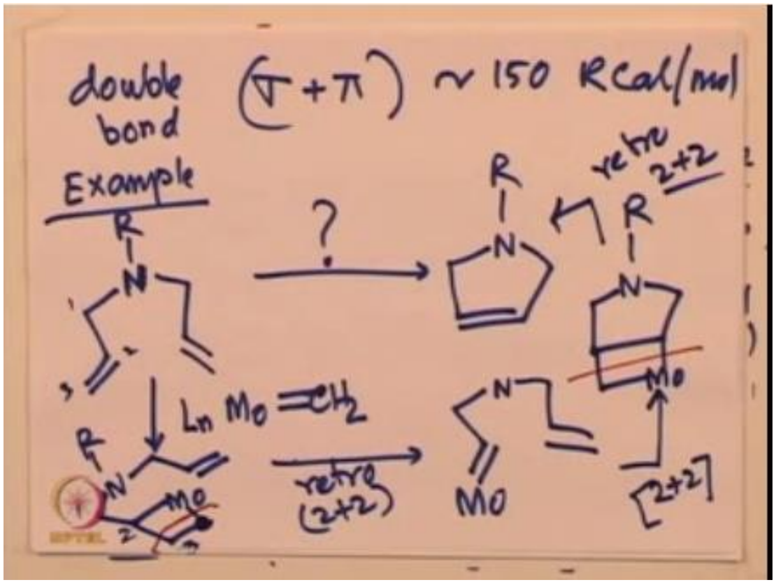

So in this case if you see that you know double bond σ +π combined you are having 150 KCal/mol now one of the example that I think need to be discussed it is a very simple example let us say you start with a organic substrate like this, okay. Now beautiful reactions what you need to get is or what do you get by this process is this, so if you are not familiar with σ bond metathesis this seems very odd to you.

How can you get this product starting from this product but if you are a family at with σ bond metathesis 2+2 reaction I think it becomes obvious and it becomes so obvious that you know that one can just look at it and tell that this is a σ bond metathesis and this is what exactly would happen, for example in this particular case we are going to get these molybdenum intermediate with these are with this 2+2.

So what we are having here is this curve this olefin and this partner undergoing 2+2 reactions okay, so one two let us say three one two and three and this is molybdenum and this is molybdenum this carbon Center this carbon Center over here, so 2 & 2 2+2 reaction gives you this intermediate where one two three, one, two, three the center is there and this carbon Center over here is over here.

So you have four centered organometallic intermediate or Mottola cyclic intermediate which then can undergo retro 2+2 okay to give you out this part, so this part will go out overall you will get this molybdenum carbine is now getting into the organic substrate directly so you have now molybdenum attached or inserted into the substrate itself and once you are able to insert that and that will be it.

You should be able to get a very good reaction subsequently to give you a intermediate which will lead you to the final product formation and in this particular case as you will see this molybdenum again this is a 2+2 reaction going on so first 2+2 and then return to plus 2 and then again 2+2 these sequence of events happen to give you this intermediate which can then give you the final product.

So again it is under it will then undergo is retro 2 + 2 where this part will be broken and double bond will be formed, overall you have the retro 2+2 again, so what we have seen so far in this particular example, we have seen that you know Sigma bond metathesis type of reaction we have basically we have seen a 2+2 reaction we start with an olefin partner organic substrate there we have added a molybdenum carbine, okay.

This molybdenum carbine intermediate exchanges partner and molybdenum gets inserted into the into the organic part so 2+2 and retro 2+2 to get the molybdenum into the organic substrate but the organic substrate once it is having molybdenum then the intra molecular can participate into the 2+2 to give you once again the four centered intermediate so 2+2 followed by retro 2+2 again 2+2 to give you the intra molecular organic substrate based molybdenum four Center intermediate from their own it is very simple and straightforward pathway you get another recruit two plus two, to give you the overall the metathesis reaction so-called ring closing metathesis reaction, in this particular case the example we have seen to give you the product where you have the ring formation, let us try to look at the example one more time.

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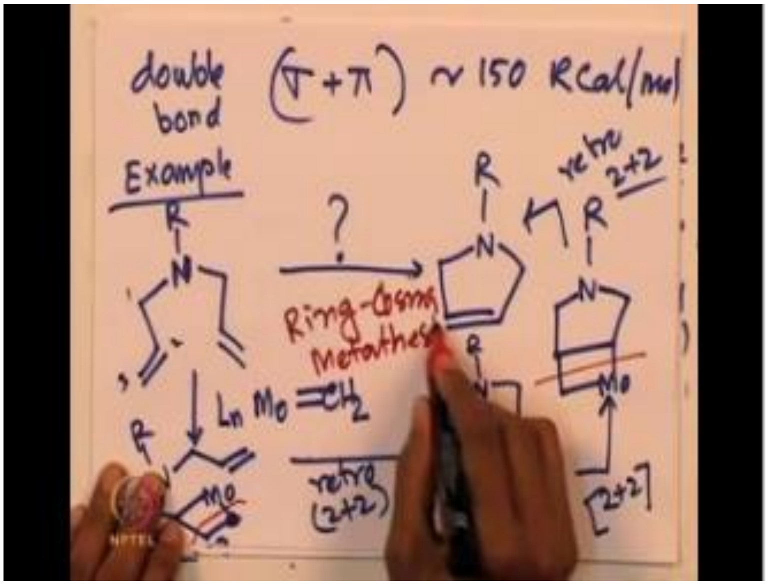

And it is very simple, we start with a substrate which has to olefin it olefin in, it one of the molybdenum this is the organometallic intermediate we take, with a carbon intermediate this to this olefin accented these are carbon Centre, interact with one of the olefins enter into the substrate to give you two plus two reactions.

Now these 2+2 intermediate can undergo retro 2+2 to exchange the partner, it was having carbon Centre over here, now it ends up having the molybdenum centre once molybdenum is inserted into the organic substrate of course, R is over there once molybdenum is inserted into the organic substrate, then they can undergo infra molecular 2 + 2, this is 2 and this is 2+ 2 give you 4, Centre our reaction mechanism or four Centre intermediate that is a molybdenum Milder cycle intermediate.

For Centre intermediate from there on you need to again exchange the partner, so here molybdenum was attached with this carbon now in the final product, molybdenum will attached with the carbon over there, essentially it is forming back this compound okay, this from here it rewards back to this molybdenum compound, and finally the net result is what you get is ring-closing metathesis reaction okay.

This is a beautiful reaction of considering opening metathesis reaction closing are almost similar reaction in terms of mechanism, but overall in this particular case what you see here is a ring closing metathesis, happening by simple two plus two reactions, so two plus two reactions are very popular reactions and it is widespread both in industry and academic setting, and the underlying principle as you have seen is nothing but it gives us the oculus product, there are plenty of examples you can and you can find in all over the place you can read about any of it.

You can look at even the natural product synthesis by 2 + 2, and the mechanism is no different it is the simplest of all and the product formation is I guess most beautiful of all, that is why that is why this reactions has caught the imagination of the scientific world remick's world, and people are you utilizing this method quite efficiently.

With this would like to conclude do late season, so today we have tried to discuss mainly for Centre reaction mechanism, and the Sigma bond metathesis we have taken one example each of course you can go-ahead and look at many more example, the basic or the fundamental steps remains very simple, and if it should be straightforward to understand if you have any queries please get back to us, and till then for the next class we will discuss the you know ligand exchange reaction, or ligand attack on an on an organometallic intermediate so the nucleophile.

You will attack from the outside and, these are the very classic example of another wide variety of the exits please keep studying we'll discuss for that in the next class bye.

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