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

Module No # 04
Lecture No # 20
Cross Metathesis (Part -2)

Welcome to this course on transition metal organometallics in catalysis and biology in this course we have been exploring the depth and the breath of organometallics chemistry particularly with regard to the applications of organometallic compounds in large scale industrial processes. In this context we have looked into various types of organometallic reaction which have been practiced in industry in the large industrial scale.

And to start with we have looked at Reppe chemistry which is the convolution of C2 feedstock acetylene to other functionalized forms. So after Reppe had been looking into another very interesting reaction which is olefin metathesis we have looked at olefin metathesis followed by alkyne metathesis and now we have been discussing about cross metathesis reaction which was taken up in the previous lecture.

Now cross metathesis reaction as we have been discussing is being developed or has been developed in conjunction with industrial process particularly shop or which is better known as shell Heir olefin process and which was mainly used to utilize unwanted feedstock from these shop alpha olefin polymerization process.

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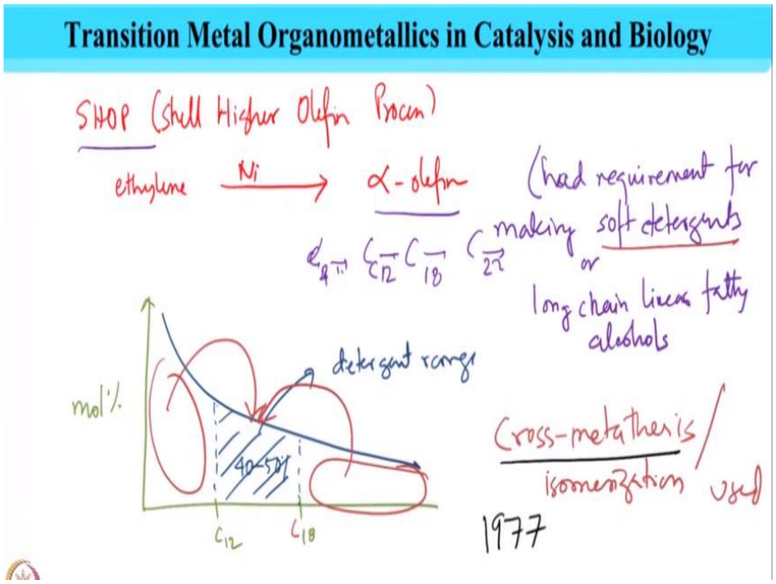

Transition Metal Organometallics in Catalysis and Biology

SHOP (Shell Higher Olefin Process)

ethylene $\xrightarrow{Ni}$ α - olefin (had requirement for making soft detergents or long chain linear fatty alcohols)

C_4 C_{12} C_{18} C_{22}

Cross-metathesis / isomerization used

1977

So let me just illustrate this or shell higher olefin process would convert ethylene to alpha olefin using nickel catalyst. Now these alpha olefin's was primary source which was from ethylene feedstock and this was used or had used for making had requirement for making soft detergents which has long chain fatty alcohols linear fatty alcohols. So prior to these alpha olefin they were accessed through cracking's as well as hydroformylation of alpha olefin's and they were synthesis from other methods and shop provided easier and convenient access to this alpha olefin other than the prevalent method of cracking or from alkaline sources that gives alpha olefin and then the hydro formylation acts to this.

So this was the better method to get alpha olefin but the only problem which arose was that it was churning out alpha olefins of various fragment from C4 to C12 to C18 to C22 and so on forth. So a large range of oligomers were obtained and this was best represented by this (()) (04:51) distribution C12 C18 and the distribution was something of the type this the now as for the requirement for detergent was this region which are about 40 to 50% and they were for making the detergent range.

So cross metathesis was then successful cross metathesis actually cross metathesis followed by isomerization another reaction. So cross metathesis as well as isomerization was used to convert the unwanted lower fragment and the unwanted higher fragment to make something of within the range of C12 and C18 for the use (()) (06:28) soft detergent applications. So this is where the cross metathesis reaction came into being in the sense came into being applicable for using the distribution of alpha olefin which otherwise at that point of time was not usable for any commercial purpose.

So these was the interesting development which was practiced in a large industrial scale way back from 1977 in the Schrock plant and this shows how these cross metathesis reaction was employed in large scale for commercial purpose.

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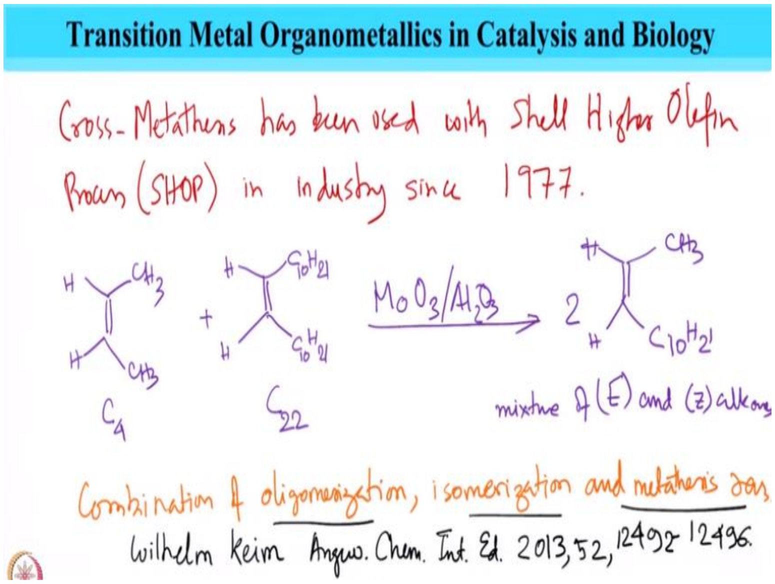

Transition Metal Organometallics in Catalysis and Biology

Cross-Metathesis has been used with Shell Higher Olefin Process (SHOP) in industry since 1977.

mixture of (E) and (Z) alkenes

Combination of oligomerization, isomerization and metathesis rxns

Wilhelm Keim Angew. Chem. Int. Ed. 2013, 52, 12492-12496.

So I am going to illustrate this cross metathesis has been used with shell higher olefin process in industry since 1977 and this is given nicely by this reaction which is a C4 fragment plus C10 H21 this is C22 fragment in presence of molybdenum trioxide it molybdenum oxide catalyst and Al2O3 giving 2 of these C13 fragment. And this was actually both E and Z mixtures where obtained and as mentioned that the process actually involved the industrial process involved indeed 3 process combination of oligomerization, isomerization and metathesis reactions.

Now these 3 processes have been discussed in detail in our previous lecture and the different for this is by an article by Wilhelm keim in Angew Chem 2013 52 12492 212496.

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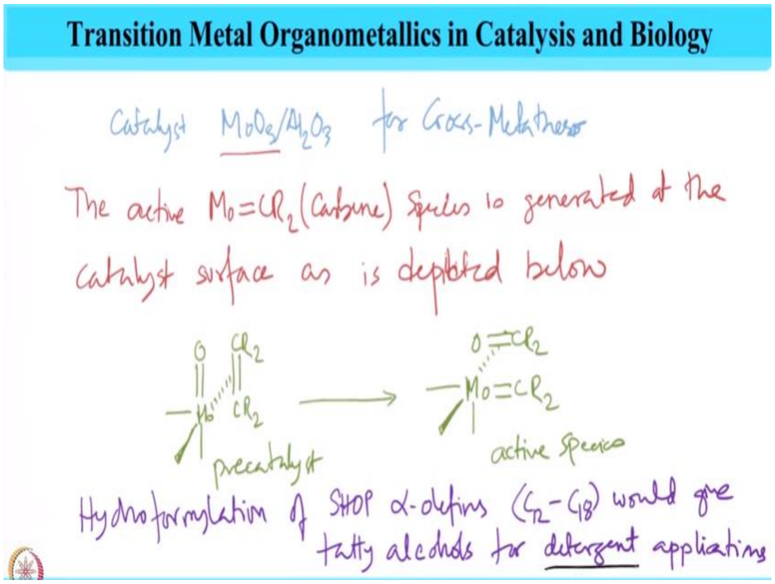

Transition Metal Organometallics in Catalysis and Biology

Catalyst MoO_3/Al_2O_3 for Cross-Metathesis

The active $Mo=CR_2$ (Carbene) Species is generated at the catalyst surface as is depicted below

Hydroformylation of SHOP α-olefins ($C_{12}-C_{18}$) would give fatty alcohols for detergent applications

The catalyst was MoO3 Al2O3 for cross metathesis reaction and then as we had observed that metal carbine species are usually involved in metathesis reactions then the question which comes to mind that how does a metal oxide in terms of molybdenum oxide carry out cross metathesis. So there is a interesting question in the sense that for the cross metathesis large scale reaction the pre catalyst to the was originally used was molybdenum trioxide and what it turns out that the active catalysis species of molybdenum carbine is generated through the following reaction as it shown below.

The active molybdenum carbine species is generated at the catalyst surface as is depicted below and this is shown by the equation given here. This is molybdenum oxide reaction with olefin giving the molybdenum carbine species as is shown here with the bound ketone and this is the active species and this is the pre-catalyst. So what is seen over here is that the pre-catalyst of the molybdenum also reacts with an olefin to generates the active species along with the metal carbine metal along with the key tone and this active metal molybdenum carbine species then carry out then it carried out these cross metathesis reaction.

And this cross metathesis reaction has been developed with the intent to use the higher and the lower alpha olefin oligomers had to produce mid-range alpha olefin oligomers which could be converted to detergents like fatty acids or through or fatty alcohols as required through the process of another important industrial scale organometallics reaction and which is hydroformylation.

So what we see is a chain of reactions all of them are performed in large industrials scales and they are effortlessly used for converting of its track to another to another to finally what is the value target that is being achieved. So hydroformylation of shop alpha olefin's which is of the range C12 to C18 would give fatty alcohols for detergents applications. So one thing to note here is that now it may seem that something as to trivial as application in detergent industry was bought about such utility of so many different reactions organized and so many different nice organometallic reactions for the large scale production of feedstock for detergent industry.

So what we see is that the organometallic chemistry can cater to all aspects of societal need bead from detergent to polymers to so on and hence so forth and all can be brought about by applying by the application of very intriguing set of organometallic reactions. So here we see that how cross metathesis along with isomerization shop and hydroformylation 4 processes practiced in large scale would finally give feedstock for producing detergents for the societal market.

So with these let me just talk bit more about the advantage and disadvantage of cross metathesis reaction and what it turns out is that the limitation of cross metathesis reaction arises due to non-selectivity in products in terms of not being able to exclusively formed one of the product that be E or Z. So one of the limitations of cross metathesis reaction is that the both E and Z products are formed in a mixture and that gives rise to less selectivity in product formation and hence in more challenges in product isolation.

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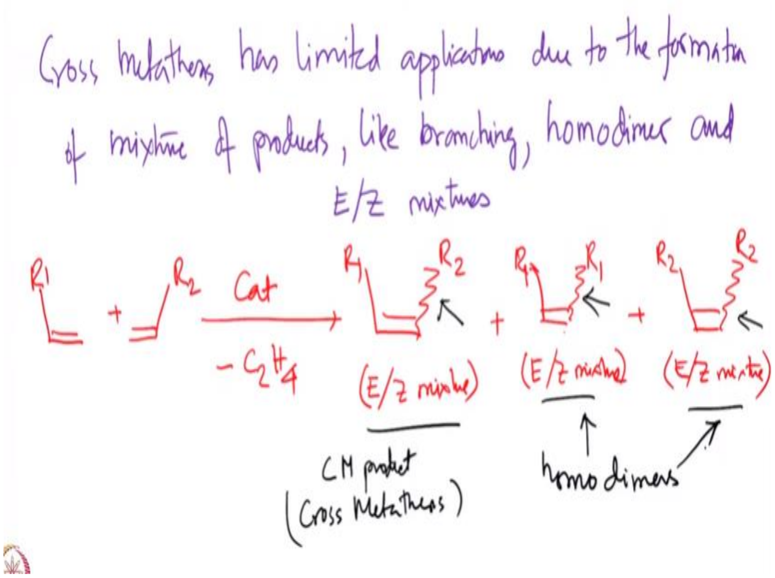

Cross metathesis has limited applications due to the formation of mixture of products, like branching, homodimer and E/Z mixtures

So these I will illustrate by the equation as its given below cross metathesis as limited applications give to the formation of mixture of products like branching homodimer and easy moistures. So this is given by the equation as it shown here R1, R2 catalyst C2H4 now the cross metathesis of this 2 catalyst can results in so many different products as it is shown here R2 so it can be R1, R2 and that can be easy mixture and that is given by this H2 bond plus R1 this is a homodimer again easy mixture plus R2 easy mixture.

So the main drawback is what we see that this selectivity is less that all of these come at more easy olefinic mixture this is the real cross metathesis product and so this is the cross metathesis product and this are homodimers. So the selectivity is a key issue of cross metathesis reaction and hence once of the important challenges is the ways to increase this selectivity of cross metathesis reaction.

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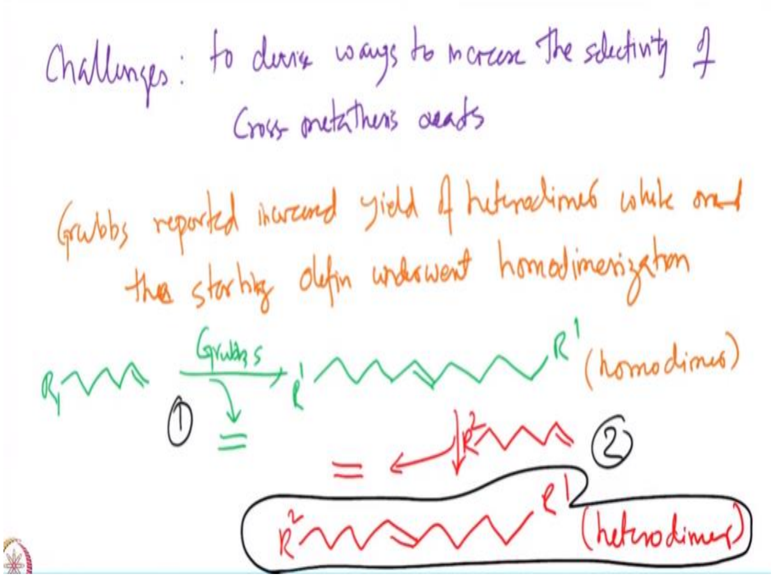

Challenges: to devise ways to increase the selectivity of Cross metathesis reacts

Grubbs reported increased yield of heterodimers while one the starting olefin underwent homodimerization

Challenges is to devise ways to increase the selectivity of cross metathesis reaction and in these regard important is to mention that Grubbs find a way of increasing the production of heterodimer while starting with the homodimerization first. So this is nicely illustrated by equation over here Grubbs reported increased yield of heterodimer while one of the starting olefin underwent homodimerization.

This is best shown by the equation given here so R1 Grubbs catalyst so the first step is illumination of ethylene R1 this is a nothing but homodimer. Now when this reacted with R2 which also eliminated ethylene then R1 which is the heterodimer so Grubbs the point to note here is that in these sequential 2 step process of introducing the sequentially Grubbs reported increased yield of these heterodimer.

So this is one way of improving the selectivity of this cross metathesis reaction then the other way of increasing the cross metathesis reaction is partially by carrying out the reaction through immobilizing by immobilizing one of the coupling partner this is best given by this sentence.

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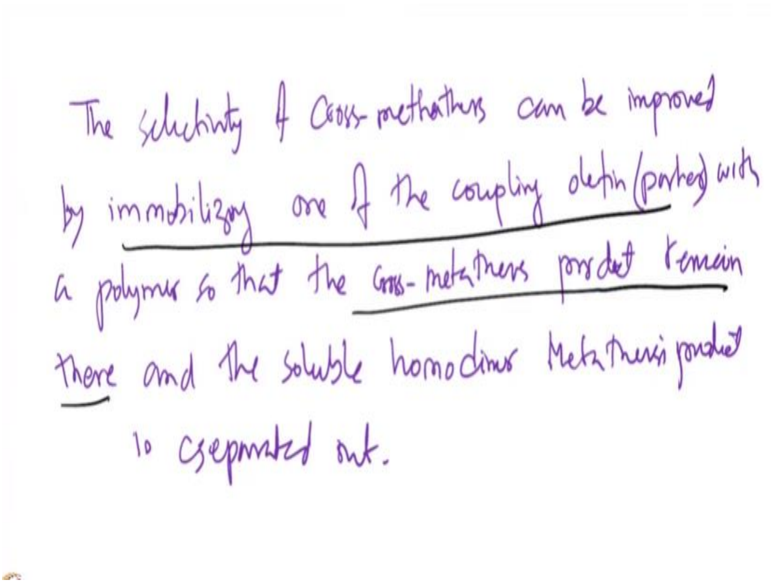

The selectivity of cross-metathesis can be improved by immobilizing one of the coupling olefin (partner) with a polymer so that the cross-metathesis product remain there and the soluble homodimer metathesis product is separated out.

The selectivity of cross metathesis can be improved by immobilizing one of the coupling partners coupling olefin with a polymer. So that the cross metathesis product remain there and the soluble homodimer metathesis product is separated out. So the other way of increasing the selectivity of cross metathesis product is by immobilizing one of the olefin so that the cross metathesis product remain in the polymer and the soluble homodimer product is separated out.

So with these I come to the conclusion of today's lecture in this lecture we had looked into the application aspects of metathesis reaction with regard to the shop olefin polymerization process and what we had discussed is the fact that all these large scale industrial application reactions have been used for making feedstock for soft detergents or fatty acids and how cross metathesis was developed to utilize the non-usable alpha olefin fragments of low and high molecular weights to produce alpha olefins of medium range molecular weight it could be used for application as detergents.

We have also looked at the issues which remain which play cross metathesis reaction and one of the main issue is the selectivity of issue of selectivity because the metathesis does not distinguish between the 2 isomers E's and Z's both are formed in the mixture for each of the products like cross metathesis products as well as homodimer homo metathesis products and when we had also looked at various attempts have been made to overcome this lack of selectivity issue and to such methods that we have discussed which is one by professor Grubbs who had reported increased yields of cross metathesis product by allowing homometathesis of the first olefin followed by the introduction of the second olefin to give the larger amount of the cross metathesis products .

We have also looked at another strategies that implies immobilizing one of the coupling partners on the polymer. So the cross metathesis products stay on the polymer surface whereas the soluble homodimer metathesis product are separated out. So with these we come to conclusion of today's lecture we are going to be talking more on the aspects of cross metathesis as well as some other olefin metathesis reaction particularly the admit reaction when we take up our discussion in the next class till then goodbye and thank you.