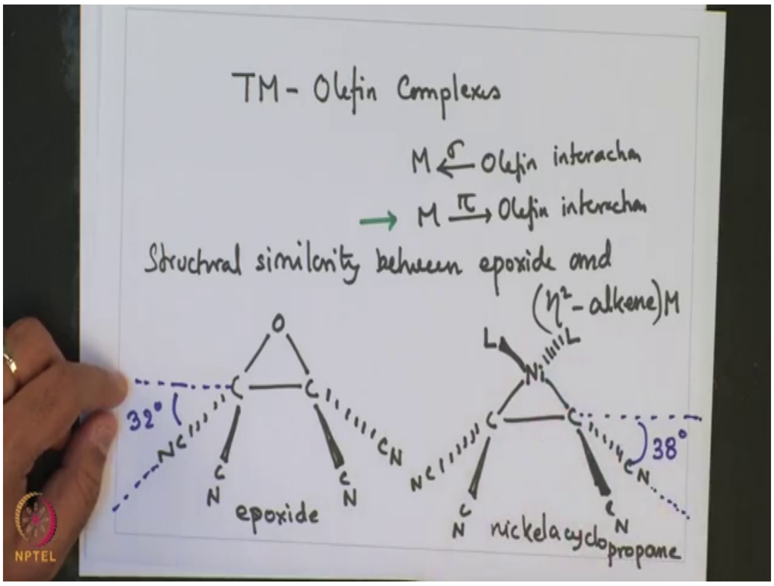
Transition Metal Organometallic Chemistry : Principles to Applications
Prof. Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology, Bombay

Week - 11
Lecture - 54
Bonding Properties in Olefin Complexes

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. We have been discussing bonding properties of transition metal olefin complexes. Now, this is a very important aspect in transition metal olefin complexes because bonding determines the reactivity.

(Refer Slide Time: 00:28)



TM- Olefin Complexes

$M \xleftarrow{\sigma}$ Olefin interaction

→ $M \xrightarrow{\pi}$ Olefin interaction

Structural similarity between epoxide and (η^2-alkene)M

So, understanding bonding provides a useful insight as to the reactivity of transition metal olefin and complexes. And from that perspective we have discussed the interactions that are prevalent for the binding of olefins to the transition metals. And what we have seen is that these transition metal olefin complexes contains olefin interacting with transition metal by two interactions; where first one is as olefin to metal sigma donating interaction and the second one is a metal to ligand pi back donation interaction that happens from the metal on to the ligand empty orbital.

Now, these two interactions that is olefin to metal sigma interaction and metal to olefin pi interaction are extremely crucial in understanding the reactivity of transition metal olefin complexes and we have seen that even though both the interactions are important of these transition metal to olefin pi interaction is a kind of a very significant.

It is it is significant in two respect: One is that that most of the transition metal olefin complexes that have been isolated, they are of lead transition metals which means that the metal has enough electron density on them to or take metal to ligand pi back donation. So, in that way it sort of one can sort of infer that the olefin complexes of transition metal can only be stabilized, when the metal has the capacity to participate in a metal to olefin pi back donation in interaction.

And to support this argument, most of the transition metal olefin complexes that have been isolated, they all contain lead transition metals. And second point with regard to the significance of this metal to olefin pi interaction is the fact that these presence of this metal to olefin pi interaction, increases the multiplicity of this metal olefin bond and that it becomes more than in a single bound character and partially double bond character. As a result this transition metal olefin pi interaction also increases the bond energy of the transition metal olefin bond.

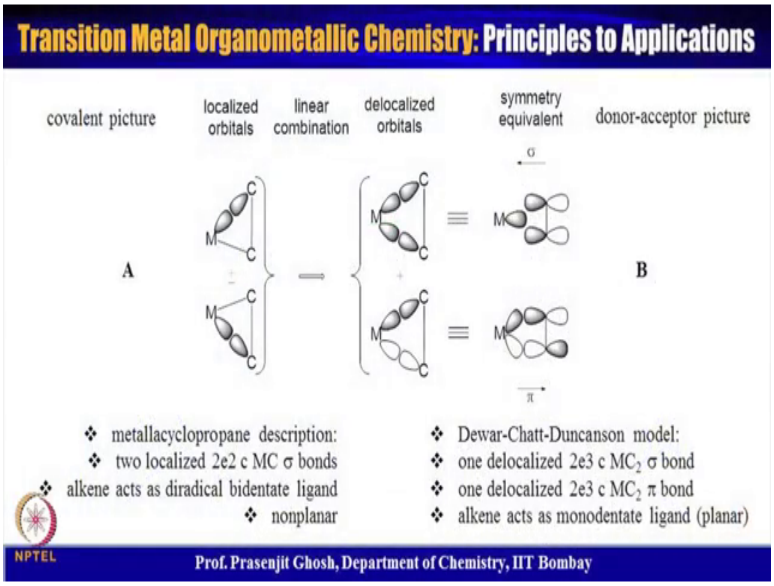
So, what we see is that the interplay of these two interactions are very important for stabilizing transition metal olefin complexes and also we have seen that they are important marker for gauging the stability of these complexes. So, with that we are going to talk more about these interactions that occur between transition metal olefin complexes.

Now, there is a similarity between an epoxide and transition metal alkene complex. So, let us look at the structure of an olefin; a epoxide. Let us say, tetra cyanide epoxide and the corresponding nickel cyclopropane system which has nickel bound two L and that is perpendicular to the ring continuing the olefin and the nickel cyclopropane ring. And what it seems over here? This is called nikela cyclopropane. So, this is similar to the epoxide with oxygen on top and nickel replacing the oxygen.

Now, these four tetra cyano groups are not in the plane and are deviated from the plane and they are deviated by about 32 degrees. So, these four tetra cyano groups are not in the plane contain CC but are below the plane containing issued by about 32 degrees and the same in the nikela cyclopropane is about 38 degrees.

So, what one can see is there is a starching similarity between a organic epoxide and a metallo cyclopropane intermediate that is formed by at a two binding of an alkene. Now, let us sort of discuss this aspect of this metallo cyclopropane in bit more detailed.

(Refer Slide Time: 07:33)



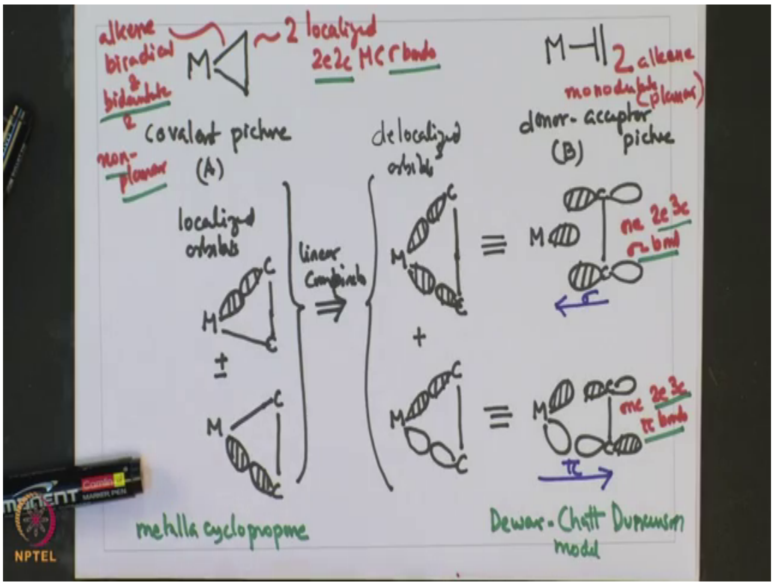
Transition Metal Organometallic Chemistry: Principles to Applications

- metallacyclopropane description:
- two localized 2e2 c MC σ bonds
- alkene acts as diradical bidentate ligand
- nonplanar

- Dewar-Chatt-Duncanson model:
- one delocalized 2e3 c MC_2 σ bond
- one delocalized 2e3 c MC_2 π bond
- alkene acts as monodentate ligand (planar)

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

(Refer Slide Time: 07:50)



Now, one can conceive of metal olefin bond to be of two type: One is a metallo cyclopropane ring where there are two covalent bonds. And the other extreme can be olefin attached to the metal where the olefinic double bond is retained. An olefinic double bond is completely lost and in present two metal carbon bonds have been formed.

So, this can be sort of spoken about as covalent picture. Let us say, this is form A and this can be called as donor acceptor picture. And this can be designated by form B; here the donor is the olefin; alkane and acceptor is the metal.

Now, one can see that, in these there are two localized bonds, the two localized single bonds between the metal and the carbon and they can be represented as localized orbital's and they can be represented something like and the other bond can be given as.

So, these 2 can undergo linear combination to give following two types of bonds. One in which all the metal orbital are in same phase, these two covalent bond in same phase or they can be in different phase.

Now, these linear combination thus gives delocalized orbital's, linear combination of localized orbital gives delocalized orbital's , which is akin to this donor both sides of the same phase is akin to the interactions something like, this is akin to this and this part is akin to something like this.

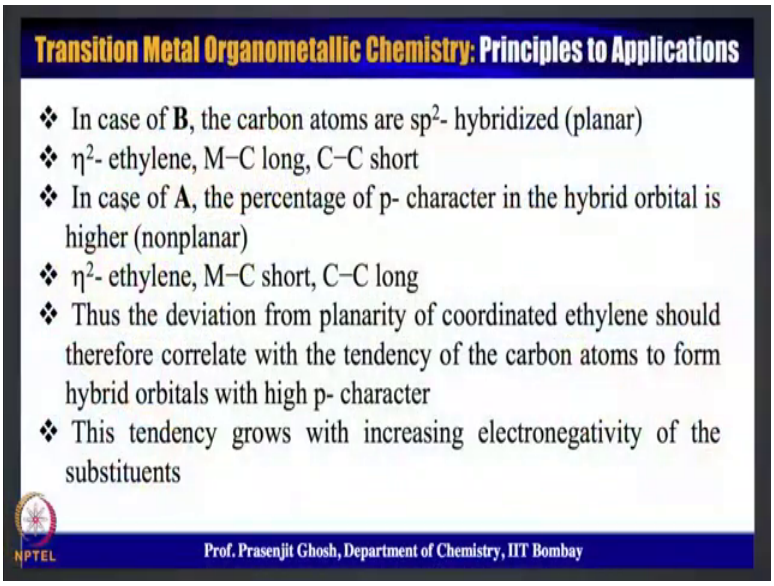
So, in this case, this is designated as sigma interaction and this is designated as pi interaction. Now, this left hand side, where there is a cyclopropane ring; this is called metalla cyclopropane description. And where there is donor acceptor model, simple olefin complex; this is called Dewar–Chatt–Duncanson model.

Now, let us look at these two interaction for metallo cyclo intermediate contains 2 localized 2 electron 2 c metal carbon sigma bonds. So, these are classical metal carbon sigma bonds contain 2 c 2 e types. On the other hand, this contains one 2 e 3 c sigma bond and another one 2 e 3 c pi bonds.

So, what we see the difference being that over here there are 2 localized sigma bonds which are classical 2 electron 2 centered. On the other hand, for the donor acceptor theory, there is one 2 electron 3 centered sigma bond and another 2 electron 3 centered pi bonds. Another interesting different difference between the two is, in this case alkene is biradical, bi dentate and also non-planar.

Now, in this case alkene is monodentate and also planar. So, what we see that depending on which description satisfies the metal olefin complex. One can get bidentate, non-planar structure containing 2 localized 2 electron 2 centered metal carbon bonds or one can get the delocalized structure which contains one 2 electron 3 centered sigma bond and another 2 electron 3 centered pi bond. And that the olefin in this present case is planar, whereas the olefin in the presence the previous case is non-planar.

(Refer Slide Time: 16:37)

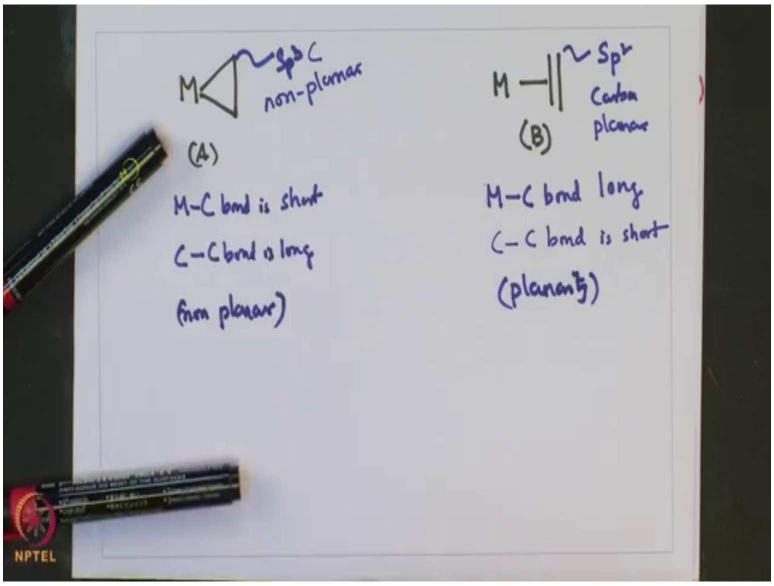


Transition Metal Organometallic Chemistry: Principles to Applications

- In case of **B**, the carbon atoms are sp^2- hybridized (planar)
- η^2- ethylene, M–C long, C–C short
- In case of **A**, the percentage of p- character in the hybrid orbital is higher (nonplanar)
- η^2- ethylene, M–C short, C–C long
- Thus the deviation from planarity of coordinated ethylene should therefore correlate with the tendency of the carbon atoms to form hybrid orbitals with high p- character
- This tendency grows with increasing electronegativity of the substituents

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

(Refer Slide Time: 16:40)

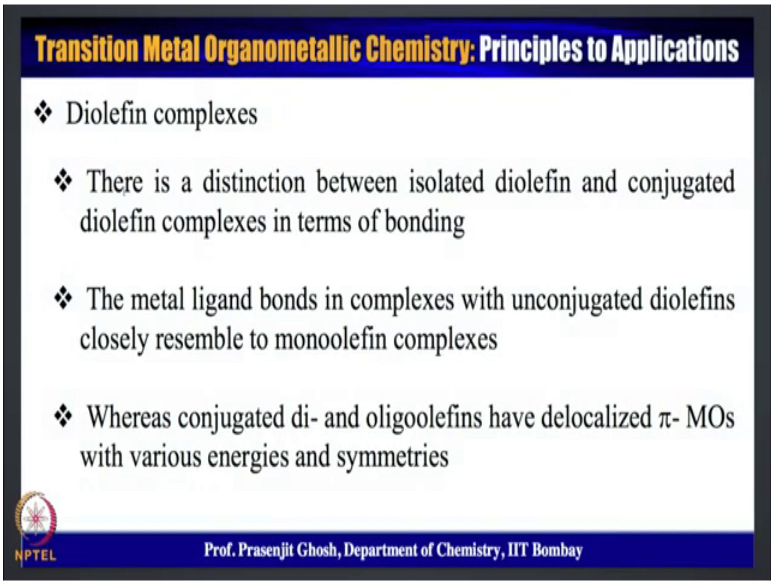


Another interesting difference between the two structures A and B, is in the hybridization of the carbon. For example, this is structure A and this is structure B. In B, the carbon atoms are Sp 2 hybridized. In structure A, carbon atoms are Sp 3 hybridized and hence non-planar. And for structure B, since it is Sp 2 hybridized, it is planar.

In B, since this interaction is short M-C bond length is long and C-C bond is short. On the other hand, the reverse is true for structure A which contains this metallo cyclopropane ring. In structure A, M-C bond is short and C-C bond is long and structure B, the planarity is maintained of the olefin is maintained; in structure A it is non-planar ok.

So, now any deviation from this planarity to non planarity is affected by the metal to ligand pi back donation which results information of the non-planar structure.

(Refer Slide Time: 19:02)



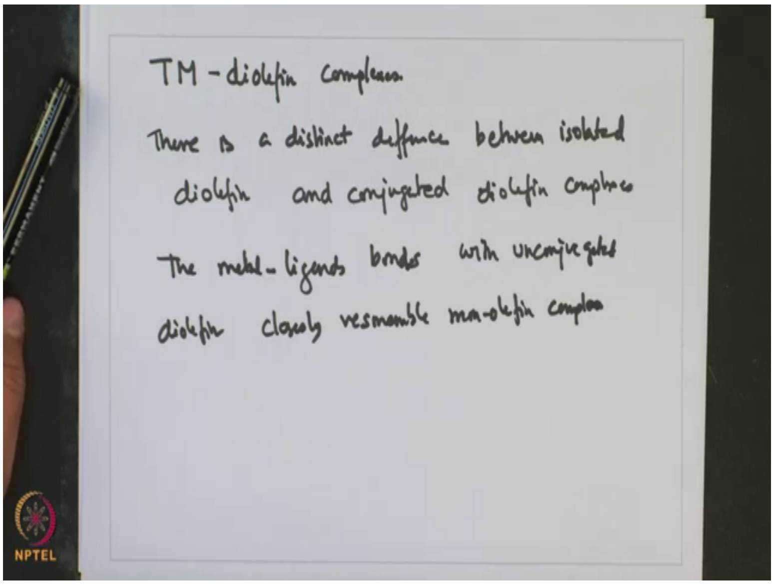
Transition Metal Organometallic Chemistry: Principles to Applications

- Diolefin complexes
  - There is a distinction between isolated diolefin and conjugated diolefin complexes in terms of bonding
  - The metal ligand bonds in complexes with unconjugated diolefins closely resemble to monoolefin complexes
  - Whereas conjugated di- and oligoolefins have delocalized π- MOs with various energies and symmetries

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Now, with that we will move on to a new topic after finishing up this reactivity and bonding aspects of metal olefin complexes. Next we are going to discuss about something which is related to transition metal olefin complexes and these are transition metal diolefin complexes.

(Refer Slide Time: 19:26)



TM - diolefin complexes

There is a distinct diffrnce between isolated diolefin and conjugated diolefin complex

The metal-ligands bonds with unconjugated diolefin closely resemble mono-olefin complex

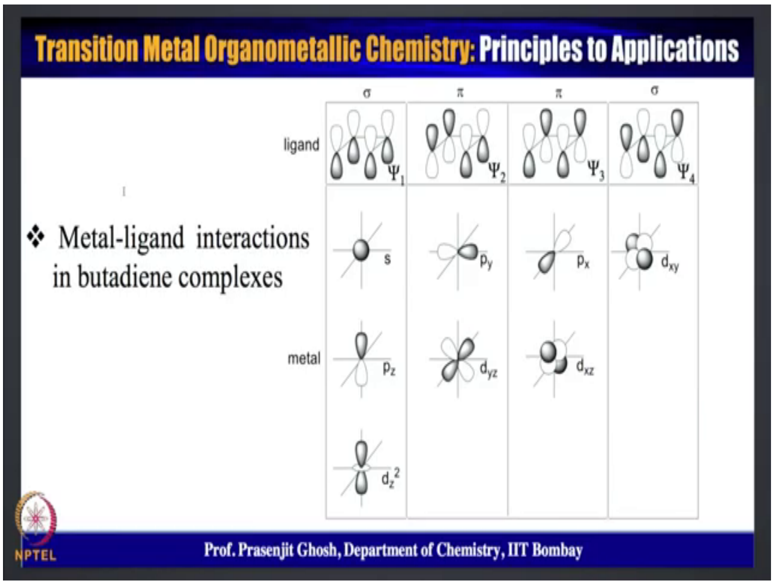
These are closed variety of transition metal olefin complexes and hence would be treated from the perspective of what we have understood on transition metal olefin complexes, when we study this transition metal diolefin complexes. One must realize that there is a distinct difference between isolated diolefin and conjugated diolefin.

Now, this is different because, now when it comes to conjugation and as a result of conjugation the bond length and structure of this diolefin would change. And hence is the statement that conjugated diolefin is different from isolated diolefin. The next thing is that metal ligands bonds in complexes with unconjugated diolefin, closely resemble the mono-olefin complex.

In metal ligand bonds with unconjugated diolefin, closely resemble mono-olefin complexes. Also wherever there is conjugated an di and oligo olefins having delocalized pi MOs, then they would exhibit different energies and symmetries ok.

So, structurally what it says that, not only energetically, but also structurally there is a change that is brought in with the existence of conjugation on going from mono-olefin to diolefin to di oligoolefin complexes. Now, with that in mind, let us take a look at how these diolefin complexes bind to the transition metal.

(Refer Slide Time: 22:36)



Transition Metal Organometallic Chemistry: Principles to Applications

- Metal-ligand interactions in butadiene complexes

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Now, this is a very important phenomenon because one of the reason of this variation or difference between conjugated diolefin with unconjugated diolefin is the fact that going to the extent of conjugation, the carbon hybridization as well as the distance between carbon carbon bonds are change. As a result the conjugated and the unconjugated are structurally a different even though they look like the same type of olefinic isomer.

Now, with that I would like to conclude about the topics that has been discussed in today's lecture. We have looked at a completion between epoxides and transition metal cyclopropane intermediates. And what we see is that because of the, similar to what had been seen in the epoxide case where the substituents and the olefin are deviated away from penalty as a result giving a non-planar distorted structure.

Similarly, in metallo cyclopropane intermediate, the substituent's of the carbon 2 are deviated and gives planar structure, similar to what has been discussed earlier. We have also looked at the type of interactions involved in the metallo cyclopropane as well as the donor acceptor metal sigma olefin complex.

And what we saw that metal a cyclopropane contains 2 classical 2 c 2 a bonds whereas, the donor acceptor metal olefin complex contain forward sigma donation from the ligands on to the metal and then backward pi back donation from the metal on to the ligand. We have also looked at how these metallo cyclopropane and metal olefin complex change as a result of spectroscopic signature that are associated with them.

So, with that I would like to conclude today's talk. And would take up topic in bit more detail particularly the transition metal di olefin complex in the subsequent lecture. Until then I thank you for being with me in this lecture and look forward to being with you, discussing transition metal diolefinic complexes in the next lecture, till then goodbye.

Thank you.