Introduction to Organometallic Chemistry
Prof. A. G. Samuelson
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore

Lecture - 7
Carbene complexes continued

In this lecture, we will discuss complexes which have multiple bonds between metal and carbon.

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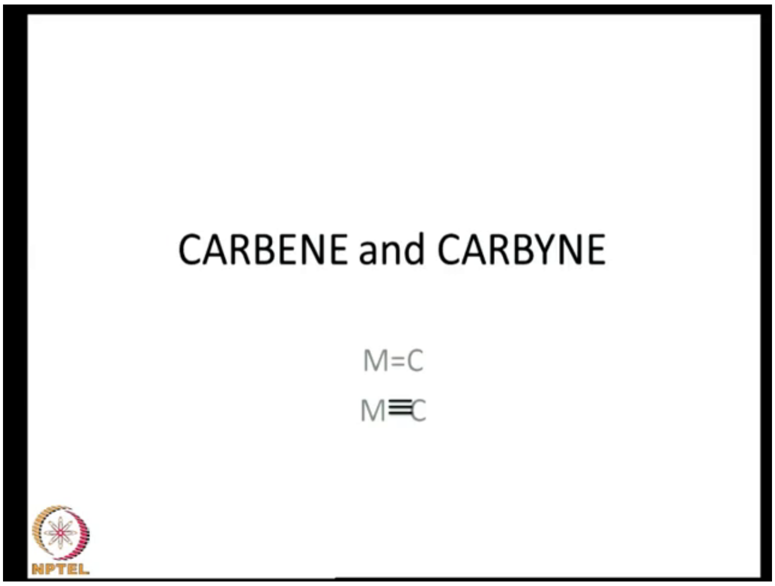

CARBENE and CARBYNE

$M{=}C$

$M{\equiv}C$

We have already seen carbon monoxide and few other ligands.

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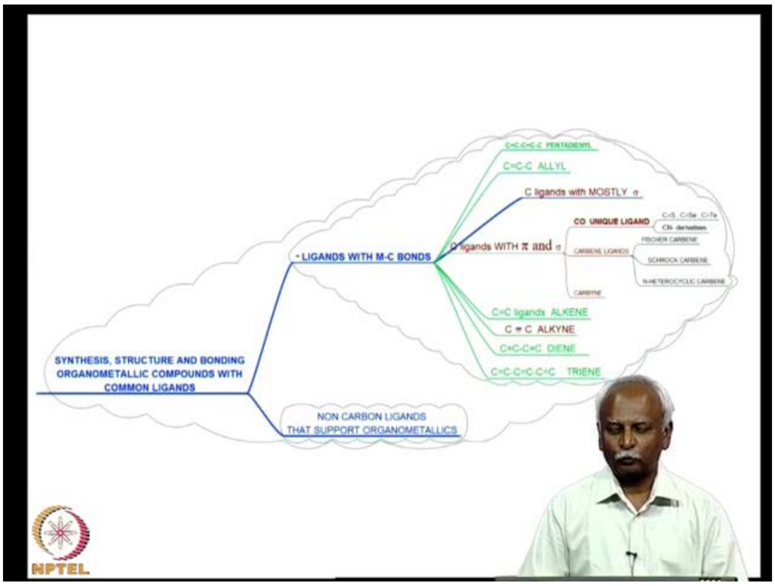

SYNTHESIS, STRUCTURE AND BONDING ORGANOMETALLIC COMPOUNDS WITH COMMON LIGANDS

LIGANDS WITH M-C BONDS

C=C-C=C-C PENTADIENYL

C=C-C ALLYL

C ligands with MOSTLY σ

C ligands WITH π and σ

CO UNIQUE LIGAND

C=S, C=Se, C=Te

CN- derivatives

CARBENE LIGANDS

FISCHER CARBENE

SCHROCK CARBENE

N-HETEROCYCLIC CARBENE

CARBYNE

C=C ligands ALKENE

C ≡ C ALKYNE

C=C-C=C DIENE

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

NON CARBON LIGANDS THAT SUPPORT ORGANOMETALLICS

And I have shown this in this ligand map which I have drawn. So you can see that, carbon monoxide occupies a unique place, carbon monoxide occupies a unique place and the ligand space. So, there are some derivatives of carbon monoxide such as, the cyanide which I am highlighting here, which have a special ability to, transform in the coordination sphere of the metal to some other ligands.

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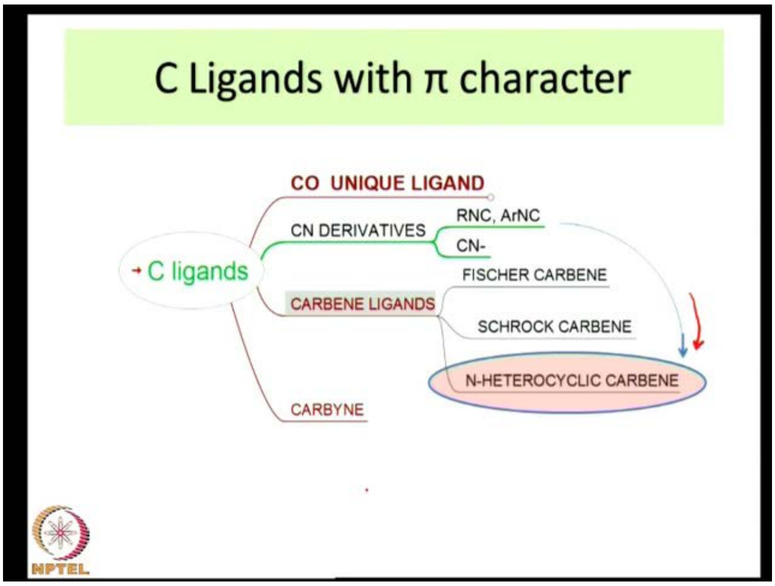

C Ligands with π character

C ligands

CO UNIQUE LIGAND

CN DERIVATIVES

RNC, ArNC

CN-

CARBENE LIGANDS

FISCHER CARBENE

SCHROCK CARBENE

N-HETEROCYCLIC CARBENE

CARBYNE

We have seen this in the lecture on N heterocyclic carbenes. So you have isocyanides, which are CN derivatives and these isocyanides can be converted into Fischer carbenes, which are in turn, related to N heterocyclic carbenes, the nucleophilic heterocycliccarbene which we discussed in the previous lecture; where, the carbene is in fact stabilized by resonance from electron donation, which is coming from the heterocyclic atom. You could also have E cyclic system where the carbene carbon is stabilized by donation from the hetero atom.

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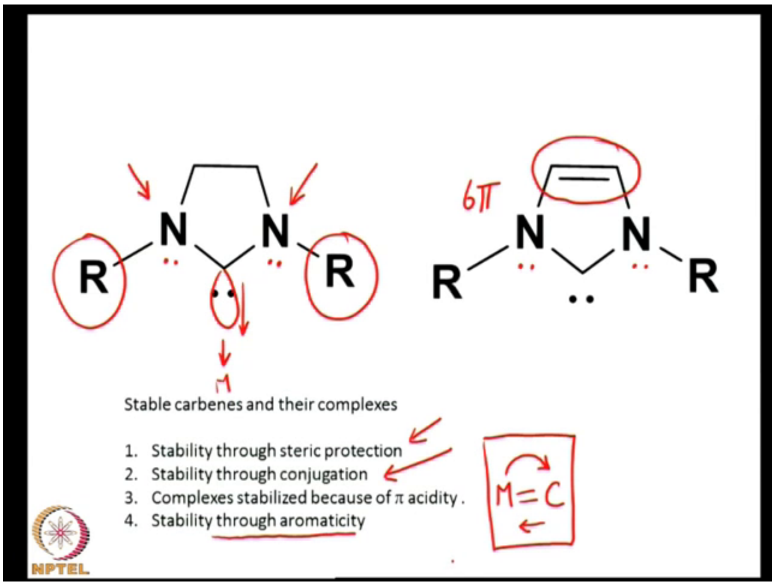

Stable carbenes and their complexes

1. Stability through steric protection
2. Stability through conjugation
3. Complexes stabilized because of π acidity .
4. Stability through aromaticity

So, in the lecture on N heterocyclic carbenes, we encountered carbenes, which have got two nitrogens or two hetero atoms. And these are the two hetero atoms that we are talking about. These two hetero atoms are stabilizing the carbene carbon which is having a pair of electrons, which can be donated to the metal atom. And perpendicular to the plane in which this lone pair is positioned, perpendicular to this plane there is a vacant P orbital, which is in resonance with the lone pairs on the two nitrogens. So, this is the factor, which stabilizes the carbene carbon.

So, stability through conjugation is an important factor, and this in fact essential for the stability of these carbenes and stability of their complexes. But there is yet another factor, which stabilizes these carbenes and that is a fact that you have rather large bulky R groups which are situated adjacent to this carbene carbon. So, stability is achieved through steric protection of the carbene carbon. It is also achieved through, conjugation of the vacant P orbital on the carbon, with the nitrogen lone pairs.

And these complexes are stabilized, because of pi acidity, when the metal forms are complex with the carbene, it has two interactions which are typified by donation from the lone pair, that we refer to. And there is a back bonding, as in the Dewar Duncanson Chatt model, from the metal there is some dative bonding, which occurs, which pushes electron density in the opposite direction. These two factors stabilize the complexes.

So, we also encountered in the lecture in N heterocyclic carbenes the fact that there can be stabilization through aromaticity. And this stabilization through aromaticity, comes about because if you have an extra pair of electrons, as in a pi system, which is in resonance with the two lone pairs on the nitrogen. Then you have, a total of 6 pi electrons and the 6 pi electrons are the ones, which lead to an aromatic ring system and it stabilizes the carbene to a great degree.

So, there is stability through steric protection, stability through conjugation, stability because of the aromatic system that is formed in this ring system. And all these factors stabilize the carbene. In addition the carbene, when it complexes to the metal is stabilized because of pi acidity or the type of Dewar Duncanson Chatt resonance, which occurs from the metals some electron density is pushed into the carbene carbon. So, these are n heterocyclic carbenes and they occupy a special place in the literature.

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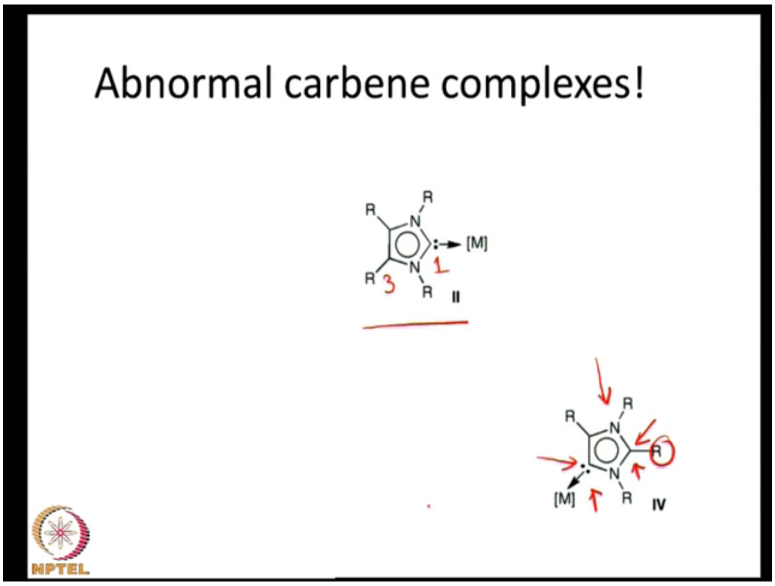

Abnormal carbene complexes!

And today I want to introduce to you, arelated system which is a system which is been called an abnormal carbene complex. There is nothing really abnormal about these carbine complexes, but we will explain how they are slightly different from the N heterocyclic carbenes that we discussed just now. You will remember that, the stability of the carbene itself is coming from several factors. All these factors can be maintained and still there can be as light variation. Just imagine that, you have instead of the carbene anion or the lone pair on the carbine carbon, being situated on a second carbon, which is not the one between the two nitrogens.

So, it is not this nitrogen, which is holding the lone pair or the pair of electrons, but let us assume that it is this carbon. In this instance also, you can have stabilization due to aromaticity. Because you still have 6 pi electrons, those 6 pi electron system is, the 6 pi electron system is not affected, when you move the lone pair of electrons from this carbon. Which is usually the, see 1 to the 3 carbon atom, which is this carbon atom.

So, moving the pair of electrons from the place where it was originally present in the N heterocyclic carbenes, to a different place is not affecting the stability of the system, in terms of aromaticity. In fact, it is going to be equally aromatic and it can have pi acidity, as in the previous system so, all those situations are still maintained. But it is abnormal because, it is different from the usual place where it is formed. So, how can one move this pair of electrons or this carbene carbon from this position 1 to position 3.

This can be done if, we block it with an R group in the appropriate position. So instead of, a hydrogen if I have an alkyl group in this position then, in the first position as shown here, as it is shown here. If I have, an alkyl group which is placed in carbon atom 1, then the carbon atom 3, if it, there is a hydrogen atom it can be deprotonated and the carbene carbon can be formed.

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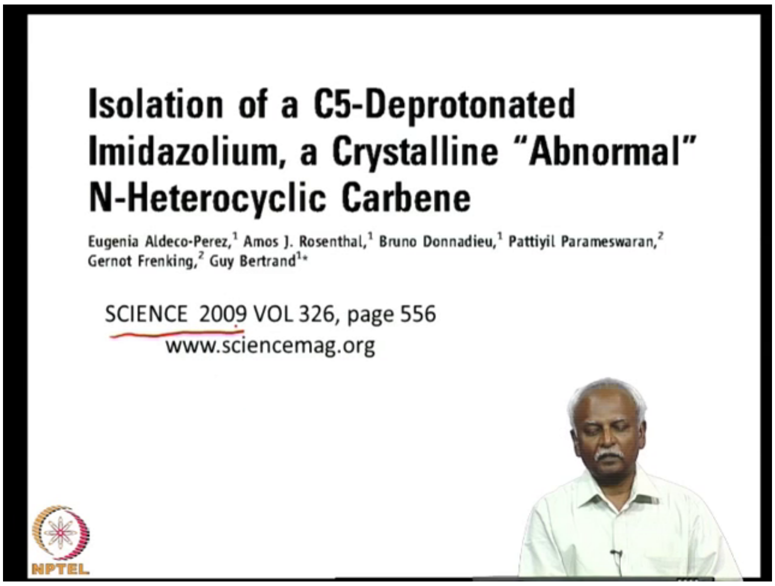

Isolation of a C5-Deprotonated Imidazolium, a Crystalline “Abnormal” N-Heterocyclic Carbene

Eugenia Aldeco-Perez,[1] Amos J. Rosenthal,[1] Bruno Donnadieu,[1] Pattiyil Parameswaran,[2] Gernot Frenking,[2] Guy Bertrand[1*]

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You will remember that, it is only 10 years ago before 200. So, it was in the year 1999 that you had a synthesis of the first N heterocyclic carbene. So, the anomalous heterocyclic carbeneor the C5 deprotonated imidazolium N heterocyclic carbene, was discovered in 2009.

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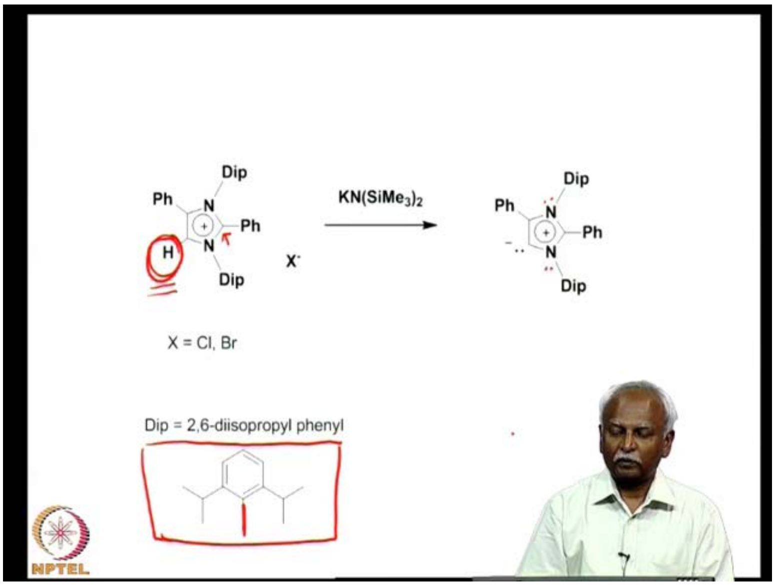

X = Cl, Br

Dip = 2,6-diisopropyl phenyl

So, the way this was carried out was by taking N substituted N alkalated ring systems, along with both C1 carbon here and the C5 carbon, both of them. Where in fact, substituted with phenyl groups and a hydrogen was positioned in this place and it was deprotonated using a very strong base. Which, will abstract the proton present in this position.

So, the base that is used is trimethylsilyl substituted. This trimethylsilyl amiditanion and the bistrimethylsilyl amidit anion is particularly suited for deprotonation, rather than nucleophilic attacks, because of the very bulky nature of the true trimethylsilyl groups. Which are present on the nitrogen so, if it was less bulky then a nucleophilic attack could have been made on this negatively, on this positively charged ring system, which is present here.

So, having protected the two nitrogen atoms with very bulky groups, that is a 2, 6 diisopropyl phenyl group which is pictured here. Which has been abbreviated to, Dip this is, that 2, 6 di-isopropyl phenyl group, which is present here. And it is connected to, the nitrogen atom through this carbon and you can deprotonate now, this ring system on this only carbon, which is bearing this hydrogen. So, you form a carbene carbon now, this has got both the positive charge delocalized here, because of this nitrogen lone pairs, which are delocalized into this carbon. And it has this negative charge, which is in the plane perpendicular to the plane of the pi system.

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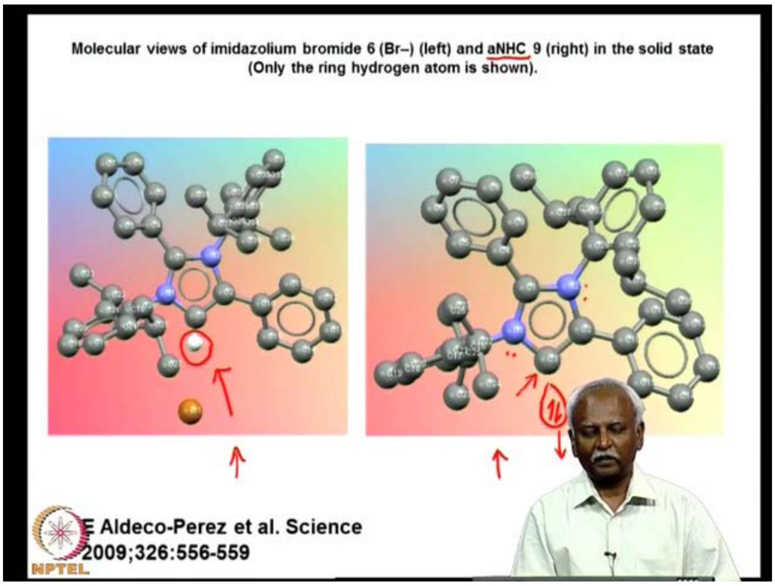

Molecular views of imidazolium bromide 6 (Br–) (left) and aNHC 9 (right) in the solid state
(Only the ring hydrogen atom is shown).

E Aldeco-Perez et al. Science
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So, let us see what happens if you take a crystal structure of these molecules. You find that, this is the original molecule which has been also crystallized and characterized. It is a imidazolium cation, that means it is got a positive net positive charge, but when you deprotonate it using the n dialkalated or the di-isopropylamidit anion. Then you can deprotonate it, only in this position. So, you deprotonate, this carbon and you end up with a carbene, which is pictured here. The lone pair is in the same plane, as the ring system so, there is a pair of electrons here and that is a carbene carbon.

But now we call it abnormal only because, you have the usual carbene carbon bearing a phenyl group now and the unusual position for the carbene carbon is in the third position. It is stabilized only by, the vacant P orbital on the C3 is on the C3 atom has got a vacant P orbital that is stabilized by the pair of electrons, which is present on, in one. But it cannot be stabilized by the lone pair, which is present on N2 nevertheless, this now forms a carbenic system and it can be coordinated to the metal atom. Just like, we coordinated the normal N heterocyclic carbene. So these are called a NHC and that is pictured here abnormal N heterocyclic carbene.

But you can notice one thing, the two structures are extremely similar. The two structures which are pictured here, this is the imidazolium cation, this is the imidazolium cation here. And the carbene are extremely similarand that is because the pi system, which is perpendicular to the plane of the ring, is not affected by this deprotonation. And the lone pair that is available for donation to the metal atom, is present perpendicular to the, it is in the plane of the ring system and perpendicular to the plane of the pi system. So, these two the carbene and the imidazolium cation were characterized perfectly using single crystal structure determination and so we have, a good idea about how the bond distance is vary in these ring systems as well.

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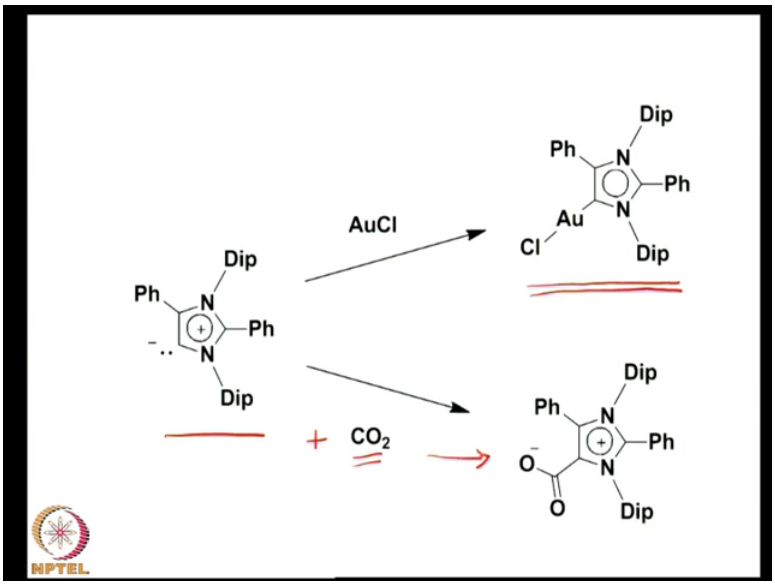

What is interesting is that, these compounds which is the carbine, abnormal N heterocyclic carbine is equally capable of forming metal complex. Pictured here, is only the gold complex, the gold complex is formed by simply treating the carbene with AuCl that is gold mono chloride, that is a gold one oxidation state. And that forms a very nice complex, with this carbene abnormal N heterocyclic carbene. What is interesting is that, this molecule also interacts with carbon dioxide, to form a carboxylate anion.

And this carboxylate anion, is interestingly, it is exactly the reverse, it is this, the structure that, was used to prepare the normal N heterocyclic carbene, by decarboxylation. So, the reverse reaction was known, for the preparation of N heterocyclic carbenes, but now we find that this molecule is reactive enough, this molecule is reactive enough to react with carbon dioxide, to form a carboxylate anion.

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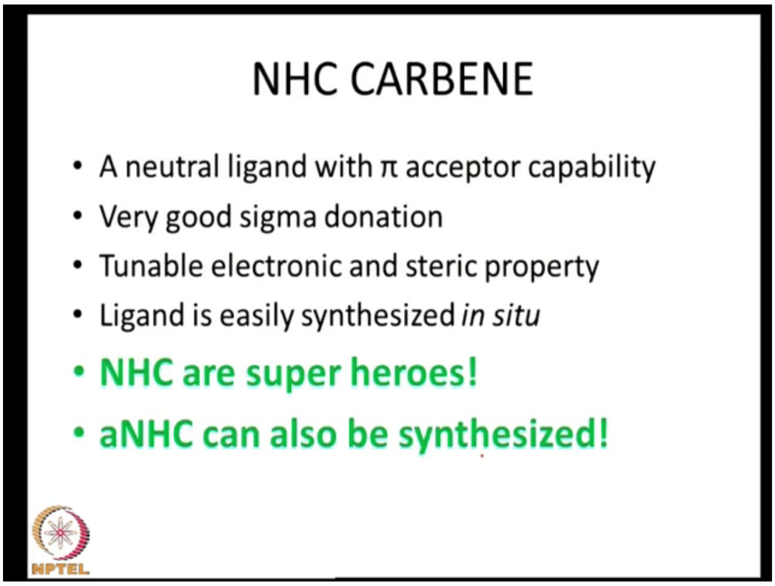

NHC CARBENE

- 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!**
- **aNHC can also be synthesized!**

So let me just, summarize what we have just been discussing N heterocyclic carbenes are great ligands because, they can have different donor properties depending on the ring system, that is there, you have tunable electronic property. You also have, tunable steric property because the substituents of the nitrogen can be changed. What is interesting is that, the ligand is easily synthesized many times in situ, it can be synthesized and reacted with the metal atom. And they are super heroes primarily because, they have been shown to have very good catalytic properties and these catalytic properties, we will be dealing with towards the end of the course.

The abnormal N heterocyclic carbenes, that we just saw can also be synthesized very easily in the coordination sphere of the metal atom. And they can be synthesized, as isolable carbenes also and so, they have been touted as very interesting species, which can be used for catalysis. However at the moment, not many abnormal n heterocyclic carbenes are known. What characterises both the NHC and the abnormal NHC is a fact that, they have very good sigma donation. Much better sigma donation to the metal than, carbon monoxide itself and so their properties are significantly different.

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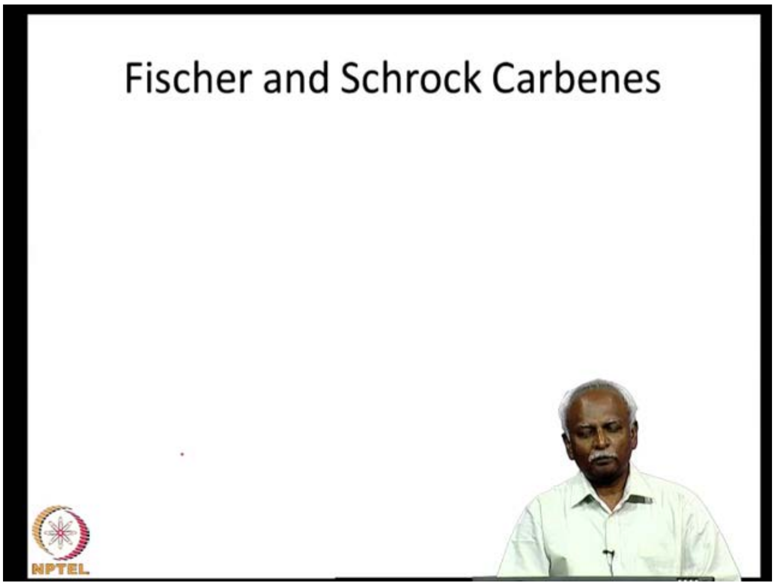

Fischer and Schrock Carbenes

Now, I want to move on to another topic which is related and I will show you how they are related. The topic that I would like to discuss is the fact that, you can have compounds where there is a metal carbon double bond.

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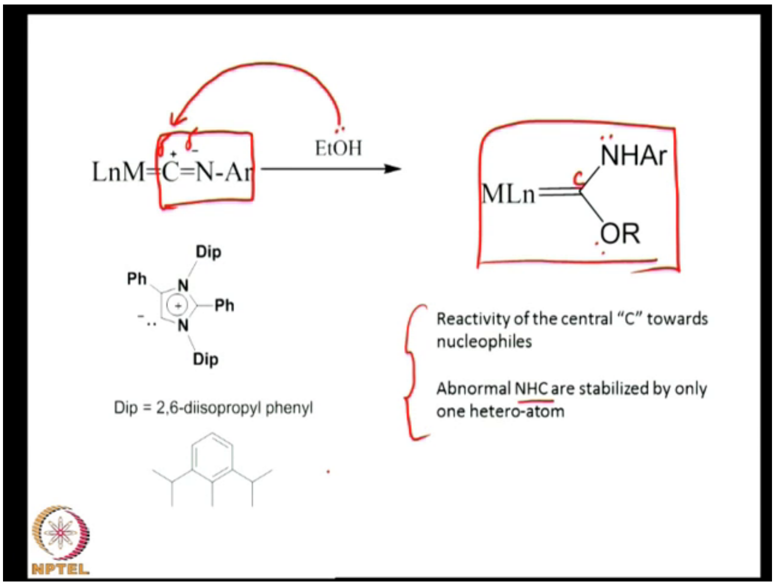

Dip = 2,6-diisopropyl phenyl

Reactivity of the central "C" towards nucleophiles

Abnormal NHC are stabilized by only one hetero-atom

And this carbene complexes are in fact, the carbene complexes are in fact stabilized by a hetero atom, which is attached to the carbene carbon. So, here I have shown you, the reaction that led to hetero atom stabilized carbene complex. If you take, the metal isocyanide compound, this is the metal isocyanide complex we noted that there is a resonance structure, which can be written as a M double bond C double bond M.

And in this structure, you have polarization of the carbon as delta plus and the nitrogen as delta minus, because of the electron activity differences. And because of these differences, you can have a nucleophilic attack by the ethanol which is used which is used as a solvent on the carbon. So, this nucleophilic attack leads to the formation of a molecule, which I told you is a, is a disadvantage because you cannot use isocyanide itself.

It very often, reacts with a solvent or with the nucleophile and generates a different molecule altogether, but this molecule by itself is a stable species very often. Because, you have a carbenic carbon which is stabilized by two lone pairs just like, you have these N heterocyclic carbons, which are stabilized by two nitrogen atoms. So, what I want to emphasis is the fact that, the abnormal N heterocyclic carbene carbon is stabilized by only 1 hetero atom, only 1 nitrogen. And it was still, forming a nice complex with the metal and here we have, a system where when the carbon is polarized in a positive fashion. You can have, an attack by nucleophile so, if you combine these two factors together, if we can combine these two factors then we have a new system which is been formed.

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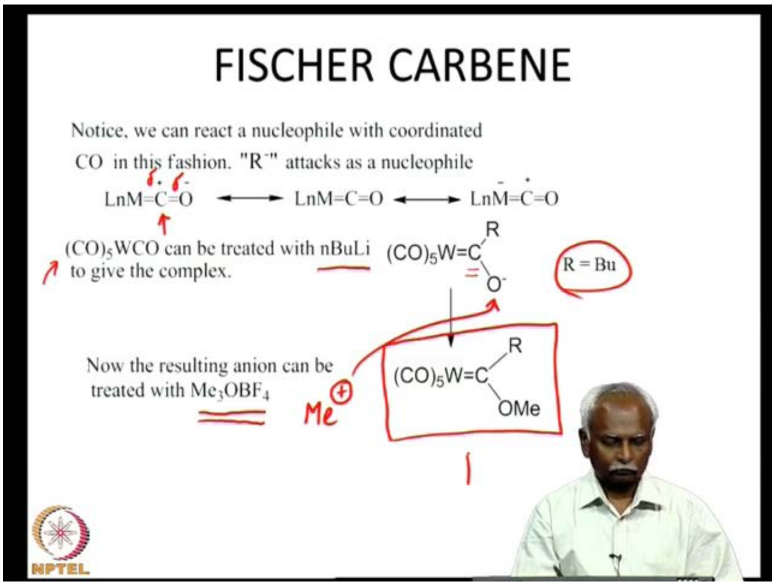

FISCHER CARBENE

Notice, we can react a nucleophile with coordinated CO in this fashion. "R^-" attacks as a nucleophile

(CO)$_5$WCO can be treated with nBuLi to give the complex.

Now the resulting anion can be treated with Me_3OBF_4

Let us look at, a one other resonance structures of a carbonyl complex. And here is the carbonyl complex which I have written here, with the same type of resonance structure LnM double bond C double bond O. And this should also be polarized, such that you have a small positive charge on the carbon and a small negative charge on the oxygen. So, in this particular resonance structure you can have a nucleophile attacking the carbon, which is the carbonyl carbon. If I treat tungsten hexacarbonyl, which is pictured here, tungsten hexacarbonyl which is pictured here, if I can treat it with n butyl lithium, the butyl lithium is a good nucleophile and it will attack this molecule at the positively charged center.

In this particular molecule, it happens to be the carbon and so, one would form an intermediate, where the R group which is the butyl group. The butyl group is attached to the carbon, which is originally from carbon monoxide. So you can have, an intermediate in which the negative charge is pushed onto the oxygen and the carbon is attached to the R group or the alkyl group, which originally came from the alkyl lithium. So, you have a negatively charged species, you can now treat it with trimethyl oxonium ion, this is trimethyl oxonium ion which is a good donor of methyl cation. Which is a convenient source for methyl cation, this methyl cation will now react with your O minus species, which is present here.

And so, we form a new complex now, which is molecule which can be called Fischer carbene, because Fischer was a first person who made these molecules. And these were characterized long before, N heterocyclic carbenes. However, we have looked at these in the light of the reactions that can happen with isocyanides, which are coordinated to the metal.

So, there are there is a conceptual relationship between the two, an isocyanide is also polarized with a carbon bearing the positive charge. And the carbon monoxide is also polarized, with a positive charge on the carbon when, they are both coordinated to the metal atom. Once this happens, you can have a nucleophilic attack and that nucleophilic attack can be used to generate a carbene complex, which is this particular species, which I have pictured here.

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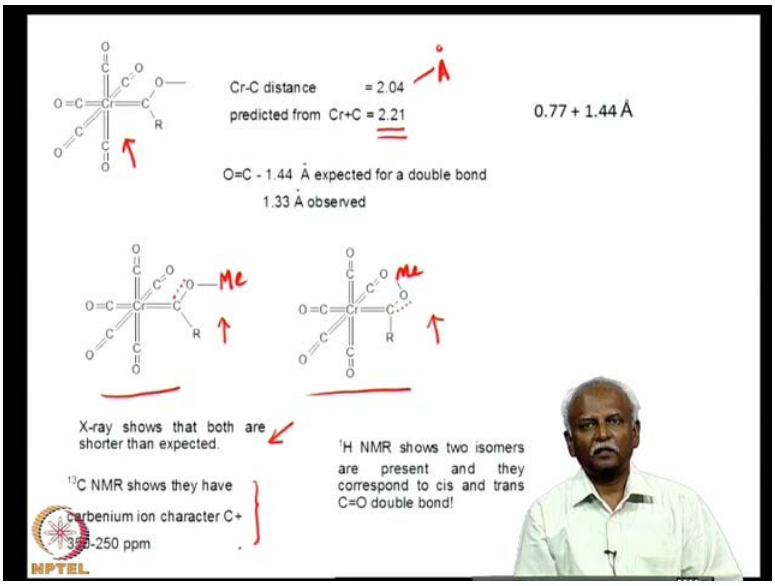

Cr-C distance = 2.04
predicted from Cr+C = 2.21

0.77 + 1.44 Å

O=C - 1.44 Å expected for a double bond
1.33 Å observed

X-ray shows that both are shorter than expected.

^{13}C NMR shows they have carbenium ion character C+ 35-250 ppm

^{1}H NMR shows two isomers are present and they correspond to cis and trans C=O double bond!

So, let us now move onto the hexacarbonyl chromium complex I have just pictured i there to show you that, one normally does not write the carbonyl complex, as a metal double bond C double bond O structure. That makes it look, very awkward because we are not used to chromium bearing 12 bonds, as it is pictured here. But we have to bear this in mind that, there is partial double bond character between the metal atom, which is the, in the center which is attached to the carbon monoxide. So, the chromium carbon distance for example, in this case is 2.04 angstroms and this 2.04 Angstroms is in fact, this 2.04 angstroms is much less than, what you would expect for a single bond.

I want to emphasis this fact, because we are going to look at some more complexes today, which you have bond distances which are less than what you would expect. But they may not be perfect double bonds so this, double bond character which is there in the chromium hexacarbonyl is responsible for the nucleophilic attack. That can take place between alkyl lithium onto the carbonic carbon. Which is in fact carbonyl complex in this particular instance. So, the first thing we note is that x rays shows that, the bond distance is much less than expected. So, there is in fact a double bond character.

Secondly, we note that proton NMR of molecules which are pictured here, that is a Fischer carbene pictured here, shows that there are two distinct isomers, for these molecules. And these two isomers come up because the methyl group which is attached to the oxygen has 2 different environments, depending on whether it is closer to the metal system or away from the metal system. In this isomer, it is shown away from the metal system here, it is shown closer to the metal system. And that happens because, you have partial double bond character, which I am indicating here.

So, if this CO bond has got partial double bond character then, you can have two distinct isomers, as I have shown you. Here which might be pictured as isomers. So, it is very clear that this double bond that we draw is in fact, a partial double bond and this partial double bond, is responsible for the presence of 2 isomers. If you look at, carbon 13 NMR you also find out that there is some carbenium ion character. In this chromium hexacarbonyl and in the Fischer carbene complexes because, the value for thecarbenium ion is quite high. The chemical shift is quite high and that is indicative of depletion of electron density around carbon.

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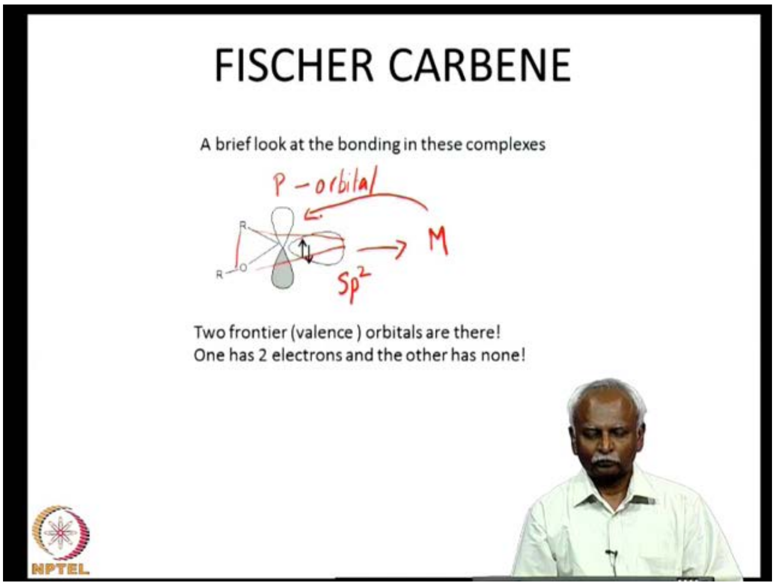

FISCHER CARBENE

A brief look at the bonding in these complexes

Two frontier (valence) orbitals are there!
One has 2 electrons and the other has none!

So, these Fischer carbene complexes are those systems, where you can have metal carbon double bond character. And that is possible because of the fact that, you have a carbene carbon which is diamagnetic and it has two pair, which has a pair of electrons in the orbital, which is like in SP2 hybrid, this can be called as an SP2 hybrid. And the p orbital which, is perpendicular to the plane in which the 3 groups are present.

These 3 groups are present is an empty P orbital, this P orbital, this P orbital is empty and you have a pair of electrons in the SP2 orbital. Now, you have a system which can both donate electron density to the metal and it can accept electron density from the metal, into the p orbital, very much like carbon monoxide. And so you have, partial double bond character in the Fischer carbene also.

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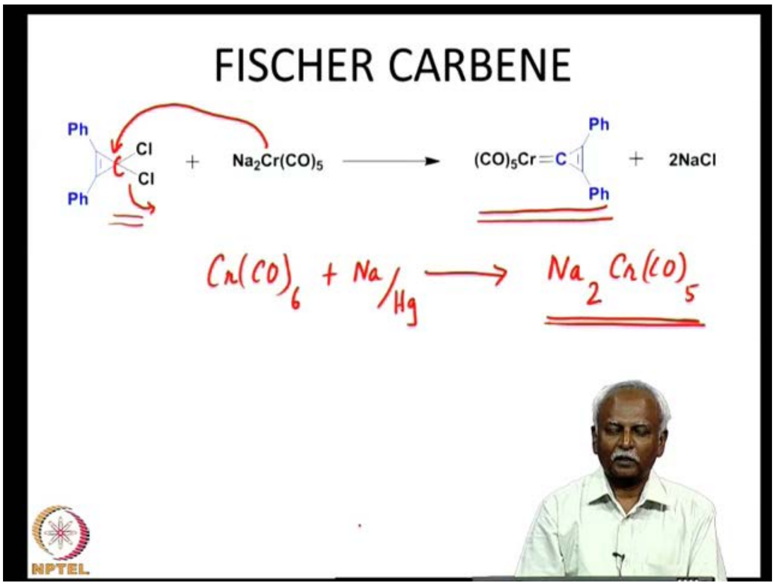

FISCHER CARBENE

$$+\ Na_2Cr(CO)_5 \longrightarrow (CO)_5Cr{=}C\ +\ 2NaCl$$

$$Cr(CO)_6 + Na/Hg \longrightarrow Na_2Cr(CO)_5$$

So, let us now look at some examples where you can synthesis these carbene complexes. Apart from the fact that, you can generate them by nucleophilic attack on carbon monoxide. It is also possible to employ other techniques and here I have shown you the sodium salt of CrCO6, if you take chromium hexacarbonyl, if you take chromium hexacarbonyl and reacted with sodium amalgam. You can pump in electrons into this, CrCO 6 and this results in the formation of NA2, NA2CrCO5 and this salt, is extremely nucleophilic and it can carry out nucleophilic attacks on a carbon center. Which, there is 2 chlorine atoms here, so if you do a nucleophilic substitution from by using the electron density which is present on chromium.

If you make an attack on, this carbon which is present here this spirocyclic looking carbon, this carbon then you can remove the 2 chlorines, in successively you form a carbene complex, which it is pictured here. So, this carbene complex now has got a cyclopropenium character also and it is quite stable and you can synthesis a limited number of complexes, in this particular fashion. Nevertheless, this just illustrates the fact that there are other ways of making the carbene complex.

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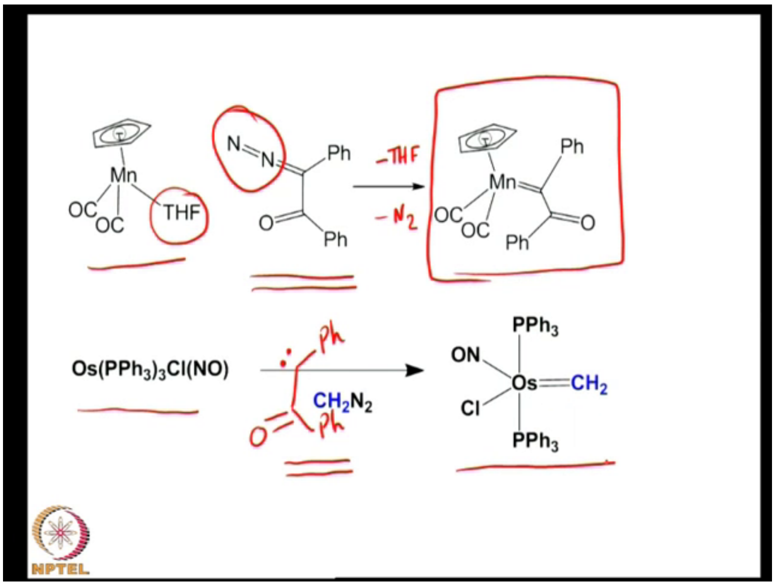

Let us look at another technique now, this is probably a more general technique we take a carbene precursor which is used in organic chemistry. So, this is a carbene precursor, which is used by organic chemistry generate the carbene present in this molecule. And that carbene is in fact, this particular moiety that I am going to draw here. So this is the carbene, this is the carbene that we are talking about and this can be generated by elimination of a molecule of nitrogen, this molecule of nitrogen can be eliminated and you can form this carbene. This carbene is infact, stabilized by some resonance with the CO bond and so, it is stable species that can begenerated.

And then it can react with, this molecule which has got a labile ligand, the labile ligand in this particular instance is tetrahydrofuran THF, fairly labile ligand compared to the carbon monoxide, which is also present in the manganese complex. So, if the THF leaves so, if you have minus THF then, minus nitrogen we eliminate the molecule of nitrogen from here and if you eliminate a molecule of THF from this manganese complex, you end up with coordination of the 2 remaining species. And you form this nice complex, where you have a carbene center coordinated to the manganese.

So, this is just an example of, how you use a precursor which diazo molecule, which is a precursor for a carbene to generate it, in the co-ordinations you are in presence of the metal complexes. So, the two reactive species react together to form a carbene complex it is also possible for us to use a different precursor and that is diazomethane. So diazomethane can be used, as a precursor for CH2 which is also a carbene, which is a simplest carbene that we can think of. So, if we treat this osmium complex, with diazomethane it forms a diazo elimination happens. The two nitrogen atoms leave and a CH2 group is now coordinated to the osmium. So, this molecule also, has been made by using a precursor for the carbene carbon, which is familiar to most organic chemist.

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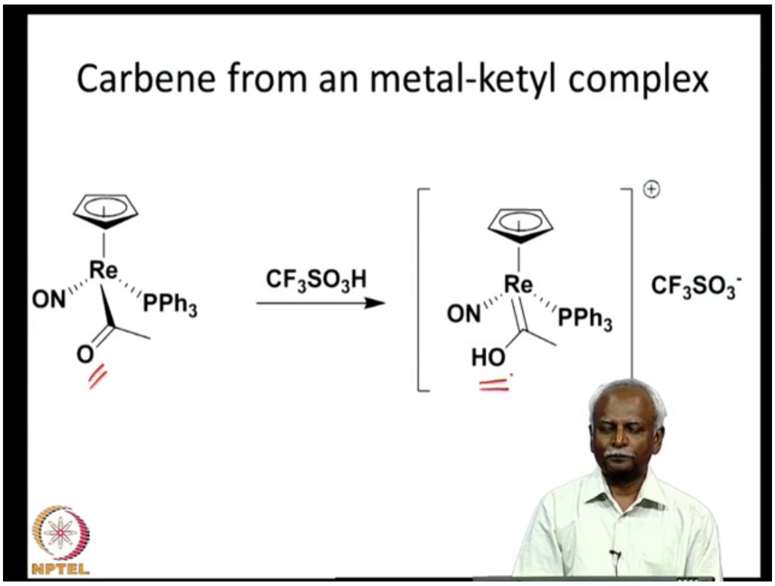

Carbene from an metal-ketyl complex

Now, apart from these reactions it is also possible to use some techniques, which are fairly unconventional. One often thinks that, organometallic compounds are not stable in the presence of water or that, they would decompose in the presence of acids. Surprisingly, this is not always the case, here is a case, here is a system which has a got a rheniumketyl complex. This is a metal complex where, you have a rhenium atom coordinated to a CH3CO group and this CH3CO group.

Now, can be protonated with a strong acid. And this trifluro methane sulphonic acid, triflic acid can now protonate this oxygen atom. This oxygen atom can be protonated and that leads tocarbene, which is now stabilized by a single hetero atom, which is the OH group. And surprisingly, this can be quite stable and can be isolated and characterized. So, this suggests that organometallic compounds are not necessarily unstable, in the presence of water. This is particularly true of, metal atoms which are either 4d or 5d transition metal series because, they have greater resistivity towards water molecules and they are more stable towards hydrolysis. We will discuss this, as practical little later on also.

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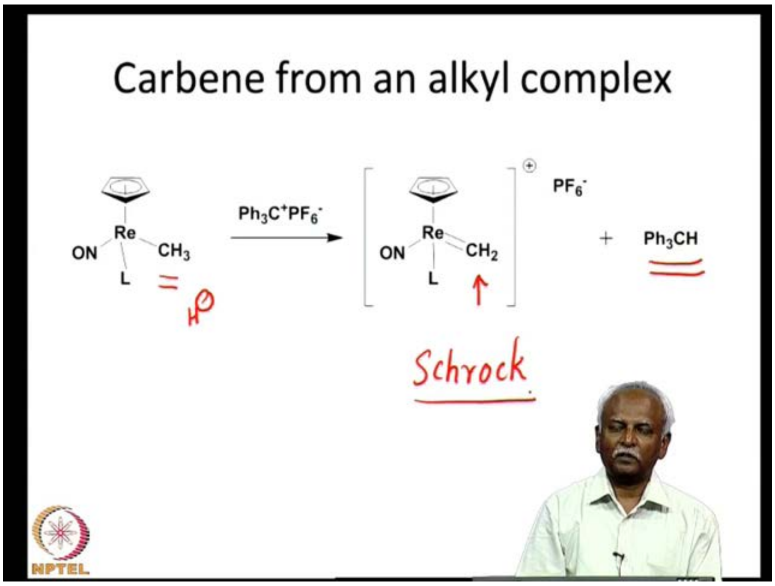

Carbene from an alkyl complex

So, we can also have an another system where we can deprotonate using a base. In the previous instance, we used an acid to protonate and generate a carbene center. Here we are going to take, an alkyl group which is attached to rhenium and this alkyl moiety has got a hydrogen atom adjacent to the metal, hydrogen atom on the carbon adjacent to the metal. And these hydrogens are mildly acidic so, if I use a molecule which can remove a proton, as in this case where we use dtrityl cation. And trityl cation is an excellent species, for removing H minus species. So, here we are removing H minus, H minus is removed from this CH 3 and it can, it reacts with Ph 3C plus.

In order to generate Ph3CH and you end up with a positively charged rhenium atom, which is coordinated to a CH2 group. So, in both instances we have in fact, treated either the molecule with a proton in and that is what we did here. Here we reacted the molecule with the proton or we have treated the molecule with species, which will remove a hydride atom H minus to generate a positively charged rhenium complex, which is bearing a carbine. Notice that, in this particular instance we do not have a hetero atom to stabilize this carbene carbon.

So, this is a system, which is called a schrock carbene. Fischer carbenes are those carbene complexes, which I have got a hetero atom to stabilize the carbene carbon. The schrock carbenes, schrock carbenes are those carbenes which are not stabilized by hetero atoms after the discover of this series of compounds, where you have only carbons with non-electron negative substituents on the carbon.

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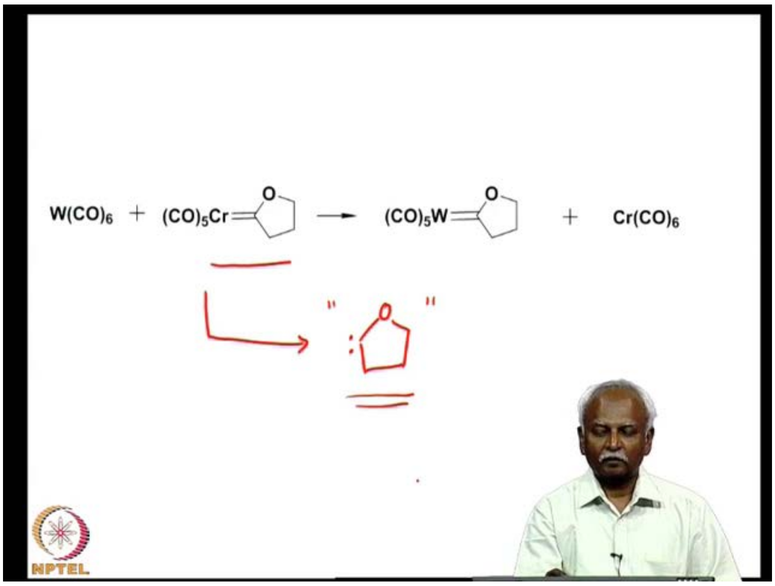

So, I now go back to another example of making carbene complexes and these carbene complexes are now, generated by transferring a metal. The carbene center from one metal center to another metal center. This can be done if you are moving from a system, which has got a 3d metal center and a 4d metal center. Basically, you end up exchanging ligands such that, the 4d or the 5d metal center then, if it is from a stronger metal carbon bond. In this particular instance, we have tungsten hexacarbonyl and the chromium pentacarbonyl with a carbene, with, this is a Fischer carbene attached to the chromium.

And this Fischer carbene, is now transferred to the tungsten whether, this reaction happens in a bimolecular fashion or whether there is an equilibrium between the carbene and. Whether, there is an equilibrium between this system and the free carbene is not particularly clear, but nevertheless it is clear that the final product is the tungsten, which is coordinated to this carbene, which is also a Fischer carbene. So, this compound is formed by reaction of this chromium carbene complex, with the tungsten carbonyl complex. And the tungsten, gains this carbene and forms the carbene complex.

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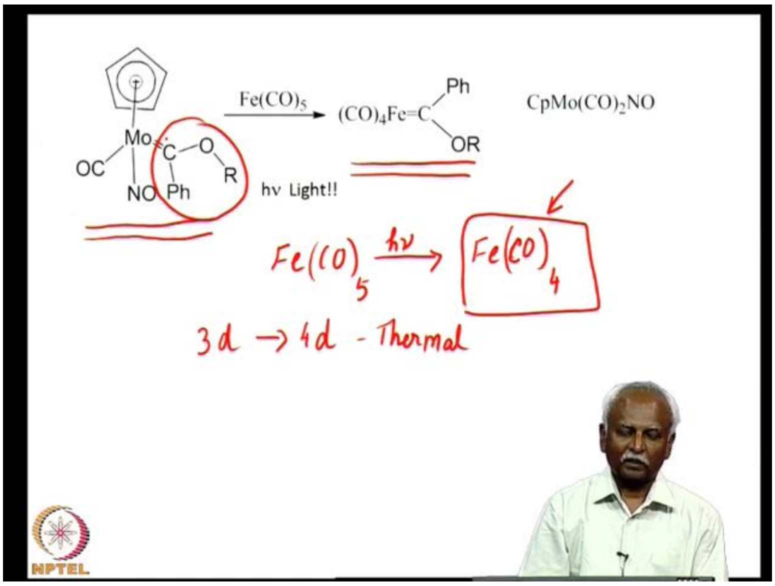

$$Fe(CO)_5 \xrightarrow{h\nu} \boxed{Fe(CO)_4}$$

3d → 4d - Thermal

There is yet another example, in this particular case because of the presence of light, we are going to generate a coordinatively unsaturated species. FeCO5, is a bright yellow colored, yellow orange colored compound and if you shine light on FeCO5, it loses a molecule of carbon monoxide and forms a coordinatively unsaturated FeCO4 molecule. This FeCO4 molecule, is extremely reactive and it is able to remove the least, the most weakly held carbene, which is attached to the molybdenum center.

So, you have a molecule which has got 4 ligands on the molybdenum and one of them is weakly held. And so, the most weakly held carbene ligand is transferred from the molybdenum center, from the molybdenum center to the co-ordinatively unsaturated FeCO4. And FeCO4 molecule now gains a carbene carbon. So, in this instance you notice that we are moving from a metal atom which is molybdenum, which is a 4d metal atom and that 4d metal atom loses the ligand to a 3d metal atom.

So, this is contrary to, apparently contrary to what I told you in the previous example that, the carbene will move from 3d, from a 3d system to, a 4d system. And that is true for, thermal reactions, in thermal reactions this is what you would expect. But because we are having a photochemical reaction, we are generating an extremely reactive, coordinatively unsaturated carbon monoxide ligidate species, which is FeCO4. This FeCO4 is able to grab the most weakly held carbene, which is coordinated to the molybdenum and forma nice new complex, which has got ion coordinated to the carbene.

So, you can transfer the net result that we need to understand is that, we can transfer a carbene carbon, from one metal center to another metal center. As long as the final result leads to a stable structure, we can always transfer the carbene from one metal center to the other.

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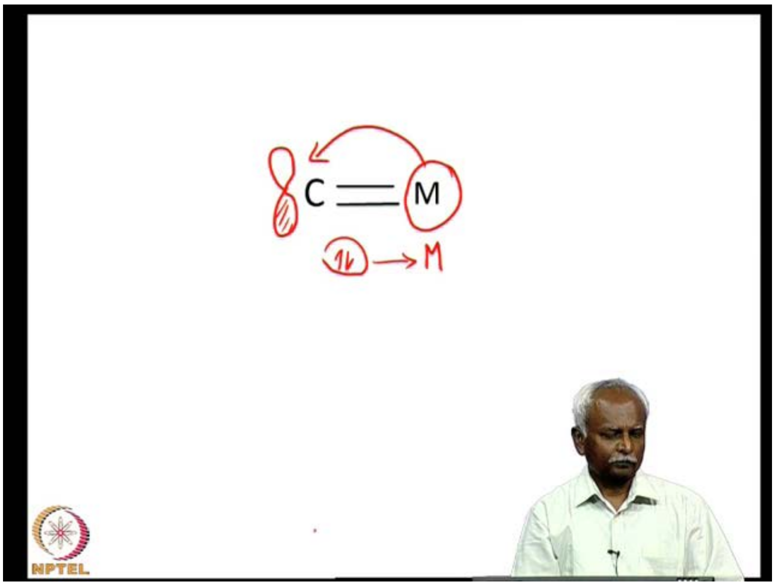

So, we have been talking about carbene complexes, where you have a system with a carbon which has got a pair of electrons, carbon with a pair of electrons. And that carbon donates, this pair of electrons to the metal and the metal has an empty orbital into which it accepts the pair of electrons. And the metal donates, a pair of electrons from it is filled manifold into an empty p orbital on the carbene. So, this type of give and take between the metal and the carbon is responsible for stabilizing all these carbene complexes, but one has to, one has to choose a metal system such that, the metal has got some electron density, which can be donated into the carbon center.

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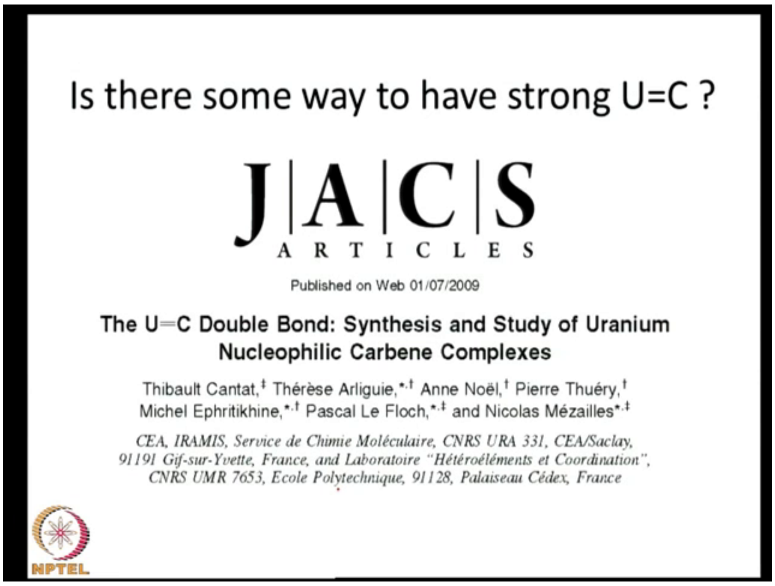

Is there some way to have strong U=C ?

J|A|C|S ARTICLES

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The U=C Double Bond: Synthesis and Study of Uranium Nucleophilic Carbene Complexes

Thibault Cantat,† Thérèse Arliguie,*,† Anne Noël,† Pierre Thuéry,† Michel Ephritikhine,*,† Pascal Le Floch,*,‡ and Nicolas Mézailles*,‡

CEA, IRAMIS, Service de Chimie Moléculaire, CNRS URA 331, CEA/Saclay, 91191 Gif-sur-Yvette, France, and Laboratoire "Hétéroéléments et Coordination", CNRS UMR 7653, Ecole Polytechnique, 91128, Palaiseau Cédex, France

So, in the case of molecules which have for example, a uranium metal center then, it will be very difficult for the uranium, if it is in the plus 4 oxidation state. For the uranium atom, to give electron density to the carbon that is because, it has already exhausted all it is valence electrons. And so, there would be no electron density on the uranium to form a double bond. So, recently in 2009a molecule has been synthesized, where you have a uranium carbon double bond. And this has been achieved, by a particular using a particular trick and that is as follows.

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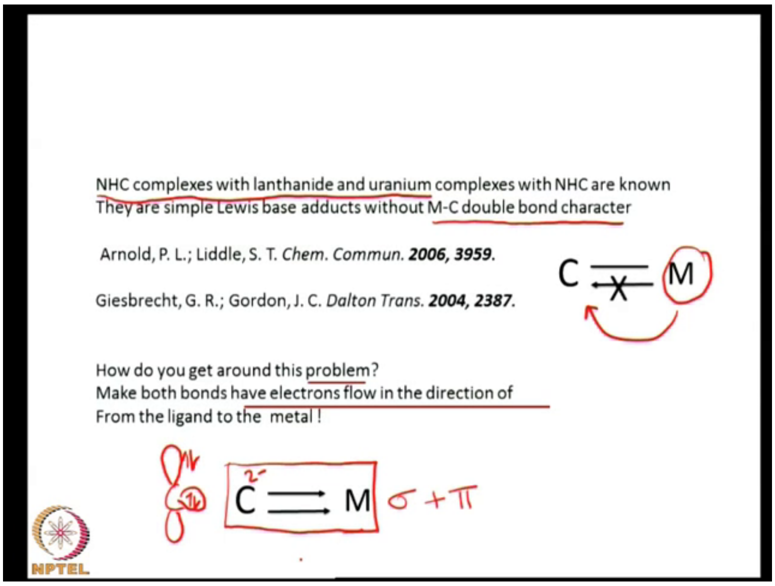

NHC complexes with lanthanide and uranium complexes with NHC are known
They are simple Lewis base adducts without M-C double bond character

Arnold, P. L.; Liddle, S. T. *Chem. Commun.* **2006, 3959.**

Giesbrecht, G. R.; Gordon, J. C. *Dalton Trans.* **2004, 2387.**

How do you get around this problem?
Make both bonds have electrons flow in the direction of
From the ligand to the metal !

If you have a carbene carbon, where there is no possibility for donating electron density from the metal, to the carbon center, where there is no possibility because, there are no valence electrons on the metal. If there are no valence electrons on the metal and you cannot form a double bond because of this type of resonance happening then, it is possible that we can get around this problem by making the electron density flow from the carbon, to the metal in both sigma and in the pi fashion.

So, how can one do that, in fact before I go further, I should tell you that there are N heterocyclic carbene complexes of lanthanide and uranium which have been made, but these are systems in which there is a metal carbon single bond. So, there is very little metal carbon double bond character in these complexes, they are best characterized as simple Lewis base adducts of the carbene system with the metal.

So, in the systems that we are going to discuss just now, there is in fact a very clear formation of a carbon metal double bond. And that happens because you have generated a carbene or a carbon center, which has got electron density both in the sigma and in the pi manifold, with the pair of electrons. So, if you have C2 minus, C2, C2 minus and then both electrons can be donated to the metal in the same direction. Let us take a look at these complexes now.

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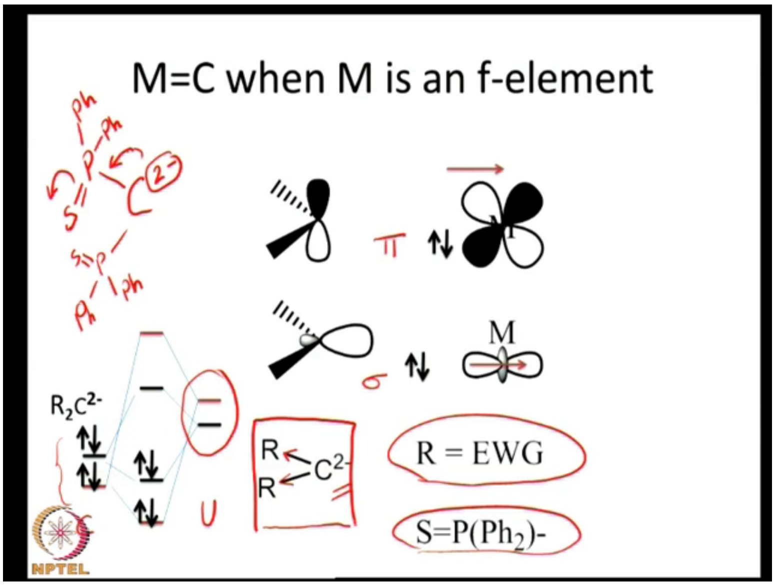

M=C when M is an f-element

The electron, the bonding picture that we can think of in these cases, is a fact that, if you have a carbene carbon, which has attained an extra pair of electrons. And so that will be, a carbene with 2 minus, there is a 2 electrons formed to extend charges on the carbon. So, you have both sigma bond, which I have pictured here that, has also got a pair of electrons. And you have a possibility for, a p orbital on the carbon and that has also got a pair of electrons.

And the energy level diagram is shown here, in the, on your left bottom of this screen and that shows you 4 electrons present on the carbon and the vacant orbitals on the uranium are pictured here. And they lie at a much higher energy, but both of them are vacant and they can accept electron density. So, these two orbitals on the uranium are stabilized by donation from carbon, in both a sigma fashion and that is, this sigma fashion here and also in the pi fashion.

So, you have a unique situation where it is no longer a carbene, but it still forms a metal carbon double bond. And this is made possible, because of the fact that you have electron donation both in the sigma manifold and in the pi manifold, both occurring from carbon to the metal. So, how can one stabilize the two negative charge, the two extra pairs of electrons on the carbon. If you have, a very strong electron withdrawing group on the carbon then, it is possible that a electron withdrawing group can draw away, the extra charge that is present on the carbon, by pulling electron density towards itself.

And this will lead to stabilization of such a dianionic species so, this dianion is stabilized because, you have 2PPh2S groups, which are present on the carbon. So, let us picture this molecule, this molecule, I can draw this molecule in this fashion. I have P, a Ph group, a Ph group and a double bond S and I have two of these groups. So, I can draw them like so, and I have 2 minus this, 2 minus charge is extra electron density is delocalized on to the phosphorous or in other words, you form you can push this electrons into this, phosphorus carbon bond.

And make a partial double bond and this can in fact, be stabilized by further resonance structures, by pushing this double bond and making this minus species. So let us look, take a look at this molecule,I am going to show you a structure where you have the uranium coordinated to this particular ligand, where you have R 2, 2 minus where the R group is actually a PPh2S.

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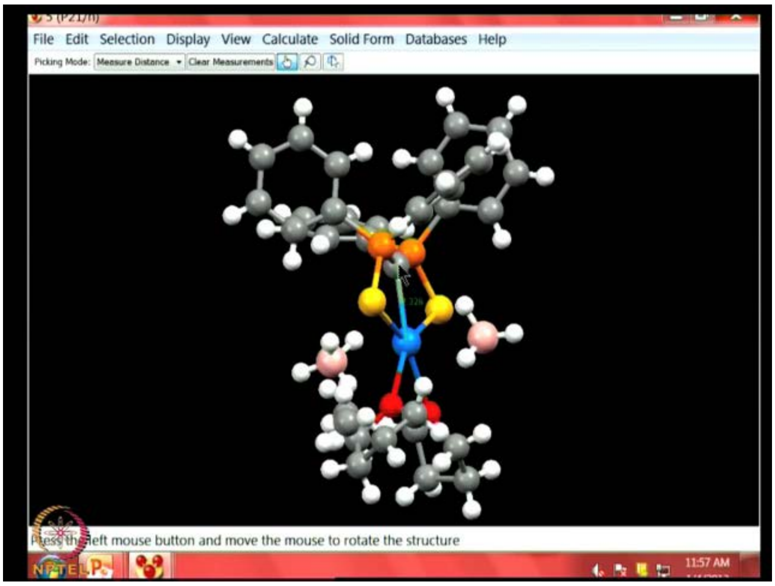

Press the left mouse button and move the mouse to rotate the structure

So, here is this molecule you have a uranium atom and this uranium atom is present in the place where I am, I am pointing it to, it with my the arrow. So, this is the uranium atom and it is coordinated to a carbon which is at a distance of 2.326 Angstroms. So, you have a carbon, which is about 2.326 Angstroms from the uranium atom and you will notice that, the carbon is flanked by two phosphorous atoms. And I am pointing to the phosphorous, with the cursor and that is the orange color. So, the orange color phosphorous atoms on either side of the dark colored carbon is, what you are seeing and the two sulphurs are in yellow, the two sulphur atoms are yellow in color.

And I am pointing to them right here and these two yellow sulphurs are also coordinated to the uranium. So, you have the uranium atom which is flanked by two sulphurs from the PPh2S groups because, you have partial S minus character, which I just explained to you. That S minus character will lead to, extra coordination ability for the sulphurs and so, they are pointed towards the uranium. And you have, a carbon which is having the two minus charge.

Now, how do we know that there is a double bond between the uranium and the carbon. The uranium single bond radiuses, are around 1.8 or 1.77 Angstroms according to some estimates and so, if you estimate carbon to have a single bond radius of 0.77 angstroms. You will notice that, this distance is 2.326 angstroms so it is much less than 2.4 or 2.5 angstroms, which some books estimate. So, because of this shortening of the bond distance between carbon and between carbon and the uranium, you can say that there is partial double bond character between the uranium and the carbon.

These, it is interesting that in this molecule right here which I can in factrotate slightly and show you. This is a beautiful molecule, where the uranium atom is in fact surrounded by 2BH4 units, BH4 minus units and the hydrogens are in fact pointed towards the uranium. So, you can see the 3 hydrogens that, are on the BH4 units they are pointed towards the uranium. They are also, coordinating to the uranium and you have these two sulphurs coordinating. In addition, you have the carbon which we are interested in this lecture, that is coordinated to the uranium as well. So, here is a case where you have, a very strong indication of the formation of a double bond between the uranium and carbon.

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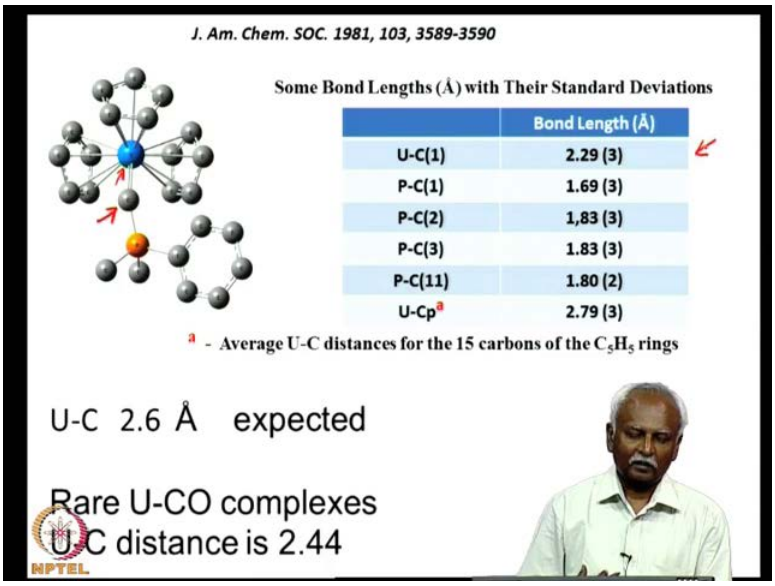

J. Am. Chem. SOC. 1981, 103, 3589-3590

Some Bond Lengths (Å) with Their Standard Deviations

	Bond Length (Å)
U-C(1)	2.29 (3)
P-C(1)	1.69 (3)
P-C(2)	1,83 (3)
P-C(3)	1.83 (3)
P-C(11)	1.80 (2)
U-Cp[a]	2.79 (3)

[a] - Average U-C distances for the 15 carbons of the C_5H_5 rings

U-C 2.6 Å expected

Rare U-CO complexes

U-C distance is 2.44

Getting back to this particular structure, I would like to show you another molecule where, also you have evidence for some carbon uranium double bond character. And that comes from a different structure, which was characterized fairly long ago, but this is not a system which has got 2 negatively charged, two electrons on the carbon. This is in fact, a system where you have a CH2 minus and you expect a distance of 2.6 Angstroms and the uranium carbon distance.

This is a carbon distance, this is a carbon that we are talking about and this is the uranium atom that is present in this structure and this distance is around 2.29 Angstroms.

So, there are instances where you can form short uranium carbon contacts and these are indicative of the fact that, even in the case of uranium you can have stabilization of the MC double bond. And these are relatively rare, but nevertheless it is possible to have this double bond character between the actinide or lanthanide element and the carbon center.

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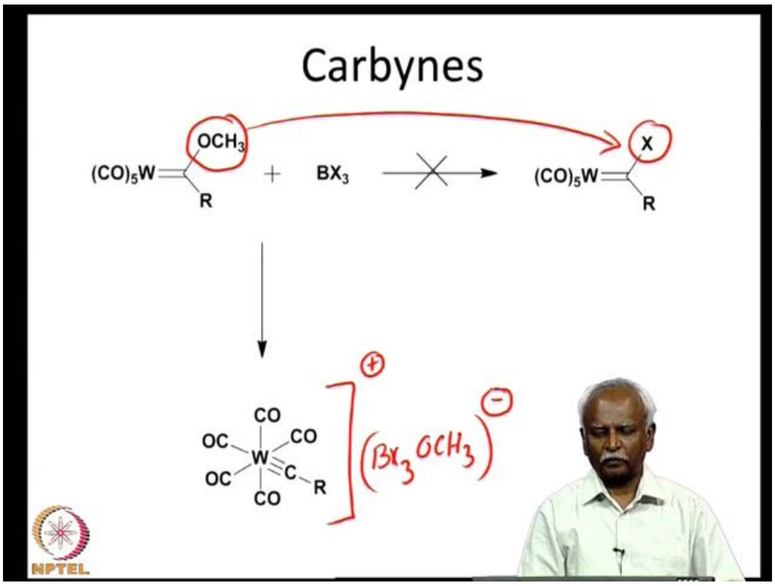

Carbynes

So, let me now move onto another system briefly and that is a carbyne system. This was accidentally discovered and the reaction of the Fischer carbene with, BX3 or a trihalo boron molecule BX3, BCl3 or BBR3 led instead of a substitution of this OCH3 by the X group. Instead of converting the, OCH3 to an X group one end up with elimination of the OCH3 leading to the formation of a carbyne complex.

So, carbynes are relatively tricky to understand because of the fact that you have now a molecule, which is apparently a neutral donor. And you have the possibility for forming, three bonds between the tungsten and the carbon. So, let us take a look at a some of these molecules, how they are made. And this would have a net positive charge and BX3, OCH3 and a negative charge to compensate for the extra halogen atom on the boron.

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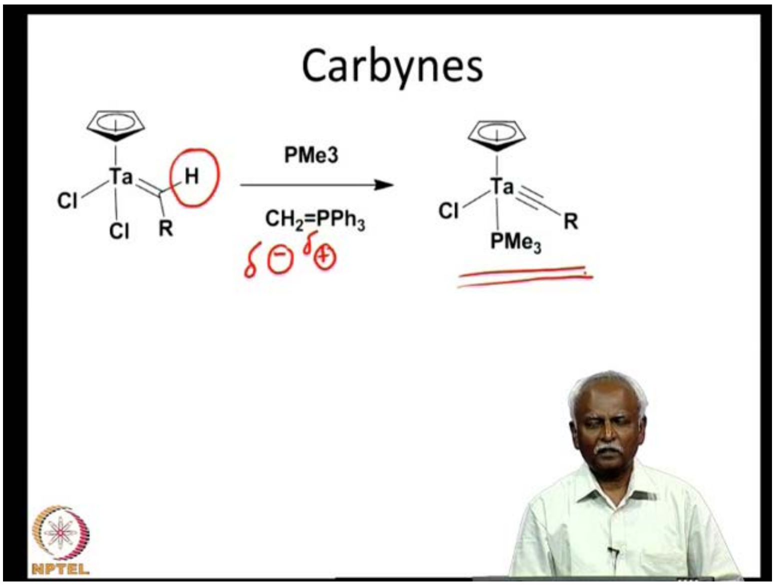
Carbynes

So, you could also do the abstraction of a proton or a hydride. In this particular instance, this molecule is polarized in this fashion, you have CH2 minus and a PPH3 plus. We can write it, in this fashion and this can abstract this hydrogen which is on the position, leading to a tantalum carbon triple bond.

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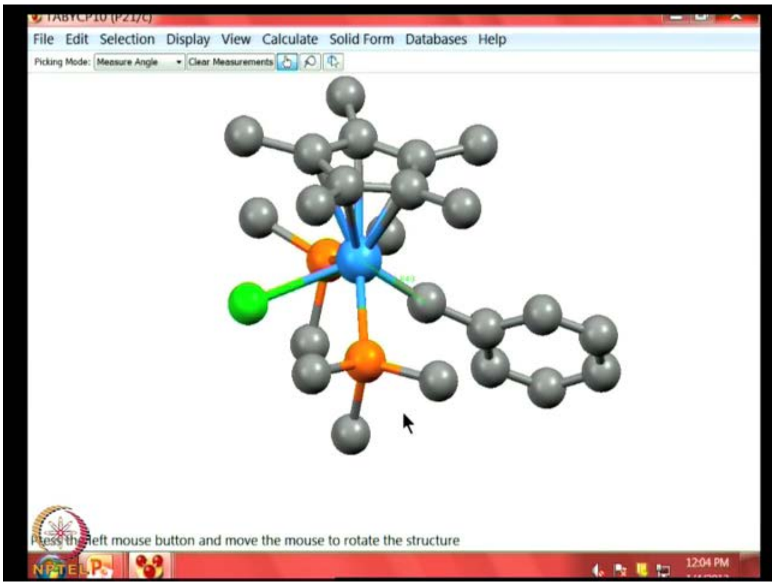
Press the left mouse button and move the mouse to rotate the structure

Now, let us take a look at these molecules and once again let me show you, this molecule which is pictured here. This is a tantalum carbon carbyne complex, in which you have the carbon at a very short distance of 1.849 Angstroms. And so, this is a distance which is assumed to be a triple bond, it is much shorter than a metal carbon double bond. And it is much, much shorter than a metal carbon single bond. And so, the best formulation of this molecule is to assume that they have a triple bond between the metal, and the carbon atom.

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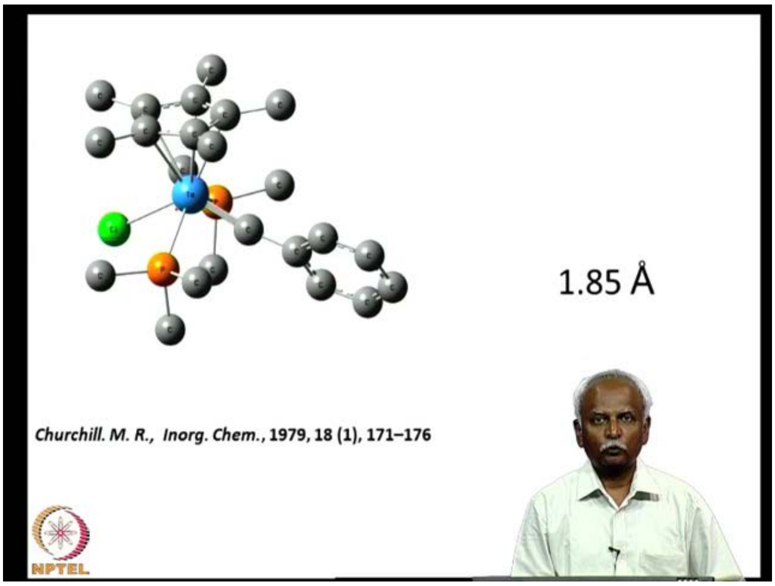

1.85 Å

Churchill. M. R., Inorg. Chem., 1979, 18 (1), 171–176

So, let me now proceed further. You here, you have the picture of this molecule, where you have the benzene ring attached to the carbon, which is attached to the tantalum. And you can see that, the distances are very short. So, you have metal carbyne complexes just like you have metal carbene complexes.

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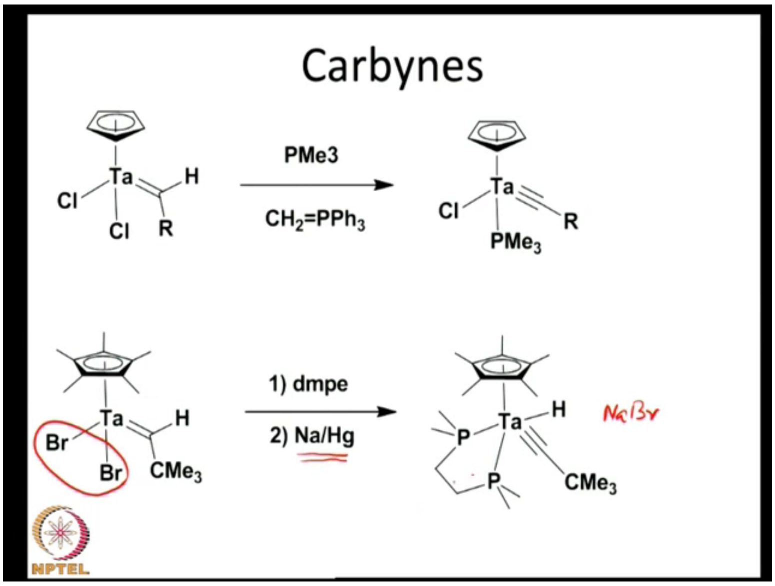

Carbynes

PMe3

$CH_2=PPh_3$

1) dmpe

2) Na/Hg

NaBr

And they can be made in a variety of ways, I will show you quickly two different ways. One is to use a light to abstract the proton. Another is to use sodium amalgam again, to reduce the tantalumoxidation state of the tantalum, from what it was earlier, by eliminating this bromine as a sodium bromide. And this sodium bromide is eliminated and you form a tantalum carbyne complex.

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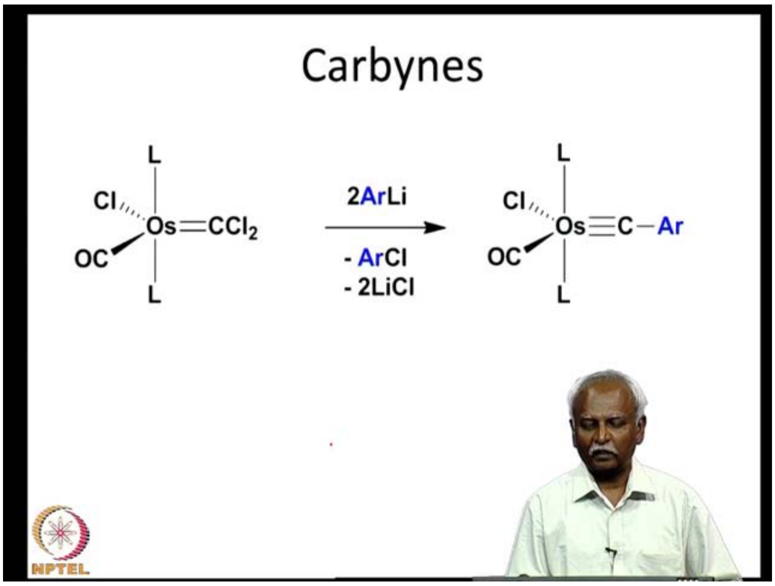

Carbynes

2ArLi

- ArCl

- 2LiCl

Here is one more instance, where you can have a CCl 2 group attached to the osmium, and we have done a substitution reaction with aryl lithium, it can be any aryl group. But phenyl lithium would do, and you can end up with a carbyne complex as pictured here.

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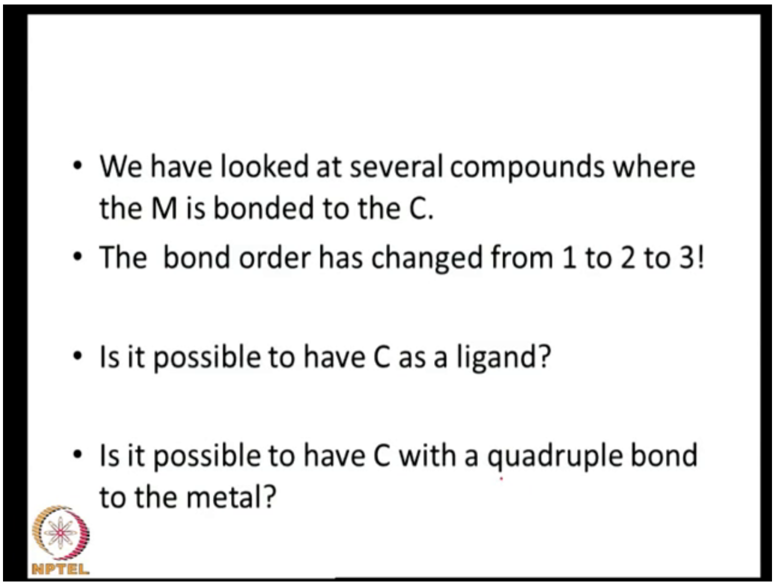

- We have looked at several compounds where the M is bonded to the C.
- The bond order has changed from 1 to 2 to 3!
- Is it possible to have C as a ligand?
- Is it possible to have C with a quadruple bond to the metal?

We have looked at several compounds, where the metal is bonded to the carbon. The bond order has changed from 1 to 2 to 3. Now, is it possible to have just carbon as a ligand, we will see this in a future lecture. We have looked at the possibility of a carbon metal bond order of 3, can we have a quadruple bond between the metal and the carbon.

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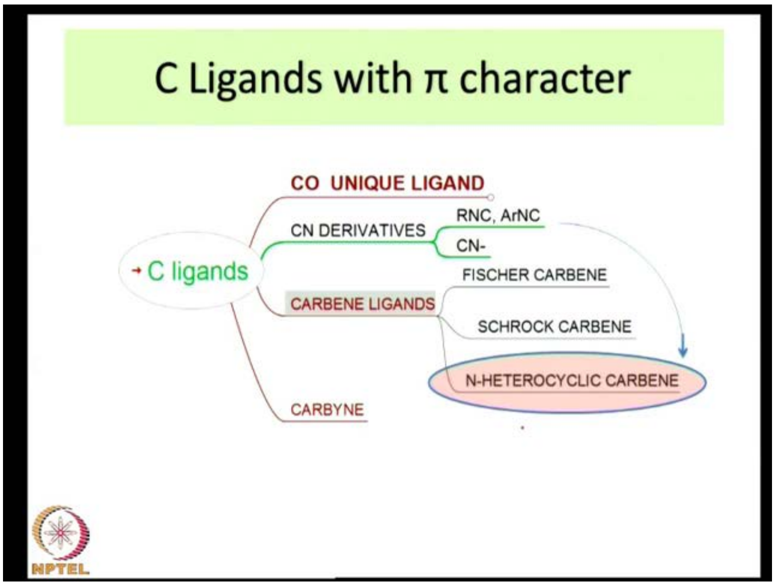

C Ligands with π character

This is again something that we need to explore later as well. So, to summarize let me say that we looked at heterocyclic, hetero atom stabilized carbene complexes, we looked at N heterocyclic carbenes.

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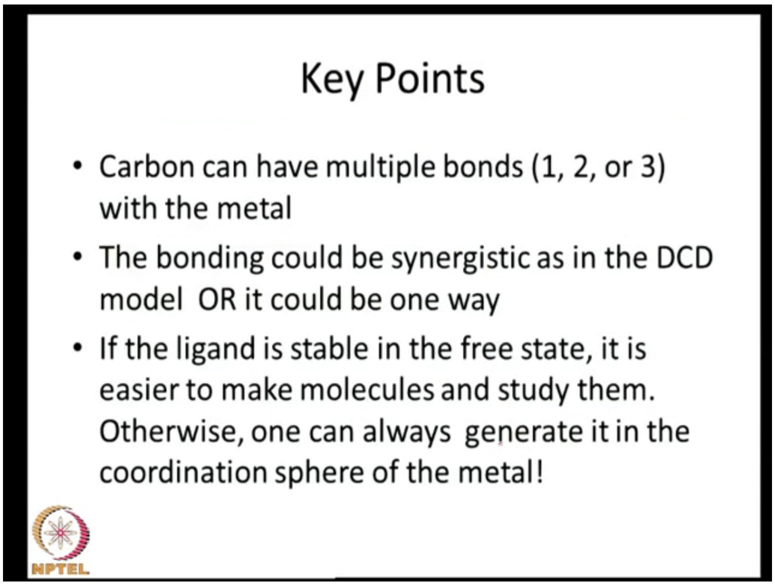

Key Points

- Carbon can have multiple bonds (1, 2, or 3) with the metal
- The bonding could be synergistic as in the DCD model OR it could be one way
- If the ligand is stable in the free state, it is easier to make molecules and study them. Otherwise, one can always generate it in the coordination sphere of the metal!

And the key points that we have learnt is a following carbon can have multiple bonds between the carbon and the metal. And we can have synergistic interaction between the metal, so that you can have a give and take which stabilizes the metal carbene complex. And if the ligand can be stable made in a stable form, then it is easier to make these molecules, and study them in the coordination sphere of the metal. So, metal carbene complexes and metal carbyne complexes have been extensively studied and are very useful species in organometallic chemistry.