Transition Metal Organometallic Chemistry : Principles to Applications

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Week – 11
Lecture - 55
Transition Metal Diolefin Complexes

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. Now in the last few lectures we have been discussing about a transition metal olefin complexes, we have looked into their bonding, their preparations, as well as reactivity aspects of these very important class of organometallic compounds. We have seen as to how these compounds are important from catalytic perspective because they are important intermediates in many catalytic reaction we have discussed that also. We have also looked at the bonding scenario that exists between olefin, and the transition metal in the transition metal olefinic olefin complexes.

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Transition Metal Organometallic Chemistry: Principles to Applications

Transition Metal Diolefin Complexes

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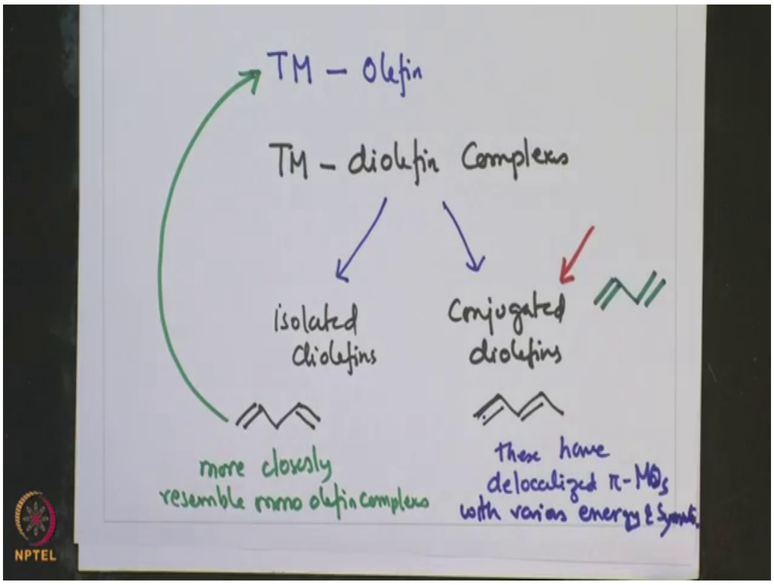

So, we in the last few lectures what we have seen is we have looked into details of transition metal olefin complexes from all perspectives right from synthesis, bonding, structure, and reactivity as well as characterization of this complexes. Now, in this lecture we are going to start another new class of organo metallic compounds, these are mainly a transition metal diolefin complexes. Now one may think that, what is the need for studying transition metal diolefin complexes? Once we have studied transition metal olefin complexes. The reason being simple is that there is a difference in properties of transition metal diolefin complexes as opposed to simple transition metal olefin complexes.

These difference not only is reflected in the bonding as well as the reactivity a thing, but also in the other preparations and other aspects of it. So, there is a definitive need for studying the transition metal diolefin complexes despite having spent quite a few lectures on transition metal olefin complexes. Now for example, this diolefin can be of two types; that means, that it can be isolated di olefins.

For example where these two olefinic bonds are not in conjugation of each other, or it can be conjugated di olefins where these two olefinic bonds are in conjugation of each other. So, what it turns out that unconjugated or isolated diolefins resemble more more reasonable more closely the uncommon olefin complexes, more closely resemble mono olefin complexes.

So, when they these two olefinic bonds are not conjugated the sort of resembles the mono olefin complexes which are somewhere over here. On the other hand when this olefinic is conjugated as a result of conjugation they have a difference scenario and that needs to be treated separately and hence the reason for studying these diolefin different complexes.

So, these have delocalized pi mos mole pi molecular orbitals, with various energies and symmetries with various energies and symmetries such that they require different treatment. Now with that being in mind we are going to focus on some of these types of ligand, in the this part of the lecture where we are going to look at how does conjugated diolefins interact with the transition metal. And with that ah being apart let us take a look at this simple example of a conjugated diolefin which is just butadiene.

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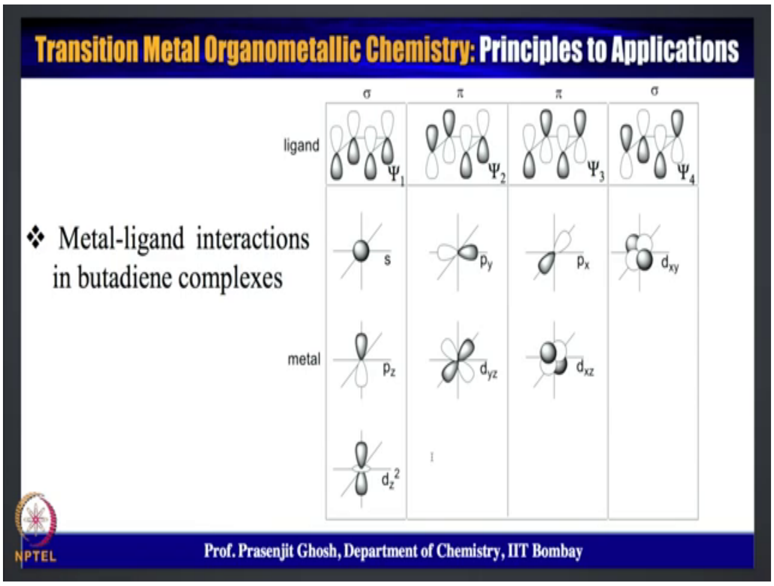

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- ❖ Metal-ligand interactions in butadiene complexes

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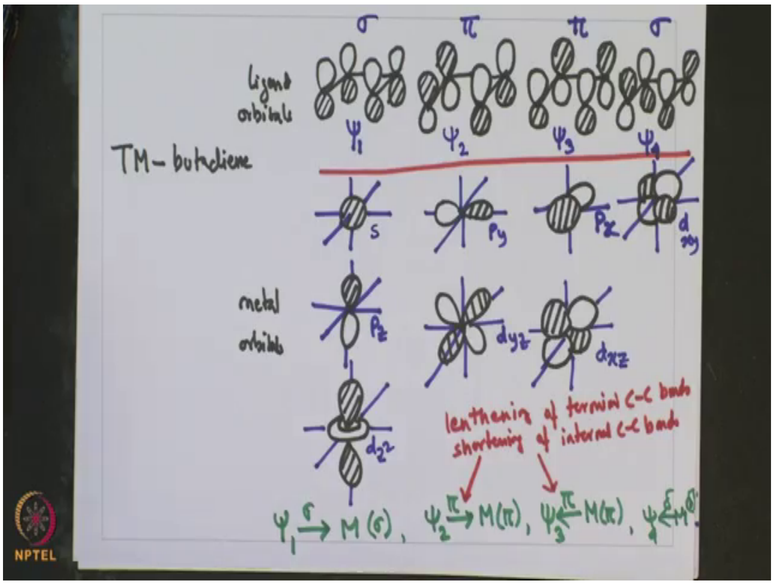

So, to begin with let us sort of take a look at the molecular orbital structure of a metal butadiene complex as is represented by this formulation TM dash butadiene. And let us I take a look at the ligand orbital's and as well as the corresponding metal art orbital's that interacts with them. Now so there are 4 p orbital's of the type shown over here, where all the bondings are in one phase, and this is a sigma type orbital and represented by psi 1.

Since butadiene has 4 p orbital linear combination will give 4 frontier fragment molecular orbital FMOS, and that would react with the corresponding atomic orbital of the metal. So, this is the combination where it is bonding on one side all the 4 edges in same phase, so that is psi 1. The other possibility is that it be that it would have one node, they said new node all have same pace that the possibility is that it has one node; that means, that it is one phase in the top, another phase at the bottom.

This is a psi 2 and this is a pi type orbital. The third combination can be where it is same thing is at the back and opposite in the front. And this is denoted as psi 3, and also is a pi type orbital and the last combination is where it is anti bonding in nature and it has opposite phase. And this is also designated as psi 4, and it is a sigma type orbital.

Now this gives a idea as to how this butadiene orbital's are located. So, you have psi 1 when all 4 are bonding and in sync then you have one with next has one node and then you have the other one where it is plus minus minus plus. And then you have plus minus plus minus 4 orbital's of which two first and the last one are sigma type and the second one and the third one are pi type and we let us see how they interact with the metal orbital's; the metal orbital's involved s s orbital.

For example so this is a s orbital s orbital approximately can interact with a ah these psi 1, or p z orbital. So, this is p z, or these square orbital which is dz square orbital. Similarly for this psi 2, the corresponding metal orbital which can interact with psi 2 are that is p y orbital as well as d y z orbital.

So, it is d y z orbital as for the psi 3 orbital's, which can interact is p x orbital, which is p x orbital, and that is given by that or d x z orbital. Now as for the anti bonding orbital which is psi 4, the middle orbital that can interact is d y x which is given by and this is the x y. So, what it does is it gives an idea as to which ligand orbital interacts with what kind of metal orbital?

So, what we see is the metal orbital that interacts with the particular ligand orbital has same phases to interact with for example, it is black at the bottom, this is all black or this can top is black it can go up there, and the z square also is this. Now over here where there is one mode are the metal orbital's which can interact has the similar thing white, and black as similar to that or white and black as similar to this is a d orbital, this is a p orbital. So, orbital of appropriate symmetry come and match and the same applies to these orbital.

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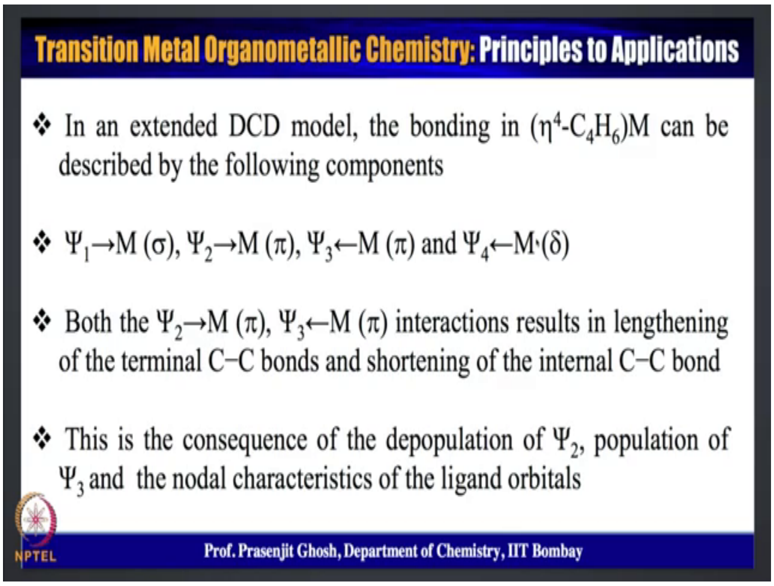

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- ❖ In an extended DCD model, the bonding in (η^4-C_4H_6)M can be described by the following components
- ❖ $\Psi_1 \rightarrow M$ (σ), $\Psi_2 \rightarrow M$ (π), $\Psi_3 \leftarrow M$ (π) and $\Psi_4 \leftarrow M$ (δ)
- ❖ Both the $\Psi_2 \rightarrow M$ (π), $\Psi_3 \leftarrow M$ (π) interactions results in lengthening of the terminal C–C bonds and shortening of the internal C–C bond
- ❖ This is the consequence of the depopulation of Ψ_2, population of Ψ_3 and the nodal characteristics of the ligand orbitals

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So, frontier molecular orbital of the ligand puts a little restriction on the metal orbital that can interact with these elements with these metals, and can provide and inside as to what kind of interactions these can give threw.

In these butadiene binding then one can see that psi 1, or the first interaction is a sigma donating interaction, where psi 1 into metal sigma bond is happening which is a sigma interaction. Now psi 2 metal is a pi kind of ligand to metal interaction, and the third one is metal to psi 3 pi kind of interaction.

Now, this is reverse a metal is donating and psi 4 is metal it is a delta interaction metal to this delta x interaction. Now so this is kind of a side on interaction where these lobe all 4 lobes are interacting with all 4, so this is a delta kind of interactions and these sort of tells what kind of bonds if at all this interaction will form what kind of bonds they would form this says that the first one would be a sigma, these two a pi, and that one a delta bond also one must note that these bears some more significance for example both psi 2 M this interaction, as well as M 2 psi 3 interactions ok. These two would this two psi 2 to M, or M 2 psi 3 interaction. So, these two would result in lengthening on lengthening of terminal C C bonds; that means, these two side ones would be lengthened and shortening of internal C C bonds.

So, what is interesting is that predominance of these two interaction would ensure that these terminal C C bonds are lengthened, and in contrast the internal C C bonds are shortened. And ah that is a very interesting observation that has emerged out of this frontal molecular orbital diagram.

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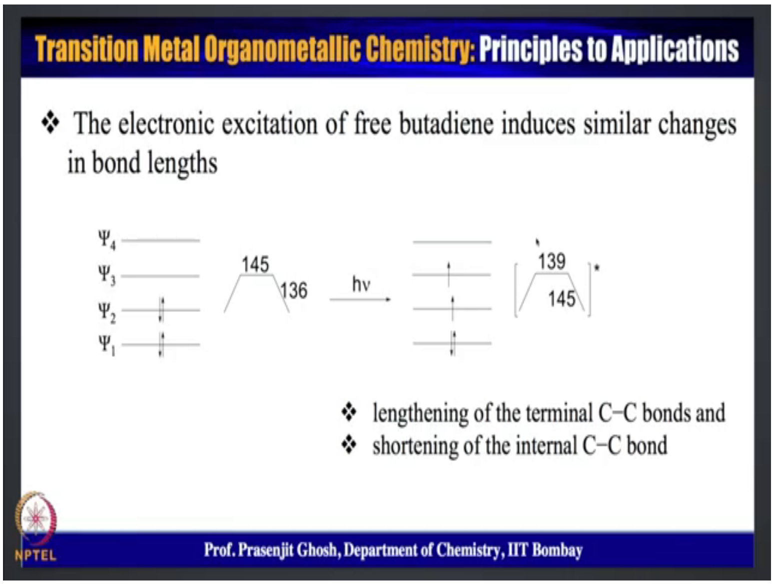
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- The electronic excitation of free butadiene induces similar changes in bond lengths

- lengthening of the terminal C–C bonds and
- shortening of the internal C–C bond

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And we are going to see the implications of these in bit more details. Particularly when we look at the energy diagrams of all these 4 molecular orbitals, so the electronic excitation.

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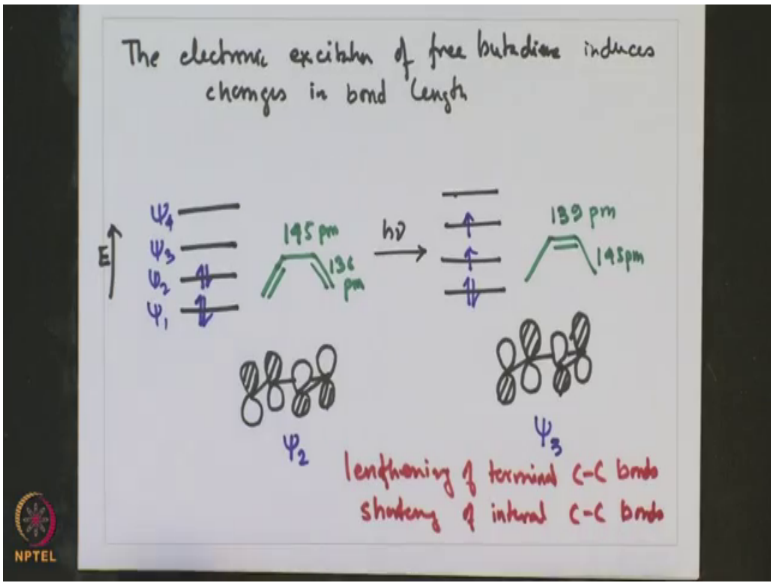
The electronic excitation of free butadiene induces changes in bond length

lengthening of terminal C–C bonds
shortening of internal C–C bonds

For example the electronic excitation of free butadiene induces changes in a bond lengths to comparable to the one that we have just discussed. Let us just sort of illustrate these as follows. For example there are butadiene orbital, this is let us say the energy and there are 4 butadiene orbital which are psi 1, psi 2, psi 3, and psi 4 of which two of them there are 4 electrons.

So, two of them are populated and that would sort of give the butadiene fragments to be something like that or, so the bond distance of the internal C C bond is much longer about 145 pico meter, whereas the one with double bond character is much shorter about 136 pico meter. Now, when the butadiene is excited one of the electron is excited to a higher orbital then again we have these 4 a energy states. And what we see that one of the frontier electron which is over here gets excited to psi 3.

Now, what has happened is the psi 3 which had a population of similar phase that gets populated. So, to understand that let us sort of look a psi 2, and psi 3; psi 2 is this is psi 2. And when it gets excited let us take a look at the structure of psi 3, structure of psi 3 which is the internal double bond is double bond in character.

So, these this is a bond order of that is increased is something like that. And indeed now the internal bond has decreased and it has become 139 pico meter whereas, the external one is now 145 pico meter. So, as a result what one observes is that lengthening of terminal C C bonds, as well as shortening of internal C C bonds.

So, that is a interesting observation that we see that electronic excitation of free butadiene would leads to shortening of internal bonds and lengthening of terminal bonds and the same thing can be also be seen when the butadiene coordinates to metal. There also we see that the population of psi 2 and population of psi 3 would result in analogous a lengthening of terminal bonds and shortening of C C bonds.

So, with this let me conclude today’s lecture which was diolefin complexes, we begin the lecture by looking at how is the di olefin complex is different from olefin symbol simple mono olefin complexes. We have also looked at the bonding scenario of di olefin complexes out there this molecular orbital interacts with that of the fragment molecular orbital.

And how that leads to change in the bond lengths of the internal, as well as terminal C C bond length of the di olefinic ligands, and that provided a very useful insight as to we see that the impact of the metal coordination to a conjugated di olefin, or as well as the excitation light excitation of the di olefin have similar effects.

So, with that let me conclude today’s lecture on di olefinic complexes. We are going to take this a bit more and a few other examples are few other new types of organometallic complexes in the next lecture, till then goodbye. And I look forward to seeing you in the next lecture.

Thank you.