Transition Metal Organometallics in Catalysis and Biology
Prof. Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology-Bombay

Lecture - 23
Ring Opening Metathesis (Part-2)

Welcome to this course on Transition Metal Organometallics in Catalysis and Biology. In continuation with our earlier discussion on various type of olefin metathesis reaction, we have been talking about ring opening metathesis in particular, we have been talking about two variations of ring opening metathesis. One is just simple ring opening metathesis. The other is ring opening cross metathesis reactions.

Now in this discussion it is important to note that this ring opening metathesis reactions are favorable for substrates which are under strain. Like they have physical ring strain, which is the driving force for carrying out this ring opening metathesis reactions. So today we are going to look at various examples of both types ring opening metathesis as well as ring opening cross metathesis reactions.

And see how they have been used for synthesizing a variety of novel structures which are of importance commercially as well as from biological point of view. So with this let us move on to various examples of ring opening metathesis reactions that we would be discussing in today's lecture.

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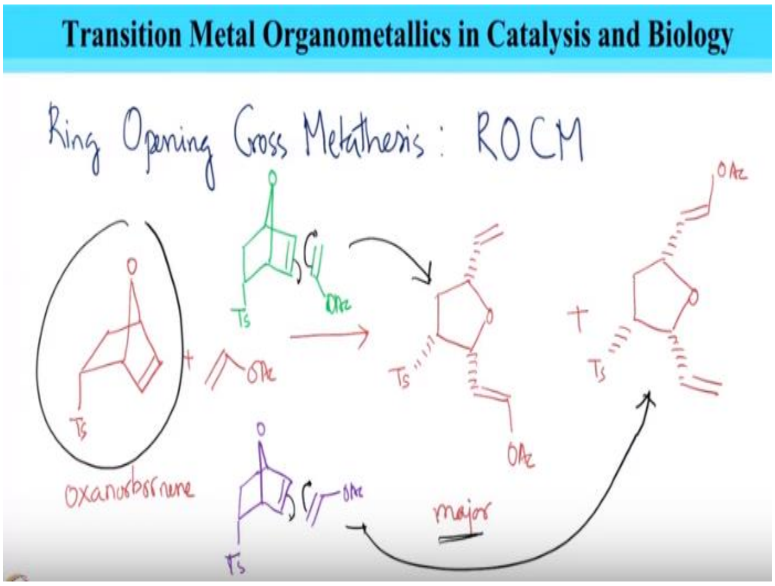

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Ring Opening Cross Metathesis : ROCM

ROCM, this is popularly called. And a nice example is given by the reaction as shown. This is called oxanorbornene. The reaction of this with vinyl acetate gives this five member cyclic compound which is a major product along with the other product which is we will see.

Now this reaction can be understand in the context of the transient state that may arise from binding of O-acetate in one way resulting in the formation of this product or the same can be understood, also understood by the reaction with the substrate in opposite way which will give the other product. And now this will lead to formation of two different products, of which the major product is the one which is shown over here.

And as seen that here, we see that the ring strain of oxanorbornene is the driving force for carrying out this cross metathesis, ring opening cross metathesis reaction. Now as we had discussed earlier that these metathesis reactions are often are thermoneutral reactions in the by the fact that the energy required for breaking a double bond is also almost equal to energy required in the formation of double bond.

So there is no enthalpic gain as much from in metathesis reactions. However, there are other factors like the ring strain or elimination of a gaseous ethylene molecule which is formed as a product, which sort of leads to the formation of these ring opening cross metathesis products. Look at another interesting reaction for ROCM.

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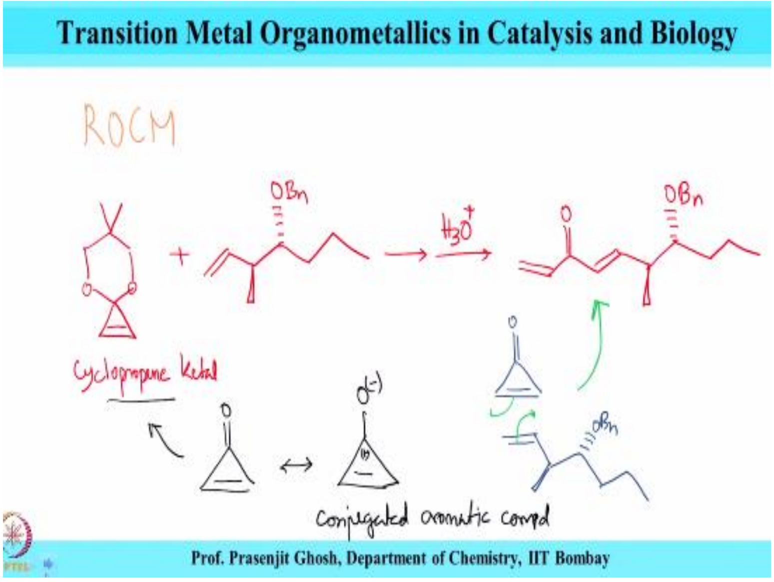

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Ring opening cross metathesis another interesting example. This is a cyclopropene ketal that reacts with and subsequent hydrolysis give this product. Now this is a interesting molecule, this cyclopropene ketal. If seen closely this is nothing but derived from the production or production of the carbonyl group to give this ketal moiety and this is cyclopropane ketone. Now this in this structure is not very stable.

It has more stable structure, which is in its zwitterionic form. Now this is cyclopropyl cation and now this is conjugated aromatic compound. So this cyclopropane, propene cation is an interesting compound which is sort of derived from cyclopropane ketone and which is stabilized in its zwitterionic resonance form. Now as far as these ROCM, cross metathesis reaction goes then one can sort of envision the reaction between the two olefinic substrates leading to the formation of the desired compound.

Proceeding further we are going to take a look at another example of ring opening cross metathesis reaction.

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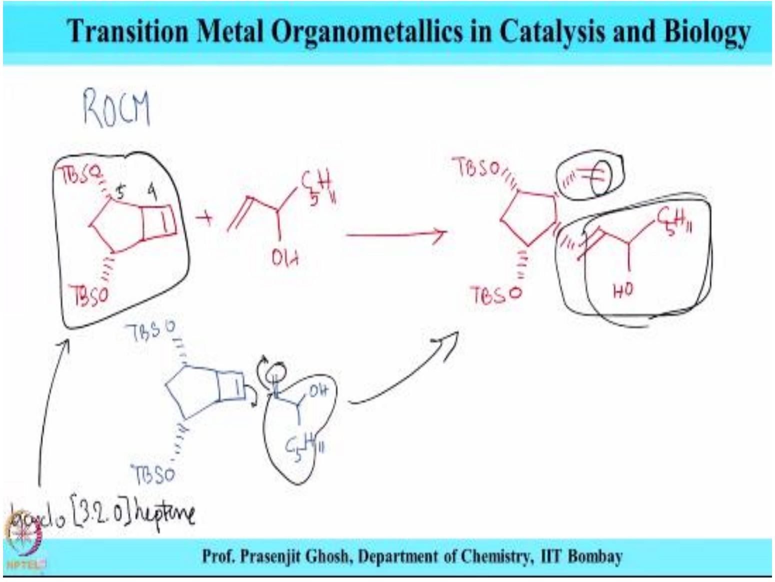
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And in this case, the substrate is also a strained compound by cyclic compound with considerable ring strain that reacts with this olefin to give this compound. So it becomes a five-membered cyclic compound as is shown over here. And if one looks at how the reaction goes plus 11 and then the orientation of the two olefins as such.

Then this goes through the four member cyclic intermediate transition state to give the desired product which would have one moiety of this and the other moiety this CH 2 group arising on this end and the rest of the fragment being over here. And here also we see that this is a highly strained substrate, where there is a five membered as well as a four member ring.

And of this the most the four membered ring which is under severe strain opens up to give the corresponding ring opening cross metathesis product and this compound is called heptane bicyclo by psychlo 3.2.0 320 heptane. Now this have gone beyond achiral substrates to even the chiral forms of this has been reported. And in this case the catalyst obviously, the metathesis catalyst used for the study is achiral compound.

So we are going to take a look at several of the chiral examples that have been reported for ring opening cross metathesis reaction.

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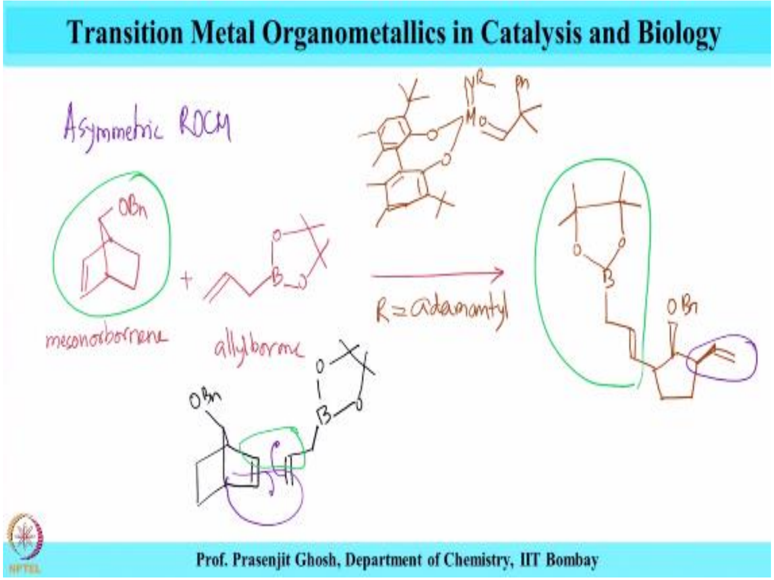

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Asymmetric ROCM or ring opening cross metathesis reaction and the substrate for this is called mesonorbornene the structure of which is shown here. Mesonorbornene in reaction with allylborane. In this cross metathesis reaction, the catalyst is an asymmetric or chiral complex as is shown here. There is a tributyl group and this is highly sterically demanding with another tributyl group both bound to molybdenum.

And this is a molybdenum imido carbene compound with phenyl and 2-methyl R equals adamantly to give the compound which is shown over here. And the transition state can be envisioned from the reaction of the reaction of this allylborane in a confirmation similar to this so that this is corresponding to the vinyl substituent over here and this fragment is corresponding to the boronic ester substrate over here.

And needless to mention that this also has considerable ring strain that is so characteristic of this ring opening cross metathesis reaction and has been successfully utilized for preparing this asymmetric chiral compound using asymmetrically opening cross metathesis reaction.

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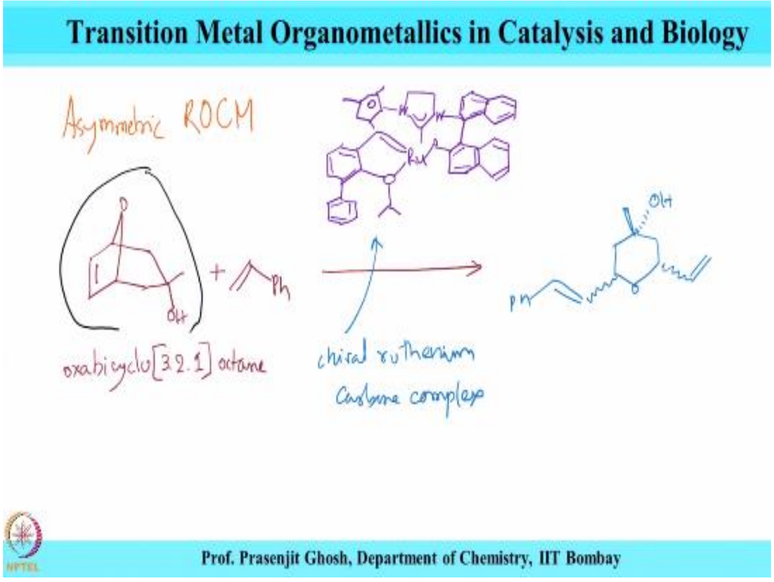

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We are going to look at another interesting example of asymmetric ring opening cross metathesis reaction. And here also another bicyclic steric substrate is used which is oxabicyclo 3.2.1 octane that reaction with styrene again using achiral catalyst which I will draw over here ruthenium and N-heterocyclic carbene with a mesityl moiety on one end and binol with oxygen bound to ruthenium as is shown over here to give the corresponding product and the catalyst used is chiral ruthenium carbene complex.

Here too we see that highly strained bicyclic octane ring has been used using achiral sterically demanding chiral ruthenium carbene complex to give the product.

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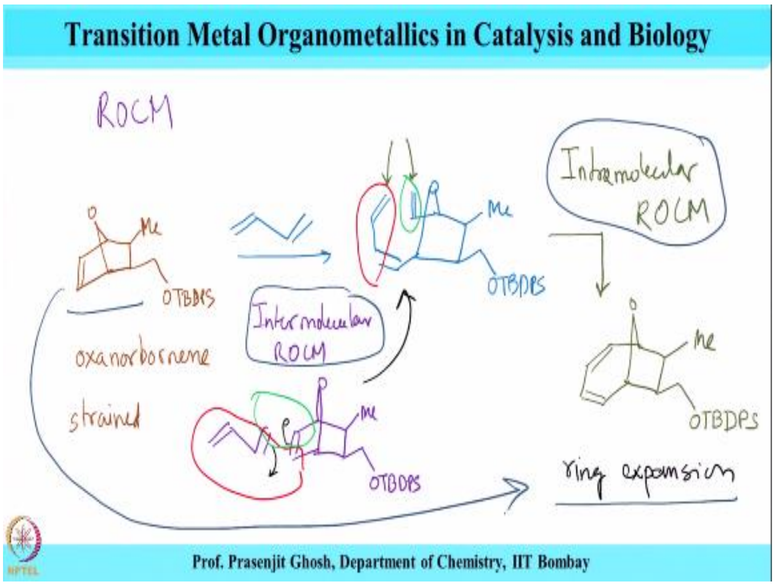

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Proceeding further we are going to take a look at another example of ROCM, ring opening cross metathesis in which this reaction has been attempted two times. First one is a intermolecular cross metathesis and the second one is a intramolecular cross metathesis. This is a interesting reaction. So here too one starts with an strained oxanorbornene which is highly strained ring that reacts with butadiene to give the corresponding ring opened cross metathesis product. This is a protecting group.

So one can see that this is intermolecular ROCM and that happens from the reaction of two substrates as is shown here giving to the desired product in which the fragment comes from the reaction of this and the other fragment comes from the reaction of this. So the reaction does not stop here. It further undergoes a intramolecular ROCM in which these two olefin reacts in a intramolecular fashion to give the product as is shown here.

And this is a ring expansion that happens over here. So this is a interesting example where we saw two types of ring opening cross metathesis happening. The first one is intramolecular ROCM followed by intermolecular ROCM followed by intramolecular ROCM again resulting in a bicyclic ring. However, this is in much more expanded form than it is over here.

And hence this release of ring strain on going from here to here occurs using this nice example of intermolecular and intramolecular ROCM ring opening cross metathesis reaction. So with this I come to the end of today's discussion, where we have seen various example of ring opening cross metathesis reaction starting from there achiral variant to their asymmetric variant.

And what we had observed that in all of these cases of link opening metathesis reactions that the substrates are bicyclic compounds, mostly bicyclic compounds with substantial ring strain which is which provides the impetus for the reaction. We have also looked into the chiral versions in which sterically demanding chiral catalysts had been used mainly with binal fragments bound to the metal.

And they also successfully carry out these ring opening cross metathesis in the symmetric fashion. We have also looked at a very nice example in the last slide in which oxonorbornene compound undergoes reaction with butadiene first in a intermolecular ROCM fashion followed by intramolecular ROCM fashion resulting in the ring expansion to give another bicyclic compound.

So with this I come to the conclusion of today's lecture. We are going to take up this more on this ring opening reactions particularly with regard to ring opening metathesis polymerization or ROMP as we start in the next lecture. Till then, goodbye and thank you.