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NATIONAL PROGRAMME ON
TECHNOLOGY ENHANCED LEARNING

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Organometallic Chemistry-I

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Module No. 1

Lecture No. 1

INTRODUCTION OF ORGANOMETALLIC CHEMISTRY

Hello welcome everyone, I am Debabrata Maiti from IIT Bombay. I would like to welcome all of you for this course organometallic chemistry I. In this course we have decided to discuss mainly about the synthetic aspects of organometallic chemistry. This will be both for in organic chemist and organic chemist as well. I am sure both of you have taken some courses in organometallic chemistry so far, and you have introduced, you have been introduced to this topic before.

Now on the less there are some prerequisite for this course which I will briefly outline, but major aspects we will try to focus in this, in our course is the fundamentals of organometallic chemistry, what is the basis of different reactions of organometallic chemistry. Often we see both in, you know textbook or in industry, number of reactions going on and number of catalyst is going on. And by looking at the transformation we just simply get mesmerized how that reaction might be possible okay.

So this is the beauty of organometallic chemistry seemingly difficult reactions which is otherwise not possible by let us say traditional organic or inorganic type of reaction, organometallic chemistry can do wonder. So therefore, knowing different varieties of organometallic reactions will be of fundamental and as well as very synthetic importance.

As you know organometallic chemistry in often term in often it is discussed in the way that it is the metal, carbon bond formation reaction or if a compound is having metal carbon bond that is usually defined as the organometallic compound or the chemistry derived from it is classically defined as organometallic chemistry.

But there exist nowadays we do not really restrict the term organometallic chemistry to this basic definition, we also use various non-metal or, you know semi-metal species and their carbon complexes also under the banner of organometallic chemistry. And actually there are number of examples with boron, silicon, phosphorous, arsenic for example to discuss about their carbon complexes as are these metal or non-metal and or metal, semi-metal, carbon complexes as the organometallic species.

So all actually derives from the fact that the electronic negativity difference between the that is a metal and the carbon centers. Now without going into too much of the history of organometallic chemistry and what organometallic chemist has done so far we will try to focus and we will be discussing about what organometallic chemistry can do, what are the type of reactions we are going to see okay.

So the prerequisite for this course, I would like to point out that one should learn before getting into the discussion of this course.

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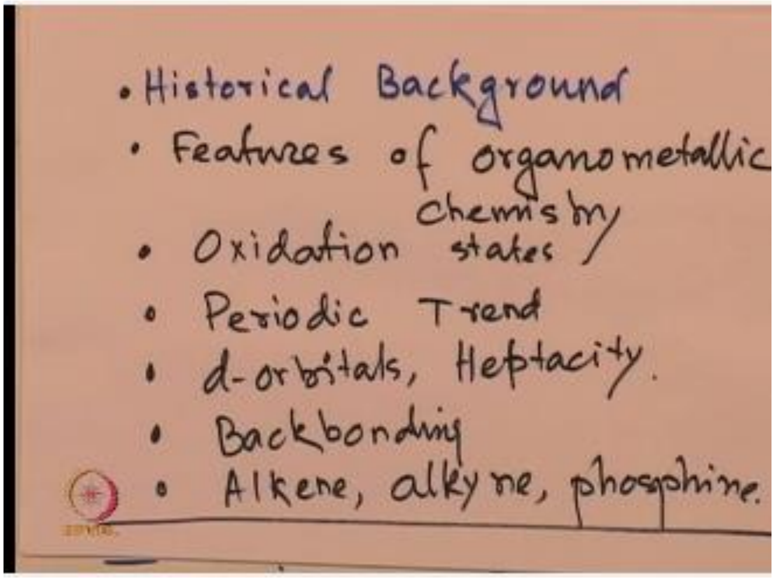

- Historical Background
- Features of organometallic chemistry
- Oxidation states
- Periodic Trend
- d-orbitals, Heptacity.
- Backbonding
- Alkene, alkyne, phosphine.

If we should know about the historical background that is essential, since it is in our course we will try to restrict on that and of course different features of organometallic chemistry features of organometallic chemistry these are thing one is expected to know and you know oxidation states fundamental To learning to in learn in chemistry oxidation states as well as period trend this is hopefully all of your families are with.

and you can rephrase your memory with these and of course d orbital’s electron count and Hephtacity back bonding these are of course another famous topic of organometallic chemistry and such back bonding and knowing the properties and knowing the properties of alken alkenes all will be useful alken, alkenes all these things one is expected to of course Phosphine are all is going to be useful.

So for these are things I expect all of your familiar with are you can phase your memory little bit long will be about more about the periodic table periodic trend and little bit about the electronic configuration of each and every metal that will be very important because when we will be counting the electron for a given complex those will be useful the balance let in may lead like to you get an idea about and of course the oxidation step and periodic trend and different carbon monoxide alkynes.

There electronic configuration and everything once one is expected to know okay without term speeding dual much on that I think I will take you to the syllabus what we might will be discussing for this course for this course before getting into the syllabus they exits a number of books and you know quite a helpful for this organometallic chemistry one is expected to learn of course my learning as been influence by various furthers which I have come across during my bachelors masters PhD and post studying.

But a since they are number of books which you are certainly encourage to read about any books should be okay to so to speak in terms of fundamental of the chemistry that we will be discussing but mainly I would say the basics of organometallic chemistry.

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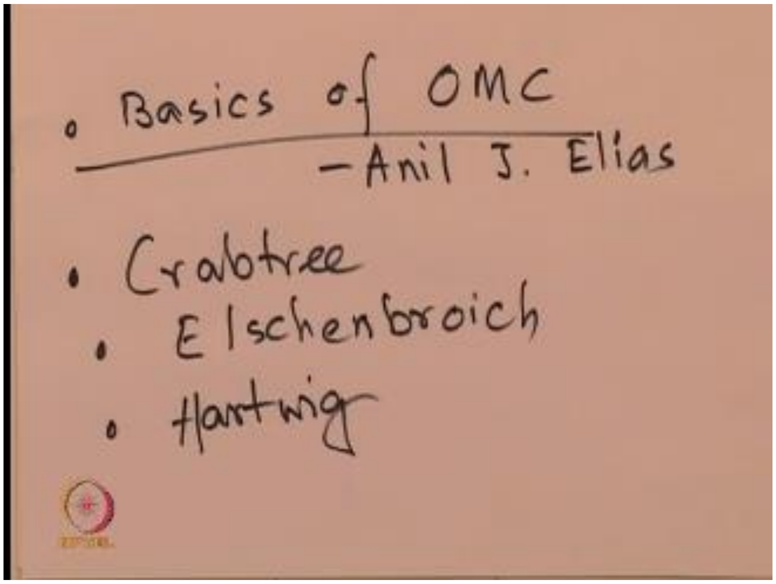

- Basics of OMC
  —Anil J. Elias
- Crabtree
- Elschenbroich
- Hartwig

Basics of organometallic chemistry by a Anil J. Elias it is our colleague at IIT Delhi of course the other fundamental books include Crabtree organometallic chemistry and Elschenbroich as well as very I do not know excellent book by John Hartwig these are the books one can consult other than that any I think any other book of organometallic chemistry can also be consulted or you know I hope for if you try to focus on this course and pick up any other book that should be good enough for this activity.

Now mainly we will try to outline the syllabus of this course okay for this purpose we would like to usually go one topic at a time on a half an hour class bases so although it is like a total ten course so definitely there will divide into 20 class so 20 small, small class each class roughly will discuss one topic sometime it will spin over to another class but most often in half an hour slot you will try to discuss one topic sometime two topics priory will discuss one topic into the two half an hour courses if the topic happen to be little bit of a more importance and we need to discuss more about it, okay. So let us look at the syllabus roughly.

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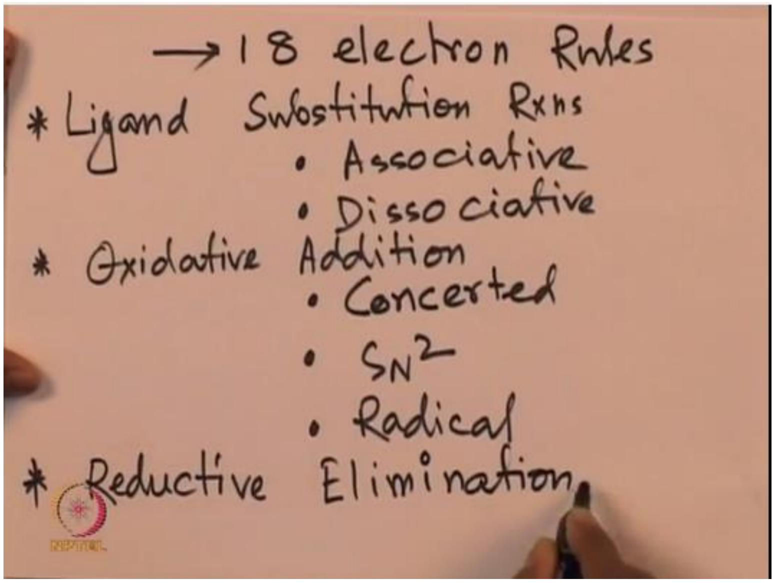

→ 18 electron Rules

* Ligand Substitution Rxns
  - Associative
  - Dissociative
* Oxidative Addition
  - Concerted
  - S_N2
  - Radical
* Reductive Elimination

While you will start as almost every you know chemist need to discuss the 18 electron rules briefly we will discuss that okay, 18 electron rules and expecting you are familiar with but you will just try to discuss electron count of it and electron count of the organ material complexes and try to give some example and then move on from the top the major focus from their won will be the ligand substitution reaction, ligand substitution reactions, okay.

These are, are of two types one will be on associative mechanism another will be the dissociative one okay, this is the first topic major topic we will be focusing regarding the substitution reaction followed by you know one of the most important topic will be the oxidative addition with the plenty of example all of them will be discussing each of every topic with 20 of the example oxidative addition.

These examples again are influenced by my previous exposure or from different books and so on, so these are going to be concerted mechanism oxidative addition there are 3 different mechanisms it will be so consorted $S_N{}^2$ and the radical mechanism these three different mechanism will be discussed, of course almost the microscopic green house of oxidative addition will be the reductive elimination which is again although it is microscopic reverse we need to discuss quite efficiently on this elimination, okay.

Moving on farther from this we will be discussing the migratory aptitude, migratory insertion and elimination reaction there would be α and ß migratory insertion and elimination.

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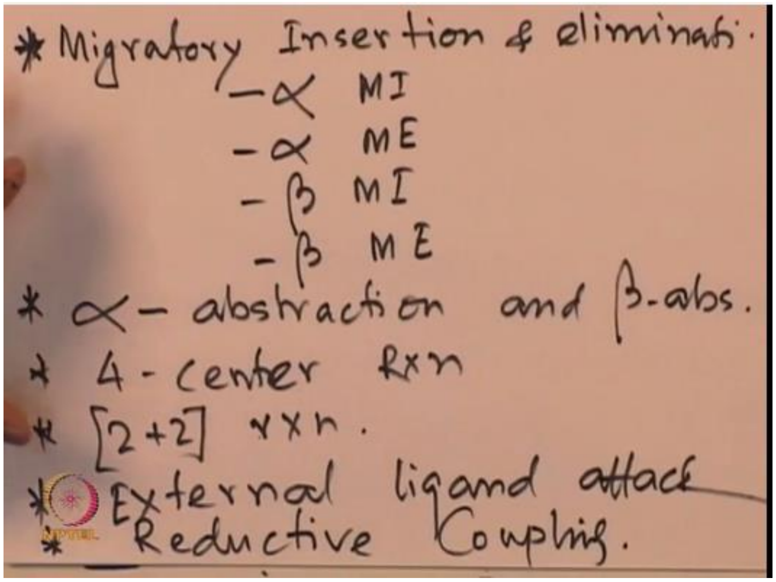

* Migratory Insertion & eliminati.
- α MI
- α ME
- β MI
- β ME

* α- abstraction and β-abs.

* 4-center Rxn

* [2+2] rxn.

* External ligand attack

* Reductive Coupling.

So the next topic will be the migratory insertion and elimination reaction and elimination so here we will be discussing α of course α migratory insertion, α migratory elimination and of course ß migratory insertion, ß migratory elimination and you know will also discuss quite a lot about the example of it and lot of examples where we will combine both the ß migratory insertion and ß elimination reactions.

Subsequently we will move to α abstraction α abstraction and ß abstractions reactions and finally moving for that four centre reactions 2 + 2 reactions these are various type of reaction patterned are we will be discussing and attack by external Ligand so when let us say for example we have you know we have an Olefin and then we would like to interact to with this meta center show that is the external ligand attack external ligand attack.

And then of course the reductive coupling these are the topic mainly will be discussing. Now of course some of these topic you may have heard of we will try to discuss each and every topic in greater detail once again almost each of these topic will be discussed in half in our time scale so roughly you know 1,2,3,4,5,6 and nearly 10 topics will be discussed and each topic maybe having sub topics so one topic will have nearly one hour of discussion in some topic if you are having two sub topic on the one topic we might will discuss half an hour each of those, okay.

Of course after learning all these reaction you know pattern or reactivity pattern we then must apply some of these pattern some of these reaction types to generalize reactions scheme show to speak one of the catalytic cycle. Subsequently we would like to discuss let us say mainly we will try to focus or we will try to restrict ourselves to the hydrogenise reaction and carbon lysine reaction and try to see how some of these reaction types or protocols can be applied to the catalytic cycle.

Usually as you know a catalytic cycle will have multiple steps, right so maybe having let us say four steps, five steps and so on. Now each of these four steps is necessarily go forward by all these 10 topics or total 20 different subtopics we are talking about, each of the catalytic cycle can be broken down into these topics or subtopics, okay. So therefore by knowing these topics we should be able to discuss about any catalytic cycle with confidence and we will be able to understand the mechanism in details that is I guess will be the strongest point of these organic metal chemistry one. So once again we will be discussing the ligand substitution reaction to start with we will have associative and dissociative mechanism how the ligand substitution reaction occurs at the beginning you have your organ metallic components.

Of course the organ metallic component you are going to have is going to be usually stable 1 you need to do some chemistry with it therefore you need to undergo a ligand dissociation or association reaction, right if it is an eighteen electron spices for example you need to loss one ligand to make it 16 electron show that the metal fill encourage for an heterogeneous substance otherwise 18 electron species complex will not be really filling that much encourage to undergo any reaction, right.

So ligand substitution reaction how it occurs associative mechanism and dissociative mechanism will be discussing subsequently we will discuss the oxidatie validation again this is one of the topic which is quite popular oxidatie validation usually remains as a bound like you know insert some into the carbon bromine bond of the bromobenzene for example by a organic metallic species let us for example platinum and then we get a platinum GL oxidation state to platinum two place oxidation step right and where we have a Arial carbon metal bond allow with metal bromine bonds, right.

So these oxidatie addition reaction can be of different type it could be contortioned mechanism it could be SN2 mechanism of course it can be of radical type in nature, right. So that different types of oxidatie addition we will discuss subsequently you would like to see the reductive elements which is the opposite of it, so imagine two partners are on one metal and then we want to take out those two partners and combine those two partner together.

And then living a lot of vacancy side to the metal center those will be again essential for often regenerating the catalyst of making the catalyst more effective okay. As we go alone we will see how the migratory incursion is occurring how you have one group with the metal center and then that group is trying to my great on the another group such as all if in other unsaturated partner which is associated with the metal center now we can have various type of reaction form that angle we can have alpha migratory incursion.

So at the alpha position of that Oliphant or let us a carbonyl we will be migrating another group which is associated with the metal center then also we can have the you know incursion or elimination and form the β position of the legated partner on the metal center of course another variation of such type of reaction will be the abstraction this abstraction could be you know similar in a way it is essentially going to be similar compare to your migratory incursion or elimination reaction.

So alpha extracts and the beta abstracts in the you will be similar to the you know alpha migratory elimination or beta migratory elimination but fundamentally this are different type of reaction that you will see the difference in lot of cases we may not be having an opportunity to let say undergo traditional oscillate word or traditional reductive elimination re access. So what will then have that particular case is we might will haven opportunity to go about the four center reaction mechanism right.

So that is also essential when we need that what are the major type of reaction and when we cannot have those major type of reaction pattern alternative has to be looked up. similarly like alpha and beta migratory incursion elimination when we talk about those at the major one but when the abstracts and reaction dominant that also need to be looked at, others will be of course the 2+2 reactions where you know 2 unsaturated unit will be coupling together.

So curve you know fray famous you know reactions ewe have seen that might a three sees reactions how the reactions occurred what is the basic fundamental outline principle for this reaction would like to also discuss. Then you know simple if you take let us a simple all if new on to a react it with a nuclei file you may not be getting such any reaction but that all if in if you want to interact with the metal center then you might will have an opportunity to react the nuclear file with the all if in this is another class of reaction you know external attack by nuclei file to the olefin center.

Sub sequent of course we would also like to discuss the detective coupling which is again another fundamental class of reactions so these at the major type of reaction will be discussing in depth in detail regarding this course after discussing this we will be discussing the hydrogenous reactions, and a carbonilious reaction, in terms of hydrogenous and catalyst we have two types of catalysts, one is mono hydride catalysts, and the other will be the de-hydride catalysis, how fundamentally these two catalyst are different? What are the steps to undergo the hydro no 2, under to understand the hydrogenous reactions that will be trying to discuss.

Mainly you will see usually it's a elegant association, and disassociation reaction then of course oxidity addition, or olefin co-ordinance and sub sequent oxidity addition in suction and then derive illumination reaction, to view the product that these are going to be the simplest reaction of all, finally we will move on for this course the carbonation where we would like to look at quite lot of topics.

Such as hydro formulation reaction of course monsoon to acetic acid, process where will be discussing about the methanol getting converted in to the carboxylic acid, and in hydro formulisation reaction we will be discussing olefin reacting with the carbon monoxide, and hydrogen mix are to be viewed, al-de Hyde this al de hide can be of two different type, it could be the terminal al de hide, it could be the branch one as well, and subsequently we will be discussing the hydro carbonisation reaction.

And we will cap of the discussion why having the hydro nation reaction, and hydro nation of olefin, we also like to touch up on little bit, just little bit on the asymmetric version of this reactions. Okay we may not be able to discuss to the infests of time, wait for much about asymmetric reaction but whenever possible, whenever an asymmetric version of a catalysts' will be possible we will be discussing in briefly.

So that will be also discussed in this fundamental type of reaction, look oxidative values and reductive luminous and you know the type of reactions whenever there is a scope of a discussing the asymmetric catalysis or asymmetric accented how fundamentally it will be tell to it by a reaction type, also be a discussed during this course, okay.

So we will come again so we will total again including this one we will have total ten hours discussion, and I would like you to ask as many question as possible, of each and every section and of course there will be some evolution as want to expect for this courses, allow with it we will try to see if your understanding can be border, if you have any quarries please feel free to ask me, okay.

So in the next class, mainly we will try to discuss the eighteen lection rule, and from there on various elegance substation we will focus on them, okay so this will be all for the introductive part of this course and you know, feel free to drop me any quarries that you may be having regarding course, thank you.

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