Introduction to Organometallic Chemistry
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Lecture - 6
Carbene complexes

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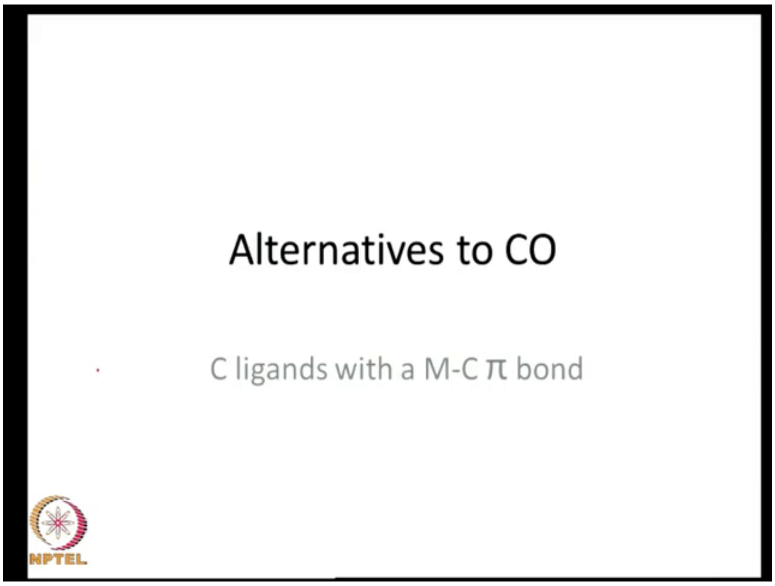

Alternatives to CO

C ligands with a M-C π bond

So, this is a lecture on a few ligands, which are alternatives to carbon monoxide. We have already seen that carbon monoxide is one of the best ligands in organometallic chemistry, because it provides unsurpassed pi bonding character. And people have always been looking for alternatives to carbon monoxide, because carbon monoxide does not exert a significant steric influence. And it is possible to have specific catalytic properties, if you can modify the steric properties of the ligand. So with that in mind people have been looking for alternatives to carbon monoxide. And today we are going to look at set of ligands, which have come out to be extremely useful in organometallic chemistry. And which rival carbon monoxide in terms of some of the properties that they exhibit.

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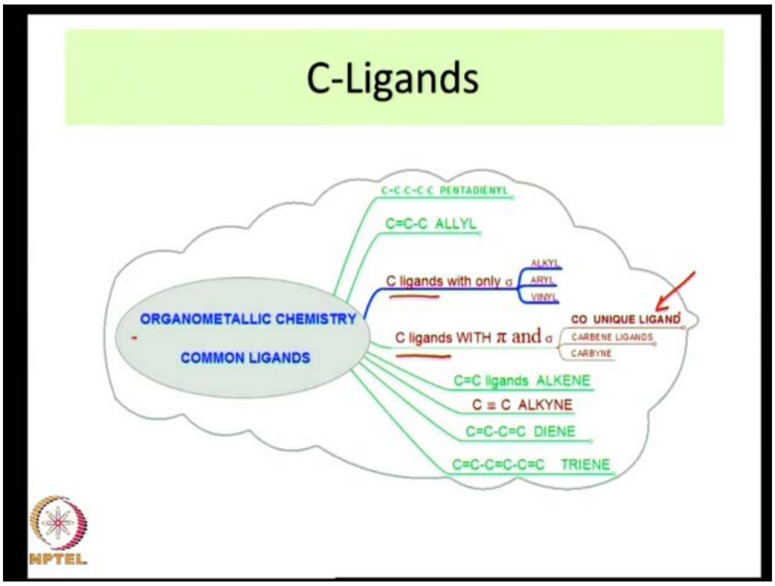

C-Ligands

ORGANOMETALLIC CHEMISTRY

COMMON LIGANDS

C=C-C=C-C PENTADIENYL

C=C-C ALLYL

C ligands with only σ

ALKYL

ARYL

VINYL

C ligands WITH π and σ

CO UNIQUE LIGAND

CARBENE LIGANDS

CARBYNE

C=C ligands ALKENE

C ≡ C ALKYNE

C=C-C=C DIENE

C=C-C=C-C=C TRIENE

If you look at all the carbon ligands, one can see this map where you have carbon monoxide. Yes am I here, it is a ligand with a single carbon, there are other ligands which have a single carbon attached to the metal. And you notice that, among the ligands which have a single carbon attached to the metal, carbon monoxide occupies a unique position.

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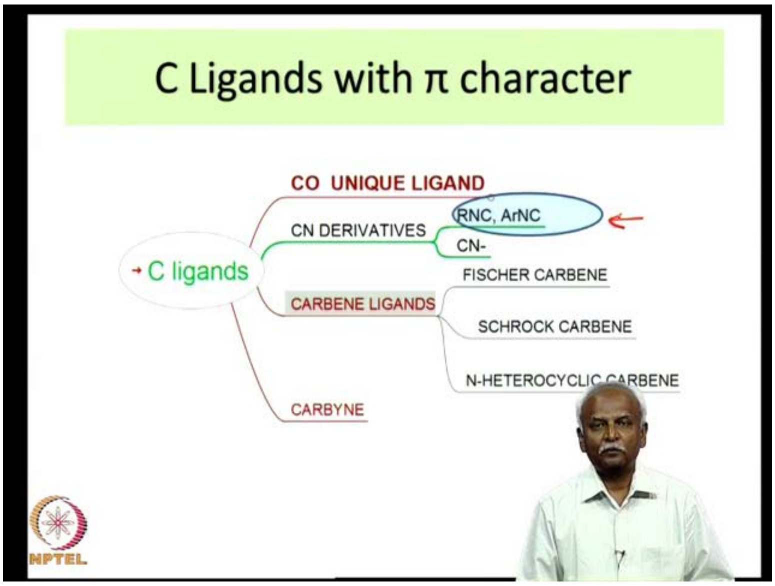

C Ligands with π character

C ligands

CO UNIQUE LIGAND

CN DERIVATIVES

RNC, ArNC

CN-

CARBENE LIGANDS

FISCHER CARBENE

SCHROCK CARBENE

N-HETEROCYCLIC CARBENE

CARBYNE

So, if you focus further on some of these ligands, you find that carbon monoxide can be replaced by CN minus or alkyl isocyanides. And if you focus further on this group of ligands, which is the alkyl isocyanide group, we can see how this will naturally lead to a set of ligands that we are going to discuss today.

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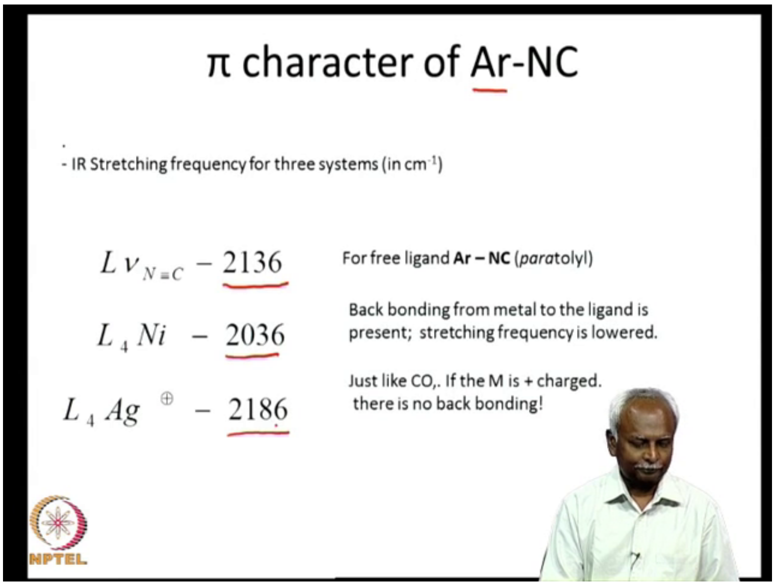

π character of Ar-NC

- IR Stretching frequency for three systems (in cm^{-1})

$L\nu_{N\equiv C}$ – 2136 For free ligand **Ar – NC** (*para*tolyl)

L_4Ni – 2036 Back bonding from metal to the ligand is present; stretching frequency is lowered.

$L_4Ag^{\oplus}$ – 2186 Just like CO,. If the M is + charged. there is no back bonding!

Alkyl isocyanides are excellent ligands and we can see that, they have pi accepting properties because the free ligand has a stretching frequency of 2136 centimetre minus 1. And when it is, complex to nickel 0, the stretching frequency reduces by 100 centimetres minus 1, which is exactly what happens with carbon monoxide also. There is a distinct advantage for alkyl isocyanides, because you can have some steric influence due to the presence of this Ar group attached to the isocyanide moiety.

A further note of similarity to carbon monoxide comes, when you compare the complex is formed by alkyl isocyanides with positively charged metal atoms. The frequency instead of going down, actually increases, this is exactly what you find for carbon monoxide also. And this has been attributed to two factors, one of them is the lack of pi back bonding and the other is the fact that you have a charge on the metal. And it influences the stretching frequency through an electrostatic phenomenon.

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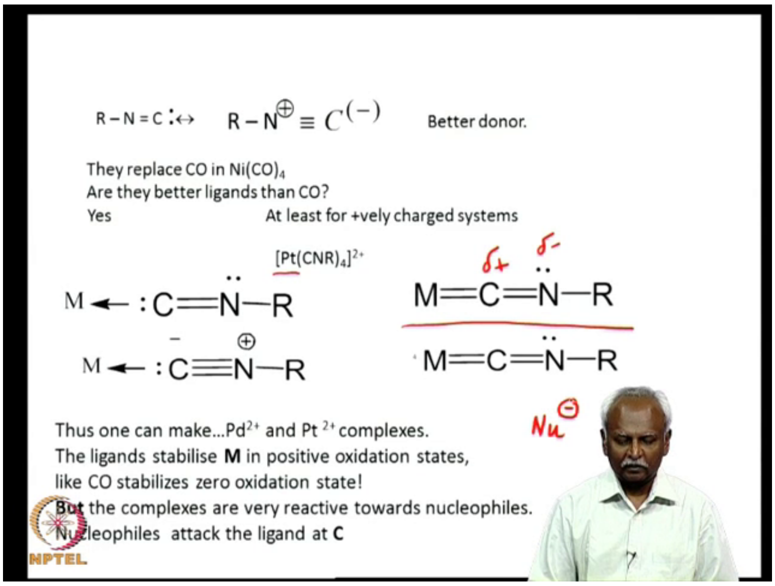

$R-N=C{:}\leftrightarrow$ $R-N^{\oplus}\equiv C^{(-)}$ Better donor.

They replace CO in $Ni(CO)_4$
Are they better ligands than CO?
Yes At least for +vely charged systems

$[Pt(CNR)_4]^{2+}$

Thus one can make...Pd^{2+} and Pt^{2+} complexes.
The ligands stabilise **M** in positive oxidation states,
like CO stabilizes zero oxidation state!
But the complexes are very reactive towards nucleophiles.
Nucleophiles attack the ligand at **C**

Unfortunately, although alkyl isocyanides are so good, they do have one disadvantage. And the disadvantage comes from the fact that, you have a complex, many times you have a complex where the metal is positively charged and the isocyanide develops a partial positive charge on the carbon of the isocyanide. So, the alkyl isocyanide ends up with a charge in the complex where, a carbon is positively charged and the nitrogen is slightly negatively charged. And so is the metal atom, now we have aproblem, because if you have a nucleophile, if you have a nucleophile, the nucleophile would like to attack the carbon, which is positively charged.

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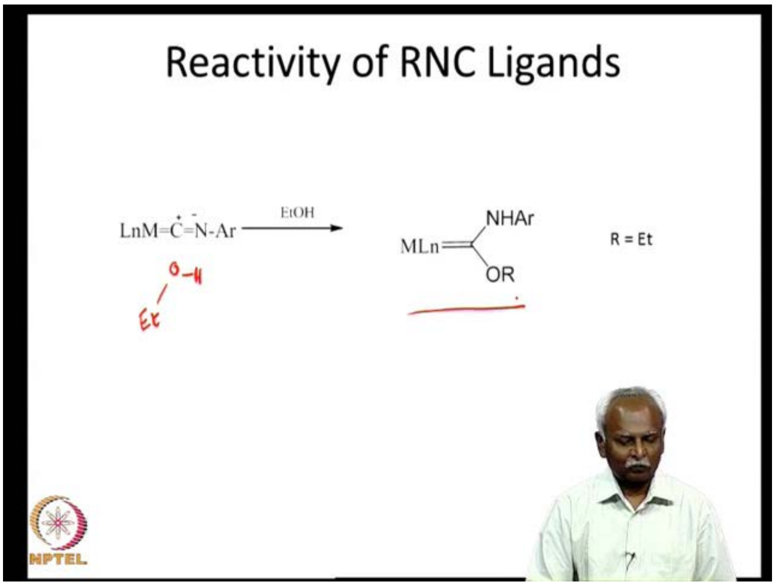

Reactivity of RNC Ligands

R = Et

And many times you have, an alcoholic solvent, the alkyl isocyanide rapidly reacts with it and forms a type of a carbene complex. Where, the ethanol or the alcohol ethanol in this example adds across the carbon and the nitrogen, so that the oxygen adds here and the proton adds at the nitrogen end. So, this is a specific example, but it is generally true that nucleophiles will add on to the carbon in such a way that, you have not an alkyl isocyanide anymore, but a carbenoid type of a complex.

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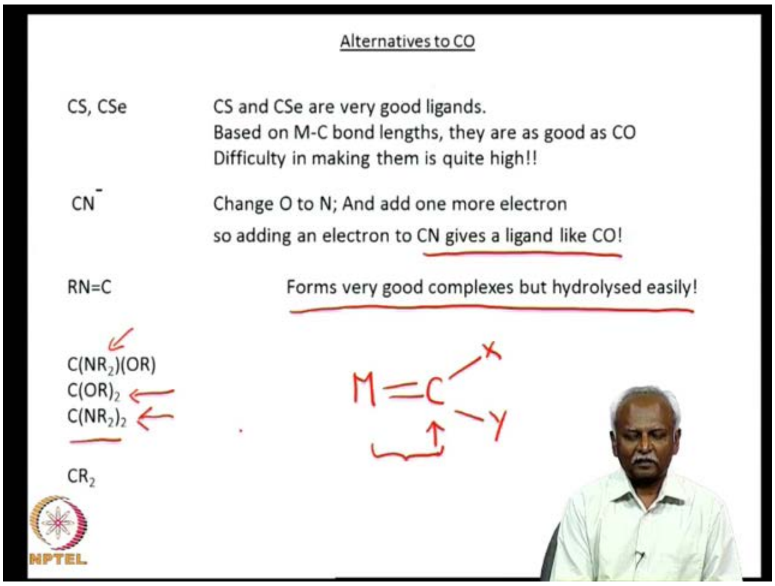

Alternatives to CO

CS, CSe	CS and CSe are very good ligands. Based on M-C bond lengths, they are as good as CO Difficulty in making them is quite high!!
CN^-	Change O to N; And add one more electron so adding an electron to CN gives a ligand like CO!
RN=C	Forms very good complexes but hydrolysed easily!
$C(NR_2)(OR)$	
$C(OR)_2$	
$C(NR_2)_2$	
CR_2	

So, let us look at the alternatives that we have examined. One of them is carbon monosulphide and carbon monoselenide, these are indeed isoelectronic with carbon monoxide. And are very good ligands, they have very good pi bonding characteristics andthey have good electron density on the metal, because carbon CS can donate electron density very well, but unfortunately there is a great difficulty in making them. They are not as good as, carbon monoxide which is readily available in a cylinder. So, we also look at cyanide CN minus, where you could change from CO to CN. And then add an electron to compensate for the number of electrons that gives you CN minus which is identical in terms of electron count to carbon monoxide.

So, CN minus should have been a good ligand, but because of the negative charge it tends to, generate excess electron density on the metal. So, it cannot stabilize low valent metals, so then we moved on to alkyl isocyanides, but unfortunately as we have just seen these, complexes hydrolyse very easily. And they generate complexes where, you have a carbene and the carbene has got an NR2 group. In the previous example, we had NRH and a OR group attached to the carbon. So, these carbenes or these carbene complexes are those systems in which, you have 2 hetero atoms attached to the carbon, which is complex to the metal.

So, we have a metal complex to a carbon and this carbon has got 2 hetero atoms attached to this central carbon atom. And this metal carbon bond, has some pi bonding character. So, these set of ligands where you have a hetero atom stabilizing the carbenecarbon are, in fact called hetero atoms stabilized, carbene complexes or Fischer complexes. And these Fischer complexes can have either an NR2 group, and an OR or they can have two OR2 groups. This is also equally valid and so is this alternative where you have two NR2 groups. In this lecture, we are going to specifically concentrate on a set of ligands where, you have 2 nitrogens attached to the central carbon and in this group of complexes, because of the formation of a ring you have a cyclic ligand.

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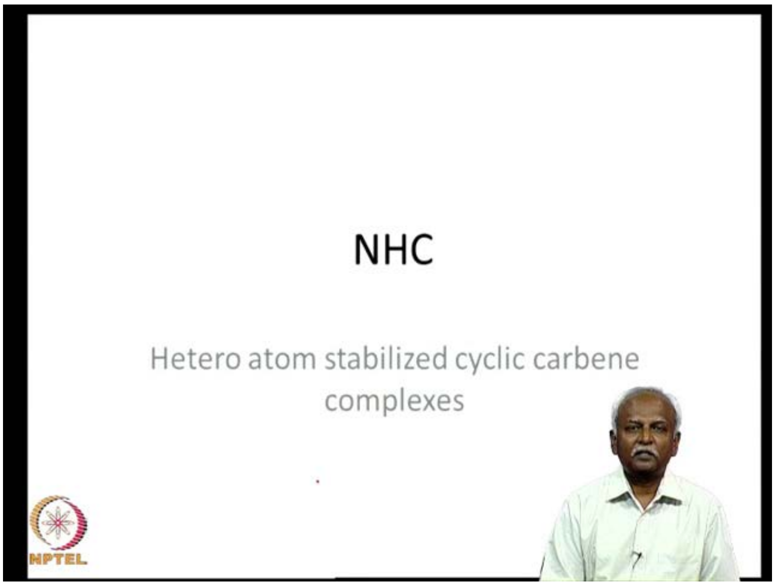

NHC

Hetero atom stabilized cyclic carbene complexes

So, these are called N heterocyclic ligands and these hetero cyclecarbene complexes are, extremely stable when they are complex to the metal. So, let us just look at a little bit of the history of these ligands and these complexes, because these complexes have been made only very recently, fairly recently about 20 years ago. They were discovered only in 1990’s and they have become very popular since then. So, let us take a look at how they were discovered and what led to their popularity.

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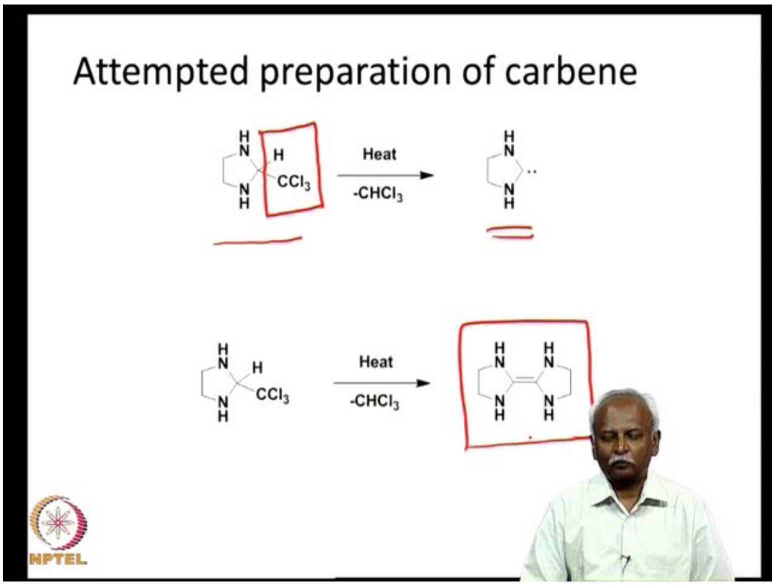

Attempted preparation of carbene

Initially, the interest in these complexes started with the attempts to prepare a free stable carbene. And one way to prepare a very stable carbene is, to carry out an elimination reaction where, you would start with a molecule which can eliminate a neutral moiety like chloroform. So, if you heat this particular heterocycle, to a high temperature you will eliminate chloroform and this elimination should lead to a carbene centre.

This was the hypothesis and when this reaction was carried out, it was found that you did not form a free stable carbene, but that carbene rapidly. And formed a olefin molecule and this olefin molecule is pictured here. So, if you can make this olefin people wondered, if this olefin would have some reactivity with metal complexes.

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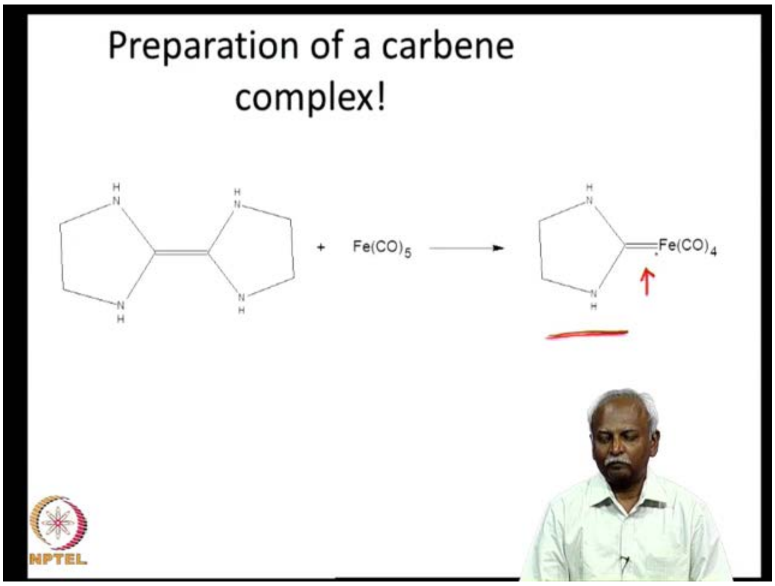

Preparation of a carbene complex!

And surprisingly, if you treat it this dimeric species, dimeric carbene or this olefin with iron pentacarbonyl, you tended to form an iron carbonyl complex, which had this carbene now, it is a heterocyclic carbene and this heterocycle is having two nitrogens stabilizing, the carbene carbon. And it is forming a stable iron complex where, the metal carbon distance is in fact, less than what would you expect for a iron carbon single bond. And it is more towards, a double bond, and we will look at this electronic characteristics shortly.

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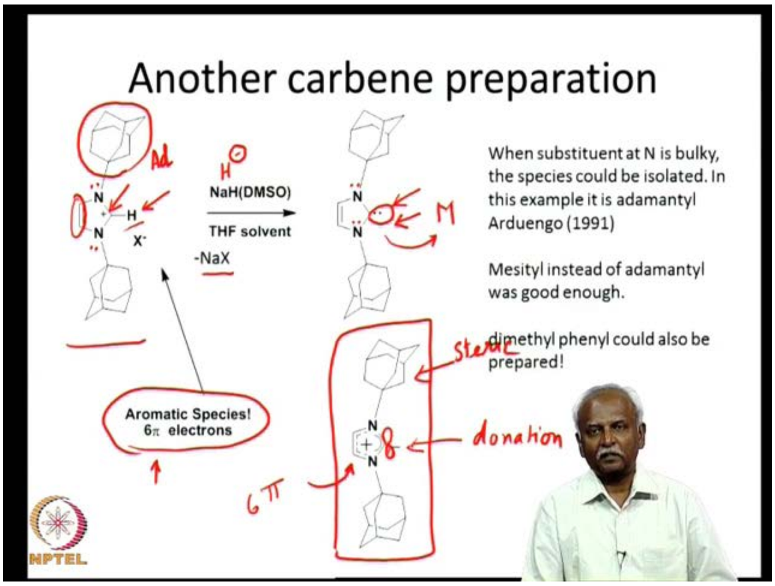

Another carbene preparation

When substituent at N is bulky, the species could be isolated. In this example it is adamantyl Arduengo (1991)

Mesityl instead of adamantyl was good enough.

dimethyl phenyl could also be prepared!

Let us look at another carbene now, this carbene was in fact the main reason why carbenes became extremely popular, because it could be very readily generated from salts, the salts are stable, because they are aromatic species. They are 6 pi electron aromatic species, which could be stabilized and kept in a bottle. They could be easily stored in a bottle and because of their stability and they were stable for two reasons. One is the fact that, you, the 6 pi electrons, 2 lone pairs on the nitrogen which, I am indicating here with red dots. And you also have, a pair of electrons between these 2 carbons so that, is the next pair of electrons.

So you have, a total of 6 pi electrons and you have a positive charge here a empty orbital. So you have, 5 p orbitals on this ring system, which have got 6 pi electrons and so it is an extremely stable aromatic system. And furthermore, the positively charged carbon which has got an empty p orbital, this carbon is stabilised or protected from attack by nucleophiles. By this, very large adamantyl group, this is a popular sterically protecting group. And this adamantyl group is the one, which protects this carbon from nucleophilic attacks. So, this particular cation is extremely stable and it can be stored in a bottle.

Now, this stable cation can be deprotonated by using a base or by using sodium hydride. If you use sodium hydride, the H minus from sodium hydride will now react with this proton which is here. And this proton will react with, this H minus andit will generate H2 or you can use a base which will remove HX as a salt. And that can also lead to a stable carbene moiety. So, this is a stable carbene moiety it is either generated by a elimination ofhydrogen andany X as it is pictured here or if we use an organic base you can just remove it as an salt.

So, either way you can generate a neutral carbene complex, which is extremely stable also because it is still an aromatic system this lone pair which is pictured here, is stored in the plane of the pi system. And the 6 pi electrons which we talked about earlier, are still present perpendicular to the plane of this ring system. You have a total of 6 pi electrons perpendicular to the plane of this ring system, and you have in the plane of the ring, you have a pair of electrons in an orbital, which is like an SP2 hybrid orbital pointing away from this ring system towards any other species, which might come towards this ligand, so if this is to be used as a ligand a metal will be approaching this ligand and this pair of electrons can be donated to this metal.

So, this carbene, was in fact quite stable it was prepared and it could be crystallized and the crystal structure of these ligands could be characterized very readily. And to add to that, one could also characterize the salt. So, you have a system which you can compare very readily, in terms of geometrical parameters and which you can use for further reactions very easily. So, let me just summarize the good features of this carbene.

This is the carbene that, we are talking about it is sterically protected so it has got steric protection, it has got a pair of electrons for donation. So, it has a pair of electrons for donation, it has got 6 pi electrons in its ring system perpendicular to the plane of the ring. And that stabilises it and makes it aromatic and then it has a vacant orbital on this carbon and this vacant orbital can be used in terms of electron acceptance from the metal, in case it is necessary. So that will destroy the aromaticity of this ring system, but nevertheless that possibility exists.

So, with this introduction let us just a look at, what would happen if we replace this very bulky adamantyl group with a mesityl group. That was also enough, to stabilize this aromatic ring system, the steric protection was sufficient. In fact, what is interesting is that dimethyl phenyl could also be used to prepare this particular ring system and make it stable.

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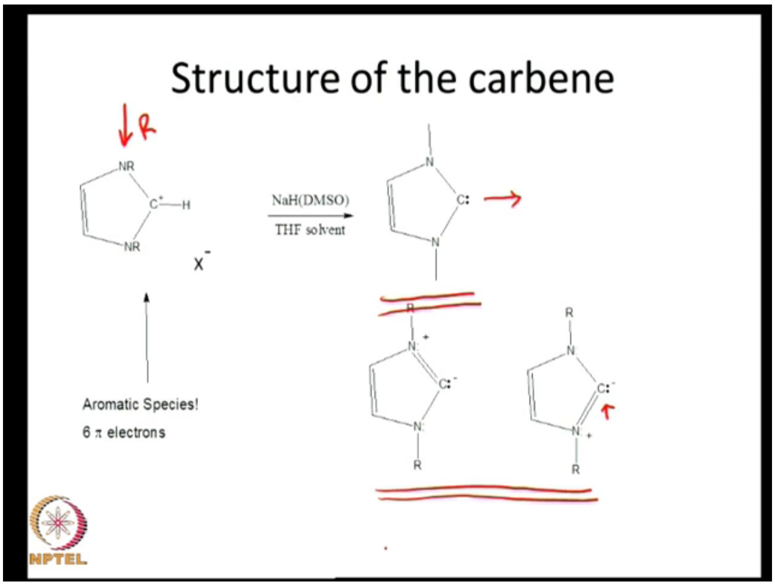

Structure of the carbene

Aromatic Species!
6 π electrons

So, a variety of R groups that, are pictured here, a variety of R groups could be used dimethyl phenyl or isopropyl or tertiary butyl, you name it and you can have it. You can make this cation and subsequently, you can deprotonate that cation, using sodium hydride or a base in order to generate the free and stable carbene. So, this carbene which is a N heterocyclic carbene could be stabilized and very easily generated. Not only that, it had this pair of electrons which could be donated to the metal and as I explained just now perpendicular to this pair of electrons present on a SP2 hybrid, which makes it a nucleophilic carbon. There is an empty P orbital, this makes the ligand a pi acceptor. From the metal, electron density can now be pushed into the empty P orbital, under carbene carbon making it a pi acceptor ligand, as well as a nucleophilic ligand. This pi acceptance actually arises, because you have this type of a resonant structure, which is present here. This resonant structure is the one which stabilizes, the carbenoid species and this carbon is the one, which is now both electron rich and which can accept electron density from the metal.

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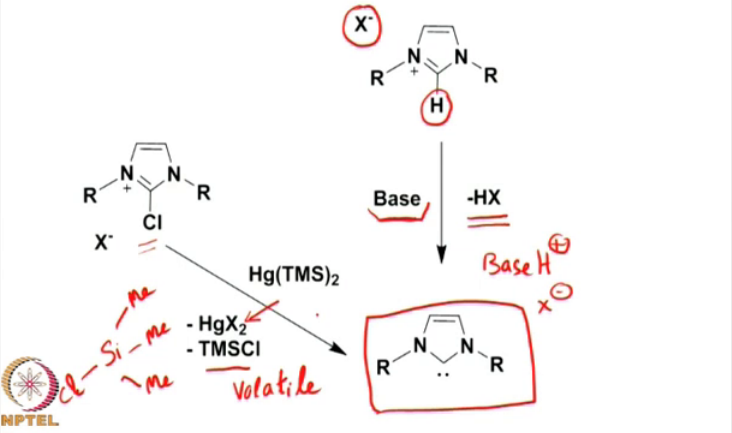
Ease of preparation from the imidazolium salt



So, not only is a imidazolium cation capable of being a precursor for this carbene. There are a variety of other systems, which will also generate this carbene. Here I have pictured a couple of other possibilities, this is a imidazolium cation reacted with a base and I have already mentioned this. But if you use a base, you would just replace a or you would remove the HX molecule, which is available here. And you would remove them as a base plus, base H plus and X minus as a salt and you would generate the free carbene. It is also possible now, to use a slightly different species.

If you have a chloro substituted imidazolium cation, the chlorine can be removed using trimethyl cylyl group. The trimethyl cylyl group which I am writing here, is excellent for scavenging chloride ions, because of it is, it will form trimethyl cylyl chloride and trimethyl cylyl chloride can be removed in this reaction. And the X minus can be removed by mercury and so you would have precipitation of HgX2 and you would form TMS chloride, which is extremely volatile.

So, this is a convenient way of making, it is a convenient way of making this neutral carbine ligand starting with this imidazolium salt, by treating them with mercury compounds. And trimethyl cylyl chloride is eliminated from this reaction and it can be readily removed. And the stable carbene is isolated in the pure form because HgX2 usually precipitates out, in the reaction medium that is dichloromethane or tetrahydrofuran.

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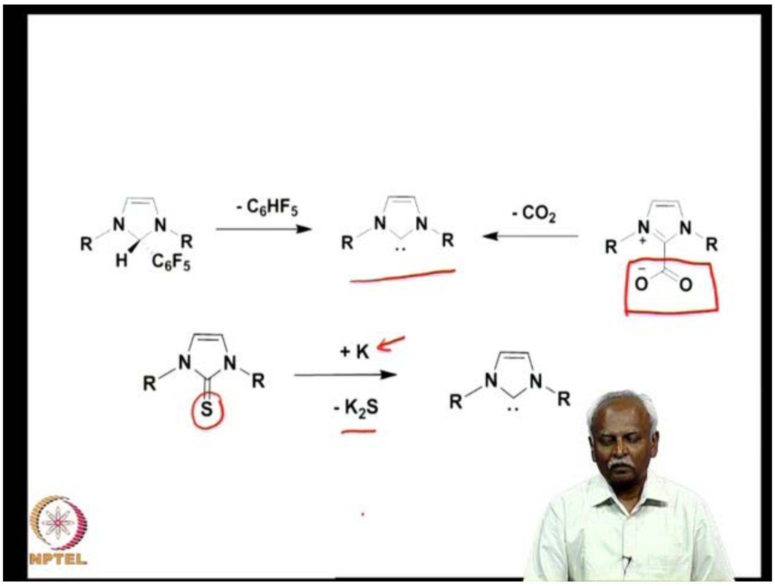

So, there isyet another method for making this carbene andhere you have elimination of a neutral molecule. This time, it is pentafloro benzene which is eliminated. C6F5 and H are eliminated from this imidazolium group or the precursor to the imidazolium carbene. And you can also eliminate a neutral molecule like carbon dioxide so here, carbon dioxide is eliminatedfrom this species.

This carboxylate imidazolium compound and you can form this neutral carbene. I am showing you, so many methods of making this carbene molecule because the ability to make this carbene is in fact, a key point. It is a key feature of this whole chemistry, because you can make this carbene readily, it is available for chemist to use in a variety of systems and study them very easilyand very effectively.

The last method is to remove a sulphur atom, from this urea derivative and that can be done with reactive potassium, you add metallic potassium and you can eliminate potassium sulphide. And because you have eliminated potassium sulphide, you again form a neutral carbene and this potassium sulphide can be just removed through filtration. So, here is a ligand which is extremely easy to generate through a variety of methods and it is possible to make them in good yield and so it is become an extremely popular ligand.

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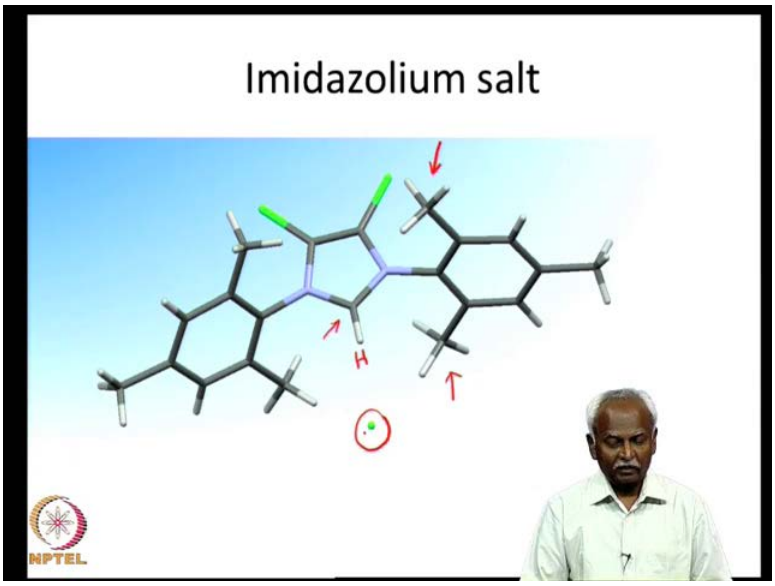

Imidazolium salt

And very often, it is possible to characterize both the imidazolium salt and the free carbene, in using crystallography. In this particular picture, I am showing you the picture ofa ligand where, you have the mesityl group, 2 methyl groups are here attached to thephenyl ring. And that is the, group which is providing steric protection for this carbon, which is right here, this carbon which is positively charged. In this structure you have, of course a proton here, which is pictured in white and you have the counter ion, which is your X minus.

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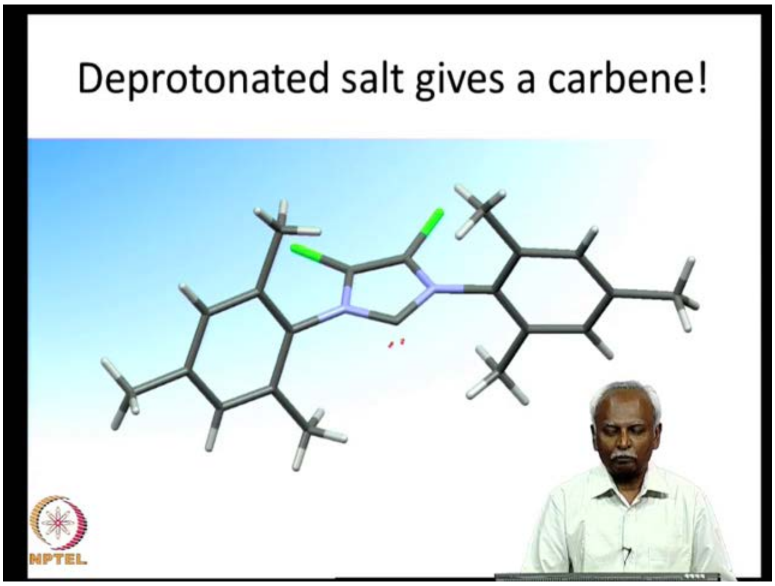
Deprotonated salt gives a carbene!

Now, this imidazolium salt can be deprotonated as we have just seen and you can generate the carbene. The reason for showing these two pictures, is to emphasize the very close similarity between these two structures. There appears to be very little change when, you go from the imidazolium salt which is pictured here, to the carbene which is pictured here. The structure seems to be extremely similar and it is now possible for you, to use this carbene carbon with the negative charge on the carbene carbon, which is actually located as a pair of electrons on this carbon in the plane of the ring to form metal complexes.

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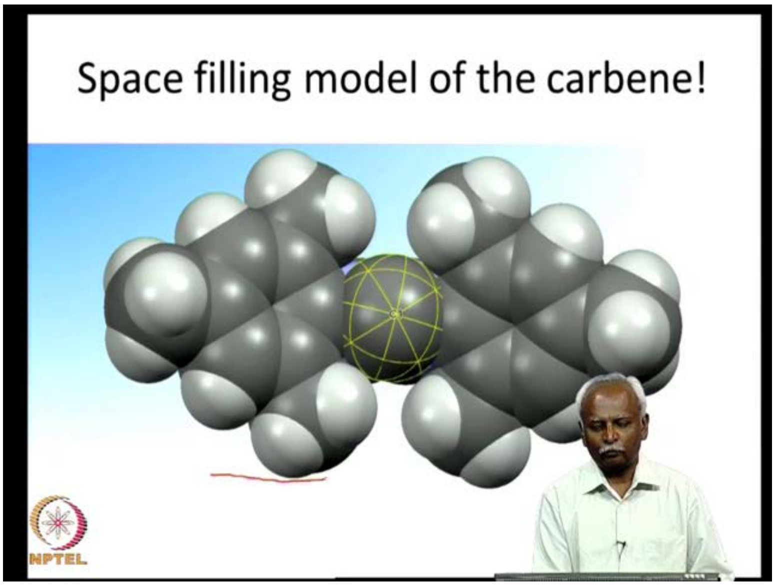

Space filling model of the carbene!

I have shown you here, a three dimensional model or a space filling model of the carbene. Reason for doing this, space filling showing you this space filling model is toshow you that, the carbene carbon which is which has been selected and shown using this yellow, which has been marked in yellow, in this particular picture. This C as C1, this carbene carbon is visible to us and that is visible to the metal also to form a nice complex, but at the same time you have substantial steric protection because of the presence of these bulky groups, on either side of the carbene carbon.

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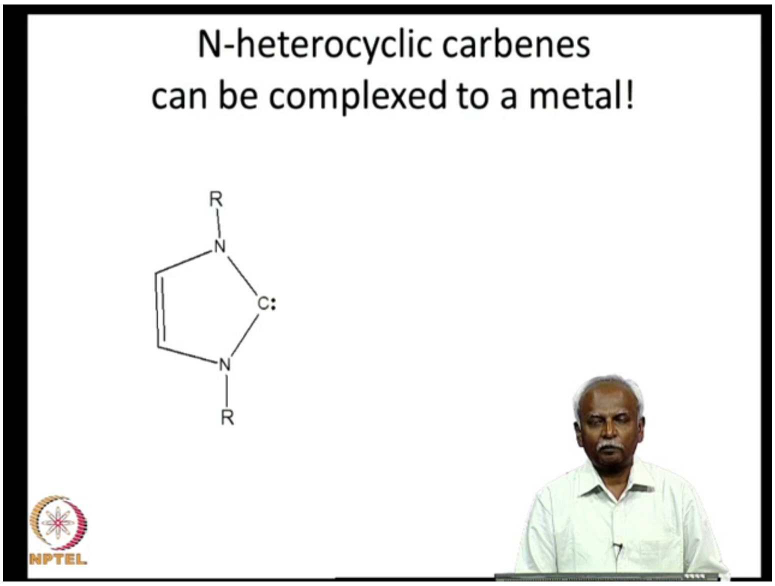

N-heterocyclic carbenes
can be complexed to a metal!

So, let us just look at some chemistry which follows the preparation of this carbene.

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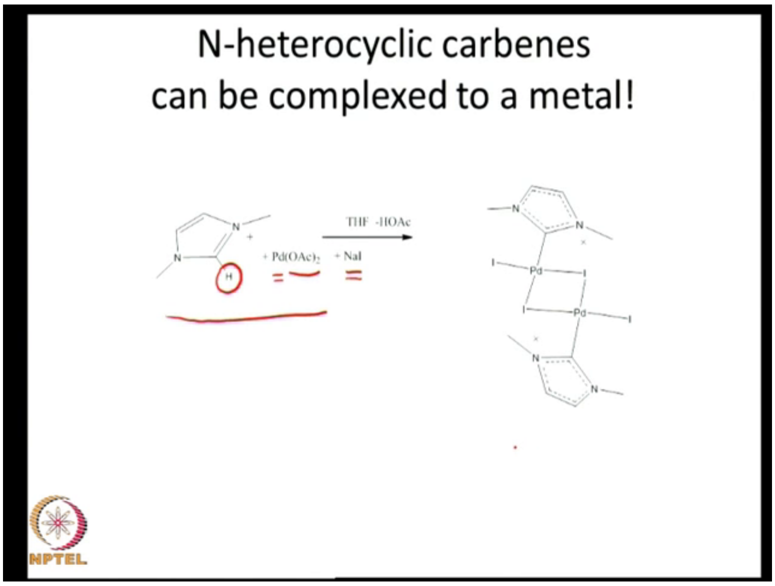

N-heterocyclic carbenes
can be complexed to a metal!

These carbenes, which have been generated by various means can be readily complexed to a metal and in some instances and in some instances, they can be reacted. The imidazolium cation, can be directly reacted with a metal salt, in order to generate a carbene complex. So, that is yet another advantage not only do you have, the precursor to the carbene, but you can use the carbene itself to form the complex. So in both instances, you can form nice carbene complexes with a metal salt.

So, here you have in this particular picture, you have the, you have the palladium atom which was generated using palladium acetate. In the presence of sodium iodide, it forms a complex where you have the iodo group which is complex to the palladium and the carbine, which has been generated in the presence of this palladium acetate by removal of HOAc. So, the acetate group comes from here and the proton comes from here and so you can eliminate, HOAc to generate this carbene in the presence of the palladium acetate. So, the palladium forms a dimeric species.

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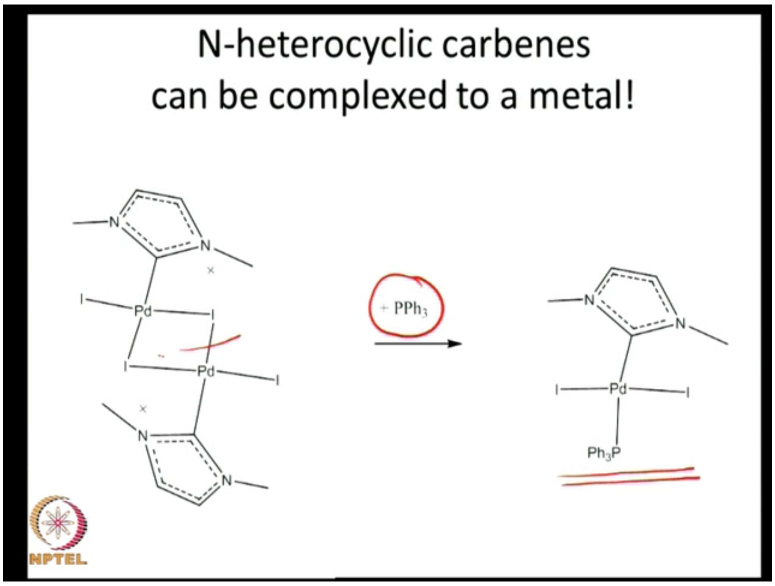
N-heterocyclic carbenes can be complexed to a metal!

And you can break this dimeric species using, yet another ligand, if you add another ligand such as triphenylphosphine, you can form a monomeric species starting with this dimeric species. I am showing you this simple chemistry, which is in fact a general principle, to move from a polymeric system, to a monomeric unit. You normally add, a second ligand which is a fairly good and strong ligand, to break the dimeric species and to form a monomer. So, this turns out to be a general principle for forming a monomeric complex starting with a dimer, but this also tells you that the, triphenylphosphine does not displace the carbene ligand, which is complex to the metal. Instead, it only breaks this dimeric bridge and it forms the monomeric complex.

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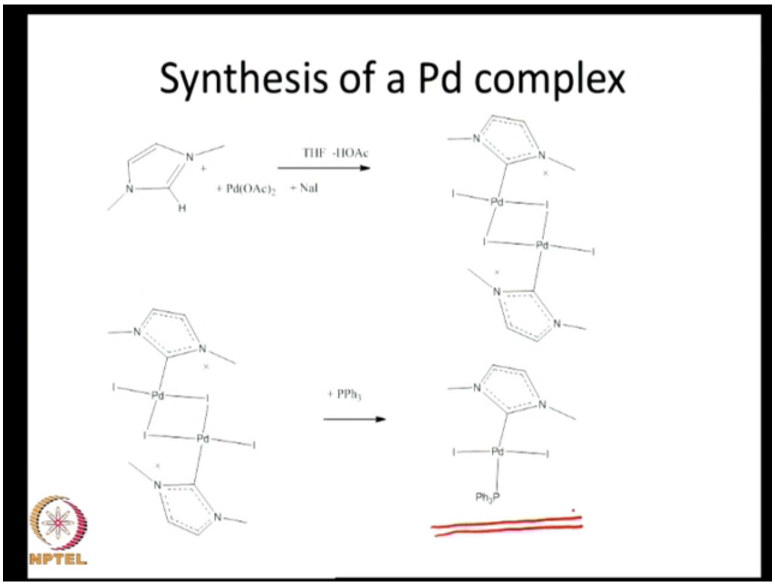

Synthesis of a Pd complex

So, let us now form look at the, so let us look at the structures which are formed using these carbenes.

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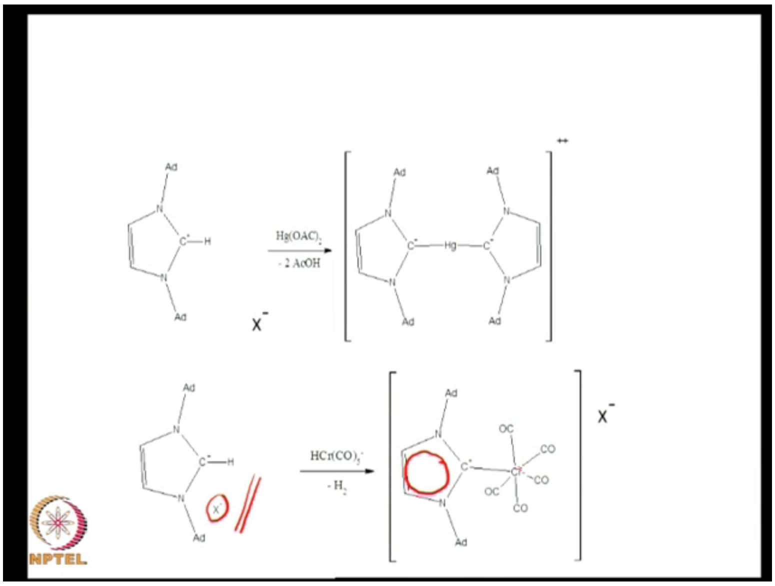

And before doing so I will give you just a few more examples. Here is yet another example, where once again you have used mercuric acetate, in order to generate a carbine. This time, you have mercury coordinated to, two of these carbene units in a linear fashion. As mercury one normally does, you can have this, you can have this mercury complex where, you have two carbenes which are both interacting with metal atom. Here I have pictured, a chromium carbonyl complex, which is a carbonalate and this carbonalate reacts with the propanated imidazolium salt. Once again, this is an example where the imidazolium salt can be directly used for generating the complex.

And here, you have the carbene which is having a positive charge on this ring, but this is in fact delocalised all over this ring system. So you have, this positive charge delocalised on this ring system and that is complex to the chromium. And as a counter ion, you have an X minus which is coming from this imidazolium salt that, we used to prepare the complex. So, you can have very interesting and very nice complexes, where carbonyl group is attached to the metal atom and also a carbene is attached to the metal atom.

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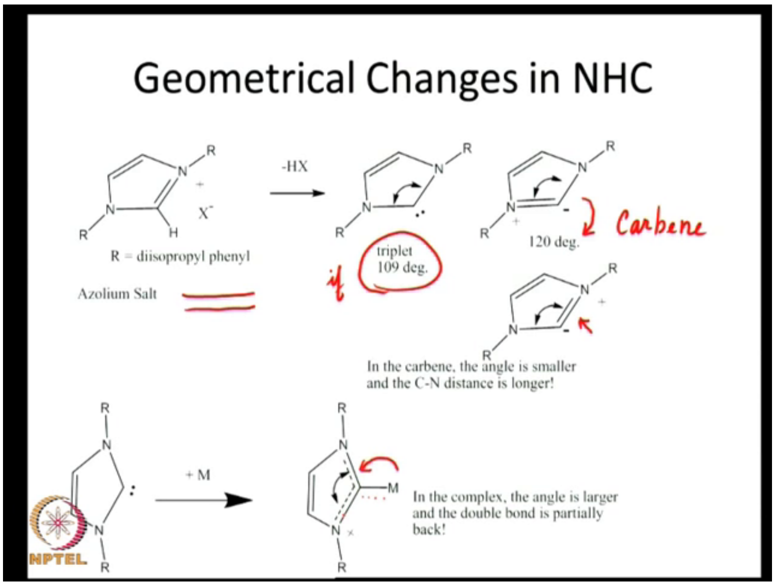

Geometrical Changes in NHC

In the carbene, the angle is smaller and the C-N distance is longer!

In the complex, the angle is larger and the double bond is partially back!

Let us look at some of the geometrical changes, that occur in n heterocyclic carbenes. A little bit, because these will give us an insight into what is going on in a carbene complex. If you look at the imidazolium salt, the imidazolium salt is pictured here on the leftmost side of the screen. And this imidazolium salt, if it is deprotonated forms a carbine. If it was a triplet carbine, if it was a triplet carbene then one would expect this ring system to have an angle of 109 degrees or this carbon to have an angle of109 degrees. But we know that, it is something more of a singlet carbene where the two electrons are in a plane perpendicular, to the plane of the ring.

So this angle, which I have pictured here is more like 120 degrees so this angle is close to 120 degrees, and the lone pair or the pair of electrons from the carbene is localised on an SP2 hybrid. And because of this delocalisation of this double bonds, you now have angle which is close to 120 degrees. And a carbon nitrogen distance which, is shorter than what you would expect for a carbon nitrogen single bond. So, this delocalization has got two effects, it shortens the CN double bond, CN bond and makes it a CN double bond and it also has this effect of having the angle similar to 120 degrees.

Now, when you form a complex so this is the carbine, this is the neutral carbene which we are talking about. And when it is complex to the metal atom, it forms a cyclic ring system, cyclic or delocalized ring system where, this charge is now delocalized on this ring system. And that leads to a metal carbon single bond, but as I told you before it is possible to push some electron density into this ring system, through the metals filled orbitals into the ring's vacant orbitals.

And this will, partially destroy the aromaticity of the heterocyclic carbene ring system, but nevertheless it stabilizes the complex as a whole. So, these are some of the small changes that happen, when you move from the partial double character to the metal complex. Here, you would have some small changes in the angle usually, the angle becomes slightly larger, it becomes closer to what you would expect for 109 degrees and it and the double bond is partially back. So you have, a greater double bond character between the metal and the carbon and also delocalized bond between the carbon and the nitrogen.

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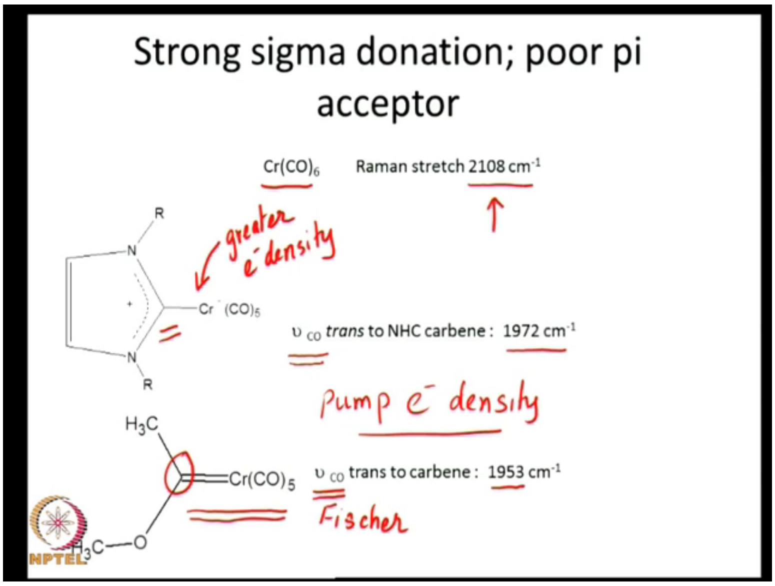

Strong sigma donation; poor pi acceptor

$Cr(CO)_6$ Raman stretch 2108 cm^{-1}

υ_{CO} *trans* to NHC carbene : 1972 cm^{-1}

υ_{CO} trans to carbene : 1953 cm^{-1}

greater e^- density

pump e^- density

Fischer

So, let us look at now the pi donation. Why did we say that, it is possible to push electron density into the ring system. There is sufficient evidence for this particular phenomenon, in fact if you have simple hexacarbonyl chromium, you would have stretch, corresponding to 2108 centimetre minus 1. And when, it is complex to a heterocyclic carbene then the carbonyl stretching frequency decreases. A decrease in the carbonyl stretching frequency, is indicative of the fact there is greater electron density on the chromium.

So, you now have greater electron density, you have greater electron density on the chromium, compared to what you had when you had CrCO6. In CrCO6, the stretch was 2108 centimetre minus 1. And now it is decreased further to 1972 centimetre minus 1, because of the presence of the same heterocyclic carbine. Now, one has to compare it with the other ligands and we do that here by looking at a Fischer carbine. This is an example of a Fischer carbene, Fischer carbenes also have the ability to push electron density into the chromium and they in fact do that much more effectively.

For an example, we have this Fischer carbene stabilized chromium pentacarbonyl complex. And this has got a stretching frequency of 1953 centimetre minus 1. We are always talking about, the stretching frequency of the carbon monoxide which is Trans to the ligand, which we are discussing. So this is the ligand that we are discussing, this carbene carbon complex. And here we are talking about, this N heterocyclic carbene and we are talking about the trans carbine carbon monoxide and the trans carbon monoxide has a stretching frequency of 1972 centimetre minus 1. And in the case of the Fischer carbene, we have a stretching frequency of 1953 centimetre minus 1.

So, these two ligands, they pump electron density into the metal, pump electron density into the metal and that is responsible, that is responsible for lower stretching frequency compared to CrCO6 itself. Where, the stretching frequency was 2108 centimetre minus 1. So we always compare, we have a reference complex and the reference complex for us in this case is CrCO6 and we put a carbene in the system and then look at the carbon monoxide stretching frequency of the trans carbon monoxide.

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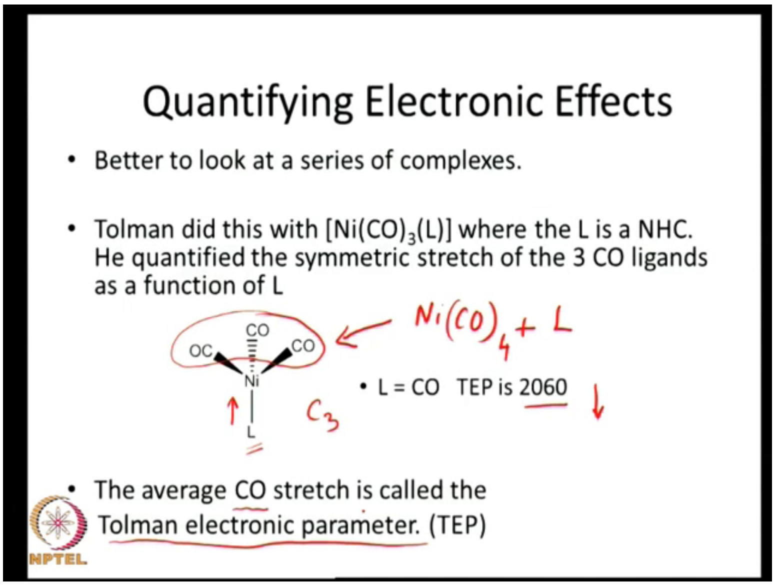

Quantifying Electronic Effects

- Better to look at a series of complexes.
- Tolman did this with $[Ni(CO)_3(L)]$ where the L is a NHC. He quantified the symmetric stretch of the 3 CO ligands as a function of L

$Ni(CO)_4 + L$

- L = CO TEP is 2060

C_3

- The average CO stretch is called the Tolman electronic parameter. (TEP)

So, one way to look at these electronic effects is to look at a series of complexes. It is better to look at a series of complexes, because we are not looking at an isolated incident, but a phenomenon where you have very clear indication of electronic effects. Tolmandid this with a series of complexes, which he could easily prepare starting with nickel tetracarbonyl. So he took, nickel tetracarbonyl. So, that is NiCO4, NiCO4was treated with a ligand and he formed this particular complex and this complex now, has got three carbon monoxides attached to the nickel. And a particular ligand L which we want to discuss and he looked at the carbon monoxide stretching frequencies of these three carbon monoxides.

Because you have a C3 symmetry, you would end up with two different stretching frequencies and he took the average of both. And the symmetric stretching frequency that you would have is the one that he parameterised as Tolman's electronic parameter. Tolman was the person who carried out this experiment first and this average CO stretch, for the carbon monoxides which are trans to the ligand, not really trans, but on the other side of the nickel. So, the symmetric stretching frequency of this two three carbon monoxides, is called the Tolman's electronic parameter.

Now, let us take a look at, what would happen if you have carbon monoxide itself. So that is nickel tetracarbonyl and then this stretching frequency is 2060 the actual stretching frequency in dichloromethane is 2057. But I have rounded it off to 2060 centimetre minus 1 and it is always convenient to have round figures, in order for us to remember easily. So, let us just remember that, nickel tetracarbonyl has a stretching frequency of 2060 centimetre minus 1. And when you substitute it with a ligand then you have a change in the stretching frequency. And this stretching frequency, is now something that we are going to call as Tolman's electronic parameter.

When you have a ligand, which donates a lot of electron density to the metal, to the nickel then the stretching frequency would go down. So, the greater the electron density given by the ligand, when this electron density donation goes up, the stretching frequency would go down. So, the Tolman's electronic parameter has an inverse correlation with, the electron donation from the ligand. So, this can be done for, a wide series of ligands and Tolman chose NiCO4, because it was easy to do spectroscopy with it. And it is also easy, to synthesize these metal complexes very readily starting with nickel tetracarbonyl.

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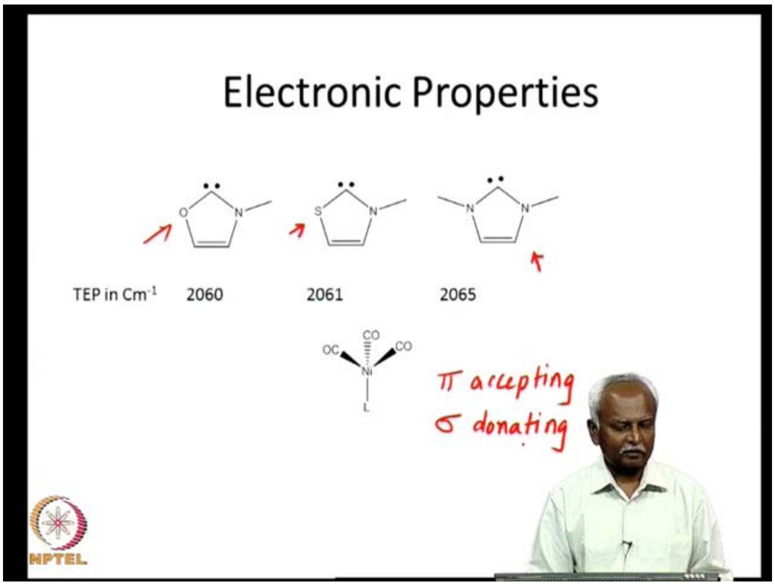
Electronic Properties

TEP in Cm^{-1} 2060 2061 2065

π accepting
σ donating

So, here is the Tolman's electronic parameter, given for a series of ligands. I have given here, a three different N heterocyclic carbenes and you will notice that, this is the type of carbene ligands that we were talking about. And this has got 2 nitrogens stabilizing the carbon atom, bearing the lone pair. But you can also have a sulphur or an oxygen here, we have a sulphur and here we have an oxygen, which is stabilizing the carbene carbon. In all these cases, in all these cases you have the carbene carbon stabilized by a hetero atom and when it is complex to nickel tricarbonyl, as in this complex we are talking about.

Then the stretching frequency of these three carbon monoxides, the symmetric stretch goes down to 2060 centimetre minus 1 or it is close by. As in the case of sulphur you have, 20601 and in the case of this N N dimethyl stabilized heterocyclic carbene, you have a frequency of 2065 centimetre minus 1. These are very close to carbon monoxide's stretching frequencies and so that is indicative of the fact that the pi accepting character of these ligands are similar to carbon monoxide.

So, if you, so by comparing the Tolman's electronic parameter, one would be able to identify whether, the ligand is capable of pi acceptance. Whether the ligand is capable of pi accepting character, whether it has pi accepting character or whether it has sigma donating character. And which of these characteristics is predominating in the complex.

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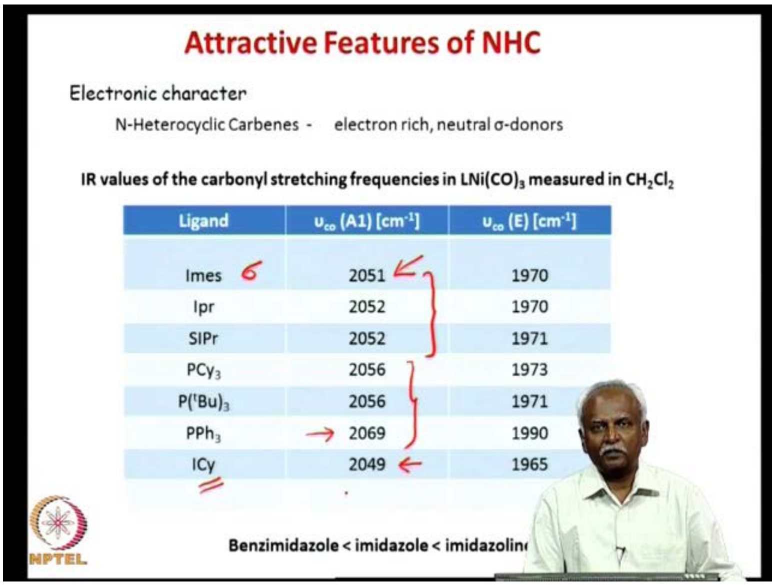

Attractive Features of NHC

Electronic character

N-Heterocyclic Carbenes - electron rich, neutral σ-donors

IR values of the carbonyl stretching frequencies in $LNi(CO)_3$ measured in CH_2Cl_2

Ligand	υ_{co} (A1) [cm^{-1}]	υ_{co} (E) [cm^{-1}]
Imes σ	2051	1970
Ipr	2052	1970
SIPr	2052	1971
PCy_3	2056	1973
$P(^tBu)_3$	2056	1971
PPh_3	2069	1990
ICy	2049	1965

Benzimidazole < imidazole < imidazolin

So, let us take a look at some of these complexes in the N heterocyclic carbenes, when you have a mesityl group, which is stabilizing the imidazole then the stretching frequency in fact goes down to 2051centimetre minus 1. So, here you see that it has gone down further from 2060 centimetre minus 1. So, the pi accepting character is indeed there, but nevertheless the sigma donation property of this imidazolyl, mesotyl stabilized imidazolyl carbene is better. The sigma donation is much better, in the case of the imidazolering, which is bearing the carbene carbon. If you have instead of a mesityl group, if you have an isopropyl group in the imidazolyl carbene carbon then you end up with a frequency which is 2052 centimetre minus 1.

You will notice that, all of them, all of these 3 have got very close stretching frequencies and these are indicative of the fact that, the imidazolyl group is capable of giving a large amount of electron density. Much more than carbon monoxide tothe nickel tricarbonyl complex. Now, if you want to compare it with the phosphorous bearing complexes then you will notice that the phosphines also have got good electron donating capabilities. And they have poorer pi accepting characteristics compared to carbon monoxide. This is indicative of two factors, one is the fact that, they are poorer pi acceptors compared to carbon monoxide and the other is the fact that they donate more electron density to the metal compared to carbon monoxide.

So, here are a series of phosphorous ligands and all 3 of them are having very similar stretching frequencies, except for PPH3. This is triphenylphosphine, which has got a stretching frequency much higher than the complexes, that we are, the ligands that we are discussing here. Triphenylphosphine has got a stretching frequency of 2069 centimetre minus 1 and that seems to indicate that, in this particular instance you have PPH3, which is giving less electron density compared to these ligands to the metal. And it has got very good pi accepting characteristics, as well.

When you have, an imidazolyl group which is flanked by two nitrogens, two nitrogens bearing cyclohexyl group then the stretching frequency has gone down significantly below 2060 centimetre minus 1. And it is 2049 centimetre minus 1 and this seems to indicate that, you have very good electron donation from, the imidazolyl carbon to the nickel complex. So, this way of comparing a series of complexes and looking at the stretching frequency, has helped in quantifying the type of electron donation or the type of electron accepting properties of the ligand.

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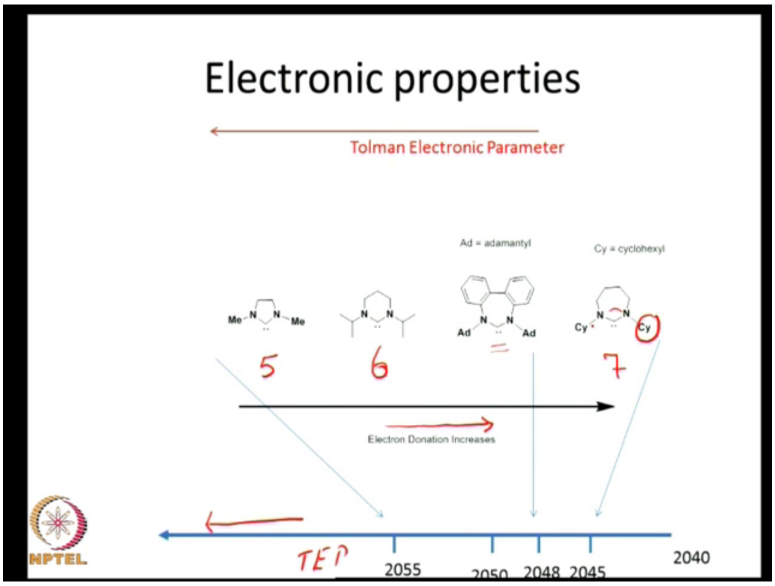

Electronic properties

Tolman Electronic Parameter

It is also possible for us, to draw it or show it in a graphical form here, I have tried to show it in a graphical form. The frequency is increasing, in this direction, in the direction of this arrow so the frequency is increasing in the side and the electron density is, that is being pumped into the metal is increasing in this direction. I told you that, there was a inverse correlation and in fact, the this inverse correlation between the electron donation and the frequency, that you observe for the three carbon monoxides. So, Tolman's electronic parameter, which is abbreviated as TEP, is plotted here. This is TEP and it is increasing in the direction from right to left and the electron donation is increasing from left to right.

So if you have cyclohexyl groups, these are cyclohexyl groups and cyclohexyl groups are obviously electron donating groups, on the, present of the nitrogen. Then the electron donation seems to be the maximum and the stretching frequency has gone down all the way down to 2045 centimetre minus 1. These are close, they are rounded off to some close numbers so that, you can easily remember them. Here is another one where, you have an adamantyl group, but the ring system that is bearing the carbene carbon has got some unsaturation.

So, the frequency has got a higher number, as you have a change in the ring size then you have a change in the amount of electron donation to the metal atom. So, if you have a large ring, the electron density that is moved from the ligand to the metal seems to be high. So, if you have a seven membered ring, here is a seven membered ring that seems to donate more electron density compared to a six membered ring. Here, is a six membered ring and then you have a five membered ring here. So, the seven membered ring donates more electron density compared to the five membered ring.

You will also notice that, we can have unsaturation in the ring system and you can also have a saturated ring system. Both ways, you can have stable carbenes which are attached to the metal atom. But in general, as the angle increases, as the angle, NCN angle is the one that we normally talk about that. As this NCN angle increases you have greater and greater electron density donated to the metal atom.

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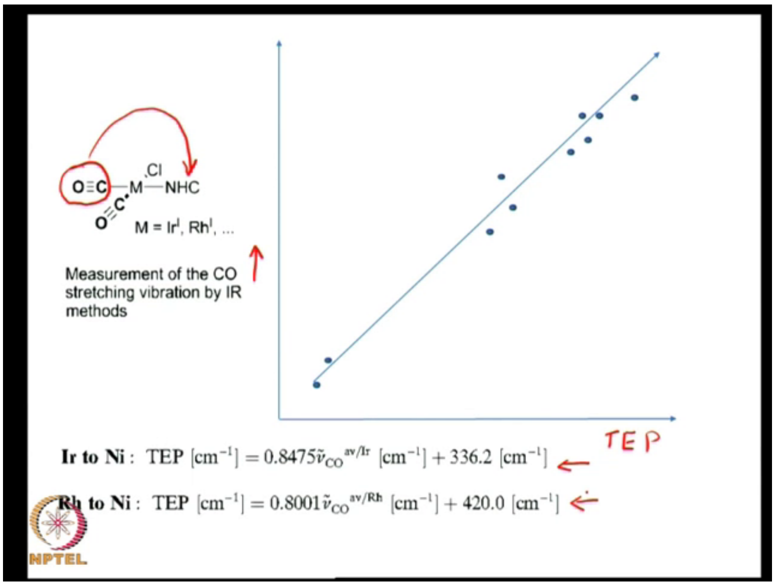

Measurement of the CO stretching vibration by IR methods

Ir to Ni: $\mathrm{TEP}\ [\mathrm{cm}^{-1}] = 0.8475\tilde{\nu}_{\mathrm{CO}}{}^{\mathrm{av/Ir}}\ [\mathrm{cm}^{-1}] + 336.2\ [\mathrm{cm}^{-1}]$

Rh to Ni: $\mathrm{TEP}\ [\mathrm{cm}^{-1}] = 0.8001\tilde{\nu}_{\mathrm{CO}}{}^{\mathrm{av/Rh}}\ [\mathrm{cm}^{-1}] + 420.0\ [\mathrm{cm}^{-1}]$

So, it is not always possible to prepare the nickel tetracarbonyl complex and so I have pictured here the iridium complex and a rhodium complex, which can be easily generated. These are similar to complexes and you have two carbon monoxides attached to the metal atom, and the carbon monoxide, which is Trans to the N heterocyclic carbene, which is this carbon monoxide.

This stretching frequency is very typical or is affected to a great degree by that ligand, which is present in the transposition. So, that is the N heterocyclic carbene that, we are going to talk about. So, depending on the electron density donated by the N heterocyclic carbene, this carbon monoxide stretching frequency changes.

The advantage in using this metal complex or this metal complex system is the fact that, you have only one stretching frequency. But that needs to be observed, so this stretching frequency has been measured for a series of ligands. And if you plot the Tolman's electronic parameter on the X axis so this is the Tolman's electronic parameter and you plot the iridium complexes stretching frequencies on this axis. You find a linear correlation so that, is just indicative of the fact that, these two frequencies are related. The electronic affects that you observe, in the nickel complex can also be observed in the iridium complex.

If you have greater electronic density, donated to the metal from the N heterocyclic carbene then the stretching frequency goes down. So, as the TEP increases the electronic density donation decreases. So, you can in fact have linear relationships quantified. And they gives us and they give us, they give us a very good confidence that, in fact the type of relations that we are observing are in fact proper scientifically valid relationships, which are very clear indicators of the electronic effects of the ligand.

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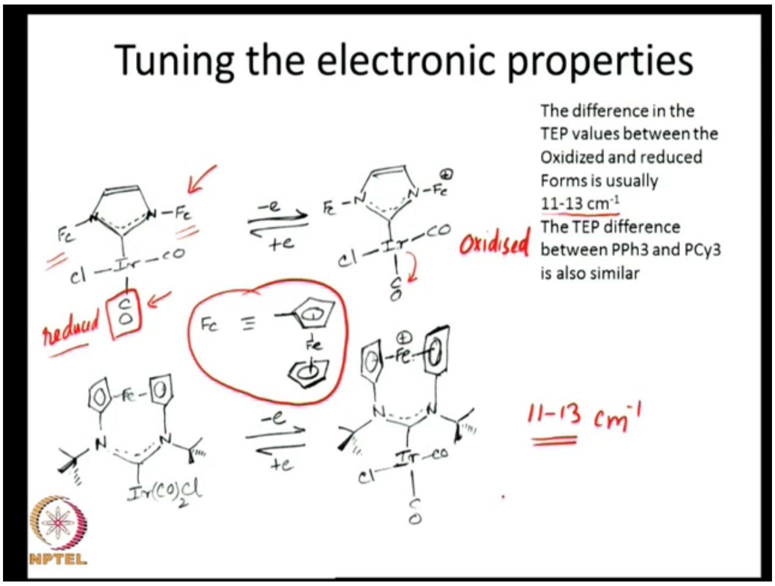

Tuning the electronic properties

The difference in the TEP values between the Oxidized and reduced Forms is usually 11-13 cm^{-1}

The TEP difference between PPh3 and PCy3 is also similar

Now, it is possible to tune the electronic parameter in a variety of ways. A very ingenious way of tuning the electronic parameter is to not use electron withdrawing groups, but to remove an electron completely, say using electrochemistry. And it is possible to do this, in the case of these ferrocene stabilized ligands. So, in fact Fc is indicative of this ferrocenyl group, Fc is indicative of this ferrocenyl group. And if you have, two ferrocenyl groups substituted on the nitrogen then you can have a very nice ferrocene stabilized carbene.

And this ferrocene stabilized carbene can be, attached to the iridium one complex and you can look at the stretching frequency of this carbonyl, which is the carbonyl group, which is Trans to the heterocyclic carbene. So, you can now remove an electron from this complex and this electron is removed from the ferrocene moiety right here. So, you can have a reduced species or you can have an oxidized species, this is the oxidized species.

So, this is the oxidized species and this is the neutral form or the reduced form. So you can compare, the Tolman's electronic parameter or the iridium carbonyl stretching frequency. And you will notice that the oxidized form has got a difference of 11 to 13 centimetre minus 1, between the system which is neutral and the system which is oxidized.

When you oxidize it, then the carbene becomes electron poor, if the carbene is electron poor then it donates less electron density. If the iridium has less electron density then less electron density is pushed on to the carbon monoxide. If less electron density is there on the carbon monoxide, then the stretching frequency is not reduced significantly and the frequency is increased. So, the oxidized form, has got a stretching frequency of 11 to 13 centimetre minus 1, greater than what you have for the neutral form. So, the neutral form, has got a less stretching frequency or a lower stretching frequency and the oxidized form has got a higher stretching frequency.

Another interesting complex has also been made and this is a similar iridium complex where, you have a carbon monoxide Trans to this ferrocene stabilized unit. But this time the ferrocene units are in fact, attached directly to the nitrogen. A very ingenious way of controlling the electronic effects, but unfortunately the difference between the oxidized and the reduced forms are mostly in the range 11 to 13 centimetre minus 1 in all these cases.

And so the type of electron density change that you have on the carbon, the carbene carbon is not very large. For a comparison, I have given here the change that occurs between PPH3 and PCy3, Cy is cyclohexyl group and in fact is much more electron donating compared to PPH3. And that difference is also, 11 to 13 approximately, in the range of 12 centimetre minus 1. So, this is a surprising phenomenon, but nevertheless it is a very interesting factor that has been observed.

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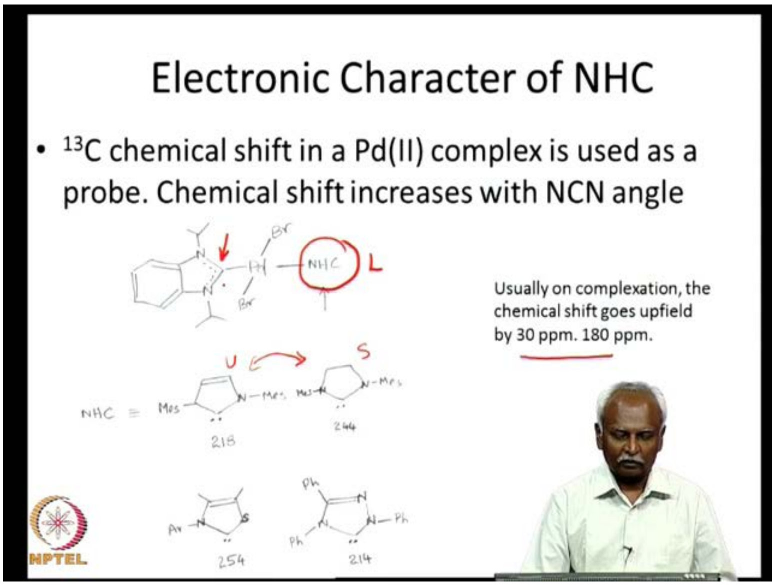

Electronic Character of NHC

- ^{13}C chemical shift in a Pd(II) complex is used as a probe. Chemical shift increases with NCN angle

Usually on complexation, the chemical shift goes upfield by 30 ppm. 180 ppm.

So, people have been able to observe this electron density being donated from a carbene carbon, to the metal in a variety of different ways. Another easy way to do it is, to look at the carbon 13 chemical shift that, you can observe readily for diamagnetic complexes. As long as you have, an organometallic system which is diamagnetic and most organometallic complexes are in fact diamagnetic. You would be able to observe, the carbon 13 chemical shift and that chemical shift changes when, you have a neutral carbene and when you have a complex, which is, where the carbene is attached to the metal atom.

The chemical shift is usually shifted, up field by 13 to 180 ppm and this chemical shift is indicative of the fact that, there is electron density which is shielding the metal atom. The metal atom’s electron density is, shielding the carbene carbon and giving it some extra protection from the external field. And that is why you have to go upfield, in order to observe these carbene carbons. So, this is in fact the type of chemical shift changes that you observe in the carbine carbons. Here I have, 2 mesityl groups attached to the nitrogen and the only difference between these two ring systems is that, this ring system is unsaturated and this ring system is saturated.

And you can see that, there is about 20 ppm chemical shift difference between, these two units. And people have tried to, derive an electronic parameter based on the chemical shift of this carbon, versus the ligand which is present in the trans position. So, if you can look at the, very this ligand and measure the chemical shift of the carbene carbon, which is in the trans position. You would be able to derive an electronic parameter, but this has not been as popular as Tolman's electronic parameter. So, we will not discuss this further, but sufficed to say that, the electron density changes are sensitively reflected in the chemical shift of the carbene carbon.

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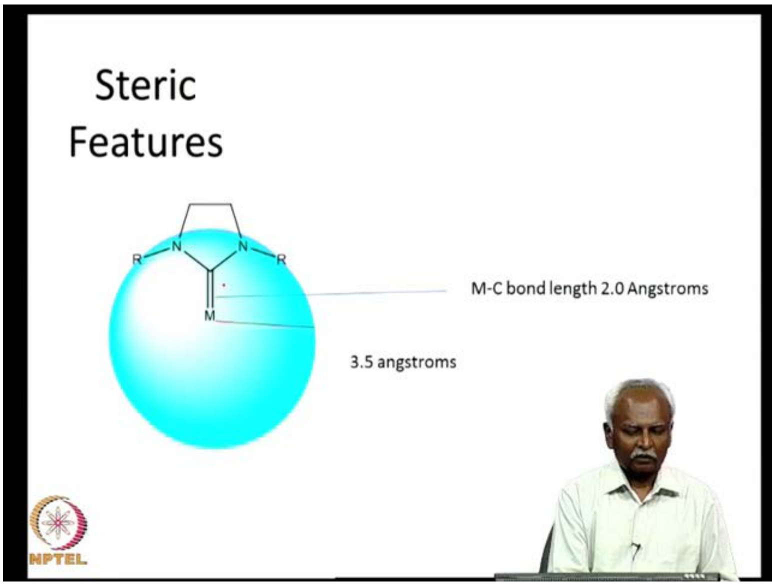

Steric Features

M-C bond length 2.0 Angstroms

3.5 angstroms

So, with this we will close this lecture and we will discuss the steric phenomena, that is associated with N heterocyclic carbenes in the, in the next few lectures.

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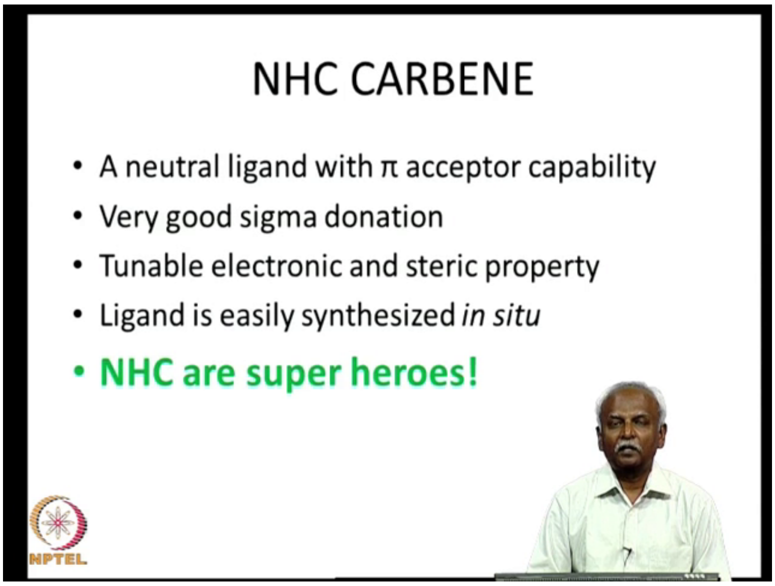

NHC CARBENE

- A neutral ligand with π acceptor capability
- Very good sigma donation
- Tunable electronic and steric property
- Ligand is easily synthesized *in situ*
- **NHC are super heroes!**

I will now, summarize what we discussed so far by going to end, we have discussed a series of N heterocyclic carbenes. This is a neutral ligand, with good pi accepting capability. It has got a p orbital, which is substantially large in character and it is able to accept the electron density for the metal d orbitals. It has got, good sigma donation properties and we have seen this from the Tolman's electronic parameter, and because of the steric properties, which can be tuned which we will see later. Both the electronic and steric properties are substantially modifiable and so this tuneable character, character gives it a very great advantage. A ligand can be easily synthesized, in situ and that makes them the N heterocyclic carbenes super heroes as ligands.