# Advanced Transition Metal Organometallic Chemistry

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## Module - 12
## Lecture - 60
## Summary of Advanced Transition Metal Organometallic Chemistry

Welcome to the last lecture of the course Advanced Transition Metal Organometallic Chemistry. In this lecture I am going to summarise the topics that has been covered in this course. Now to, even before I do that, let me just on a personal note mention that, this has been a wonderful journey on my front, as well in talking to you about the applications of organometallic complexes through this Advanced Transition Metal Organometallic Chemistry.

Now, in this day and age where the relevance of academic research is being questioned, this course sort of provided an opportunity once again to show how the discoveries made in academic world can translate to something useful in form of industrial processes or large-scale applications. So, from that perspective, this journey of, that I made through this course Advanced Transition Metal Organometallic Chemistry had been extremely gratifying.

The focus of this course was on talking about the applications of organometallic chemistry particularly from the industrial point of view. And what we had covered in this course, large number of reactions which has made it big from the laboratory, confines of the laboratory from their initial days stages in the confines of the laboratory to the large scale utility in industrial scale synthesis.

So, in this lecture today, I am going to summarise on the topics that we have covered during this course. but before I begin that, first and foremost, I should acknowledge and thank the people who had made this course possible. And they are the teaching assistants as well as the whole of IIT Bombay, NPTEL team.

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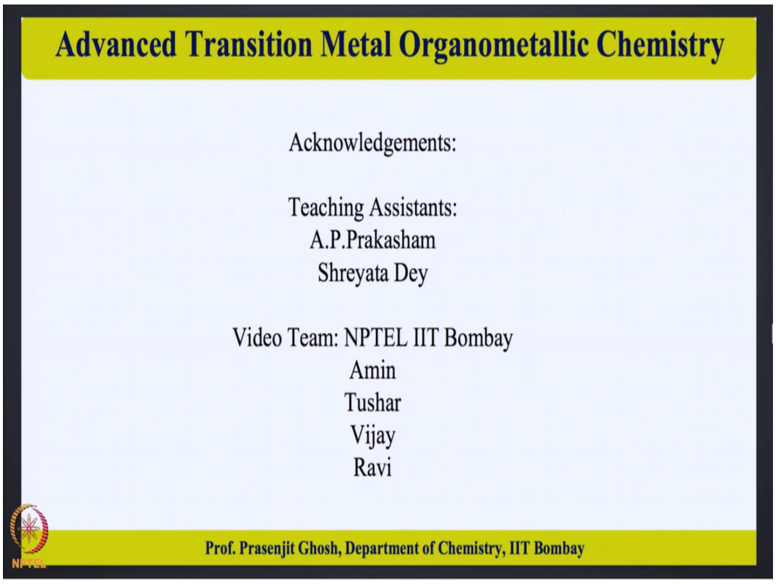

**Advanced Transition Metal Organometallic Chemistry**

Acknowledgements:

Teaching Assistants:
A.P.Prakasham
Shreyata Dey

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Tushar
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Now, to begin with the teaching assistants where Mr. A.P.Prakasham and Miss. Shreyata Dey, they had been instrumental in carrying out, making all the slides and collecting information putting them on the PowerPoint slides and then working on the questions, so on and so forth. So, a big thank to the teaching assistant Mr. A.P.Prakasham and Miss. Shreyata Dey. The video team at IIT, Bombay, NPTEL office did a wonderful job in running, making this course possible.

In particular, my thanks goes to Amin, Tushar, Vijay and Ravi who had tirelessly worked behind the scenes in recording all the lecture. 1 thing which stood out is their look out for details. So, everything was done in a perfect manner by this wonderful group of people. And that is what made this recording as well as this overall journey a very pleasant one, here at NPTEL, IIT, Bombay. So, with this, let me just go over the topics that we had covered. So, to begin with we started our course on allyl and enyl kind of complexes.

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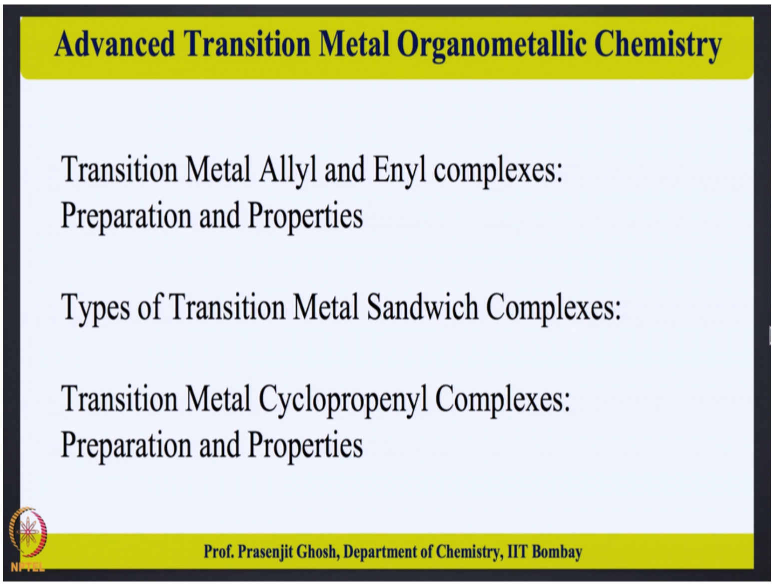

Advanced Transition Metal Organometallic Chemistry

Transition Metal Allyl and Enyl complexes:
Preparation and Properties

Types of Transition Metal Sandwich Complexes:

Transition Metal Cyclopropenyl Complexes:
Preparation and Properties

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This allyl and enyl are eta 3 type of complexes which has sigma bi component. And we had seen how these complexes were synthesised, prepared; we had also looked at the bonding and the electronic structure of this complexes. And we were, we looked at how the molecular orbital diagrams were constructed for these complexes. The electronic energy diagram of these complexes provided insight into the major reactivity of this complexes and how they defined the course of various reactions.

The, moving over from allyl and enyl kind of complexes, we looked into transition metal sandwich complexes. This transition metal sandwich complexes are of prime importance, particularly from the days of their initial discoveries synthesis and discovery in 50s. One of the intriguing question which plagued the community or which bothered the community at the time of their synthesis and discovery is, how does the P orbitals of the cyclopentadienyl ring bond with the metal and to form this sandwich complexes.

So, the interesting thing was that, how do this metal orbital interact; how, what is the nature of bonding, because these are anionic ligands bound to metal; what would be their reactivity; and so on and so forth. So, this transition metal sandwich complexes were subsequently synthesised and a proper detailed molecular orbital diagram providing inset, insight into their electronic structure was also subsequently discovered and has been discussed in this class as well.

Now, from that perspective, the nature of engagement which the cyclopentadienyl ligand engages the metal orbitals through its conjugated pyorbital becomes very important and relevant. And we had looked into those molecular orbitals in plot details, constructing this molecular orbital from individual fragment molecular orbital of the cyclopentadienyl ligands and the metal ion itself.

We have also looked into the various ways of making this transition metal sandwich complexes. And what we had also spoken about is, what are the reactivity difference or what are the unique reactivity that this transition metal sandwich complexes exhibit. And what we had seen, that this transition metal sandwich complexes can undergo this nucleophilic aromatic substitution or substitution on their CP ring at much faster rate than what a normal aromatic ring or benzene might do.

And that is a quiet pronounced effect with transition metal sandwich complexes. And such a reaction has been attributed to the molecular orbital correlation diagram that one can construct from the fragment molecular orbital interaction with this CP ligands. So, on that context, we have looked into transition metal cyclopropenyl complexes. These are interesting compounds. Cyclopropenyl ligand is on the lower end of the aromatic system in sense that, it has only 2 pi electron.

However, they behave in a aromatic, as a aromatic ligand while they bind to the transition metal. And we had also looked at how this ligand based on their cationic, anionic or radical nature can affect the binding to the transition metal. So, these are the simplest of the aromatic ligand to start with, that we had discussed. We have looked into the preparation properties as well as the molecular orbital diagrams of these transition metal cyclopropenyl complexes.

Now, we have done a full-fledged exploration of various kinds of cyclo aryl ligands. And then, moving on from cyclopropene, we have looked into cyclobutadiene complexes; their preparational properties.

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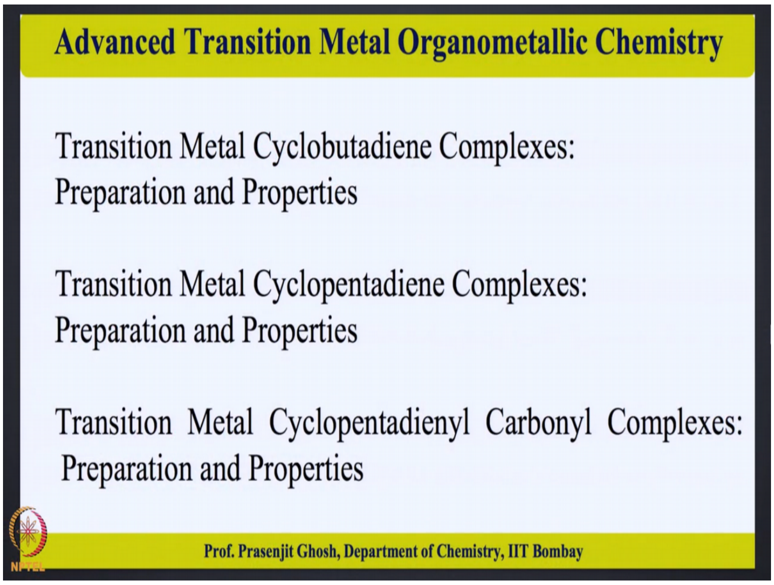

**Advanced Transition Metal Organometallic Chemistry**

Transition Metal Cyclobutadiene Complexes:
Preparation and Properties

Transition Metal Cyclopentadiene Complexes:
Preparation and Properties

Transition Metal Cyclopentadienyl Carbonyl Complexes:
Preparation and Properties

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Now, interesting thing about cyclobutadiene complexes are that they by themselves are non-aromatic in the sense that they have 4 pi electrons. And that they by accepting to more electron from the metal become aromatic, but that is when they become dianionic in nature. So, that has interesting fall out because cyclobutadiene by itself have, should have 2 longer bonds and 2 shorter bonds.

That means 2 single bonds and 2 pi bonds. However, upon complexion to the metal, what has been observed in the structurally characterised metal cyclopentyl butadiene complexes is that the metal carbon bonds are all equal. And that has been attributed to the fact that they become aromatic upon binding to transition metals. And they by accepting 2 more electron form the filled metal, partially filled metal d orbitals making them dianionic in nature.

And as they become dianionic nature and aromatic, they become fully conjugated in the ligand. And as a result, they are all, bond lengths become equal. So, that is a interesting observation we made while we discussed this cyclobutadiene complexes. We have also looked into the electronic structure of cyclobutadiene complexes with regard to generation of their molecular orbital diagrams.

And we have also looked at how this P orbitals of the cyclobutadiene ring engage in constructive or destructive fashion to give the various molecular fragment molecular orbitals. And then, how the FMOs react with the metal d orbitals to give these electronic structure of the overall metal cyclobutadienyl complexes.

Now, what, throughout this course, over and over again what we had made is an attempt to justify reactivity of the transition metal complexes with regard to their electronic structure which is obtained by constructions of the molecular orbital diagrams from the individual fragment molecular orbital of the atom and the ligand in the same orientation in which they are placed in the metal complex.

Not only that, we have also tried to explain the reactivity of this complexes not only with respect to their electronic structure and looked at which are the orbitals occupying the valence shell and what are the orbitals which are in the anti-bonding region. And then, looking at their homo and lumo and orbitals we tried to rationalise the reactivity observed for these complexes.

In addition, we had also looked at the oxidation state, the electronic saturation as well as the steric saturation or unsaturation of each of these metal complexes in trying to explain the steric bulk of the (()) (13:00) to explain the chemical reactivity of this complexes. Now, moving on from cyclobutadiene, we have moved on to cyclo metal cyclopentadiene complexes.

These are, these so-called sandwich complexes that we have been talking about. Now this sandwich complexes are important milestone in the field of organometallic chemistry, because they define a new set of interactions in which the p orbitals of the conjugated aromatic ring interacted in a bonding fashion with the transition metal orbital. And this, of this type of interaction when discovered was completely new and unknown.

And from that perspective, these transition metal cyclopentadienyl complexes occupy a very important special place in the nature of understanding of metal ligand orbital. So, these kind of a interaction at that time was completely new and unknown and also very radicle in nature and similar to the forward donation and sigma bi donation with the ethylene orbital of the Dewar-Chatt-Duncanson model, which explained how ethylene with its pi orbitals bind to the transition metal.

So, this is even much more complicated to that. And I must say that this Dewar-Chatt-Duncanson model was developed in 1950s, even though Zeise's salt, the compound structurally first characterised to have these ethylene metal interaction, was synthesised over a century back in 1820s. So, even though the compound, this Zeise's salt which had olefin metal pi interaction was synthesised in 1800.

But there were no theory in trying to explain the nature of bonding that existed between ethylene and transition metal, till in 1950s when Dewar-Chatt-Duncanson explained this metal ligand interaction of metal ligand, ligand metal sigma donation and metal ligand pi back donation occurring in this ethylene transition metal complexes.

And in this context, what is relevant here is that the metal transition metal cyclopentadienyl complexes which would, which had even more higher order of engagement between the conjugated 5 P orbitals of the CP ring to that of the metal orbitals, many fold complicated, more intriguing interaction; that was also sort of discovered around the same time of Dewar-Chatt-Duncanson model; may be in within the same decade or so.

So, from that perspective, the transition metal cyclopentadienyl complexes had been object of intense interest and excitement generated was remarkable. We have in that context, we have not only looked at the bonding interaction by looking at the, by constructing the molecular orbital diagram for metal cyclopentadienyl complexes. But also looked at the preparation properties and the reactivity of these complexes in greater details.

Now, we have not only looked at this metal cyclopentadienyl complexes as a part of our discussion on sandwich complexes. This sandwich complexes are homolytic complexes of metal and arene ligands, where there was only 1 type of arene ligand which interacts with the metal. Moving on, we have also looked into half sandwich complexes like transition metal, cyclopentadienyl carbonyl complexes.

These are interesting set of complexes which not only has the cyclopentadienyl ligand attached to the metal, but also have carbonyl ligand attached to the metal. So, these are heteroleptic complexes of transition metal and so, from that perspective they are interesting. And in these ligand, what we see that not only the anionic cyclopentadienyl ligand is bound to the transition metal, they also have highly acidic carbonyl ligands bound to the same transition metal.

So, they are heteroleptic transition metal complexes. So, we have, in this context, we have looked into various ways of preparing these complexes. And one of the main strategy had been in reaction of metal halide with carbonyl and cyclopentadienyl reagent or metal carbonyls with cyclopentadienyl reagent, so on and so forth. So, these complexes are sort of more reactive, more amenable for various catalytic transformations, as they have 2 different kinds of ligand.

And the reactivity of the metal centre or the electronic structure of the metal centre is controlled that way. Moving on, or looking into other variation of this half sandwich complexes, we have looked into transition metal nitrosyl complexes.

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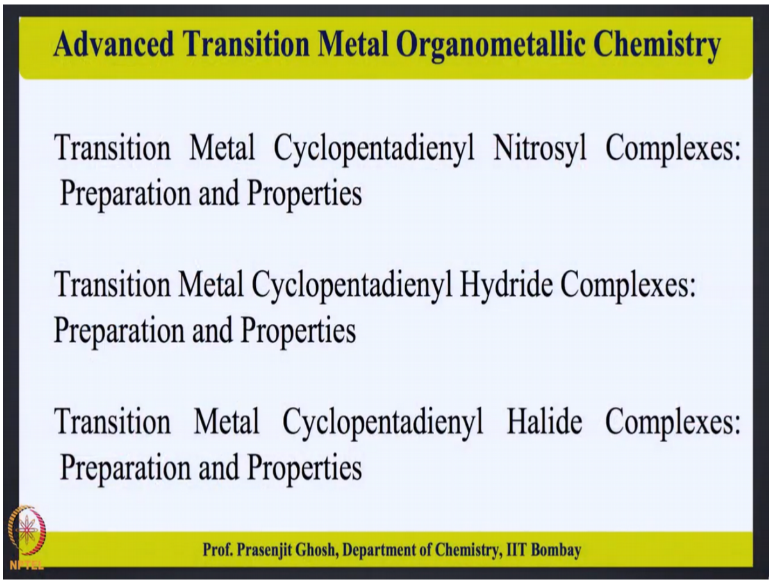

Advanced Transition Metal Organometallic Chemistry

Transition Metal Cyclopentadienyl Nitrosyl Complexes: Preparation and Properties

Transition Metal Cyclopentadienyl Hydride Complexes: Preparation and Properties

Transition Metal Cyclopentadienyl Halide Complexes: Preparation and Properties

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These nitrosyl complexes are important because eno as a ligand has also aroused a considerable interest. Now, eno can bind in several ways. It can be, it can act as a 1 electron donor and form a bent compound or it can form a 3 electron donor and bind in a linear fashion. So, eno has 2 binding modes. 1 is bent and linear and on top of that eno can also from terminal ligand or act as a bridging ligand.

So, in that way, eno has 4 different ways it can bind. 1 is, it can be a 1 electron donor or a 3 electron donor. In 1 electron donor case it is a bent ligand whereas in a 3 electron donor case it is a linear ligand. And also, eno can act as a bridging ligand and between, more than 1 metal centre. Or it can act as a terminal ligand. And all of these eno binding to the metal centre can be studied using infrared frequency and to some extent these can accurately predict the nature of binding of enos to the transition metal cyclopentadienyl nitrosyl complexes.

For this, we have as usual we have looked into the preparation and catalytic properties. Now, looking under various variation of transition metal cyclopentadienyl hydride complex variation, we have also looked at transition metal cyclopentadienyl hydride complexes. Now, these hydride complexes are very interesting because they are active intermediates in very many catalytic cycles and like, 1 such example can be hydroformylation reactions that we just discussed in the last class and which is the largest scale ever industrial process under homogeneous catalysis.

So, there are many more or hydrogenation reactions where again the metal hydrides are active intermediates in hydrogenation reaction. So, from that perspective, we have looked into ways and means for preparations of this transition metal cyclopentadienyl hydride complexes. Now, of these, the important aspect is the hydride moiety. The hydride moiety for dimiotic compounds can be easily characterised through its characteristic resonance which appear highly a fill shifted in (()) (21:52) and which gives a handle for observing the formation or the presence of the metal hydride moiety.

The hydride moiety can also be observed or characterised infrared and or isotope levelling studies. So, with respect to transition metal hydride complexes, we have also looked into the preparation and properties of this intermediate compounds in a large details. Moving further to the variation of transition metal hydride complexes, we have also looked at transition metal halide complexes.

These halide complexes are important not more as a intermediate or active intermediate in part of a catalyst cycle. But what this halide transition metal cyclobutadiene halide complexes are important more for, is their, they are important starting precursors for generating very many kinds of other transition metal organometallic complexes. For examples, halide complexes can be converted to hydride complexes, alkyl complexes or they can be abstracted.

And then subsequently can be converted to olefin adduct or some other adduct in their cationic forms. So, these halide, the moiety can not only act as a terminal ligand, but also can act as bridged ligand. And we have looked into the preparation and properties of this transition metal halide complexes and discussed them in detail, from this perspective. Moving on, we have moved from 5 membered cyclopentadienyl systems to transition metal arene complexes.

We have looked into their preparation and properties. These are neutral complexes as opposed to the cyclopentadienyl ones which are more anionic in nature.

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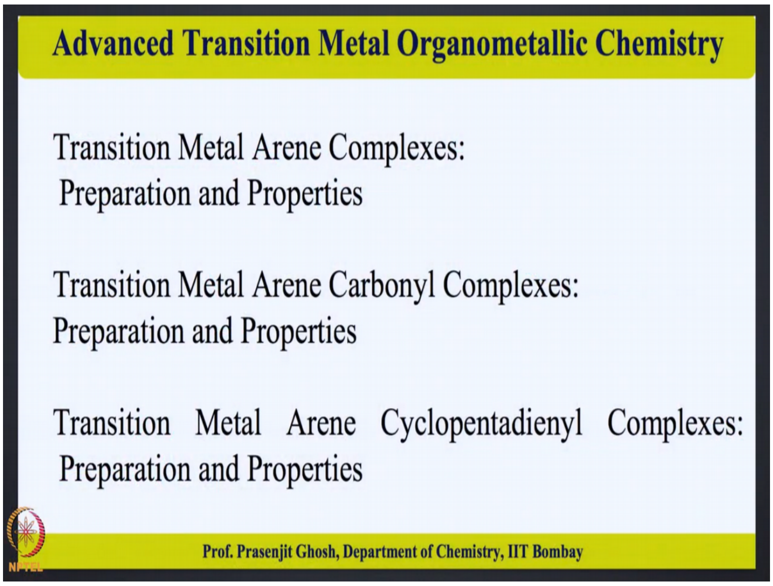

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Transition Metal Arene Complexes:
Preparation and Properties

Transition Metal Arene Carbonyl Complexes:
Preparation and Properties

Transition Metal Arene Cyclopentadienyl Complexes:
Preparation and Properties

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And hence, the arene interaction, arene metal interaction is slightly weaker than the anionic CP metal interaction. We have looked into the preparation and the properties. We have looked into, continuing further, the half sandwich complexes of transition metal arene carbonyl complexes. We have looked into the mixed CP arene complexes. These are interesting complexes where one has a neutral arene ligand bound to transition metal and anionic cyclopentadienyl ligand on the other side bound to the same transition metal.

So, these were looked from the preparation point of view because they are challenging, in which now 2 ligands are to put in place on the same metal. And we have looked at various strategies that exist out for preparation of this metal and thus corresponding properties. Moving beyond further, we have looked into the C 7 H 7, 7 membered complexes, the C 8 H 8 complexes.

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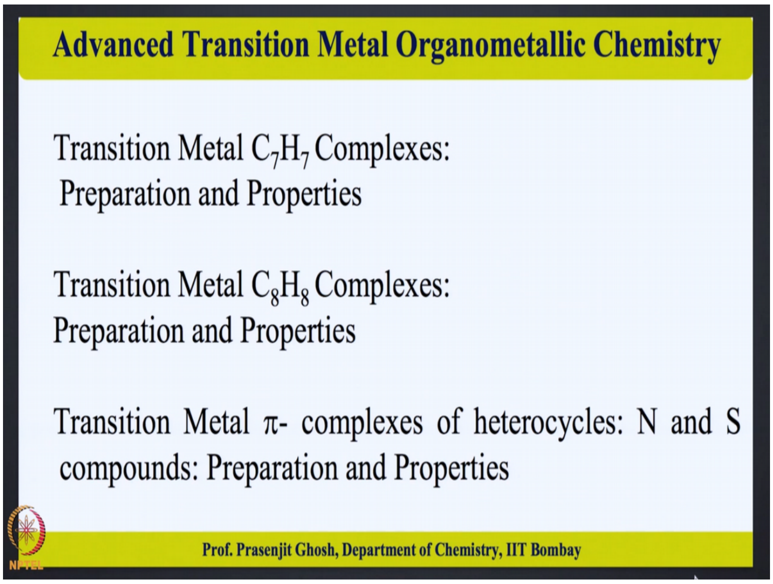

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Transition Metal $C_7H_7$ Complexes: Preparation and Properties

Transition Metal $C_8H_8$ Complexes: Preparation and Properties

Transition Metal $\pi$- complexes of heterocycles: N and S compounds: Preparation and Properties

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And then, we have moved, looked also looked at various metal heterocycles pi complexes of sulphur and nitrogen, their preparation properties and applications. And then, we have looked at the set of reactions, examples of reactions which sort of defines organometallic chemistry particularly with respect to their application in industry and academia. And from that perspective, we have looked at various kinds of C-C bond forming reactions. This C-C bond forming reactions can also be used for cross coupling reactions.

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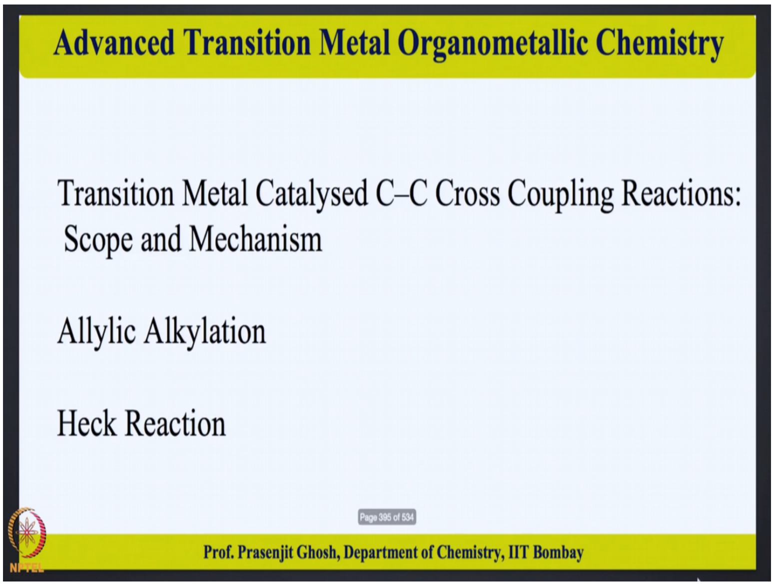

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Transition Metal Catalysed C–C Cross Coupling Reactions: Scope and Mechanism

Allylic Alkylation

Heck Reaction

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And we have looked in all of them. And what stands out is the ability of palladium in all of these reactions to be able to carry out these reactions in a very selective regio fashion. And in a very high yielding selective fashion. So, in this context, we have looked at allylic alkylation reaction of great industrial as well as academic challenge, Heck coupling reaction. Then among the cross coupling reactions we have looked at;

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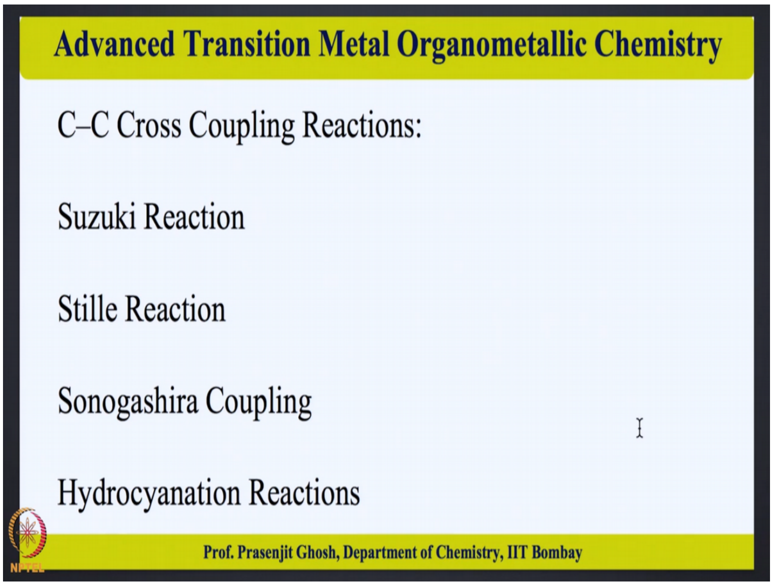

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C–C Cross Coupling Reactions:

Suzuki Reaction

Stille Reaction

Sonogashira Coupling

Hydrocyanation Reactions

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Suzuki reaction, Stille Reaction, Sonogashira reaction and then on the addition reaction, we had looked at hydrocyanation reaction. So, I must note that this Suzuki, Heck have been awarded Nobel Prize because of their impactful discoveries. Hydrocyanation reaction is another way of affecting carbon-carbon bond formation. However, this is done through addition reactions.

Now, carbon-carbon bond formation can be done through addition reactions or through metathesis reaction involving single bonds and hydrocyanation reaction is the example for the addition counterpart. The hydrocyanation reactions produces a C-C bond which can eventually be converted to amines and hence is of interest. We had looked into various kinds of coupling reactions. 1 is aryl amination reactions.

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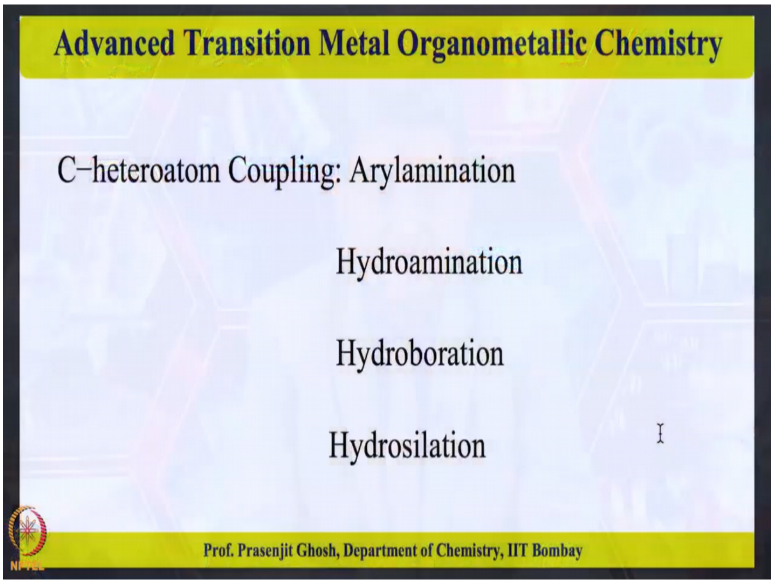

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C–heteroatom Coupling: Arylamination

Hydroamination

Hydroboration

Hydrosilation

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This is also palladium is a player in that. And then, we have looked into various addition reactions on olefins and alkynes involving hydroamination reactions, hydroboration reactions, hydrosilylation reactions. I must note that all these addition reactions are important from industrial point of view, because they are atomic economic in nature and that they do not generate any industrial sideways.

However sometimes the reacting substrates are electron rich and their ability to mutually react is not a very conducive. And as a result, organometallic transition metal catalyst play a important role in making them react. And from this perspective, all these hydro addition reactions like hydro amination reactions, hydroboration, hydrosilylation are important. We have looked into regioselectivity of addition and how the catalyst altered the markovnikov or anti-markovnikov way of addition in case of hydroboration and hydrosilylation reactions.

On the organometallic catalysis front, we have looked into this famous reaction Wacker oxidation, which is olefin oxidation.

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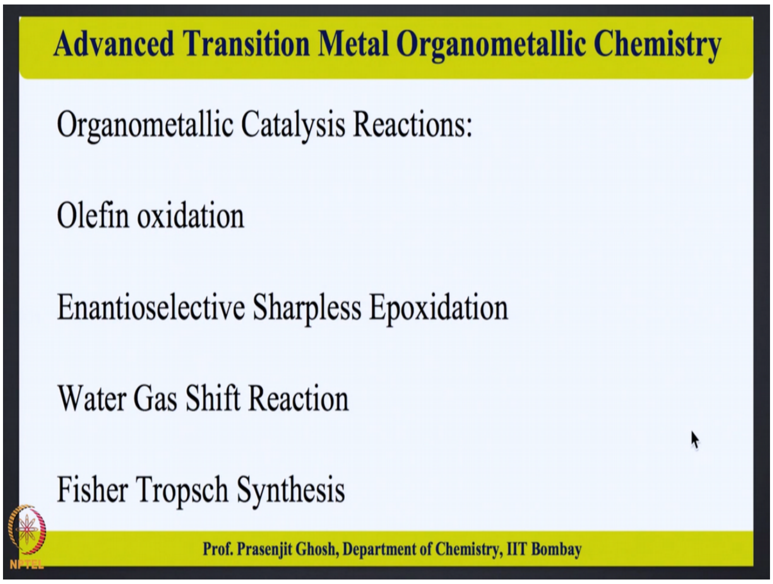

Advanced Transition Metal Organometallic Chemistry

Organometallic Catalysis Reactions:

Olefin oxidation

Enantioselective Sharpless Epoxidation

Water Gas Shift Reaction

Fisher Tropsch Synthesis

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This is the longest known industrial process known under homogeneous catalysis known till today, which has been practiced over centuries. We have looked into another oxidation which is enantio epoxidation reaction. There, propene oxide is produced in large scale using this. We have looked into the asymmetric way of epoxidation reaction. And then, we spent a lot of time on C1 chemistry looking at the reducing power of carbon monoxide in the form of water-gas-shift reaction, which converted CO reacting with H 2 O giving CO 2 and hydrogen; hydrogen being very important from the fuel perspective.

And Fischer-Tropsch sy synthesis which looked at the oxidising power of CO when CO reacting with hydrogen produced hydrocarbons and water. And here, the fuel aspect energy aspect from the hydrocarbon produced becomes very important and relevant. Proceeding further, we have looked into other important industrial interest reactions;

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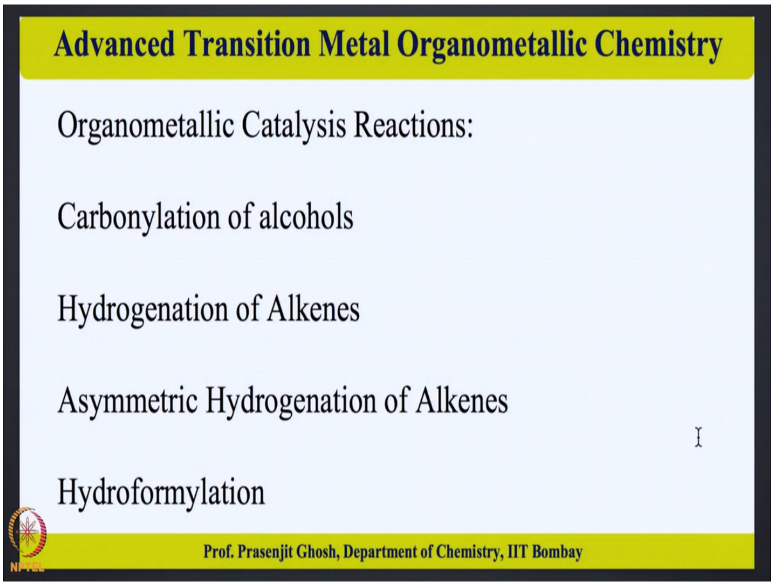

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Organometallic Catalysis Reactions:

Carbonylation of alcohols

Hydrogenation of Alkenes

Asymmetric Hydrogenation of Alkenes

Hydroformylation

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Particularly of carbonylations of alcohols, hydrogenations of alkenes, asymmetric hydrogenation of alkenes and to end with, we finished off with the largest scale industrial process under homogeneous catalysis, which is nothing but hydroformylation reaction. So, with these we have come to the end of a journey of 60 lecturers where we had covered not only the synthesis aspects of various organometallic compounds, but also stressed high on the various utility aspects of these organometallic compounds in large scale industrial processes.

It has been a wonderful journey with a lot of learning and reviewing of that area on my front. And I personally thank all of you and the, for this initiative and the opportunity for me to take this course. And also thank the TAs, supporting staffs, the people who I named and the people who I could not name; all of them, because of their unstinted effort this course became a possible and reality. I hope you have learned something.

Learned on the ways this organometallic chemistry is becoming more and more relevant in today's world and how important is organometallic chemistry and their application that can come out of it, is important to the society. So, with this, I once again thank you for being with me in all these 60 lectures. It has been a wonderful journey. And with this, we come to the end of the course. Thank you to all of you.