Transition Metal Organometallics in Catalysis and Biology
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Module No # 01
Lecture No # 01
Introduction

Welcome to this course on transition metal organometallics in catalysis and biology in the first lecture I am going to give a brief introduction about these advance level transition metal organometallics course. And then subsequently will take up a very interesting topic which is Reppe synthesis mainly from the prospective of utility and challenges of application of organometallic chemistry in chemical catalysis.

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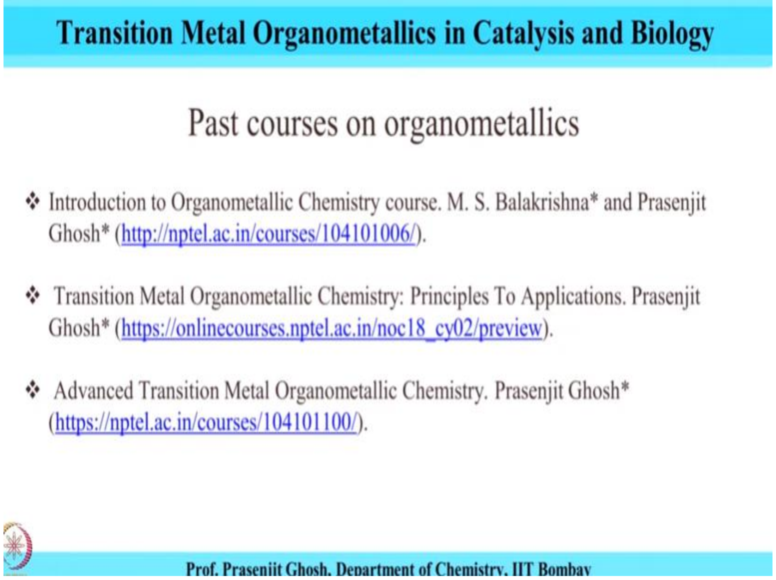

Transition Metal Organometallics in Catalysis and Biology

Past courses on organometallics

- Introduction to Organometallic Chemistry course. M. S. Balakrishna* and Prasenjit Ghosh* (http://nptel.ac.in/courses/104101006/).
- Transition Metal Organometallic Chemistry: Principles To Applications. Prasenjit Ghosh* (https://onlinecourses.nptel.ac.in/noc18_cy02/preview).
- Advanced Transition Metal Organometallic Chemistry. Prasenjit Ghosh* (https://nptel.ac.in/courses/104101100/).

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Now this particular course this transition metal organometallics in catalysis and biology is a continuation of the past 3 courses which have been offered in this series of NPTEL lecture series. To start with I had given advanced transition metal organometallic chemistry followed by organometallic chemistry from principles to applications and then introduction to transition metal organometallic chemistry.

So these are the 3 course which forms the basis and prerequisite for these current course which is transition metal organometallics in catalysis and biology and would provide the necessary foundation and platform based on these current course is floated. Now the current course focuses mainly on the application aspects of transition metal organometallics in catalysis and biology and the principles and how the rationalization had been covered in the earlier courses which I just have mentioned so far.

Now in the current time organometallics or transition metal organometallics compounds or transition metal organometallic chemistry as a field is going through and exiting time given the fact that over the last century about 9 Nobel prize have been awarded to this field of transition metal organometallics chemistry. Now these is a tremendous achievement for any field or recognition for any field to show case the potential utility of this very important say let transition metal organometallic compounds.

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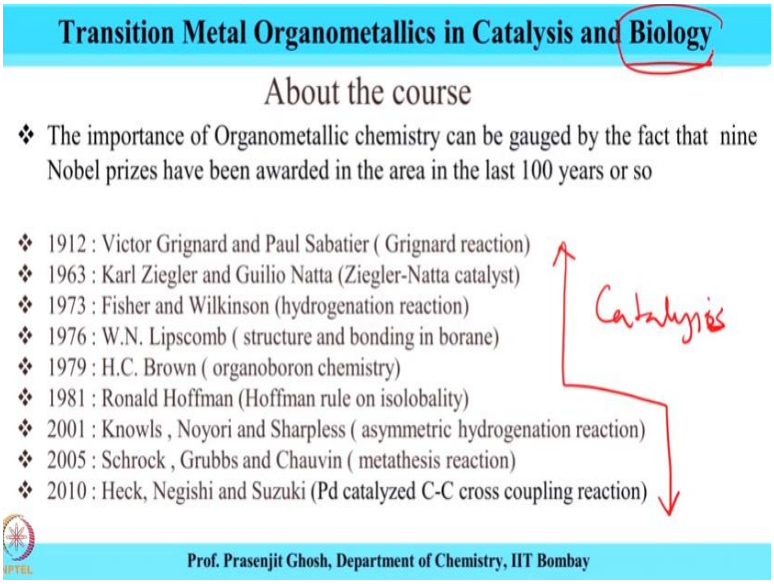

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About the course

- The importance of Organometallic chemistry can be gauged by the fact that nine Nobel prizes have been awarded in the area in the last 100 years or so

- 1912 : Victor Grignard and Paul Sabatier (Grignard reaction)
- 1963 : Karl Ziegler and Guilio Natta (Ziegler-Natta catalyst)
- 1973 : Fisher and Wilkinson (hydrogenation reaction)
- 1976 : W.N. Lipscomb (structure and bonding in borane)
- 1979 : H.C. Brown (organoboron chemistry)
- 1981 : Ronald Hoffman (Hoffman rule on isolobality)
- 2001 : Knowls , Noyori and Sharpless (asymmetric hydrogenation reaction)
- 2005 : Schrock , Grubbs and Chauvin (metathesis reaction)
- 2010 : Heck, Negishi and Suzuki (Pd catalyzed C-C cross coupling reaction)

Catalysis

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To begin with the first Nobel prize went to Victor Grignard and Paul Sabatier for Grignard reaction discovery as early as 1912. Now this if one looks at seminal discovery which allowed the chemist to form carbon-carbon bonds however there was great bit of challenge associated with it particularly going to the air and moisture sensitivities of this organo alkaline arc region like organo magnesium compounds.

And another limitation as we saw for carrying out this CC bond formation in the stoichiometric fashion. The next very important discovery in this area are came from this Ziegler- Natta catalyst for the discovery of olefin polymerization. Now these open door to this world of polymers that were synthesized by transition metal organometallic compound and lot of applications of poly olefins emerged out of this discovery.

This was indeed discovery which as broken bounds from the confines of the walls of laboratory to this large scale industries and had a lot of application in this society at large. Another important and seminal discovery was reported by Fisher and Wilkinson which is the hydrogenation reaction followed by Lipscomb in 1976 got the noble prize for structure and bonding elucidation of borane compounds which are very complex in terms of the bonds they formed and they are mainly known to form multi center electron deficient non classical bonds which are beyond the intuition of normal classical 2 electron bonds.

So here was at each world of the bonding complex bonding structures about sharing electrons in non-classical fashion between multi center for which lifts form was rightfully awarded the Nobel prize then in 1979 we saw H C Brown getting Nobel prize for developing organoboron reagents and organoboron reagents as we see has lot of applications in the chemistry of reductions particularly borohydrides and other reagents.

And we would also see the subsequently a another the second Nobel prize also was an offshoot of the discovery of arganoboron region particularly that of this palladium mediated cross coupling reaction for ahh which Heck Suzuki and Negishi was given the Nobel prize of. So what we see is that a field not only getting a Nobel prize for 1 time but in many cases has won a second Nobel prize for subsequent development of the field as we have seen in with HC Brown organoboron region getting Nobel prize in 1979 as well as in 2010.

The utility of organoboron region for palladium mediated cross coupling region Suzuki and Negishi also getting the Nobel prize. Incidentally both Suzuki and Negishi was a postdoc working for professor Brown when the excitement of organoboron chemistry was developed. So what we see that a second generation of Nobel prize coming from coming to the same junior chemist who had where the adviser as well as the post doctorial research associate both ended up getting 2 different Nobel prize in a time of about 30 years or so apart.

Then in 1981 professor Ronald Hoffman was given Nobel prize again for explaining a complex set of rule particularly for pertaining to isolobality where metal fragments behaved chemically similar or the reactivity of this metal fragment were very similar to that of their organic counterparts then in 2001 Knowls Noyori and Sharpless got Nobel prize for asymmetric hydrogenation reaction.

So again here also we see a trend that this is a second Nobel prize on the similar discovery with the first one being awarded to Fisher and Wilkinson on hydrogenation in 1973 and in 2001 Knowls Noyori and Sharpless getting the second Nobel prize in asymmetric hydrogenation in more refined techniques for hydrogenation after another 30 years or so. Again in 2005 another important ahh discovery in the area of organometallic chemistry namely this metathesis reaction was recognized and given Nobel prize to professor Richard schrock, Robert Grubbs and professor Chauvin.

And this also is in that way one can say second Nobel prize to organometallic polymerization field the first being that of Karl Ziegler and Guilio Natta in 1963 given for polyolefin polymerization and again after span of about 40 years Schrock, Grubbs and Chauvin getting Nobel prize for another discovery in the area of olefin polymerization particularly from the metathesis standpoint.

So what a intend the highlight through all this discoveries and this correlation is that fact that applications of transition metal organometallics in catalysis and biology have tremendous potential which are now being realized and also been recognized by the fact that so many another prizes have been awarded to this particular field in the last 100 years or so. Another thing that I should stress about this course is that this course not only focuses on the application of transition metal organometallics in catalysis but also in biology particularly from the prospective of bio organometallic chemistry.

Now if I may point out to all these 9 Nobel prizes that have been awarded now all can see that almost all of them have been awarded to the field of catalysis. And the area of organo transition metal organometallics in biology still remains stage in the development and as yet to be refinished as a potential area of importance. So this course also focuses on this particular aspect where one can see that how a transition metal organometallics are becoming very important in the area of biology particularly in bio organometallic chemistry.

And the course also is focus in this end now before we just go in let me recall some of the concepts that we had discussed in the earlier courses as this would be very essential in appreciating and understanding the content which would be a given in this next few lectures.

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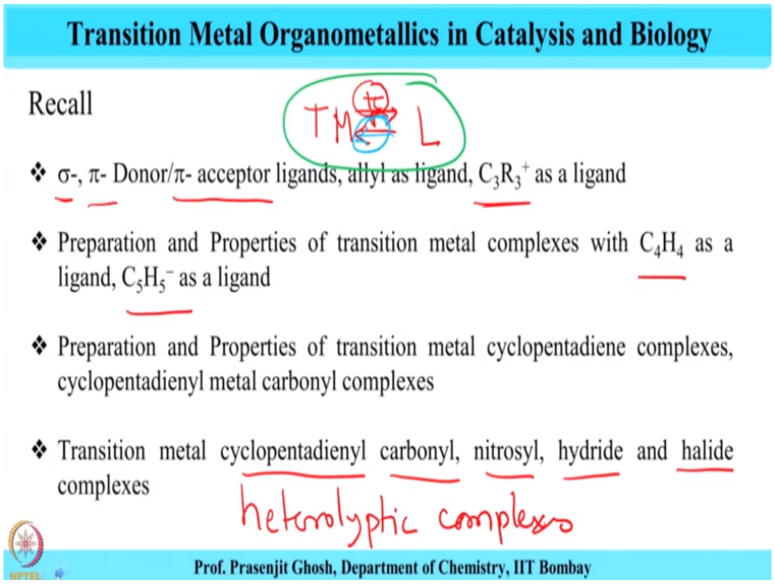

Transition Metal Organometallics in Catalysis and Biology

Recall

- σ-, π- Donor/π- acceptor ligands, ~~allyl as ligand~~, $C_3R_3^+$ as a ligand
- Preparation and Properties of transition metal complexes with C_4H_4 as a ligand, $C_5H_5^-$ as a ligand
- Preparation and Properties of transition metal cyclopentadiene complexes, cyclopentadienyl metal carbonyl complexes
- Transition metal cyclopentadienyl carbonyl, nitrosyl, hydride and halide complexes

heterolyptic complexes

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Now to begin with we had looked at various kinds of ligand systems which stabilize transition metal organometallic compounds particularly from their bonding prospective and they include sigma as well as Pi donor ligands Pi acceptor ligands. Now these in the previous courses we have looked into the various orbitals in that are involved in engaging in bonding with metal.

Now one interesting concepts about transition metal organometallics is that a transition metal ligand bond is a 2 way traffic. That means that the transition metal accepts electron a sigma electron from the ligand which is electron rich entity and also provides a second kinds of interaction which is donation of electron back from the metal to the ligand. So these is a unique property of transition metal ligand interaction where a 2 way traffic of electron flow is observed.

The first one is the sigma interaction where the ligand gives electron to the metal and the second one is the Pi interaction where the metal gives electron back to the ligand. So these there is a inter play and there is a balance between a type of flow that exist between transition ligand and bonding. And we had this phenomenon to be present in various kinds of ligand starting with the

C3 fragment which are C3R3 plus and then we have looked into the higher homologs of his ligand like cyclo butane C4H4 or the more variant C5H5.

And looked into the preparation properties of this kind of ligand which are by nature sigma donating. Pi donating or pi accepting ligand and we have also looked into heterolytic complexes where this transition metal is bound to various kinds of different ligands and that are like cyclo pentadienyl, carbonyl, nitrosyl, hydride and the halide complexes of transition metals. So in most of this cases the important take of message is the dual are 2 way interaction of metal ligand with respect to electron flow is evident and important and also they play a crucial role in being able to our stabilize the particular kind of interaction.

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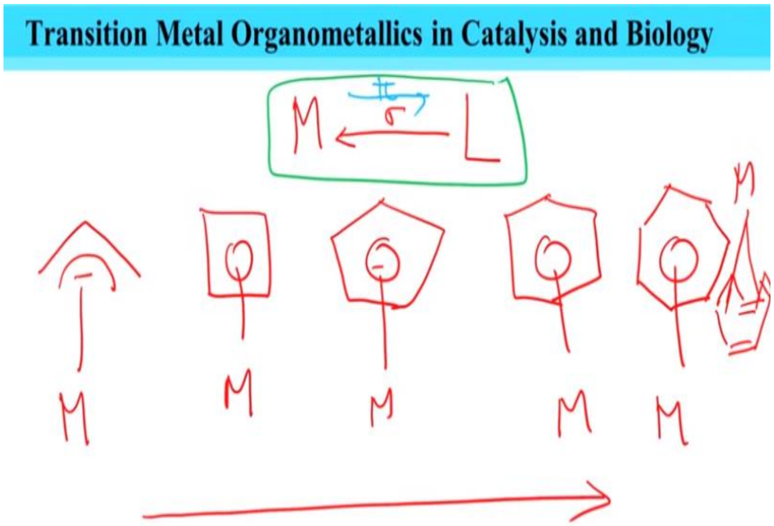

Transition Metal Organometallics in Catalysis and Biology

In the past we had seen that one has we have looked into the 3 fragment interaction with the metal the 4 fragment interaction with the metal the 5 fragment interaction with the metal then the 6 fragment interaction with the metal even the 7 fragment interaction with the metal and the last 3 the 8 fragment interaction with metal. So there is a wide diversity of range of interaction which is possible between the metal and ligand.

And in the previous course we have looked into the type of metal ligand interaction which are possible and the constant thing is all of these there is a metal ligand interaction where there is a sigma bond between the metal and ligand and there is a back donation which is happens from the metal to the ligand. So this is a unique feature of organometallic compounds and that is present in various kind of interactions that we have discussed in the previous course.

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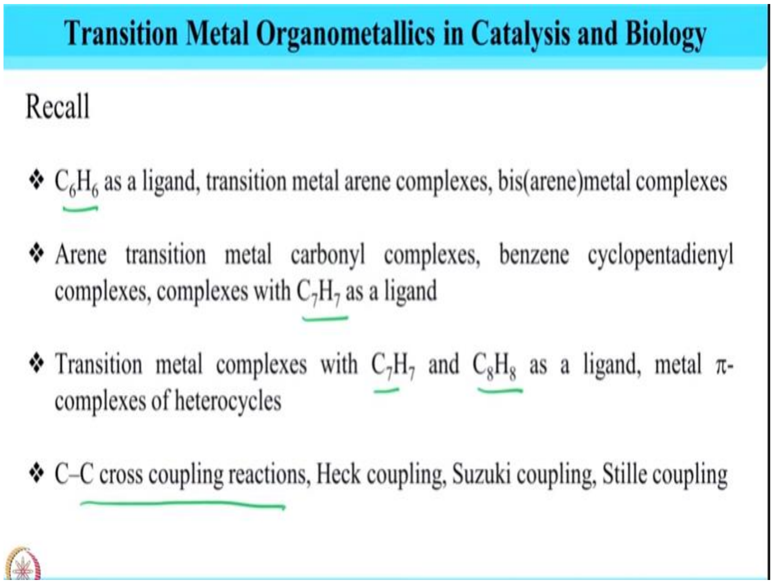

Transition Metal Organometallics in Catalysis and Biology

Recall

- C_6H_6 as a ligand, transition metal arene complexes, bis(arene)metal complexes
- Arene transition metal carbonyl complexes, benzene cyclopentadienyl complexes, complexes with C_7H_7 as a ligand
- Transition metal complexes with C_7H_7 and C_8H_8 as a ligand, metal π-complexes of heterocycles
- C–C cross coupling reactions, Heck coupling, Suzuki coupling, Stille coupling

And as we moved on from C6 fragment to the cycle hetra trynl C7H7 and C8H8 fragment looked at the interactions then in the previous class we have also looked at various applications of these transition metal organometallic compounds particularly from CC cross coupling reactions as I said that this is a very interesting area which has been recently awarded the Nobel prize where this CC coupling has been recognized an important synthetic tool for constructing various kind of organic targets and this is effortlessly done using palladium Heck Suzuki and Stille coupling and other sets of palladium mediate cross coupling reaction.

Now as I said that many when I was highlighting talking about the importance of organometallic chemistry as a field as I said that in several instances we had observed that the particular discovery a being recognized with Nobel prize not only once but even more than once and to that we had the seen the examples of olefin polymerization as well as metathesis polymerization both are transition metal mediated polymerization being recognized as important discovery and being awarded Nobel prize twice.

We have also seen like hydrogenation by Wilkinson as well as Knowls is asymmetric hydrogenation getting a this Nobel prize twice and similarly on the same flow what we saw is this CC bound forming reaction by Grignard given Nobel prize in 1912 . Again about 100 years later in 2010 again the CC bond forming reaction particularly the cross coupling reaction winning Nobel prize as given to Heck Suzuki coupling.

So this shows that field even could achieve significant milestones in terms of this discovery even about a century a part since the first major discovery recognized by Nobel prize was. So Grignard won in 1912 and then again Suzuki coupling still winning in 2010. Another important thing on this that this cross coupling which was given Nobel prize in 2010 is mainly for several improvement on with regards to CC cross coupling which this Nobel discovery bought in.

For example Grignard reactions are extremely air and moisture sensitive whereas the current Nobel prize winning cross coupling reactions are stable in air and this reactions can be performed in open air under aerobic conditions. So there has been covered in terms of improvement and discovery. Furthermore another important benefit of this more devised CC cross coupling reaction is the fact that this reactions are carried out in with the metal agent being used in catalytic compounds where large number of turnovers where observed by same catalyst.

Whereas, the Grignard discovery had mainly been a stoichiometric with respect to the very sensitive Grignard agent which were used for making the carbon – carbon bonds. And hence again a thing is that a log of grounds have been covered in terms of discovery in terms of overcoming the challenges and it is becoming more and more evident that the field is really more important as many of the discoveries or many of the areas of the discoveries have been awarded the Nobel prize.

Not only once but more than once over a span of as little as 30 years to as high as about 80 or 90 or 100 years to say that this field of organometallic chemistry is really passing through an exciting time and it is alive and kicking.

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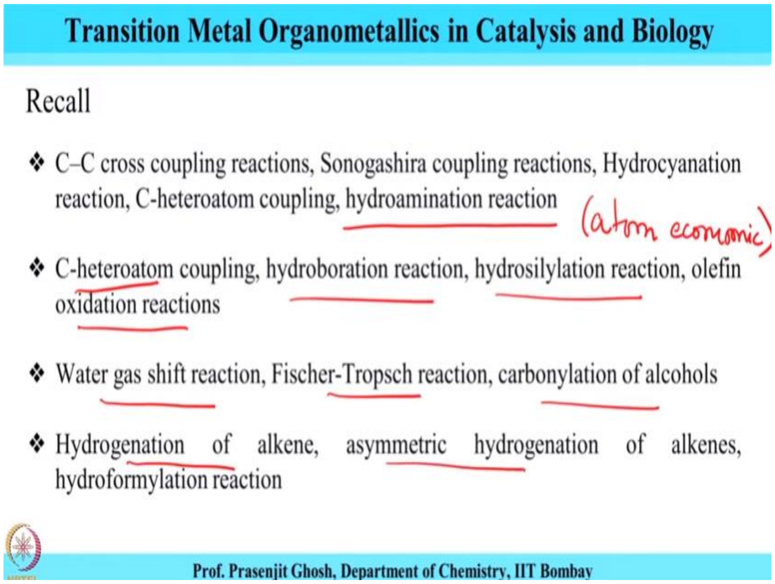

Transition Metal Organometallics in Catalysis and Biology

Recall

- C–C cross coupling reactions, Sonogashira coupling reactions, Hydrocyanation reaction, C-heteroatom coupling, hydroamination reaction (atom economic)
- C-heteroatom coupling, hydroboration reaction, hydrosilylation reaction, olefin oxidation reactions
- Water gas shift reaction, Fischer-Tropsch reaction, carbonylation of alcohols
- Hydrogenation of alkene, asymmetric hydrogenation of alkenes, hydroformylation reaction

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So we had along the same flow we had looked into some applications earlier on in a previous courses that involved cross coupling reaction sonogashira coupling hydrogenation reactions, carbo heteroatom coupling, hydroamination reaction. Now some of this are really very interesting problems even industrially from our society point of view given the fact that they pose a lot of challenges when wants to achieve.

And one such thing is hydroamination reaction which are very in sense that they are atom economic which means that there is no side product which is our bi-products which are to be produced in the course of the reaction which needs to be discarded. So this are highly desirable atom economic reaction in the sense that all the reactants getting incorporated into that product and there is nothing to discard off.

But the major challenge in hydrogenation reactions are that both making the 2 reactions because their means and the substrates unsaturated substrates like olefin’s alkynes all are electronic entities and they mutually repel each other and they would not participate in reaction with each. And here what we observe is that the solution has been provided by transition metal chemistry where the transition metal binds to these electronic species activates them that is make them more electron deficient as a result of binding to transition in metal through the metal ligand or forward sigma donation and backward Pi donation.

The those type of donation we have discussed about in the earlier slide making one of the reactant more agreeable to reacting with the other reactant and hence we see how this academic challenge of making 2 electron rich substrates react becomes possible as a result of intervention of transient metals in transition metal organometallic chemistry. Along the same line we had looked into some other very useful applications of transition metal organometallic chemistry particularly carbon heteroatom coupling, hydroboration reaction, hydrosilylation reactions.

Olefin oxidation reactions now we have also looked at some of the very important industrial process is like water gas shift reaction Fischer-Tropsch synthesis, carbonation of alcohols. We have also in the same breath we have also looked into this hydrogenation reactions their asymmetric form as a part of the previous course where we discussed some of the applications of transition metal organometallic chemistry the world of chemical catalysis.

Now today given the fact that I have just provided a glimpse of extent and the utility to which the transition metal organometallic chemistry in the world of catalysis can expand to and also being recognized with global prizes. Today in this course I am going to take up another very important applications of transition metal chemistry particularly in the area of Reppe synthesis which is nothing but the utility of acetylenes in industrial processes.

Now here I should mention that this development of transition metal organometallic chemistry is kind of unique where we see the development being carried out equally in industry as well as in the laboratory of academia. So the topic the first topic in this course is Reppe synthesis which has been exclusively or extensively developed in industry where and has been done about a century ago by Walter Reppe who was a pioneer in acetylene chemistry.

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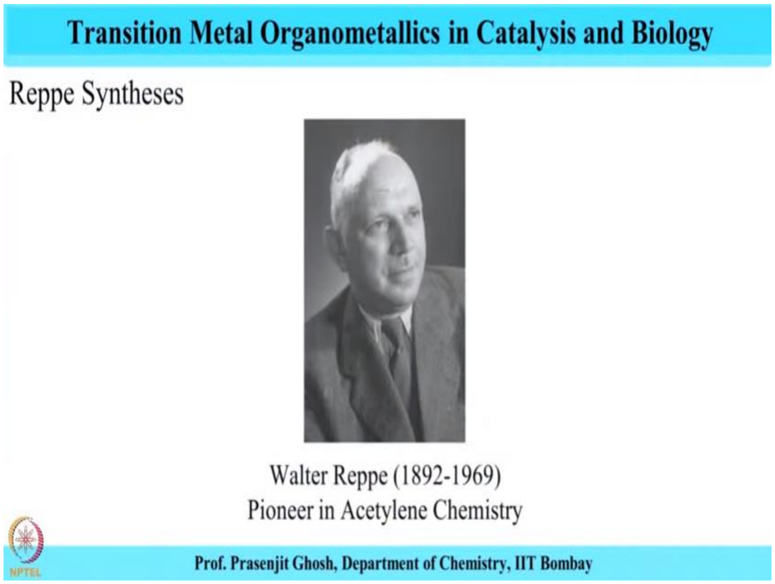

Transition Metal Organometallics in Catalysis and Biology

Reppe Syntheses

Walter Reppe (1892-1969)
Pioneer in Acetylene Chemistry

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Now we are going to looking up in this rich application of acetylene chemistry as developed by Walter Reppe and which popularly known as this Reppe synthesis in the subsequent lecture from now on. I should also mention that the most of the applications of transition metal organometallics has been by and large in the area of chemical catalysis homogenous as well as heterogeneous. However the applications of transition metal organometallics in biology is still an emerging and the new area which is getting importance by the day.

With that I want to emphasize that this course we are going to take up topics not only for the utility of transition metal organometallics in catalysis but also in biology. So with these I conclude today's lecture where had given a brief introduction about the potential importance and utility of transition metal organometallics in catalysis and I have made grounds for the utility in biology. And also introduced an important reaction that I would be talking about which is Reppe synthesis which has been developed mainly in the industry and have been a contribution from the industry in Germany and more of this today's lecture.

We are going take up these Reppe synthesis Reppe chemistry in more details in subsequent lectures till that good bye and look forward to being with you in the next lecture thank you.