Transition Metal Organometallics in Catalysis and Biology

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Lecture - 21
Cross Metathesis (Part-3)

Welcome to this course on Transition Metal Organometallics in Catalysis and Biology. Over the last few lectures we have been discussing about cross metathesis. This is the reaction of great industrial importance particularly a for its application in being used in couple with SHOP, Shell Higher Olefin Process as well as isomerization for producing feedstock of detergents and we have discussed in great details how this story of cross metathesis is being used in SHOP came into being.

Now we have also discussed the various advantages as well as disadvantages of cross metathesis reaction. And in this context what we have learned is that a major limitation of cross metathesis reaction is its lack of selectivity. Now by lack of selectivity, I mean the type of cross metathesis products olefinic products produced from the reacting two different olefins.

And they include all combinations of homodimers which can be possible by the individual reaction of each of the olefin with itself as well as the formation of the cross metathesis product which is obviously the desired product of the reaction. Another issue with lack of selectivity is that, these homodimers as the like two of the homodimers and one of the cross metathesis products, all of them also appear as a mixture of E and Z isomers.

So here we see that a large number of a mixture of products E and Z isomers of each of the homodimers as well as the E and Z isomer of the cross metathesis products they are formed and hence separation and isolation of each of the products become a problem. All the more it is important to note that these polymers may not be too easy to separate given the fact that though their molecular weight in some cases may vary like from one homodimer to another homodimer to the cross metathesis products.

However, between the E and Z isomer of each of these homodimer or cross metathesis products the molecular weight remains the same. So it is very challenging effort to separate these isomers after cross metathesis reaction. Now if one may want to think a bit and try to understand that why is so many different products being formed in cross metathesis reaction then one can see that by and large this metathesis reactions are thermoneutral in nature.

That means that there is no energy gain in formation of the product because whatever C-C bond is broken in the substrate that many C-C bond is formed in the product. So actually, this thermoneutrality brings in all the more complexity information of large number of products. So we have looked into various strategies that have been put in place to enhance the selectivity particularly with respect to formation of the cross metathesis product.

And beautiful demonstration of these towards this end was given reported by Grubbs in which he had homopolymerized one of the olefins first to give the one of the homopolymer product and then introduced the second olefin to produce the cross metathesis product in higher yields. So that was the story of sequential addition of two olefins so as to enhance the yield of the cross metathesis product and we had discussed this work of Professor Grubbs in the previous lecture.

We have also seen another strategy in which to fish out larger yield of the cross metathesis product the strategy involves immobilizing one of the olefins on a polymer surface so that the cross metathesis product so formed after the reaction with the second olefin stays impregnated on the polymer surface whereas the soluble homodimer metathesis products can be separated out or washed out from the polymer surface.

So we had looked at ways and means of enhancing the selectivity of this cross metathesis reaction. Today in this lecture, we are going to look at some more important applications of cross metathesis reactions and this will sort of indicate the total overall spread of these metathesis, cross metathesis reaction. So we are going to look at some of the examples of cross metathesis reaction today.

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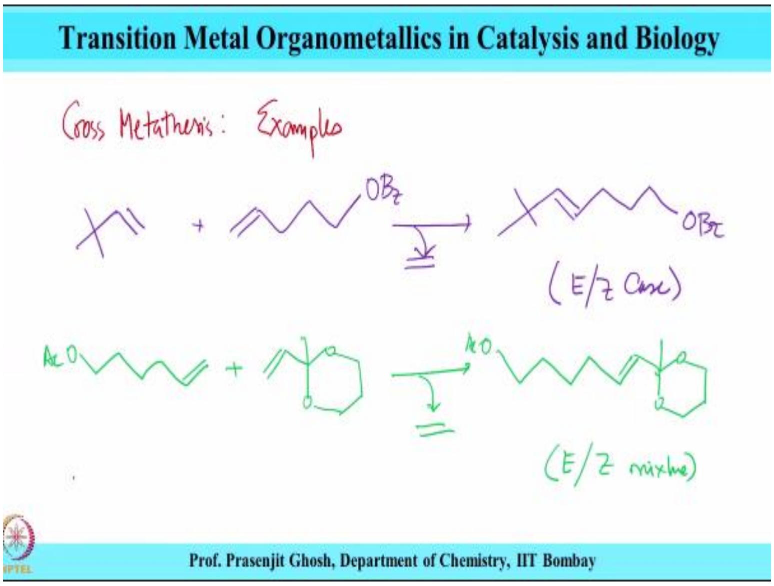

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Cross Metathesis: Examples

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And this is given by the equation hopefully alpha olefin giving the following product and obviously in this case ethylene is eliminated. The other example is this again giving out, ethylene gives the following product. So it is to be noted that both E, Z mixture is obtained in this case

as well as in the previous case.

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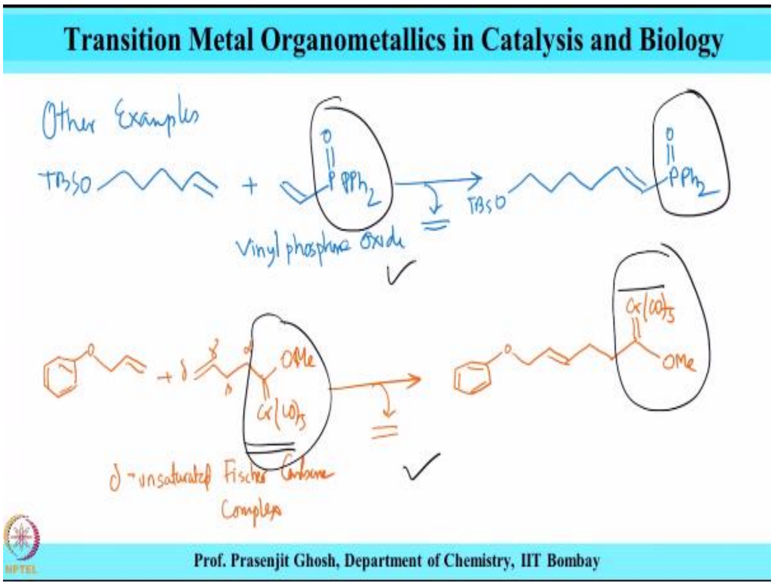

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Other Examples

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Similarly, the other examples include the following reaction. This is the protecting group of the end alcohol moiety. This is called vinyl phosphine oxides. They are reacting to give ethylene TBSO PP h 2. Similarly, another reaction ethyl moiety vinyl phenyl ethyl with a Fischer carbene complex chromium CO 5. So this is called delta alpha, beta, gamma, delta; delta unsaturated Fischer carbene complex giving CO 5.

So this is a interesting example, where one sees that even the metal carbene or Fischer carbene moiety remains intact in the process of cross metathesis and is not affected by the ruthenium catalyst. So as we had discussed in our previous lecture similarly, this phosphene oxide stays intact during the course of metathesis.

So as we had discussed in our earlier case that one of the important feature of Grubbs ruthenium catalyst is that they are functional group tolerant and the catalyst does not get affected by presence of other different functionality of the olefin.

And a big realization of that concept or demonstration of this concept is seen in for these two substrates where we can see that even a metal carbene moiety as well as a phosphine oxide moiety does not attack the metal center that carry out this cross metathesis reaction. So we have been looking at some of the important applications of cross metathesis reaction.

And with that, we come to end of our discussion on cross metathesis reaction. Let me just review how we have looked at the various important utility of cross metathesis reaction with respect to producing feedstock, feedstock for detergent and that story goes back to using the lower than C 8 fragments and higher than C20 -18 alpha olefin fragments obtained from SHOP process to convert to a range of C12 - C20 alpha olefin fragments which were then converted to feedstock for detergent by hydroformylation reaction.

We have also looked at the various limitation or the main limitation of cross metathesis reaction which had been its selectivity and then we have looked into various applications of cross metathesis reaction and there we observed that one of the primary reason for their success is the functional group tolerance and which we have seen that is survives various functional group including metal carbene complexes on of its olefin and carries out the desired cross metathesis reaction.

So we are going to now take up another new subclass of olefin metathesis and this is acyclic diene metathesis reaction, metathesis polymerization in the next part of the as a part of the lecture as a next topic.

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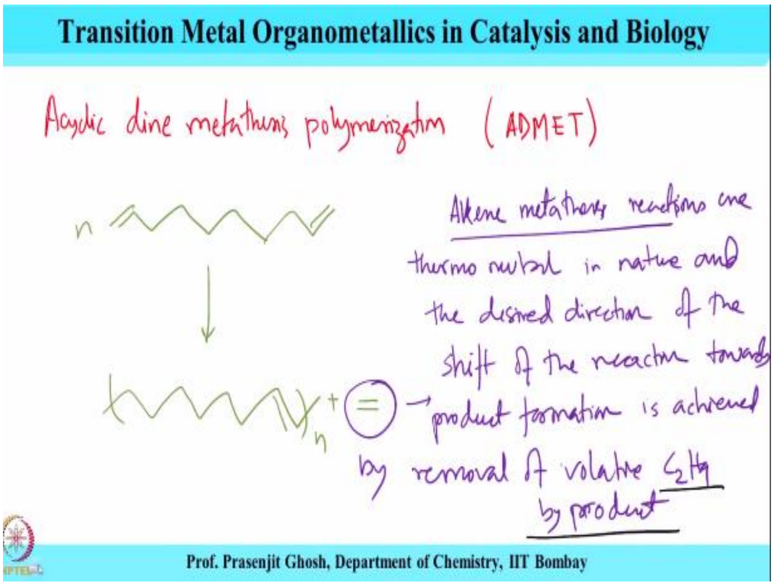
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Acyclic dine metathesis polymerization (ADMET)

Alkene metathesis reactions are thermo neutral in nature and the desired direction of the shift of the reaction towards product formation is achieved by removal of volatile C_2H_4 by product

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And this is commonly referred to as ADMET and this is designated by the following equation. Now we see that ADMET also suffers from same limitation with regard to the reaction being thermoneutral. Reaction being thermoneutral means that there is no drive for the product formation and the product formation is driven by removal of these olefin from out of the system.

So this is a nice way of tilting the equilibrium towards the product formation by removing one of the byproducts of the reaction. So point to note is alkene metathesis reactions and this includes all types of metathesis reactions RCM, ROM, ADMET olefin metathesis alkyne metathesis. So all of them per se, are thermoneutral in nature.

And the desired direction of the shift of the reaction towards product formation is achieved by removal of volatile ethylene of volatile byproduct. So this is an important strategy whereby this byproduct ethylene is removed and as a result the reaction is driven towards a product formation. We are going to look into some examples of ADMET.

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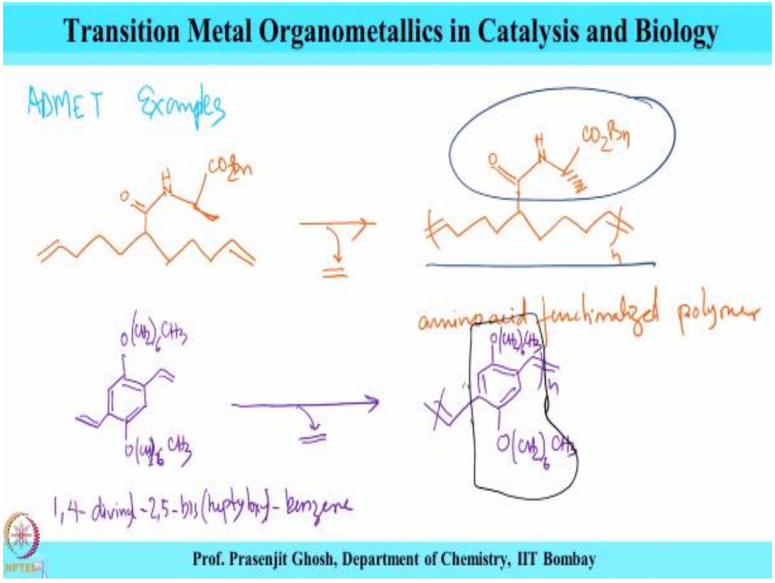

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And this is going to throw light on type of applications or materials that are produced using ADMET reaction. So one of the reaction we are considering is depicted as given below. O 2 B n, this giving ethylene and the following polymer. And these are important polymers because they are amino acid functionalized polymer. So they have this important chiral functional moieties attached to this polymer backbone, which is nonpolar in nature.

Another example of ADMET is given by this equation $(CH_2)_6CH_3$ that also gives ethylene to give this following polymer and this monomer is called 1, 4 divinyl 2, 5 bis heptyloxy benzene. So what we see that the this is a polymer of polymer of these aromatic backbone and it has its own applications. We are going to take a look at some more applications of ADMET examples.

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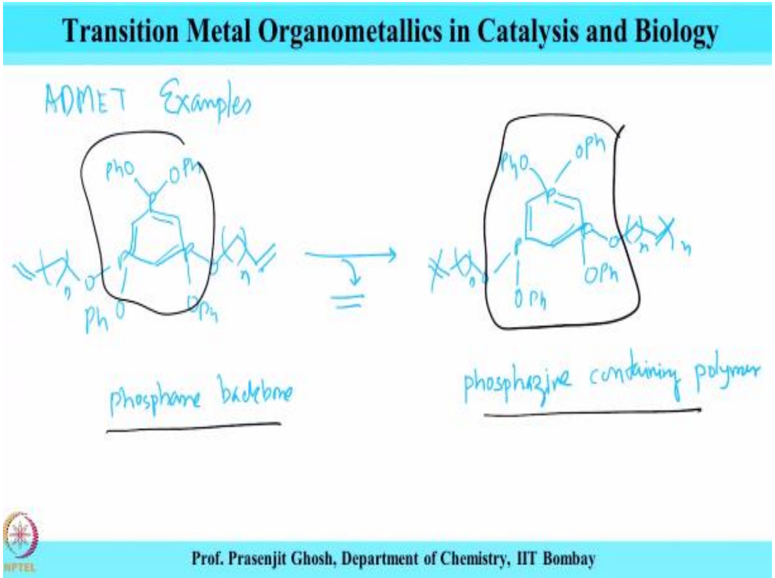

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And this is an interesting compound of phosphorus, another phosphorus with this olefinic bond. So it has long CH 2 and that eliminating ethylene to give the following compound. And this is phosphazene containing polymer and have this is phosphazene olefin backbone. So what is interesting over here is the functional group tolerance and that even the moiety is like phosphazene is unattacked by the catalyst.

And that made polymerization of phosphazene backbone is achieved and which sort of again highlights the functional group tolerance of these metathesis catalyst particularly of ruthenium. So with this we come to an end of this ADMET polymerization. I am going to end with one more example of ADMET.

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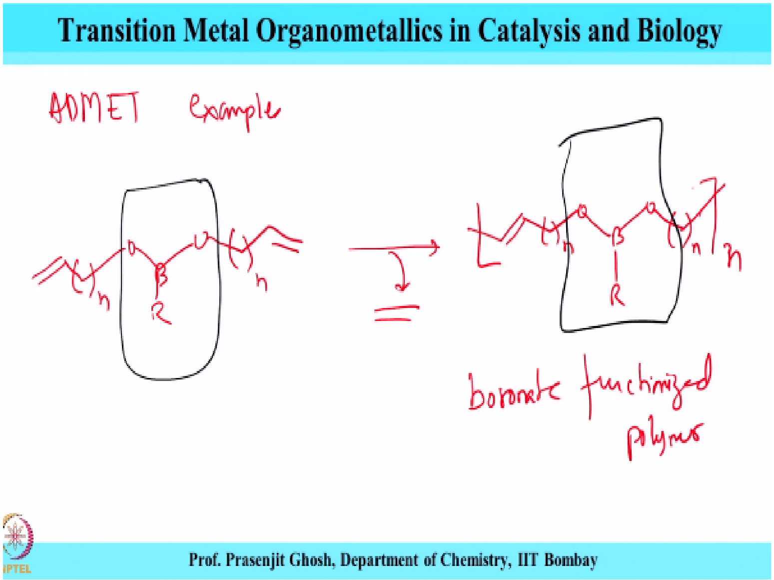

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And in this case, we will see that not only the phosphazene but also boronate compounds can be used to give this polymer and that again highlights the functional group tolerance of these ruthenium based metathesis catalyst. And here the point to note is that even this boronate moiety remains untouched by that ruthenium catalyst and the functional group tolerance of the ruthenium metathesis catalyst is highlighted.

So with this we come to an end of our discussion on ADMET reactions and this is acyclic diene metathesis polymerization reactions. What we had observed that for ADMET as well as other cross metathesis reaction since this reactions are thermoneutral in nature, so one way to drive the product formation is by removing the volatile components of the product more quickly and in this case the byproduct is ethylene by so by removing ethylene the reaction is driven forward.

We have looked into some of the examples of ADMET and what we had seen that a very many different scaffolds can be prepared using ADMET polymerization. And we what sort of highlights is that these catalysts are indeed functional group tolerant and that allows formation of different kinds of polymer using ADMET reactions. So with this we come to the conclusion of today's lecture.

In today's lecture, we discussed about the applications of applications of cross metathesis as well as ADMET. We are going to take up a new topic, a new subclass of metathesis reaction particularly ring opening metathesis or ROM when we meet next. Till then I thank you once again for being with me in this lecture. And I look forward to take up this ROM, ring opening metathesis reaction in more details when we see next time. So with that goodbye and thank you.