Advanced Transition Metal Organometallic Chemistry
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Lecture – 01
Transition Metal Allyl and Enyl complexes

Welcome to this course on advanced transition metal organometallic chemistry. As the title suggests these course focuses on various application aspects of transition metal organometallic chemistry. This course is a continuation of an earlier course that was run on NPTEL portal and the title of the course was transition metal organometallic chemistry from applications to principles.

Now the earlier course presupposes certain concepts which are prerequisites for these advanced level transition metal organometallic chemistry courses and before we start talking about the content of this particular course let me just reiterate what we had gone over in the last course which was the transition metal organometallic chemistry from principles to applications. Now as for the textbooks for this course we will be following three text books.

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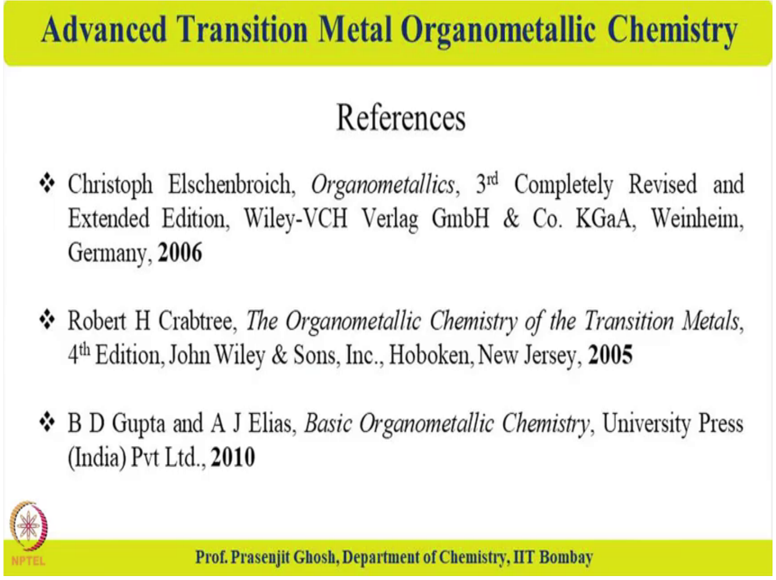

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References

- Christoph Elschenbroich, *Organometallics*, 3rd Completely Revised and Extended Edition, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2006**
- Robert H Crabtree, *The Organometallic Chemistry of the Transition Metals*, 4th Edition, John Wiley & Sons, Inc., Hoboken, New Jersey, **2005**
- B D Gupta and A J Elias, *Basic Organometallic Chemistry*, University Press (India) Pvt Ltd., **2010**

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The first and the foremost is organometallics by Christoph Eisenberg this is the third completely revised edition is it came out as in 2006 followed by another very important book in organometallic chemistry the title of the book being the organometallic chemistry of transition metal by Robert Captree fourth edition John Wiley and Sons. And last but not the least book on organometallic chemistry right from India by Professor B. D. Gupta and A. J. Elias the title of the book is basic organometallic chemistry from University Press and which came out in 2010.

These three books will form the main skeleton for the course and emphasis will be given on the first organometallic metalic organometallics by Christoph Eisenberg for the major part of the course. Apart from this other contains in the web as well as any other book on the subject area will also be useful. Now as mentioned earlier that this course presupposes certain knowledge in organometallic chemistry as this being an advanced level organometallic course.

And that is why I would like to just mention the various topics that was covered in our earlier course. The course started off with a brief overview on the history of organometallic compounds.

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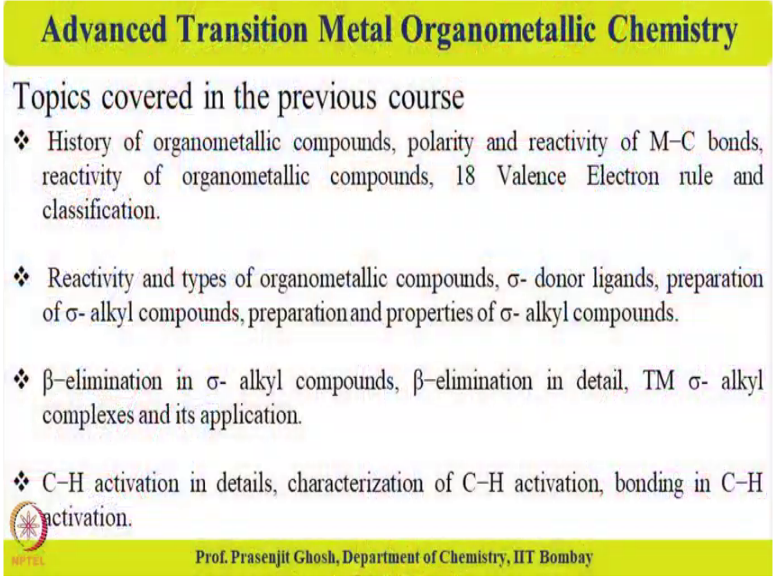

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Topics covered in the previous course

- ❖ History of organometallic compounds, polarity and reactivity of M−C bonds, reactivity of organometallic compounds, 18 Valence Electron rule and classification.
- ❖ Reactivity and types of organometallic compounds, σ- donor ligands, preparation of σ- alkyl compounds, preparation and properties of σ- alkyl compounds.
- ❖ β−elimination in σ- alkyl compounds, β−elimination in detail, TM σ- alkyl complexes and its application.
- ❖ C−H activation in details, characterization of C−H activation, bonding in C−H activation.

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Then looked at the reactivity and the types of organic compounds particularly their classifications based on their Sigma Pi donor properties the various kind of decomposition reactions in particular beta elimination in sigma allyl complexes as well as in transition metal alkyl complexes and their utility in various catalytic applications were also looked at in our earlier course. Area is contemporary areas like C-H activation the characterization of C-H activation and they are bonding aspects were also covered.

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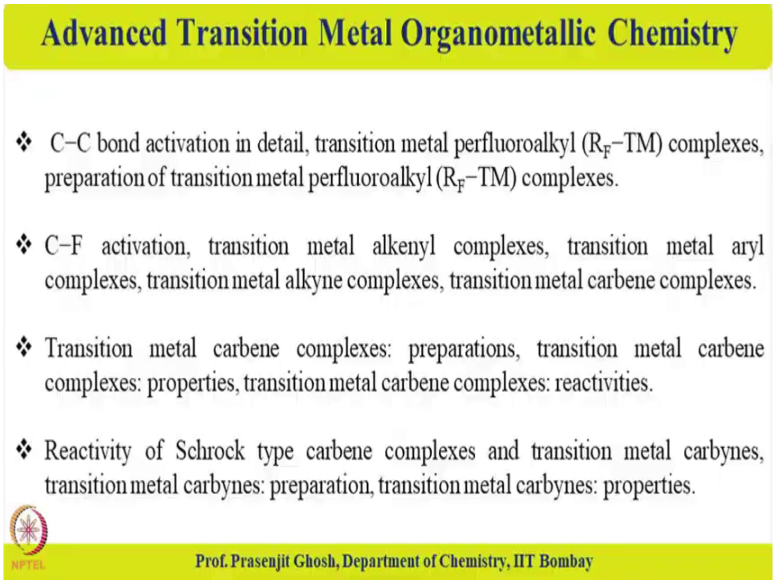

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- C−C bond activation in detail, transition metal perfluoroalkyl (R_F−TM) complexes, preparation of transition metal perfluoroalkyl (R_F−TM) complexes.
- C−F activation, transition metal alkenyl complexes, transition metal aryl complexes, transition metal alkyne complexes, transition metal carbene complexes.
- Transition metal carbene complexes: preparations, transition metal carbene complexes: properties, transition metal carbene complexes: reactivities.
- Reactivity of Schrock type carbene complexes and transition metal carbynes, transition metal carbynes: preparation, transition metal carbynes: properties.

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Not only the C-H activations detailed analysis were done on C-C activations as well as C-F activations one of the most challenging bonds to activate in transition metal organometallic chemistry particularly from the aspect of their high bond energies particularly that of C-F bond and C-H bonds. These activation reactions were covered the challenges in these activations mainly in their selectivity were also looked at.

Apart from this transition metal Sigma alkyl complexes that involved various kind of activations of carbon fluorine, carbon carbon and carbon hydrogen single bonds the course also looked at metal ligand multiple bonding and their chemistry. In this respect what mentioning our transition metal carbene complexes the two famous bonds the shags and the Fischer tied carbines and their reactivity the reason for their particular reactivity the nature of bonding in these compounds were also looked at.

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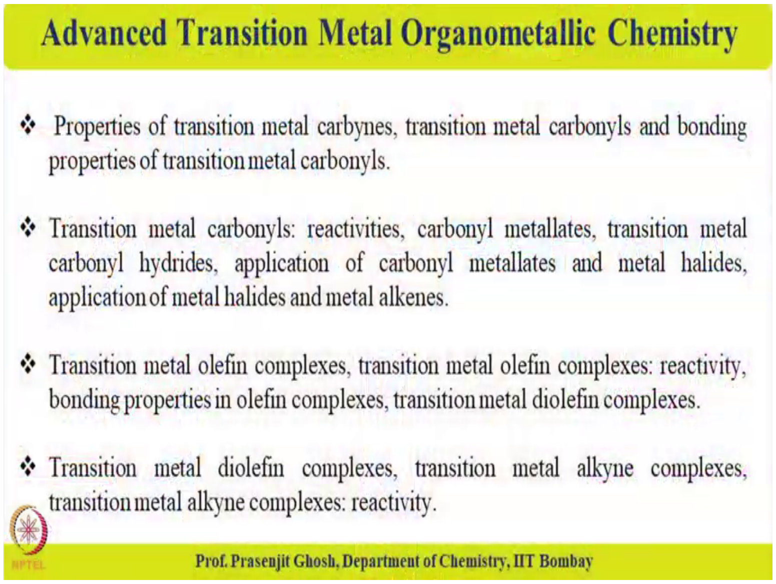

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- Properties of transition metal carbynes, transition metal carbonyls and bonding properties of transition metal carbonyls.
- Transition metal carbonyls: reactivities, carbonyl metallates, transition metal carbonyl hydrides, application of carbonyl metallates and metal halides, application of metal halides and metal alkenes.
- Transition metal olefin complexes, transition metal olefin complexes: reactivity, bonding properties in olefin complexes, transition metal diolefin complexes.
- Transition metal diolefin complexes, transition metal alkyne complexes, transition metal alkyne complexes: reactivity.

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Not only the carbons transition metal carbonyl compounds carbonyl migration reactions carbonyl metallates metal halides and their applications all these things were also discussed. A large part of the course was also dedicated to looking at the transition metal olefin complexes these are very important class of transition metal compounds as they give rise to reversal of reactivity reversal of polarity that arise from Oompa long reactivity we have looked at transition metal olefin complexes.

Not only that we also looked at transition metal diolefin complexes transition metal alkyne complexes and their reactivity. Now with this background been covered in the last course this course sort of takes off from where we had left in the last course and looks at the more advanced level of this chemistry. Now in particular in this course we are going to look at various kinds of interesting ligands.

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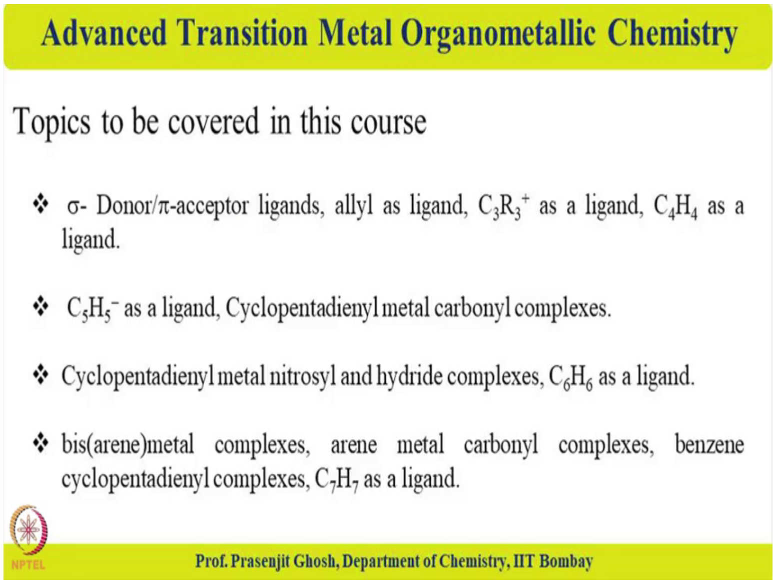

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Topics to be covered in this course

- σ- Donor/π-acceptor ligands, allyl as ligand, $C_3R_3^+$ as a ligand, C_4H_4 as a ligand.
- $C_5H_5^-$ as a ligand, Cyclopentadienyl metal carbonyl complexes.
- Cyclopentadienyl metal nitrosyl and hydride complexes, C_6H_6 as a ligand.
- bis(arene)metal complexes, arene metal carbonyl complexes, benzene cyclopentadienyl complexes, C_7H_7 as a ligand.

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We will start off with Sigma donor pi acceptor ligands these are ligands which are very interesting in the sense that they not only can donate electrons but also can accept electrons in their interaction with transition metals. These are hallmark of transition metal organometallic chemistry where ligands are not just spectator entities which just donate electrons on to the metal but in process it can also absorb electron density back from the metal and that rise give rise to these famous PI acceptor attributes of these transition metal organometallic compounds.

So, we are going to look at allyl ligands C3 R3 + C4 H4 ligands then the famous cyclopentadienyl ligands C5 H5 - they are nitrosyl and the hydride complexes we get to look also at this hydride transition metal complexes as well as the C7 H7 ligands, C8 H8 ligands and they are metal Pi complexes of heterocycles. Now with these we would sort of come to an end of various kinds of ligands that we looked at in transition metal organometallic chemistry and enter into a domain of a very exciting realm of homogeneous catalysis.

Actually transition metal organometallic chemistry plays a important role in various catalytic transformations that has been carried out lately and of them at transformations like CC cross coupling reactions.

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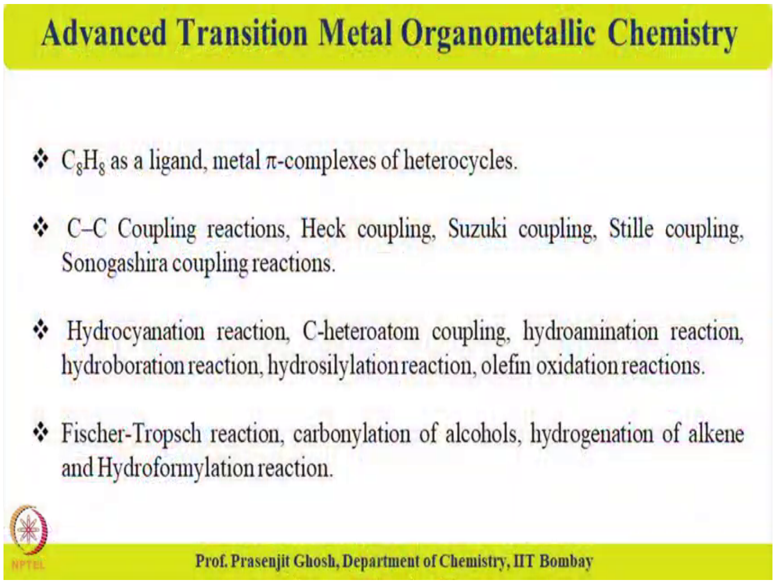

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- C_8H_8 as a ligand, metal π-complexes of heterocycles.
- C–C Coupling reactions, Heck coupling, Suzuki coupling, Stille coupling, Sonogashira coupling reactions.
- Hydrocyanation reaction, C-heteroatom coupling, hydroamination reaction, hydroboration reaction, hydrosilylation reaction, olefin oxidation reactions.
- Fischer-Tropsch reaction, carbonylation of alcohols, hydrogenation of alkene and Hydroformylation reaction.

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Including Heck Suzuki Stille Sonogashira and many other involving palladium has lately been rewarded with the recognition of being receiving this Nobel prize. There are other reactions which would also be looking at for example hydrocyanic reactions carbon hetero atom coupling reactions, hydroamination reaction, hydroboration reactions, hydrosilylation reactions, olefin oxidation reactions. For example Fischer-Tropsch synthesis carbonation of alcohols and hydrogenation of alkenes.

Now the this reactions has tremendous implications in industry which led to preparation of various kind of specialty and fine chemicals in a large scale and the source of these reactions fully lies on the organometallic compounds that often are used as catalyst for carrying out these reactions. Not to mention of the fact that last seven or eight discoveries in the last century can be traced to organometallic compounds and have been awarded recognized with the Nobel prizes.

Now as I mentioned or have been mentioning all throughout this introduction is the fact that organometallic chemistry is indeed very formidable science and is known to have made significant impact in the society in chemical at large and in chemical industry as particular and there has been a tremendous amount of translation of laboratory chemistry to the industrial world and which had been possible because of organometallic chemistry.

As I have been saying that in the last century or so about eight or nine Nobel prizes have been awarded to the field that that speaks highly about the utility of these transition metal organometallic compounds. So, the buzz word for transmittal chemistry is does this translation the translation of level-3 reaction to the industry scale reaction is what makes transition metal organometallic chemistry so interesting and so important to the society at large and chemists in particular.

Now in the last five or six minutes I have painted an overview of this advanced transition metal organometallic chemistry course that I will be talking about and it gives you brief overview of the topics that would be covered what would be the focus of this course which particularly would be on the application aspects of transient metal organometallic chemistry. Now the big thing about transition metal organometallic chemistry is the fact that the many of the reaction have gone past the confines of laboratory and ended up in industry and had resulted in blockbuster processes where billions and tons of many of the chemicals have been produced in industry using transition metal organometallic compounds. And that is why this subject becomes so very interesting and important.

Now with this interview it with this introduction let me just now start with various kinds of allele and in allyle type of complexes that we are going to be discussing as a part of this first lecture.

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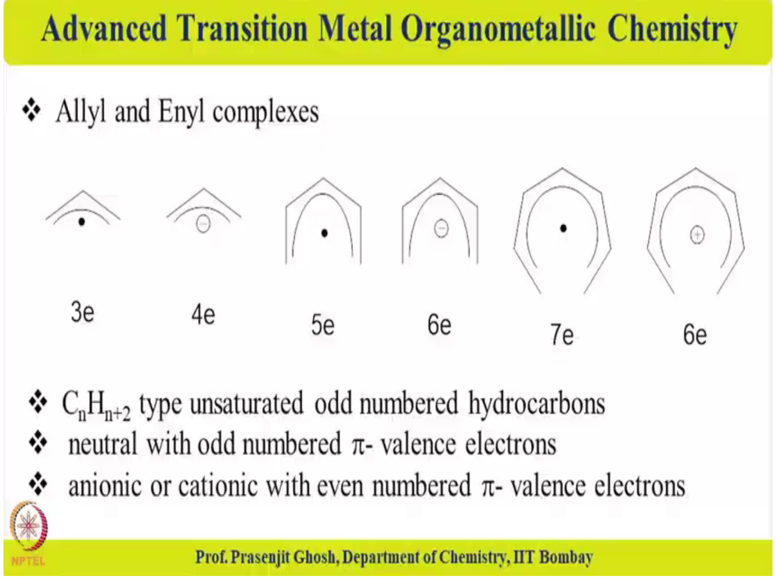

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- Allyl and Enyl complexes

- C_nH_{n+2} type unsaturated odd numbered hydrocarbons
- neutral with odd numbered π- valence electrons
- anionic or cationic with even numbered π- valence electrons

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Now these allyl and enyl and ligands are of the formula Cn H2n+2.

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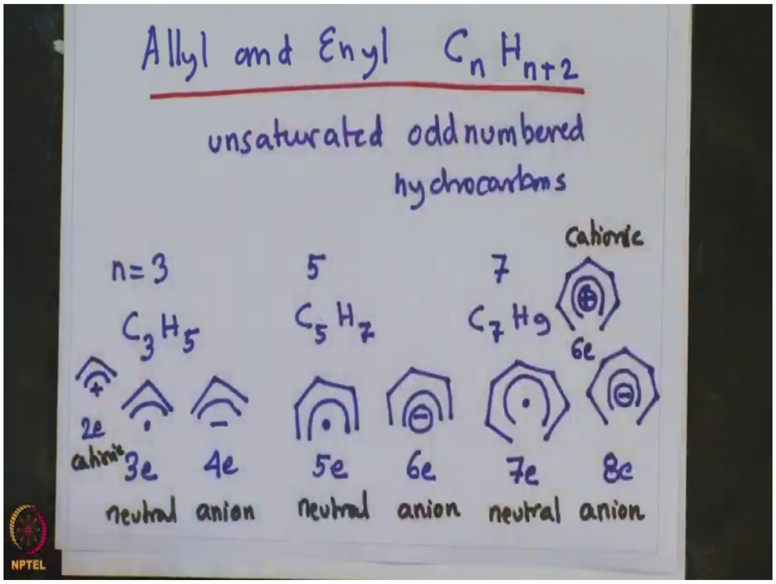

Allyl and Enyl C_nH_{n+2}

unsaturated odd numbered hydrocarbons

And these are unsaturated ligands having odd number of hydrocarbons. So, that means that for example n can be 3 so C3 H5, n can be 5 so that is C5 H7, n can be 7 so that means this is C7 H9. Now these are odd-numbered ligands and their structure is as follows now these ligands can exist in neutral form or charged form. The charged form can be anionic or cationic I will illustrate some of the diagrams over here.

For example in the neutral form C3 H3 can exist as a 3 electron donor. This is in the neutral form in the anionic form C3H exist as an anion. So, this is a 4 electron donor similarly. C5 H7 can also exist in a neutral form. So, it becomes 5 electron donor they can also exist as an anionic form which makes it a 6 electron donor. Similarly 7 electrons neutral form anionic form will make it 8 electron donor.

Now what is important over here that these ligands provide a wide range of ligands having electron donating capacity which can range from 3 electron donor to 8 electron donor. Now each of this ligand can exist in neutral anionic as well as cationic forms. For example the 7 member C7 H9 can also exist in its cationic form where it becomes a 6 electron donor and this is the cationic form and if the C3 H5 becomes; exist in the cationic form.

Then it becomes a 2 electron donor, so what is important to see is this allyl and enyl complexes provide wide whole range of binding capabilities of the ligand in terms of the electron donation. Each of these ligand can exist in three forms neutral anionic and cationic and as a result they have versatility in with respect to the electron they can donate. For example C3 H5 can donate to electron as a 2 cationic 3 as a neutral 4 is an anion and so on and so forth.

Each of these ligands C5 H7, C7 H9 they can show donated types of ligands depending on which form they are binding. Another important correlation is that the neutral species the neutral species are all odd neutral species, are all odd electron donors and the anionic and cationic species are all even electron donors with respect to their PI orbital. So, this is a very interesting correlation about various type of allyl and enyl ligands that are out there and the type of complexes they make with the transition metal.

Now one thing which is what mentioning is in the radical form that that means that the neutral form of these CN H n+2 ligands the neutral form the radical form is extremely reactive given the fact they are radical whereas the ionic ones then anionic and the cationic ones can be stabilized with respect to who their salts of alkali alkaline or transition metals. So, here we see that these are anionic of the cationic ligands when the complex with transition metals they get more stabilized than the neutral form, which are just radicals which show very high reactivity.

Now having seen how these the ligands are the structure of them with respect to their electron donation.

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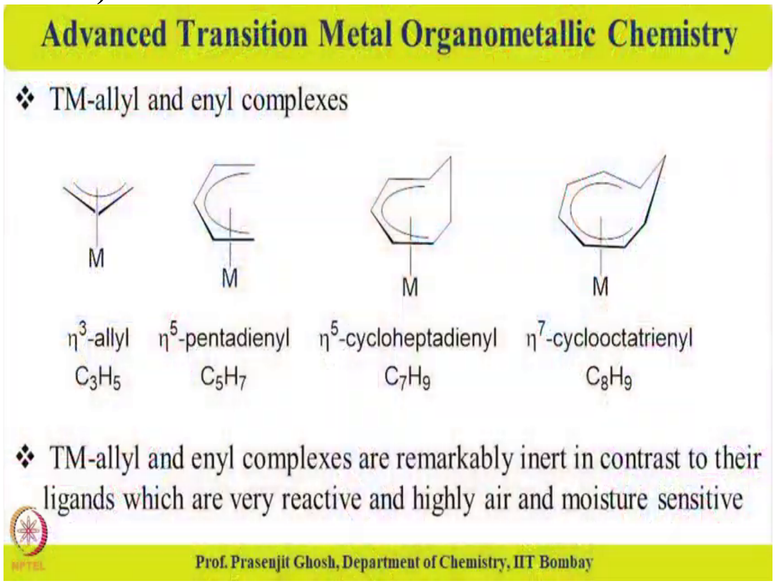

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- TM-allyl and enyl complexes

η^3-allyl C_3H_5

η^5-pentadienyl C_5H_7

η^5-cycloheptadienyl C_7H_9

η^7-cyclooctatrienyl C_8H_9

- TM-allyl and enyl complexes are remarkably inert in contrast to their ligands which are very reactive and highly air and moisture sensitive

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Let us see how these ligands bind to transition metals so this transition metal Allyl and Enyl complexes can be written as or shown by:

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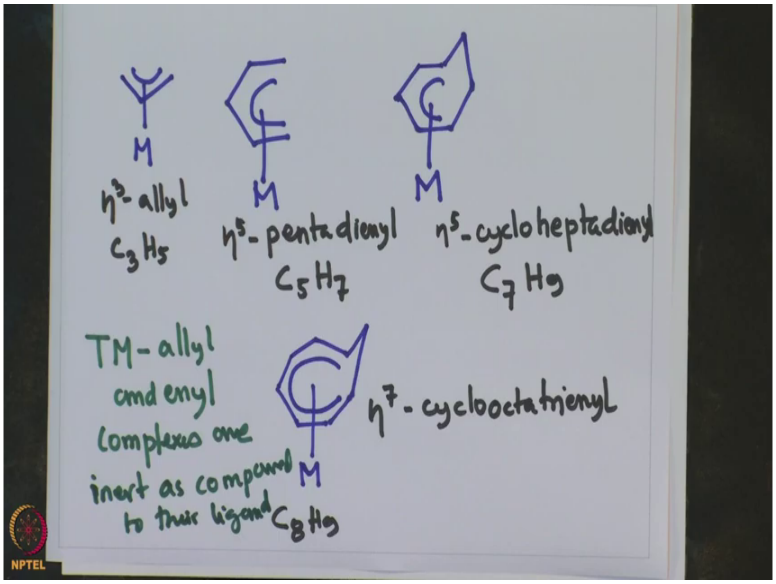

TM- allyl and enyl complexes are inert as compared to their ligand

So, this is ETA 3 allyl or C3 H5 ligands similarly so this is ETA 5 pentadineyl C5 H7 okay. Now we are very a familiar with the other C5 H5 which is cyclo-pentadineyl where this ring is sort of closed. So, many people tend to call this C5 H7 or ETA 5 pentadineyl has opens CP ligand so as if the cyclopentadienyl ring is not closed and it is open and that is why people call it open CP or more appropriately it should be called as ETA 5 pentadineyl.

Similarly there is C7 H9 which binds as this is called a Eta 5 cyclo heptadineyl or C7 H9 and as for C8 H9 this is called Eta seven cyclo octor trienyl ligands. So, these trends as mentioned earlier that these transition metal allyl-enyl complexes and allyl-enyl complexes are remarkably inert in contrast to the ligands, so, these transition metal allyl and enyl are inert as compared to their ligands neutral form because the neutral form has a radical structure.

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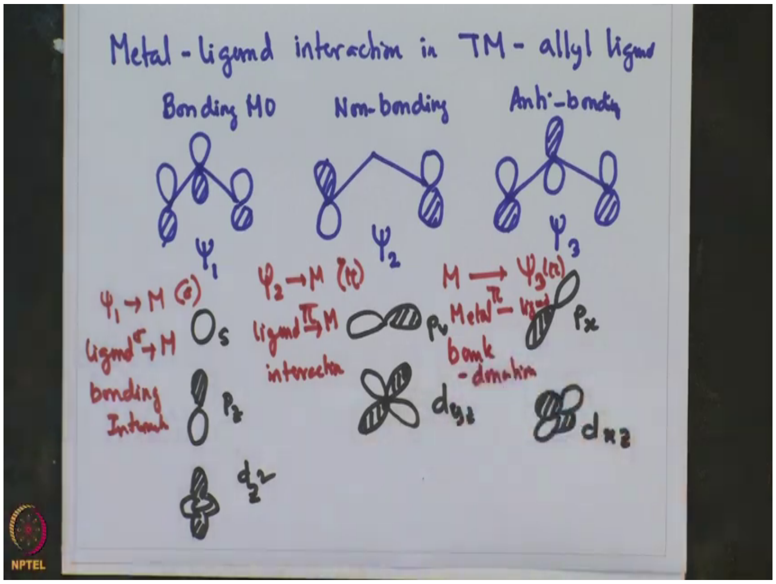

Now we are going to look at a very interesting aspect of these ligand particularly this metal ligand interaction for transition metal allyl complexes. So, in transition metal allyl ligand, now this transition metal allyl ligand has 3 molecular orbitals containing P orbitals and they are of Psi 1 Psi 2 and Psi 3 symmetry so let me just draw it over here. This can be thought of as such Psi1, Psi 2, Psi 3.

Now these is sort of the homo non-bonding, anti bonding; bonding HO nonbonding, anti bonding. Let us take a look at the metal orbitals which attract with these various kind of orbitals. For example the metal component will be s or pz and dz 2. Similarly Psi 2 would be interacting with py of metal and dyz of metal and Psi 3 simultaneously can interact with px and dxz. Now if one considers this interaction what transfers out is that Psi 1.

Psi 1 to metal is a sigma interaction this is ligand to metal sigma bond, bonding interaction Psi 2 metal is a PI type ligand to metal ligand to metal PI type interaction on the other hand metals to Psi 3 is a PI type metal to ligand PI back donation.

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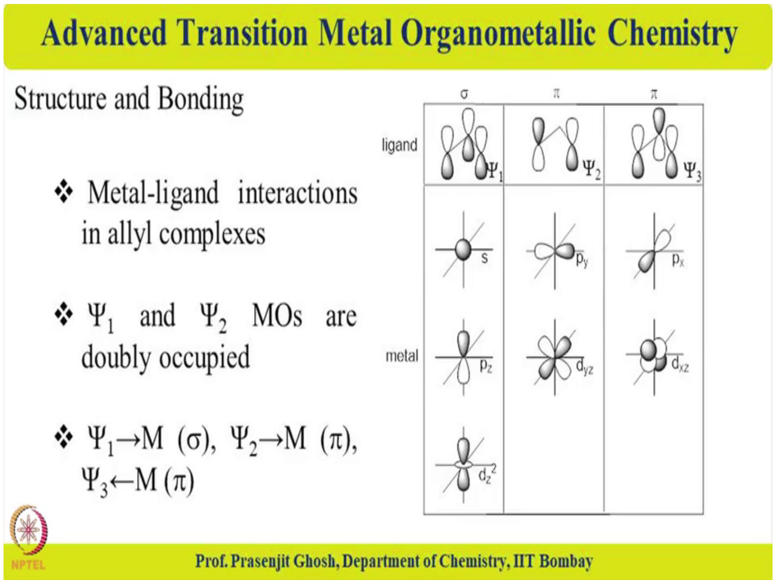

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Structure and Bonding

- Metal-ligand interactions in allyl complexes
- Ψ_1 and Ψ_2 MOs are doubly occupied
- $\Psi_1 \rightarrow M$ (σ), $\Psi_2 \rightarrow M$ (π), $\Psi_3 \leftarrow M$ (π)

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So, this gives a very important picture about how allyl ligands interact with the metal. So, it shows that there are two bonding interaction ligand to metal sigma bond, ligand to metal PI bond and metal to ligand Pi activation. So, with this we come to the end of today's lecture which are parallel primarily been on looking at various kind of allyl and enyl ligands that are out there how they interact with the metal and what kind of orbitals from the ligand interact with the metal trying and which would help us try to understand the reactivity of transition metal allyl and enyl complexes.

So, we have also given overview of what is coming in terms of the topics that would be covered in future lecture. I thank you for being with me in this particular lecture and look forward to discussing with you some more interesting and applied topics of transition metal chemistry organometallic chemistry that in the future discourses of this course and which I think you would really be excited about. So, with this let me thank you once again for being with me in this lecture and I look forward to being with you in the next lecture, thank you.