Advanced Transition Metal Organometallic Chemistry
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Lecture – 06
Transition Metal Cyclobutadiene Complexes

Welcome to this lecture on, Advanced Transition Metal Organometallic Chemistry. In our last class, we had a detailed discussion on an important class of organometallic compounds, these are sandwich complexes, and what we saw that these sandwich complexes though has its origin on ferrocene but gradually it has emerged as a new group or new class of its own with various kinds of variations observed for the sandwich complexes.

Apart from sandwich complexes which contain two cyclopentadienyl or other cyclic ligands sandwiching or encapsulating the metal on both of its sides, there are also half sandwich complexes in which there is one cyclic ligand bound to metal and the vacant site, other vacant site is occupied by other organic ligands. So apart from these we had also seen that in sandwich complexes it can be homoleptic or that is the same type of ligands binding to the metal or it can also be heteroleptic.

Where two or three different kinds of being bound to the is found bound to the transition metal. These apart we had also seen that the same ligand can bind in different fashion in sandwich complexes, for example we had looked into examples where the cyclopentadienyl ligand was bound to the metal complex in eta 5 as well as in eta 1 or eta 3 fashions which suggests that these ligands are very versatile and also can bind to the same transition metal in the within the same molecule in the same complex into two or more different ways.

Now having seen these sandwich complexes we have also looked into various preparations, preparative methods available for preparing these sandwich complexes in the last lecture. Today we are going to talk about another important class of compound; these are called transition metal cyclo butadiene complexes. Now these is not a very simple system to look at, the name is starts from cyclo butadiene.

And the raging controversy regarding the structure of cyclobutadiene, the question is what is the structure or what can be the structure of cyclo butadiene.

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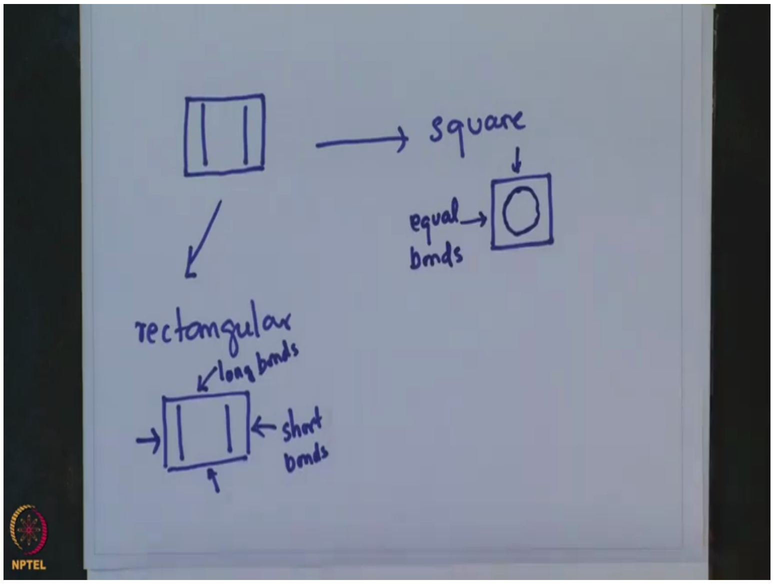

Now from a very simple perspective one can write down the structure of cyclo butadiene having 2 cyclic 4 membered ring having two double bonds then the question is what is the structure of the cyclo butadiene, is it rectangular or is it square? A rectangular structure would mean something of this kind and a square structure would mean something of this kind.

So these has different implications, like if one looks at it, one can say that why would a cyclo butadiene being rectangular, because in that case there will be two long bonds and two short bonds, and that one can possibly speculate because of the presence of double bond and single bond. Whereas if this is something similar to that of benzene where it can have a structure where all the carbon-carbon bonds are equal, then that would give a square structure with something similar to that we had observed in benzene.

Now the interesting debate sort of starts with theoretical calculations as well as spectroscopic identification of cyclobutadiene molecule and that indeed showed, that cyclo butadiene molecule, by itself should have a rectangular structure on synthetically when one made cyclopentadiene complex of transition metals, for example, cyclobutadiene moiety bound to transition metal and with an isolated with some other ligand then one found that this has a square, square structure.

So this debate gives rise to a very interesting chemistry with regard to today's topic and the topic become today is transition metal complexes of cyclo butadiene a ligand. So in order to understand what is the true nature of cyclobutadiene ligand? One has to look at its structure and bonding particularly look at how the molecular orbitals interact are evolved by neutral interaction within the ligand.

And then without beyond the ligand when it does interacts with transition metals. So, before we proceed to speak about the different chemistry's of cyclobutadiene complexes of transition metal let us sort of look at the structure and bonding of cyclobutadiene ligand and compare that with similar that of butadiene ligand which is non-cyclic butadiene ligand as well as to the allyl ligand which we have learned of earlier and then see how the molecular orbitals differ so as to address this issue of square structure or its rectangular structure.

Now if one were to draw the atomic orbitals involved in cyclo butadiene, then one would see there are 4 P-type orbital's, which will give rise to 4 sets of fragment molecular fmos fragment molecular involves orbital P-type orbital's that would be arise from the combination of various P orbital's of cyclo butadiene, the, so there will be since there are 4 P orbital's, so there will be 4 Fmo's, there would be Psi 1, Psi 2, Psi 3, and Psi 4.

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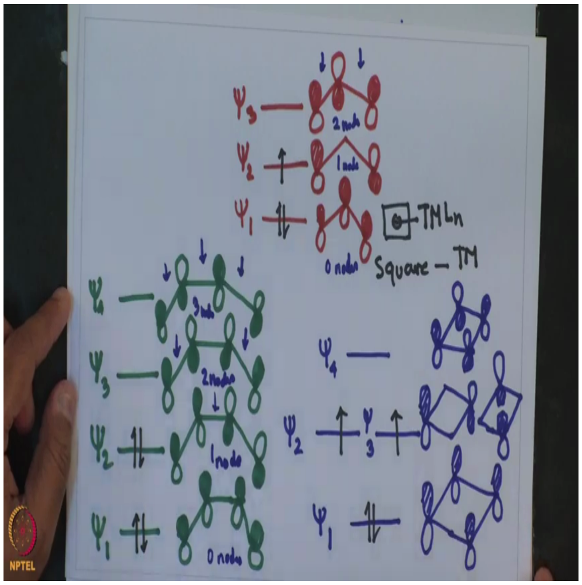

Now so Psi 1 would be all bonding in nature hence now Psi 2 and Psi 3 would be to degenerate orbital's and there molecular orbital's would be something like something like that and the third one or the fourth one would be Psi 4 which will be all the way anti-bonding in nature. So, butadiene would thus have 4 electrons and the Psi 1 will be fully occupied whereas Psi 2 and Psi 3 would be singly occupied each with one unpaired electron each. Now this scenario makes a cyclo butadiene in its square structure this configuration is relevant when the structure is square,

square structure, that Psi 2 and Psi 3 become degenerate and thus in its square structure what does it happen?

The square structure we stabilized by binding to transition metal, as we had seen earlier giving rise to complexes of the type this cyclopentadiene transition metal allene and when it interacts with transition metal the metal puts two more electrons in its Psi 2 and Psi 3 orbitals, thus pairing them up, as a result, making it di anionic 6 electron system, resulting in the aromaticity and as it becomes aromatic then all the 4 bond becomes of same size and it thus becomes a square.

So these molecular orbital diagram sort of explains how cyclo butadiene become square structure upon binding to transition metal and it does so by accepting electron from the transition metal to become a aromatic 6 Pi system, resulting in equal carbon-carbon bond lengths. Now this diagram is sort of starkly different from butadiene. Now in butadiene, again there will be 4 P orbital's however the energy is of these orbitals would not be same as it is with regard to cyclo butadiene.

So, difference between butadiene and cyclo butadiene is that there will be 4 combinations of our vitals but these degeneracy between C2 and C3 would be lifted so I will illustrate this so again there will be in butadiene there would be 4P orbitals and they would again interact to give 4 Emos of Psi 1, Psi 2, Psi 3, Psi 4. So, let us take a look at Psi 1, now Psi 1 being bonding, the orientation would be something like this, then comes Psi 2.

This is Psi 2 after Psi 2 comes Psi 3 and last comes the most energetic Psi 4, so one thing to note over here is the number of nodes, so this has zero nodes, so I am hence this is the most stable molecular orbital fragment molecular orbital Psi 2 is slightly higher it has one node here, now Psi 3 is even higher in energy than Psi 2, so it has two nodes one over here one over here and then lastly it is Psi 4 which has 3 nodes over here, here, here.

And this is the energy order and again the butadiene would have 4 electrons so that would mean that Psi 1 and Psi 2 will be fully occupied and they are diamagnetic. So now I would ask you to see the difference between the molecular orbitals of butadiene and cyclo butadiene in its square form. So what emerges out, that in cyclo butadiene in a square form, this Psi 2 and Psi 3 becomes degenerate and they are singly occupied each with one unpaired electron which allowed them to accept electron from the metal center and achieving its aromatic configuration in a two electron dynamic form.

This is an interesting observation which differentiates cyclo butadiene from butadiene and not only in their structure but also in their reactivity pattern. Now for a better appreciation of this molecular orbital I would further go further and I am going to draw the structure of the allene a moiety and that would also give you a feel, for how, the molecular orbital's overall make a difference in terms of the binding and reactivity and as well as bonding of these ah, ligands.

Similarly allyl has a 3P orbital’s and that would give rise to 3 FMOs the first one obviously would thus be Psi 1 which would be something like this, it will have 3 lobes the second one likewise would be Psi 2 which will have one node and higher in energy than Psi 1 and lastly we have Psi 3 which will have 3 nodes. So, this has zero notes this has one node this has two nodes. Now Pi allyl ligand in its neutral form would have 3 electrons and the configuration of that would thus be, so allyl in its neutral form is a radical.

And hence it is highly reactive and when it interacts with transition metal similar to what we it becomes mono anionic by accepting a electron from the metal in its Psi 2 or homo orbital’s, this phenomenon is exactly similar to that of a butadiene as it interacts with the metal there are two single paired orbitals which individually takes one electron each, H, so one can see a similarity of the neutral allyl ligand with that of the neutral butadiene ligand in its square geometry.

The similarity is that neutral allyl ligand is a radical or mono radical and square geometry cyclobutadiene ligand in this neutral form would thus be a diradical as is shown over here. On the other hand butadiene which does not have these degeneracy you know, is fully diamagnetic Psi two is lower in energy much lower in energy than Psi 3 and as a result both Psi 1 and Psi 2 are fully occupied with paired electron Psi 3 is sort of unoccupied and represents the lumo of these ligand.

So, in this discussion, I have brought out the difference in the, structure and the reactivity, that has its genesis on the atomic orbitals of the cyclo butadiene and I have also made a thorough comparison of the way these atomic orbitals interact with each other to form the molecular orbitals with respect to their acyclic just butadiene counterpart and then went on further and made a completion of this acyclic butadiene and square cyclobutadiene emos with that of the allyl emos, that we had earlier ah, discussed.

So, now we are going to look into these transition metal cyclopentadienyl complexes in much more detail particularly from their synthesis standpoint as well as from their reactivity standpoint. Preparations of our isolation of cyclo butadiene direct reactions of cyclobutadiene in with metal precursors, where came out later, but even before that, method available for preparing, the cyclo butadiene transition metal complexes whereby dehalogenation of dihalo cyclo butadiene ligand.

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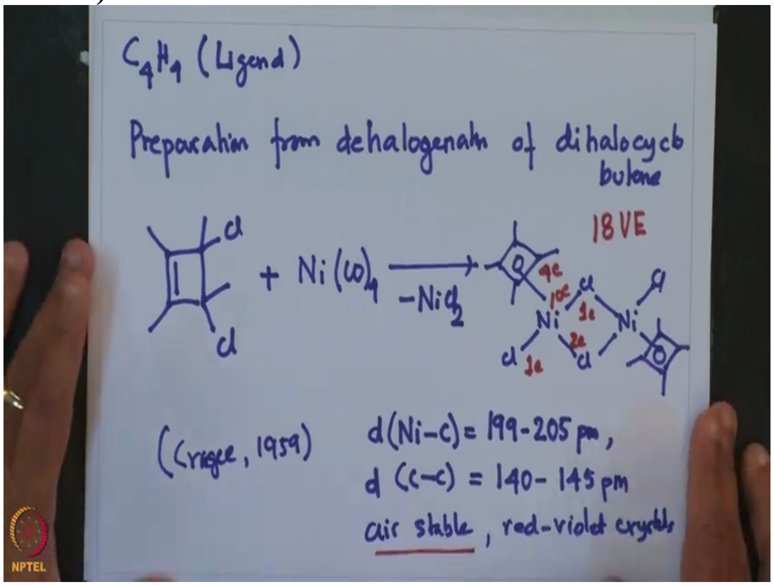

C_4H_4 (Ligand)

Preparation from dehalogenation of dihalocyclobutane

(Crigee, 1959)

d(Ni–C) = 199-205 pm,

d(C–C) = 140- 145 pm

air stable, red-violet crystals

So, let me illustrate that the first available method way back in 1959 was obtained through preparation of dehalogenation of dihalo cyclobutane, the reaction of dihalo cyclobutane where there is only one single bond, and two chlorine atoms with nickel tetracarbonyl results in elimination of nickel Cl2 , so distance of so the these are 140 to 145 picometer, which is, these carbon-carbon bond lines and nickel carbon bond lines are about 199 to 205 picometers. This compound is kind of really stable, air stable, and occurs at red-violet crystals this is an important synthesis reported by Crigie in 1959.

Now the stability of this complex can be ascertained from the electron count and that shows that it itself is a fully 18 electron valence electron compound, and one can do the counting by simple neutral covalent method which will give 4 electrons for this and then 1 for the chlorine 5 nickel is 10 so 15 and then one another covalent 16 and this is a dative bond which will be two electrons, so overall this is a 18 valence electron compound, and this being 18 valence electron compound.

No wonder this compound is air stable and can be crystallized under an ambient conditions, so what we see the power of stabilization of a ligand by complex systems of transition metal is very much evident in these synthesis cyclobutadiene in its square form is diradical in nature, so that means it should be extremely, extremely, extremely reactive, however, when the complex with transition metal, it acquires too far the electron and becomes aromatic and then it is so stable that it can be stabilized by coordination to transition metal.

The compound which is shown over here, that thus, would be an example of half sandwich complex, in the nomenclature that we have discussed earlier and with this I would like to bring on the carton on today's lecture to summarize we have looked into a various important class of organometallic ligand which is cyclo butadiene and we started off by looking at this ligand right from the point of understanding its structure.

According to simple spectroscopic evidence, or according to simple organic chemistry knowledge, cyclopentadiene, butadiene, would have two double bonds and as a result one would expect a rectangular structure with two long bonds and two short CC bonds, but when these compounds of cyclobutadiene are stabilized and with transition metal, one sees fully aromatic square structure where all the CC bonds were equivalent and that gives rise to understanding how the atomic orbitals interact to form such a structure.

And so we have in the beginning of the class we have looked at the origin for the structural variation that addresses this controversy our solve the issue of rectangular versus square structure of cyclo butadiene, not only we have looked at that, we have looked at the cyclo butadiene emos with respect of simple butadiene emos as well as with respect to allyl emos and then made a comparison in terms of the reactivity that may arise from there.

In addition to that we have also looked at the preparative methods available for preparing such beautiful class of cyclobutadiene transition metal complexes, so we will to discuss more of these preparative methods that are available for preparing this fantastic class of cyclo butadiene ligand in the next lecture ah, I again thank you for your patient hearing and we will look forward to have some more intimate discussion on this cyclopentadienyl transition metal complexes in the next lecture, thank you.