Metallocene and Metal-carbene Based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts

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Lecture 37

N-Heterocyclic Carbene (NHC) Complex _ Bonding and General Synthetic Protocol

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Metallocene and Metal-carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts

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Welcome to ourclasses on Metallocene and Metal-carbene Based Organometallic Compounds for Advanced Polyolefin catalysts.

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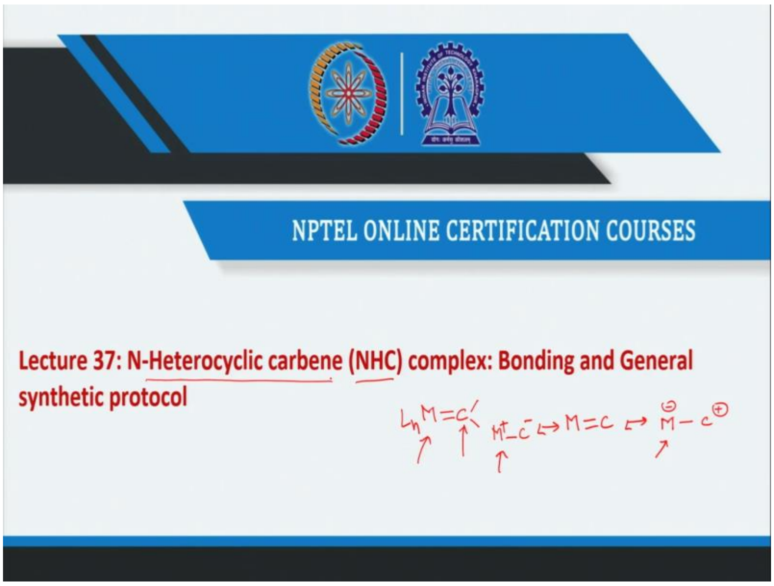

NPTEL ONLINE CERTIFICATION COURSES

Lecture 37: N-Heterocyclic carbene (NHC) complex: Bonding and General synthetic protocol

$L_nM{=}C\langle$ $\overset{+}{M}-\overset{-}{C} \leftrightarrow M{=}C \leftrightarrow \overset{\ominus}{M}-C^{\oplus}$

And as you know, we started the metal carbene complexes in the last few classes. And now we are very much aware and we have a now knowledge about the type of metal carbene complexes that is the metal carbon bond, carbon double, multiple bonds and this is the basic skeleton.

So, we now know that what are the basic chemical structure, what are the carbene ligands and we know that what is the Fischer carbene, Shrock carbene, what is the singlet carbene, triplet carbene and we know that in the Fisher carbene, the singlet carbenes ligands are associated in the Srhock carbene, shifted ligands are associated.

We know that what kind of electronic factors, electronic parameters are there on the carbon center of the carbene and on the metal center on the carbene and we know that depending on the Fischer or Shrock or singulet or triplet ligands and also on the variation of the transition metals this kind of scenario may exist like this one and, so you see here that if it is two canonical structures, two possibilities that these metal centers in this case it is nucleophilic in nature, and this one you will see just opposite.

So, we are now very much aware, we also know that the bonding parameters the simplified molecular orbitals and associated with Fischer and Shock that is the two categories. Today, we will concentrate on a specific category of the metal carbene complexes where the ligands are N H C. N H C stands for N Heterocyclic Carbene complexes.

These are very important because these complexes are actually plays a dominant role in catalytic domains, especially, for making the valuated organic compounds in medicinal chemistry and also the material chemistry like polyolefin synthesis. So, it is very much important to understand what is the basic chemical structure and the bonding and the electronic parameter associated with N heterocyclic that is the NHC metal carbene complexes.

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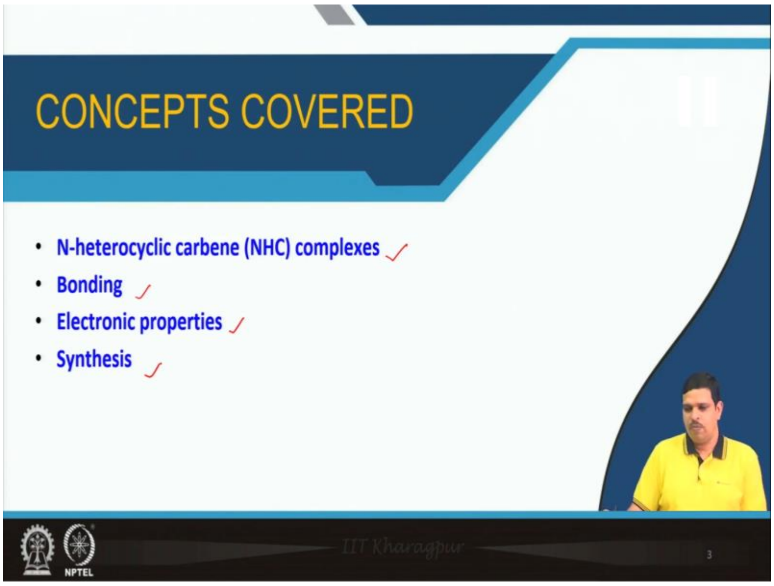

CONCEPTS COVERED

- N-heterocyclic carbene (NHC) complexes ✓
- Bonding ✓
- Electronic properties ✓
- Synthesis ✓

So, today we will discuss about the following concepts that is the N - heterocyclic ligands and complexes, the bonding, the electronic parameters and will also discuss a general synthetic protocols of the metal NHC carbene complexes.

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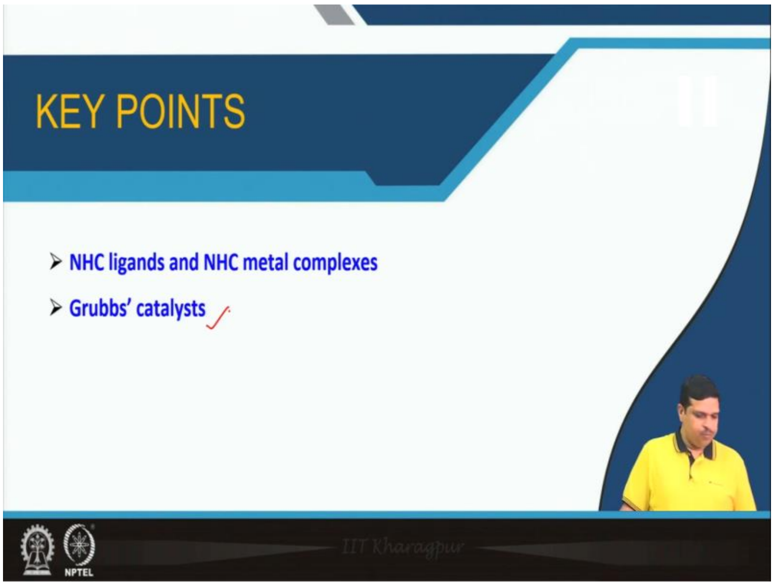

KEY POINTS

- ➢ NHC ligands and NHC metal complexes
- ➢ Grubbs' catalysts ✓

So, the key points will be covered very obviously the N H C ligands and its complexes and also we learn the very famous the Grubb’s catalyst that is actually falls in the category most of the Grubb’s catalysts, although, Grubb’s catalyst is not a single catalyst, there is a in time to time the catalysts have been developed using the different ligands that we learned today and you will see that how famous and how important the Grubb’s catalysts are. This is one of the very successful catalyst and that is why the Nobel Prize were awarded that you all we now know.

So, today we will learn this very interesting chemistry and very interesting development of the Grubb's catalysts and which are used on various type of metathesis reactions. We know briefly now we have discussed that the types of the different alkene metathesis catalysts ring closing, cross-metathesis, ring opening, all those.

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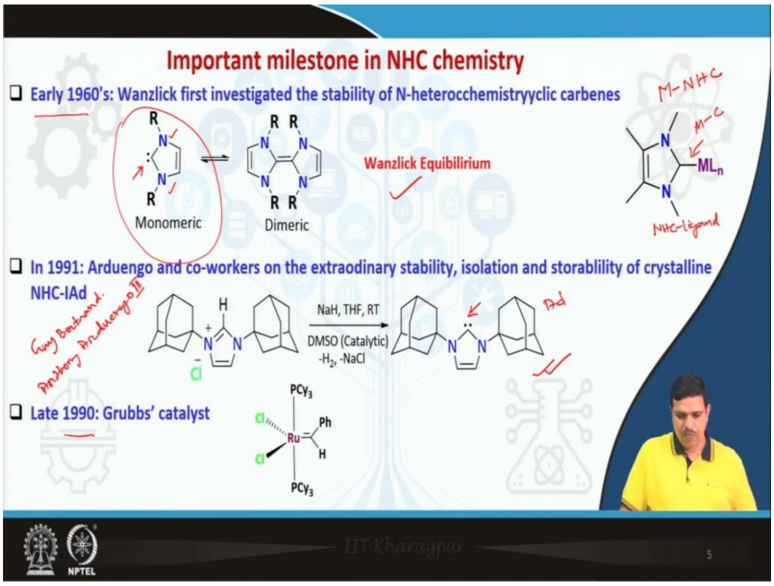

Important milestone in NHC chemistry

☐ Early 1960's: Wanzlick first investigated the stability of N-heterocchemistryyclic carbenes

☐ In 1991: Arduengo and co-workers on the extraodinary stability, isolation and storablility of crystalline NHC-IAd

☐ Late 1990: Grubbs' catalyst

So, you know that before going to the NHC, the bonding and the chemical structure in metal carbene complexes. So, this is we would try to understand what are the important milestones in NHC chemistry. That is you know that this is the first carbene ligands were reported in around 1960s by the Wanzlick and he actually first investigated the N-heterocyclic chemistry, N- heterocyclic carbons and however, that time that this kind of carbene that is you see that why we will discuss what is the NHC.

So, NHC here basic basically you see to stabilize this carbon you have to have two heteroatoms. In this case you will see, this original imidazole moiety and here you see two nitrogens and this this is important to stabilize this carbonyl... after two after two slides, why these are important.

And and this will is the basically the resultant metal carbene NHC, metal carbene complexes. So, if this is my ligand, this one is my ligand that is the N H C ligand, this one and so this if I react with metal, suitable metals precursor then this metal carbene bond that is the metal carbene bond that is the will be formed that is the metal NHC complexes.

So, this is the famous Wanzlick equilibrium, you may be aware of this one, this actually so unstable that it diverges very rapidly and once at a time it does believe that probably the this kind of free carbene may not be isolated because due to its so instability in at ambient conditions.

So, later this Arduengo and Guy Bartrand, and Anthony Arduengo, they actually, where they were successful to make the stable of, that is the first stable free carbenes which can be isolated, which are stable at normal conditions and means ambient conditions and also stable to moisture and air.

So, this is the first stable carbon which can be isolated, very nice crystalline, colorless crystalline compounds. So, you will see that this is actually adamantyl group, this one and so, it is a very strictly demanding group and is an imidazole adamantyl derivative. And see this is the singlet carbene.

So, in 19, after that after the remarkable and path breaking discovery of Arduengo and co-workers, this carbon chemistry became so popular and eventually the Grubb's, one of the pioneering scientists, who actually this discovered many catalysts and the metal carbene complexes, mostly by ruthenium complexes.

And you know that now we cannot really think any multiple step of organic synthesis without any Grubb's catalyst or alkene metathesis categories. So, after 1990 is a is called the Grubb's era and in 1992 almost like a 2005 that is a golden era of the metal carbene metathesis catalyst. So, that is one of the biggest discovery in organometallic complexes.

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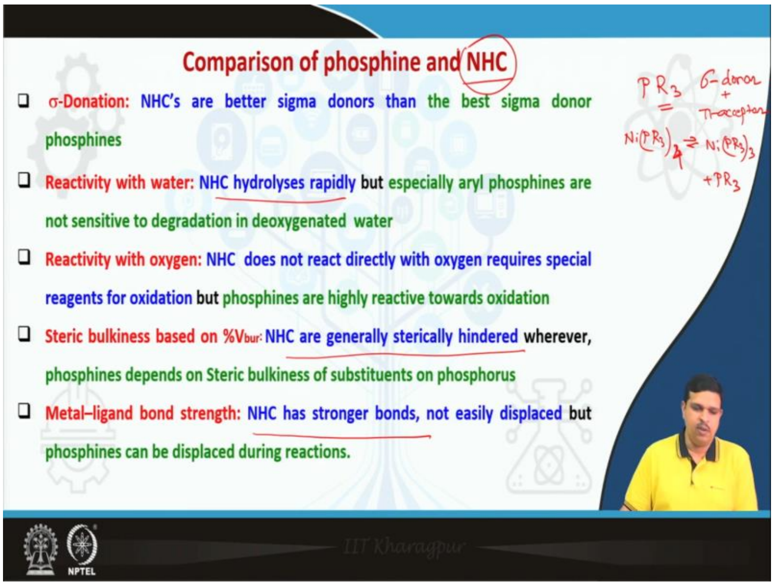

Comparison of phosphine and NHC

- ❑ **σ-Donation:** NHC's are better sigma donors than the best sigma donor phosphines
- ❑ **Reactivity with water:** NHC hydrolyses rapidly but especially aryl phosphines are not sensitive to degradation in deoxygenated water
- ❑ **Reactivity with oxygen:** NHC does not react directly with oxygen requires special reagents for oxidation but phosphines are highly reactive towards oxidation
- ❑ **Steric bulkiness based on %V$_{bur}$:** NHC are generally sterically hindered wherever, phosphines depends on Steric bulkiness of substituents on phosphorus
- ❑ **Metal–ligand bond strength:** NHC has stronger bonds, not easily displaced but phosphines can be displaced during reactions.

$PR_3 = \sigma\text{-donor} + \pi\text{-acceptor}$

$Ni(PR_3)_4 \rightleftharpoons Ni(PR_3)_3 + PR_3$

So, is very interesting and we actually very briefly discussed that what is the, why the N H C is so popular because we know in catalytic chemistry, the phosphine ligands plays a dominant role because it is you can tune the bonding properties of phosphine by choosing the right alkyl groups.

So, you can basically balance between the sigma donor and the pi acceptor ability of your the P R 3. So, that is why in the catalytic cycle you will see, whenever it is needed the P R 3 come outs and puts like this kind of, like this, like I am just writing in a very theoretical, I mean arbitrary model, so, you will see that this kind of equilibrium exists like, this is 4 and here P R 3 and P R 3 comes out. So, is it like a delegation.

And this is important, this kind of equilibrium to for giving the space for the substrate. That means if you I want to like if you remember, the Wilkinson's catalyst, the first is the previously comes out and then alkene coordinates and then you will see that the oxidative addition of H2 happens then insertion happens like that.

So, it is very much important that to give a space that means to make a coordinately unsaturated compounds, so that the substrate can approach. So, that P R, the phosphines is one of the very popular ligands not only for that one by for you can tune its bond sigma donor and pi acceptor properties and also you can induce the chirality on the catalyst by choosing the chiral phosphine ligands.

So, however there is a lot of disadvantage in the phosphines, one that many phosphines are very expensive, it reacts with water, sorry, it reacts with oxygen because that most of the alkyl phosphines are oxidation prone and it readily forms the phosphonoxide. So, how about the NHC is quite stable.

And you see that reactivity with water NHC hydrolyzes rapidly but the phosphines does not hydrolyze that this can be one of the advantage for phosphines. Steric bulkiness based on the N H C are generally, sterically hindered because you know that there is to make the stable carbon complexes, we have to have a protecting bulky organic substituents around the carbene carbon and metal ligand bond strength NHC has a stronger bonds because the sigma donor property of NHC is better than the phosphine ligands.

I will come after one or two slides, why, how the sigma donor property of N H C ligands is better than the phosphines. So, you see there is advantage of the carbene ligands are more than the disadvantage, if you compare with the phosphines. So, that is why this is one of the popular choice of the N-heterocyclic carbene ligands to replace the phosphine ligands in many successful catalytes.

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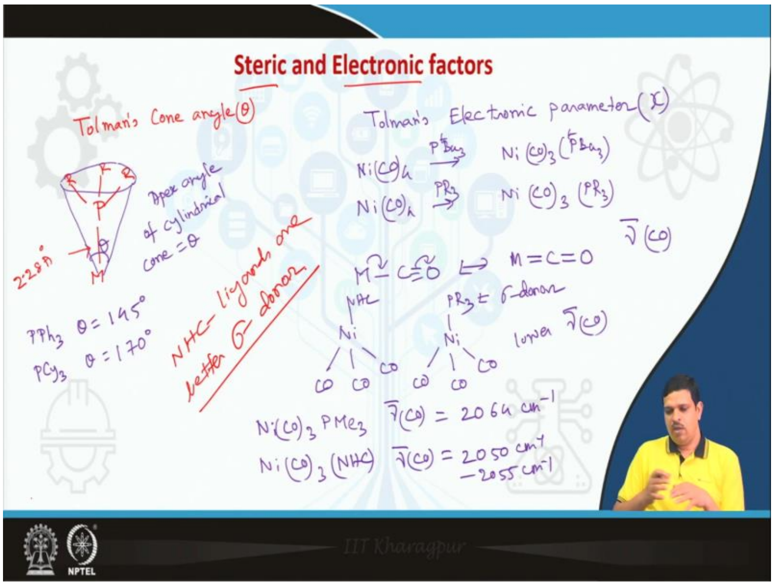
Steric and Electronic factors

So, as I told that that two factors that is one is the steric and one is the electronic factors. If you recall the metal phosphine chemistry that there is a parameter called the cone angle, Tolman’s cone angle is called is called theta. So, do you remember this, what is that? This is actually represents the steric hindrance or steric requirement of the phosphines. And what is the convention?

That if you have the phosphine ligands and and put a make is coordinatial metal and you fix the metal phosphine distance as 2.28 angstrom and there is a three substituents on the phosphine. So, like that and now what I want to do that you make a cone with this metal centers and touching the Van Der Waal ready of the outermost atom of the phosphine like that.

And if you do it then the apex angle of cylindrical cone is actually theta. So, that is the theta that is called the Tolman’s cone angle. As example, if you like pph 3, triphenyl phosphine, for that the cone angle is 145 degree and for like cyclohexyl the theta is 170 degree. That means the streric requirement for the cyclohexyl phosphine is more than the pph 3.

So, for like pma 3, trimethyl phosphine, the theta will be much less and the lowest theta is for the pas 3 that is the obvious reason. So, this is the convention and this is the to basically quantification of the steric factors of methyl phosphine. So, similarly you can also project for NHC ligands. Like that another factor that is the electronic factors.

So, what is that? That is also called the Tolman’s electronic parameter. To understand actually you have to compare with first phosphine ligands because we are comparing the properties between the phosphine and the carbenes. So, that actually is xi. Now, you will see here that if I, this is the convention if you like replacing the nickel tetracarbonyl nickel with tertiory-butyl 3, then you will get this one, that is the terci-butyl. And suppose, if I reacting with any other P R 3, then you will get like this one.

Now, we know that the, this is the metal carbeneyl bond, now, if this can exist at if there is a sufficient back bonding between metal and carbon then what happens that metal carbon becomes a kind of double bond and C double O becomes triplet to the double bond. That means the stretching frequency of the carbonyl that is the lower energy stretching frequency becomes smaller.

So, more backbonding means the more lower stretching frequency. So, if you consider like this one, so like that. So, in this case, if this is more sigma doner then is a lower stretching frequency like that. So, similarly, if I replace the NHC, in this case, if you see that stitching frequency is lower then again we can tell that NHC has a more sigma donor character.

If we compare with this different N H C metal carbene complexes then it is observed that like for Ni CO 3 P Me 3 that mu CO value is 2064 centimeter inverse. And if we compare the

NHC ligands, this falls in the range of 2050 centimeter inverse to let us say 2055 centimeter inverse.

So, form this data it is very much clear that NHC ligands are better sigma donor. So, NHC ligands are better sigma donors. So, you can, from this data it is very clear that the NHC ligands are much more better sigma donor than the phosphines, by very clearly is visible from the simple experimental that is the IR spectroscopy.

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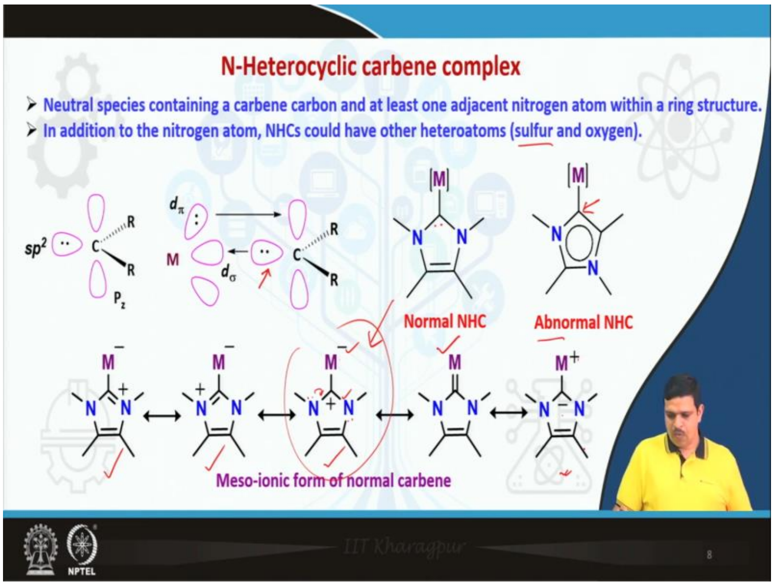

N-Heterocyclic carbene complex

- Neutral species containing a carbene carbon and at least one adjacent nitrogen atom within a ring structure.
- In addition to the nitrogen atom, NHCs could have other heteroatoms (sulfur and oxygen).

Now, here you will see that this is the metal carbene complexes and the right-hand side you will see it is written abnormal. The normal NHC is that you will see that carbon actually this is the carbon is in between the two heteroatoms, here two nitrogens and this one, the abnormal carbon you will see that if we this you you have to design the ligands in such a way that, that carbon formation is not feasible in between the nitrogen.

So, forcefully, I am making the carbon here. In this case, it is called the abnormal NHC. Not only the nitrogen, any other heteroatoms like sulfur and oxygens also possible to make the NHC kind of legands. And the bonding is very much similar as we discussed for the Fischer type carbene complexes.

So, here you will see that is the carbon at the SP2 orbitals hybridized orbitals it donates to the D sigma orbitals of the metal and it can also give form the back bonding between the suitable orbitals of the metal the orbitals and the p z orbitals of the carbon. So, it is very much similar.

Here is interesting, if you see that normal curving that is the this one, you will see, it can form a meso-ionic form.

If you see the different canonical structures, you will see that this is the M minus C plus, that is the this one. So, M minus C plus and you will see that this plus. So, if your known pair is there. So, you see here. So, this is N plus, this one and similarly, this side is also there. So, it forms the plus and is the opposite polarity.

If it is here it is M minus C plus. So, it is a M plus C minus, but you see that these are the called the meso-ionic form of the normal carbenes. So, this is the you will see that in general cases, this is the most acceptable meso-ionic form. This is not actually. So, the major contribution is the left side.

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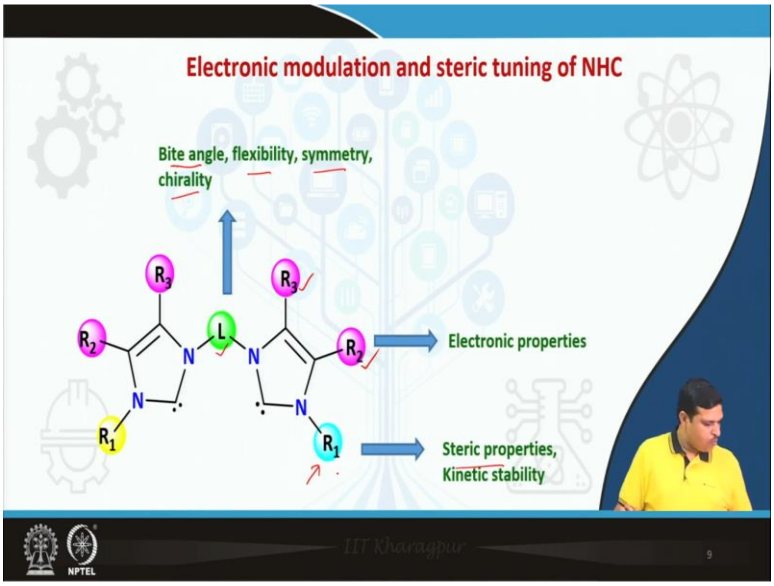

Electronic modulation and steric tuning of NHC

Bite angle, flexibility, symmetry, chirality

Electronic properties

Steric properties, Kinetic stability

So, you can design your NHC ligands by considering the different properties what actually we need. As example, like for this one the L it is actually governs the bite angle, the flexibility, symmetry, chirality, bite angle and also the steric requirement that is the Tolman’s cone angle. So, it basically governs this all these properties. These are governs the electronic properties, the donation ability, back bonding ability and also solubility.

This is again very much similar as R2 that major contribution of, the major contribution of the steric requirement of the NHC carbon ligand. So, it is basically gives the kinetic stability, this one. So, it is more steric, this R1 means the NHC carbon is more stable. So, more steric mean more stable that means it can protects the reaction from the moisture and oxygen.

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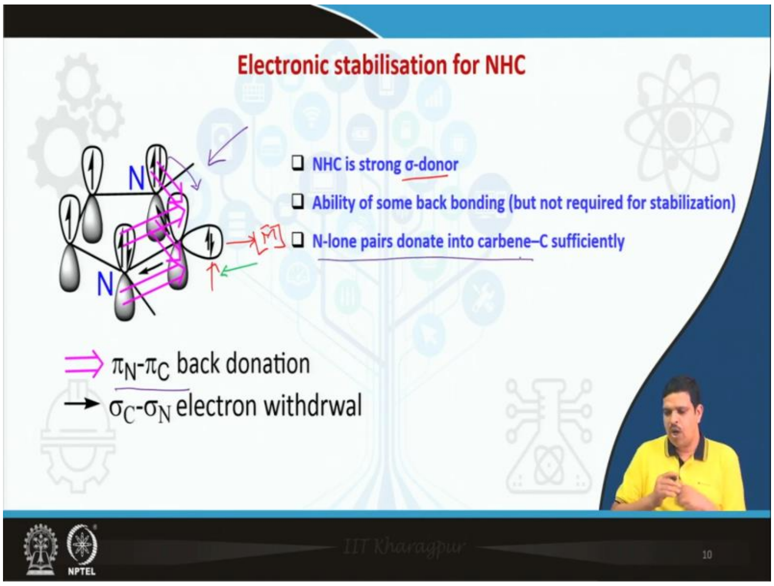

Electronic stabilisation for NHC

- ☐ NHC is strong σ-donor
- ☐ Ability of some back bonding (but not required for stabilization)
- ☐ N-lone pairs donate into carbene–C sufficiently

⇒ π_N-π_C back donation

→ σ_C-σ_N electron withdrwal

So, this one is very much important to understand that what is the bonding between the ligand NHC ligand and the metal. So, let us try to understand what is this. As I told that NHC is a very good sigma donor. So, you see that it is very much clear that this one, this the carbene ligands, this actually donates to the metal centers as like the in the Fischer carbene.

Now, similarly, in other Fischer metal carbene complexes like Fischer carbene complexes that same can be back donated to the carbene ligands. However, to make stability, to give the stability this back bonding is not very much needed for the NHC ligands. Why it is not needed?

Because you see here after this donation, the electron deficiency is actually neutralized from the loan pair of the from the nitrogen, loan pair of the nitrogen to the carbene carbon and that is that is the actually the canonical forms, this one and this one, give the contribution. So, from here you will see that one it is donated to the metal center, the electrode deficiency actually is neutralized from the donation from the loan pair of the nitrogen to the carbene carbon, like this one. So, this is called the pi nitrogen, pi carbon back donation. So, NHC. So, that is why you see ability of some back bonding is possible but not required for the stability of the metal NHC complexes. Because in loan pairs donate into carbene carbon sufficiently to make it stable.

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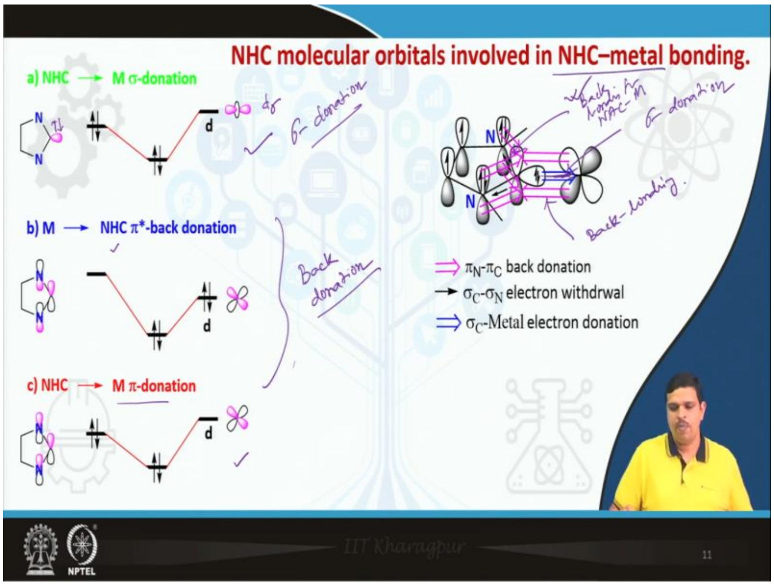

NHC molecular orbitals involved in NHC–metal bonding.

a) NHC → M σ-donation

b) M → NHC π^*-back donation

c) NHC → M π-donation

⇒ π_N-π_C back donation

→ σ_C-σ_N electron withdrwal

⇒ σ_C-Metal electron donation

So, if this will be more clearer from this picture, very simplified molecular orbitals and orbital interaction between the metal D orbitals and the carbene ligands. So, this is the normal sigma donations that is the this one, this one. So, here you will see that this carbene donates the electrons donates to the D sigma type of orbital that is the d z square here which is obvious.

And then here you will see that bonding is possible here, one is the NHC to the metal pi donation to the pi orbital of the metal that is the D square and also here you see that another one the NHC to the pi star orbital of the metal D orbitals. So, back bonding, these are the back donation and these are the sigma donation. So, this is the sigma donation from the sp2 orbitals of the field sp2 orbitals from the carbon carbon to the metal sigma orbitals.

And these are the possible back donation from the metal to the pi star of the NHC. And this one is the NHC that is the carbene ligands to the pi orbitals of the metal. So, that bonding, two pack bonding is possible here. So, here you will see, this is a conjugated. So, this is the donation, sigma donation.

This is the back bonding from the metal and this is the back bonding from NHC to metal through the carbon. So, you will see that this is more feasible and actually that is why the back bonding between the metal and the N H C carbon is not required for the stability of the metal carbene complexes. That is the one of the vital electronic properties and the important points in the NHC metal bonding.

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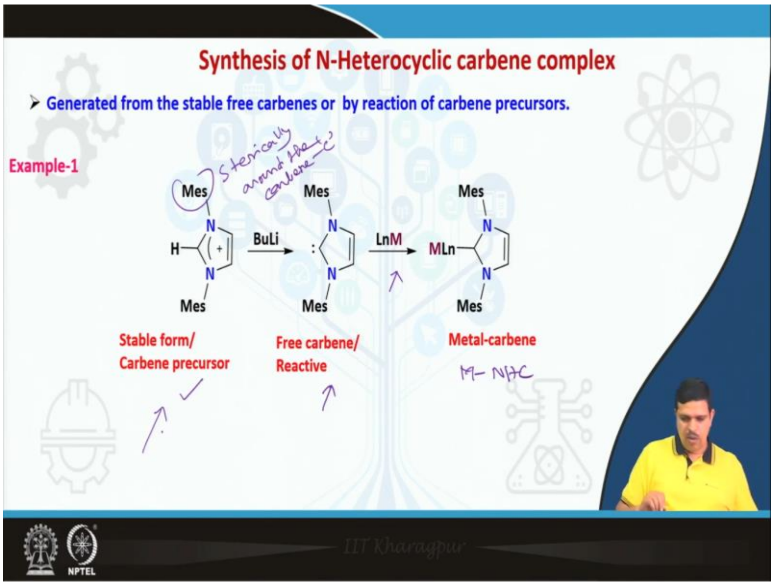

Synthesis of N-Heterocyclic carbene complex

- Generated from the stable free carbenes or by reaction of carbene precursors.

Example-1

So, now, I will briefly discuss about the general synthetic protocols of the N-heterozychic carbene complexes. So, as we discussed that free carbene to get a free carbene ligands you will have to have a judicious design of the carbene ligands. You have to have a proper subsequence so that it does not react to its moisture and oxygen and kinetically becomes stable. So, that is why you have to put a quite statically demanding ligands around the carbon otherwise it will be not stable.

So, like mesitylene, mesityl or more sterical demanding group like adamantyl like that. So, here you will see that strategy to make the this is one of the simple strategy to make the metal N H C carbene complex is that this is you take the carbon precursor that is the stable form that is the imidazole cation and if you add a strong base like butyllithium or any alkoxide, the strong alkoxide base, you can get a free carbon that is most of the cases it is not isolable, as I told, but many cases it is isolable.

If you design your carbene complex judiciously that is with more strategically demanding groups and then if you react with a suitable metal precursors, you will get the metal carbene complexes that is the metal NHC, N-heterocyclic carbon complex. So, this is the general synthetic strategy of N-heterocyclic metal complexes. So, most of the cases actually, we use from a stable form of the carbon, not we use the direct free carbon. Because in most of the cases it is not stable and is very difficult to store at ambient condition.

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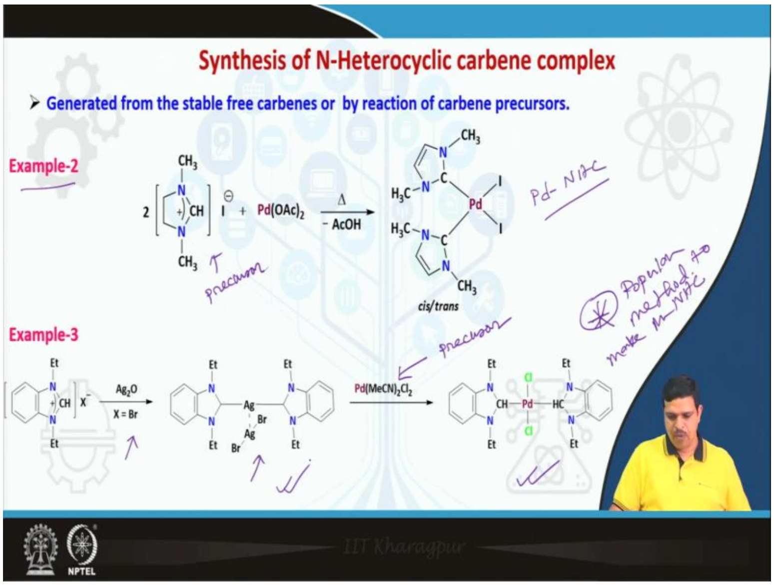

Synthesis of N-Heterocyclic carbene complex

- Generated from the stable free carbenes or by reaction of carbene precursors.

Example-2

Example-3

So, this is like example 2. So, as I told that this is the precursor and if you add with lead that is that you see that palladium acetate, you will get the corresponding the palladium NHC complexes. Its reaction is quite straightforward and very simple and very clean reactions. Most of the cases, we use the transmetalation that is you will see that first we react with silver oxide and then we will make this the this one that is in many it is isolable and you can actually store it C bar complex and then you take the your the precursor, metal precursor, what the metal carbene you want to make it and you add it and you get the your corresponding metal carbene complexes.

This one is one of the popular method to make your, to make metal carbene. So, we actually follow this method most of the times because this method is very clean, much cleaner than the other methods through the transmetelation. So, and this one is you can actually store it at least for some time, no problem.

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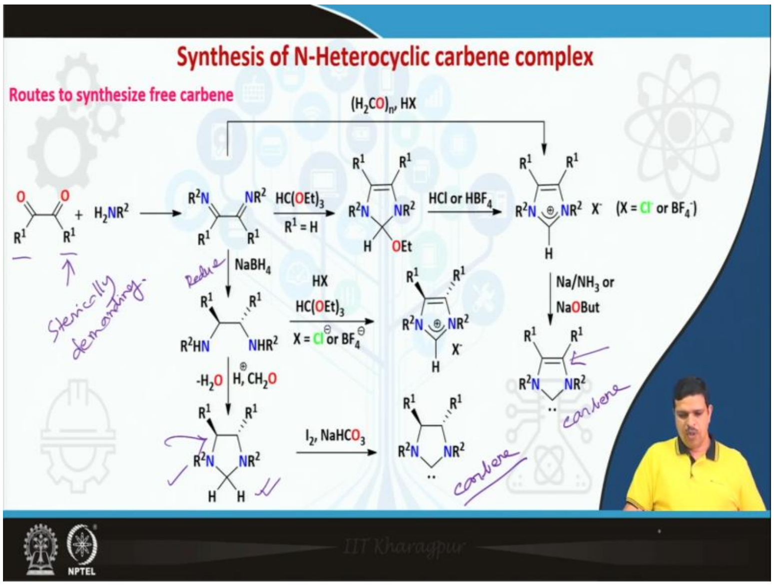

Synthesis of N-Heterocyclic carbene complex

Routes to synthesize free carbene

So, these are different routes for to make the N-heterocyclic ligands you will see that this is kind of a one kind of a guideline to synthesize a new NHC ligands. So, like if you start from the di thitone and do the simple condensation reactions, if you want to make a saturated NHC ligands then you reduce it and then the substituent reactions will give this ligand and then if you want to make a carbene then you treat with iodide and sodium bicarbonate and you get the carbene complexes.

As I told that you have to this R Group, you have to have a strically demanding group, otherwise, you cannot make the carbene complex which is stable. Similarly, if you want to make the unsaturated imidazole type carbene ligands, so, you follow this path and eventually you will get again this is the carbene complex and here you will see this is the there is a double bond and this is the saturated bond. So, these are some are the general guidelines to make N H C type of ligands and it is quite straightforward.

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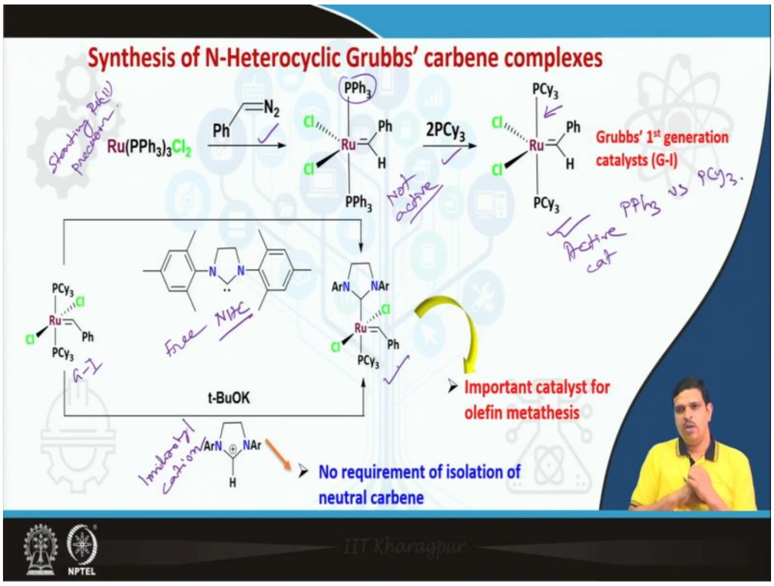

Synthesis of N-Heterocyclic Grubbs' carbene complexes

- Important catalyst for olefin metathesis
- No requirement of isolation of neutral carbene

So, this the complexes ruthenium complexes as I told that one of the biggest discovery in the recent chemistry in like last 20 or 20 years or so. So, these are nothing but a Grubb's catalyst you will see and how it can be synthesized. This is the starting material, starting precursor, starting ruthenium-2 precursor and if you react with this diazonium, the dialic compound phenyl dialic compound and you will see you will get this trigonal bipyramidal ruthenium complexes.

And this is basically the the Grubb's first-generation catalyst but with pph 3 ligands. If you replace the pph 3 by cyclohexyl phosphines ligand that is this one, you will get the Grubb's first-generation countries G 1. So, here you will see that pph3 versus pcy 3. That is the it was very important to replace the tricyclohexyl phosphine replace the triphenyl phosphine by tricyclohexyl phosphine and it was shown that that piece that this one is active catalyst but this is not active catalyst. And why it is so?

Because pph 3 makes a stronger bond between the metal and the phosphorus but in cyclohexyl phosphine this bond is much weaker. So, whenever it is necessary in the catalytic cycle the PCy3 can comes out and gives space to the substrate. For alkene metathesis reactions, it can give space to code for the coordination between the ruthenium and the alkene.

So, that is why telling the ligand design is very much important. So, this is one of the very historical and interesting example that how one phosphine, change in phosphine can drastically improve the catalyst, catalyst activity. So, if you take that this one that is the G 1 that is called the Grubb's first-generation catalyst.

And then if you react with the N H C ligands, you will get the derivatives of the ruthenium NHC Grubb's type, first generation Grubb's type of catalyst. You will see here that you no need to make the free carbon. You can also, which is the more advantageous to go, to follow this path where you no need to, no requirements of isolating the free NHC carbene.

You can easily we can go through the in situ to prepare in situ synthesis of the NHC carbene taking the imidozyl cation that is the this one imidozyl cation and in the presence of strong base, like oxobutyl oxide, you will get the free carbon which then subsequently react with your ruthenium precursor and make the this complex.

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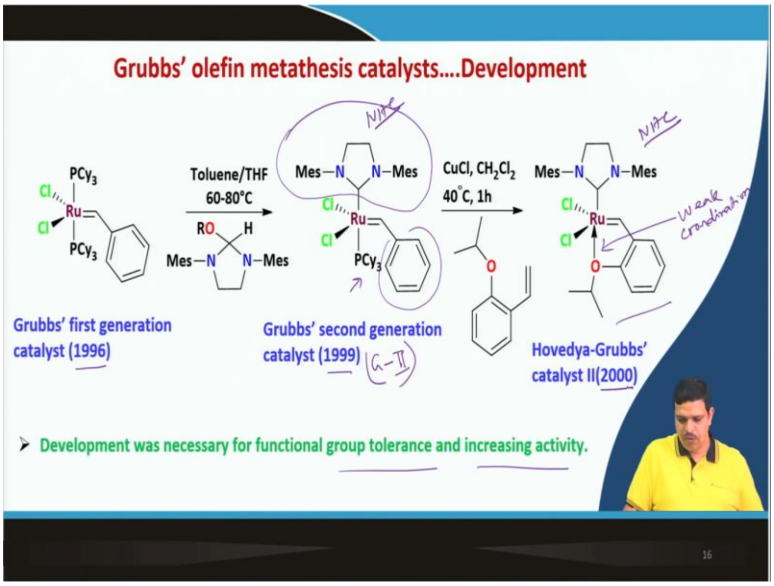

Grubbs' olefin metathesis catalysts....Development

Grubbs' first generation catalyst (1996)

Grubbs' second generation catalyst (1999)

Hovedya-Grubbs' catalyst II(2000)

- Development was necessary for functional group tolerance and increasing activity.

So, this approach eventually actually gave the second generation that is in the book you are literature you will see it is written as G2. So, it is you will get the G2 catalyst that is the second generation of catalyst. So, you will see this is by first generation developed in 1996, just after 2 - 3 years that is the G2. G2 is nothing but you will see that one cyclohexyl phosphine has been replaced by the one NHC ligands, that is all.

And you will see that subsequently, it was modified time to time and the modification of necessary to make a compatible to the other functional groups and also increasing the activity. So, for the two reasons, the different type of catalysts were developed in time to time and modified.

So, here, you will see that NHC ligands was same but here that PCy 3 ligand was substituted in a very judicious way by replacing that these phenyl groups by this, you will see that is one isopropyl ethoxy. So, this actually quickly coordinates. This is the weak coordination between the oxygen ruthenium because you know the oxygen is not a good donor.

And you will see that you will get this ruthenium complex where one is NHC and one PCy3 has been substituted by this ligand and you will get that it is called the Hovedya-Grubb's catalyst that was developed in 2000. That is another very active catalyst. So, you will see in that area, after 1990, it was a golden era in the organomic chemistry. One after one very active alkene metaphysis catalyst came.

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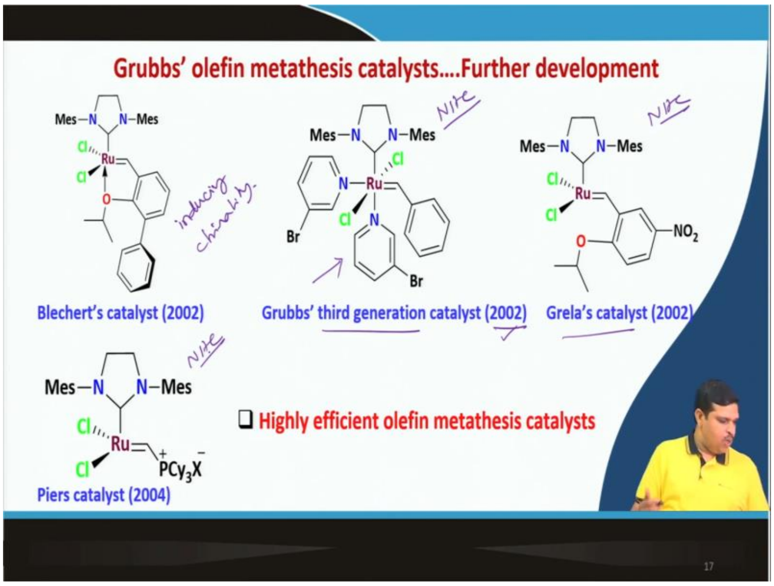


Grubbs' olefin metathesis catalysts....Further development

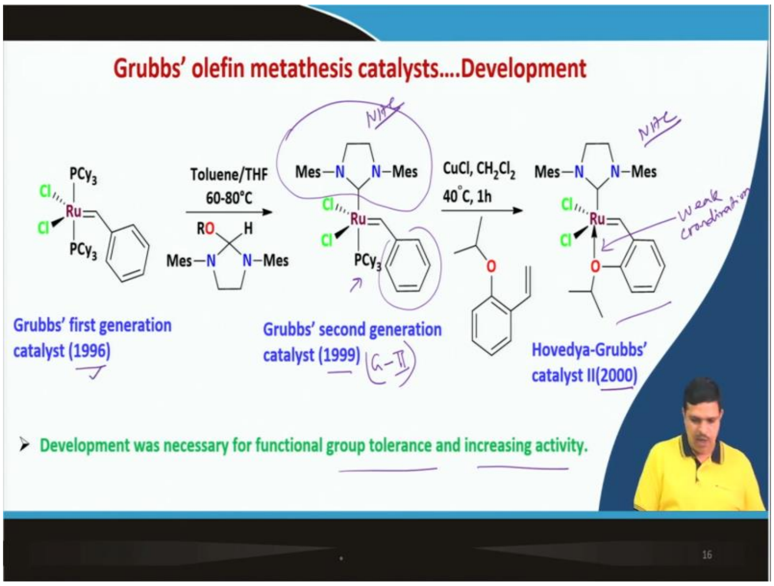
Blechert's catalyst (2002)

Grubbs' third generation catalyst (2002)

Grela's catalyst (2002)

Piers catalyst (2004)

☐ Highly efficient olefin metathesis catalysts



Grubbs' olefin metathesis catalysts....Development

Grubbs' first generation catalyst (1996)

Toluene/THF 60-80°C

Grubbs' second generation catalyst (1999) (G-II)

CuCl, CH_2Cl_2 40°C, 1h

Hovedya-Grubbs' catalyst II(2000)

- Development was necessary for functional group tolerance and increasing activity.

And after that you will see that Grubb’s third generation catalyst that is in 202. So, you will see that again in 1996 after three years generation 2 and after three years generation 3 and here you will see NHC ligand is same and here you will see in instead of PCy 3, this bromo pyridyl, 3 bromo pyridyl group has been incorporated.

Similarly, you will see that here to make the induce the chirality, here, inducing chirality in 2002, Blechert’s catalyst has been developed. Here also same, very similar, here you will see NHC, the Grela’s catalyst in same year and here also you see similar one ligand is NHC, Piers catalyst in 2004. So, all the catalysts, starting from Grubb’s 1, Grubb’s 2, Hovedya catalyst, third generation catalyst, Blechert’s catalyst are very efficient alkene metathesis catalysts.

And you will see that is why it is very important to understand the metal NHC carbene complexes, the bonding, the chemical structure, nature of the ligands nature and the electronic properties of this metal NHC complexes to understand the metathesis reactions. Because most of the complexes you will see that are based on the metal NHC type of carbene complexes.

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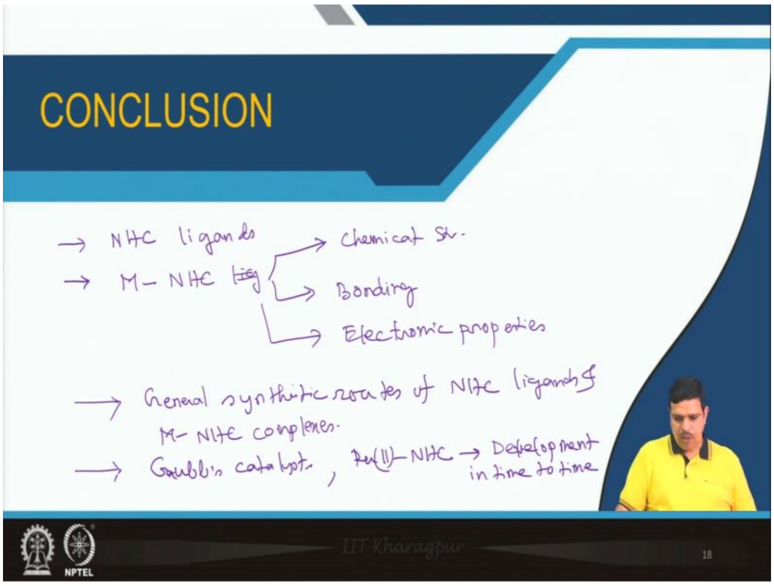

CONCLUSION

→ NHC ligands

→ M – NHC Lig → Chemical Str.
→ Bonding
→ Electronic properties

→ General synthetic routes of NHC ligands & M – NHC complexes.

→ Grubb's catalyst, Ru(II) – NHC → Development in time to time

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So, in conclusion, today what we have learned? We learned that the NHC ligands that is the N- heterocyclic carbene ligands that is and eventually we now know the basic chemical structure, most importantly, the bonding and the electronic properties. And you see that why the, what is the role of the two nitrogen atoms in the NHC legands and how these stretically demanding substance on the NHC plays a dominant role to contribute the kinetic stability of the carbene ligands.

And subsequently, we know we learn the general synthetic root of NHC ligands and metal NHC complexes. And you will see that to make the metal NHC complexes that we no need to make the free NHC ligands because in there is a stability issue, we have already discussed, most of the cases.

We make the N-heterocyclic carbene complexes by the stable form of the NHC carbene ligands that is the cationic form that we discussed. And these are very this root is very much easy compared to the first making the carbon ligands and then reacting with the metal precursor. And lastly, we discussed about the various Grubb's catalysts that is the actual ruthenium 2 based NHC complexes and the development in time to time.

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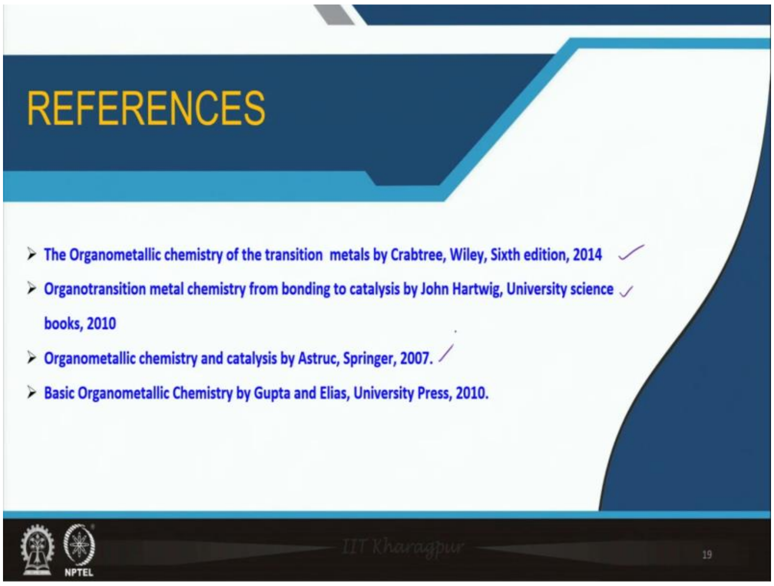

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- Basic Organometallic Chemistry by Gupta and Elias, University Press, 2010.

And these are the books you can read for today's lecture. And in the next class we will discuss about, mainly, will focus on the mechanism of the various metaphysis reactions by the Grubb's type of catalyst and that is why we today in this class, today's class we emphasize the ruthenium-based Grubb's catalyst and different type of active Grubb's catalyst G1, G2, G3, Grubb's Hovedya the catalyst, Blechert's catalyst like that. And eventually after understanding mechanism, we will discuss the its application in alkene polymeration chemistry. So, bye for now and see you in the next class. Thank you.