Transition Metal Organometallics in Catalysis and Biology
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Lecture - 22
Ring Opening Metathesis (Part-1)

Welcome to this course on Transition Metal Organometallics in Catalysis and Biology. Today we will be discussing ring opening metathesis. This topic of today's discussion is other subclasses of this olefin metathesis reaction particularly cross metathesis as well as ADMET or acyclic diene metathesis reaction that we had discussed in our earlier class.

Now one of the major drawback of olefin metathesis reaction in general is the lack of selectivity and we had observed this issue propping up in both the earlier two discussed examples, particularly in cross metathesis, as well as in ADMET reactions that we have spoken about. So today continuing further, we are going to be talking about ring opening metathesis or which is popularly called as ROM.

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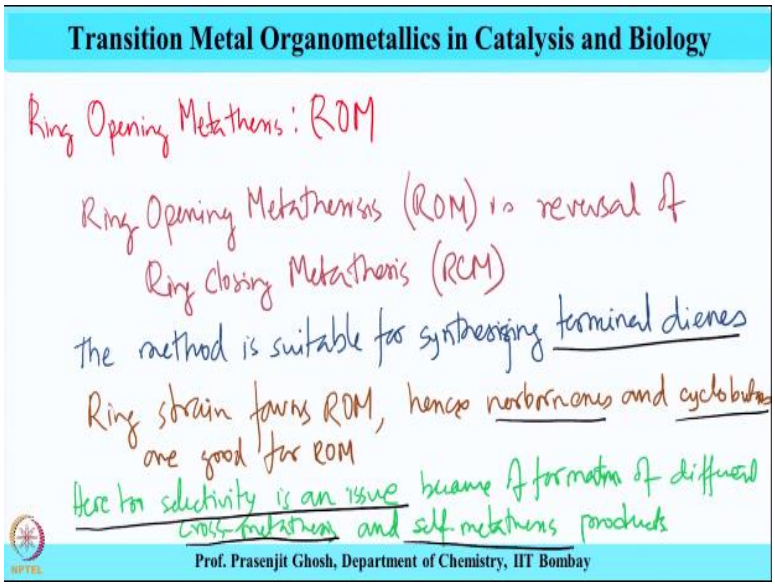

Now, ROM this ring opening metathesis is nothing but reversal of ring closing metathesis which is exactly opposite of ROM. And one of the major purpose of this ROM, ring opening metathesis is for making terminal dienes and the factor which guides ring opening metathesis is the presence of ring strain in the molecule. So ring

strain favors ROM. Hence, strains substrates like norbornenes and cyclobutanes are good for our ROM.

And as is the case with other metathesis reaction. Here too selectivity is an issue because of formation of different cross metathesis and self-metathesis products. So the point to note here is the following that ROM or ring opening metathesis is kind of opposite of ring closing metathesis. Now one important thing or one characteristic thing about metathesis reactions, olefin metathesis reaction is that these reactions are mainly thermoneutral in the sense that it they are more or less the reactant and the product are more or less of equal energy.

Because, if a double bond is broken, that is new double bond C-C double bond is formed. So there is not much of thermodynamic gain. So the driving force behind ring opening metathesis thus arises from release of ring strains in the olefinic substrate. So if the olefinic substrate containing the double bond is under strain due to constraint ring, so substrates are extremely good for ring opening metathesis and hence norbornenes cyclobutenes are good for ring opening metathesis reaction.

And this reaction is also ROM is also suitable for synthesizing terminal dienes. So this is a method in which cyclic olefins are opened up to give terminal dienes and here too selectivity is an issue because different olefins arising from cross metathesis as well as self-metathesis arise and then each of these cross metathesis and self-metathesis products they also exhibit as a mixture of E and Z isomers which further complicates the process.

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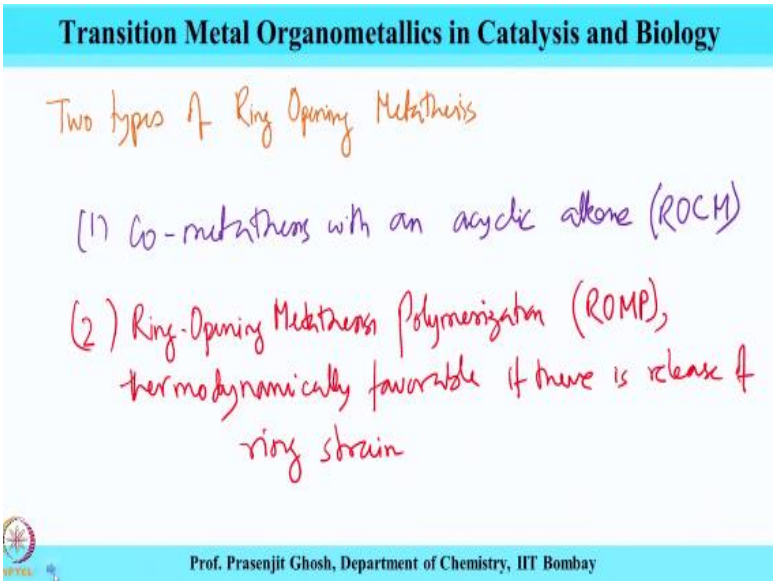

Now there are two types of ring opening metathesis reaction known. The first one is co-metathesis with an acyclic alkane and this is called ROCM and the second type is ring open metathesis polymerization or ROMP. And these are thermodynamically favorable if there is a release of ring strain.

So here we see that ROM can be of two types in which co-metathesis with acyclic diene which is called ROCM or ring opening metathesis polymerization, which is ROMP and these are favorable in case there is a release of ring strain. Now this being the case it is thus important to notice that not all substrates are suitable for ROM reaction and hence there are substrates which are specific to ROM metathesis reactions and these are the only olefinic substrates which definitely should have ring strain.

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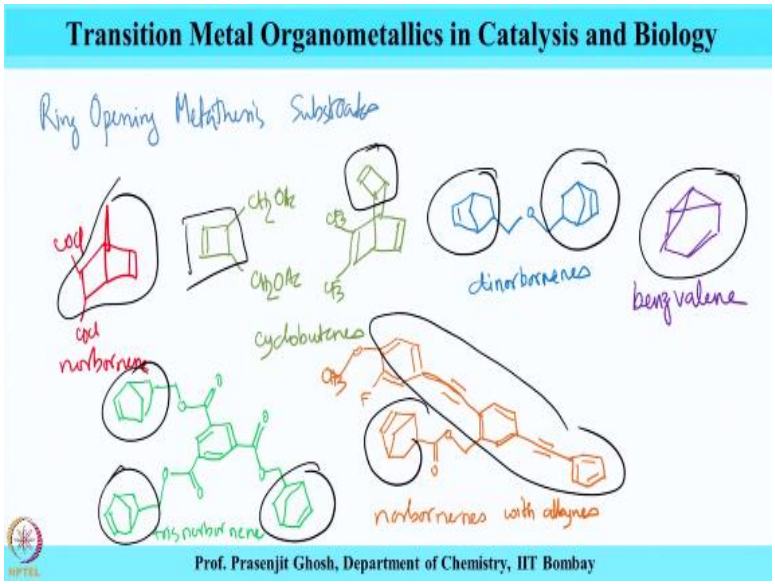

So the first that we spoke about was of norbornene then cyclobutenes or another type as is shown over here. So these are cyclobutenes then dinorbornenes then benzvalene. So there are dinorbornene, there are tris-norbornenes known as well. So tris-norbornenes and then norbornene with alkynes CH 3. So these are norbornenes with alkynes.

So what we see that primarily these are mainly strain rings and also the strain rings are of two varieties or three varieties. Now the common one is norbornene. They appear as mononorbornene, dinorbornene, trinorbornene, norbornene with alkyne substrates as it is shown over here. The other type that we had observed is cyclobutenes of the stuff over here, as well as benzvalene, which is the ring substrates like that over the one drawn over here.

So these are different types of strain ring substrates which undergo ring opening metathesis and that is because of opening of the ring chain.

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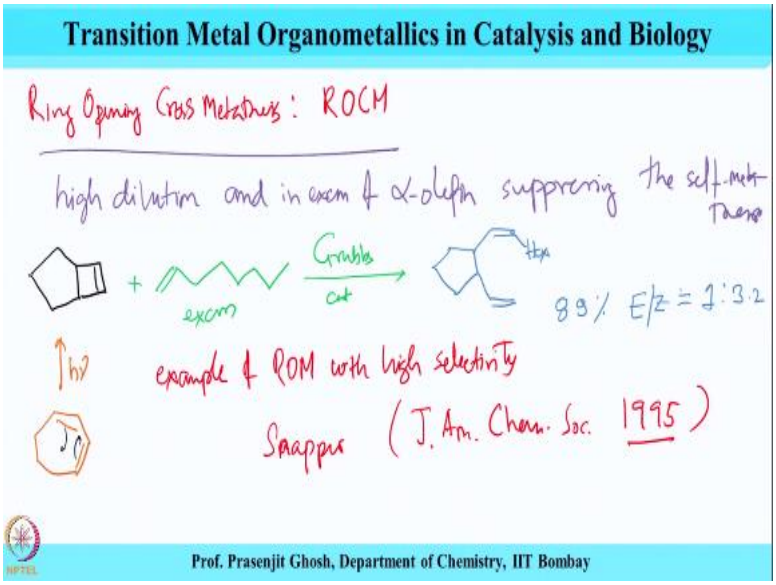

In this context, this is a nice example of the first one which is called ring opening cross metathesis or commonly called ROCM. As has been said that one of the drawbacks of metathesis reaction, cross metathesis reaction is lack of selectivity and the selectivity usually arises due to the formation of cross metathesis product in E and Z mixture ratios as well as due to formation of homo-olefin metathesis products which also appear as E and Z ratio.

This homo-olefin metathesis products are more commonly called a self-metathesis. So in order to overcome this lack of selectivity with regard to self-metathesis reactions or to suppress self-metathesis reaction, the strategy often involves carrying out this reaction in high dilution with excess of alpha olefin which suppresses the self-metathesis reaction. The reaction is performed in high dilution and in excess of alpha-olefin suppressing the self-metathesis reaction.

This is best illustrated by the reaction shown below. This 7-member diene in presence of light gives this bicyclic compound by this 2 + 2 cycloaddition giving rise to the cyclobutane derivative which is highly strained. Now when this cyclobutane derivative is treated with alpha-olefin in excess in presence of Grubbs catalyst, then following cross metathesis product is obtained in quite a good selectivity as is shown here.

The yield is quite good, 89% and even the selectivity E Z ratio is about 1:3. So this is a reaction with high selectivity and high yield. So this is an example of ROM with

high selectivity and this is demonstrated by Snapper in a Journal of American Society, Chemical Society article in 1995. So this is a strategy which was consciously implied in enhancing the real yield of the ring opening cross metathesis product.

And the two-pronged strategy involved performing the reaction under high dilution conditions along with the presence of excess amount of the alpha olefin which did the trick. Now the idea of doing this reaction under excess dilution led to separation of the self-metathesis products, and then the subsequent coupling with alpha-olefin gave the desired cross metathesis product.

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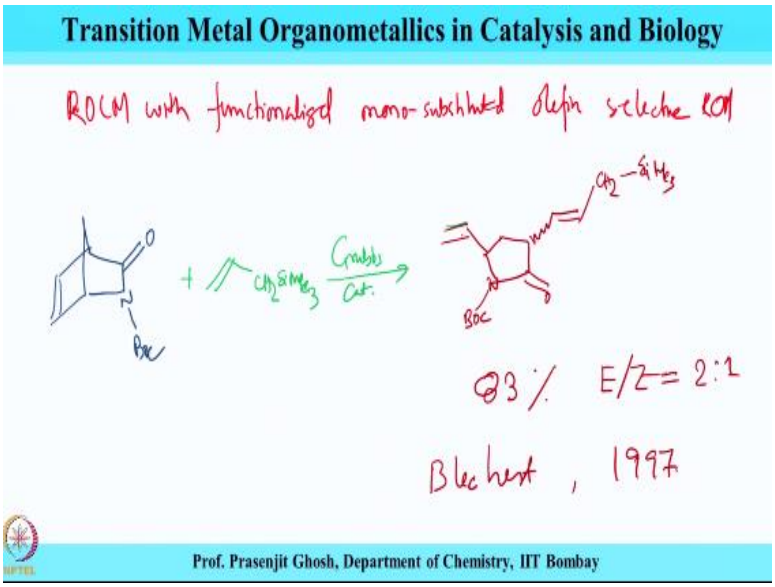

Another example of ROCM is with functionalized mono-substituted olefin selective ROM. Here also bit enhanced selectivity of ring opening metathesis was observed. This is given by this following equation. This is a highly strained norbornene like ring and that when reacted with this olefin in presence of Grubbs catalyst, then the following functionalized mono-substituted olefinic products that are obtained as is shown over here.

The yield is quite high, about 83% and E Z ratio is also in favor of 2:1and this is a work by Blechert in 1997. So with this we come to the conclusion of today's lecture, in which we have looked into ring opening metathesis particularly the challenges associated with ring opening metathesis with regard to the lack of selectivity arising from self-metathesis as well as cross metathesis.

And also because of the thermal neutrality of the olefin metathesis reaction in general, that all this varied mixture of different metathesis products being formed. Now we have also noted that the driving force for olefin metathesis, ring opening metathesis arises because of the release of the ring strength.

So one of the primary criteria for becoming a substrate for ring opening metathesis is that the substrate should have considerable ring strength and because of which substrates like norbornene or its derivatives or cyclobutene benz-fluorene they are extremely good substrates for ring opening metathesis reactions. We have also seen that ring opening metathesis are of two type.

One is ring opening cross metathesis and the other one is ring opening metathesis polymerization. In ring opening cross metathesis ring containing olefin opens up and then the metathesis happens with another olefin. Whereas, in the ring opening metathesis polymerization, the strained ring olefin opens up and undergo self-metathesis with another ring to give a polymer chain.

We have also discussed about how the yields of the cross metathesis products can be increased enhanced in ring opening cross metathesis reaction and this was achieved successfully achieved by carrying out the reaction under dilute condition in presence of excess amount of alpha-olefin. We have also seen the reaction with alpha-olefin with functionalized mono-substituted olefin using Grubbs catalyst.

So this sort of shows that this is a useful method for making olefins with terminal dienes because that is what is the product that comes out because of ring opening polymerization of strained olefinic substrates. So we are going to look into more of the applications of ring opening metathesis polymerization as we continue to discuss this in the next lecture. I once again thank you for being with me in this lecture.

And we are going to be discussing ring opening metathesis in a great more detail when we take this topic up in the next lecture. Thank you.