Advanced Transition Metal Organometallic Chemistry

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Lecture – 08

Transition Metal Cyclobutadiene Complexes: Reactivity

Welcome to this course on, Advanced Transition Metal Organometallic Chemistry. Today we will to be discussing about transition metal cyclo butadiene complexes, their reactivity, begin to look at another very interesting ligand which probably constitutes the bulk body of organometallic literature. I mean this is quickly about transition metal cyclopentadienyl complexes, so for us if you look at how this lecture is progressing.

We have started with allyl systems which are three carbon systems, then moved on to look at butadiene systems, which are 4 carbon systems, and then we have proceeded further to look at cyclo butadiene system, which is also a 4 carbon but cyclic system, and this has been the focus of our talk, in the last two or three lectures and then we will try to wrap that up in today's lecture and then move on to metal cyclo pentadiene, which is a five carbon system subsequently.

So with this, let me just talk about the reactivity of these metal cyclo butadienyl complexes, now before we have to look at the reactivity of these complexes.

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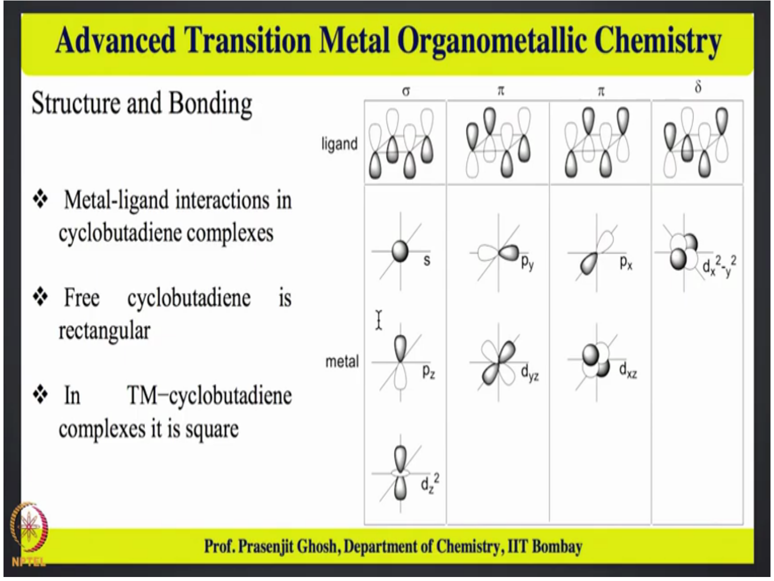

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Structure and Bonding

- ❖ Metal-ligand interactions in cyclobutadiene complexes
- ❖ Free cyclobutadiene is rectangular
- ❖ In TM–cyclobutadiene complexes it is square

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One needs to understand, the metal ligand interaction for these complexes. In our past lecture, I have sort of given a brief comparative perspective of how cyclo butadiene molecular orbitals compare it rigor to butadiene as well as with regard to allyl systems, and today we are going to look at it in bit more depth about which all metal orbitals, interact with what are all ligand orbitals of cyclo butane ring.

With regard to cyclo butane ring, I must mention that I had spoken about their structure, the degeneracy of various a molecular orbital, as a result of its square structure, as opposed to its rectangular structure in which these two Psi 2 and Psi 3 orbital's, which were degenerate would lose their degeneracy and then in that case we would be having 4 different molecular orbitals, Psi one all the way to Psi 4 as was observed in butadiene system.

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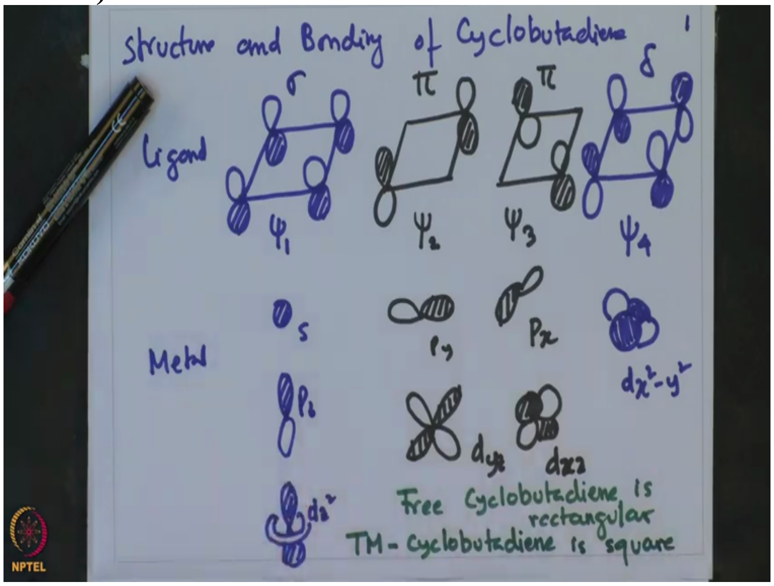

So, structure of bonding of cyclobutadiene, so the ligand would have as discussed earlier 4P orbital's the first one is Psi 1, which is a bonding orbital, so this here, the ligand orbital and the metal orbital that interacts with the Psi 1 ligand orbital, are mainly the ace orbital of the metal or the metal Pz orbital and the metal Dz 2 orbital. So these interaction of Psi 1 with the metal orbitals are primarily of Sigma type that these are Sigma interaction.

Now Sigma interaction is an interaction whereby at the, inter nuclear distance of the interacting atom in this case the ligand and the metal, the electron density should be the highest or maximum. Now if you look at the overlap that would occur between an S orbital and this bottom face of the ligand orbital, you would see, that they would form a sigma bond, and by the definition that maximum electron density resides in the inter nuclear axis between the ligand and the metal interacting atoms.

And the same Sigma bond can also be seen forming with Pz orbitals or Dz 2 orbitals, all moving up from the bottom phase of this Psi 1 ligand orbital, the next orbital for cyclo butadiene is a Psi 2 orbital and this is Psi 2 and similarly one can write Psi 3 as, so these two are shown in black, are the degenerate orbitals, that results the square structure of cyclo butadiene ring, these provides the diradical character of cyclo butadiene.

And they interact with metal orbitals, for example Psi 2 interacting with Py and Psi 3 interacting with Px. Now the orientations of this Pi and Py are such that they form Pi type overlap with the metal orbitals and corresponding the D orbitals that interact with Psi 2 are dyz and dxz, so these are metal orbitals which sort of interact or which interact with the Psi 2 and Psi 3 of the cyclo butadiene ligand, this can the middle orbitals can arise from P P orbitals Py for Psi 2 and Px for Psi 3.

As well as D orbitals like dyz for Psi 2 and the dxz for Psi 3, now these interactions, ease of Pi type, Pi type in the sense that, if this orbital were to interact with this, so this slope will interact with that, and this slope would with interrupt with this, so between the inter nuclear distance of the interacting atoms, there will be no residual electron density but it will be above and below the plane the plane of the containing the interacting inter nuclear axis.

So this interaction is a Pi type one can conceive along the same line that D orbital interacting with Psi 2, where this low will interact with that, and this low will interact with that, again such a interaction is Pi type interaction. Now Psi 2 and Psi 3 are degenerate they are complementary to each other and similarly one can envision likewise kind of interaction a Pi type when this lobe is interact with that and this will be for the Px orbital and likewise for the orbitals these two orbitals will interact with these two orbitals for the dxz.

Now the last is an anti-bonding orbital, this is sigma, then two degenerate Pi orbitals, that the both the degenerate Pi orbitals are shown in the black, and the last set of orbital is anti-bonding orbital, and so this is termed as Psi 4 and this interacts with dx 2 y 2 orbitals okay this is dx 2 y 2 orbital and this interaction is kind of one of its kind and these are called delta type of interaction where the whole of the dx 2 y 2 orbitals interact sidewise, with the bottom phase of Psi 4.

Now this diagram clearly presents to you, how the cyclobutadiene orbital interacts with different metal orbitals. Now apart from the various kind of interactions like the sigma interaction to Pi type interaction and one delta type interaction one can also see that the strength of the interaction obviously would vary. For example a sigma interaction would be the most stronger one followed by Pi type interaction, and among all these 4 interactions delta is the weakest kind of interaction, one can envision.

So, these diagram provides a brief overview of how cyclobutadiene moiety interacts with various kinds of metal based orbitals, and it also sort of gives you the feeling why after interaction of cyclobutadiene with the metal center, did not show a square geometry, whereas in free cyclobutadiene is a rectangular structure, so free cyclo butadiene is rectangular, whereas transition metal cyclo butadiene is square.

You know this diagram explicitly explains the reason for such difference in structure before and after binding to transition metal complex. As mentioned in the earlier discussion, that tension cyclo butadiene attains aromaticity by binding to transition metal, because it goes from a diradical neutral state to our dianionic aromatic state containing 6 Pi electron as a result of electron donation from the middle.

Now having attained aromatic structure, the cyclo butadiene ligand also behaves like an aromatic compound, for example, it can go exhibit electrophilic substitution reactions similar to that observed in any other aromatic compounds, for example in benzene. So now we will to look at some interesting reactions exhibited by transition metal cyclo butadiene complexes as a part of their reactivity study.

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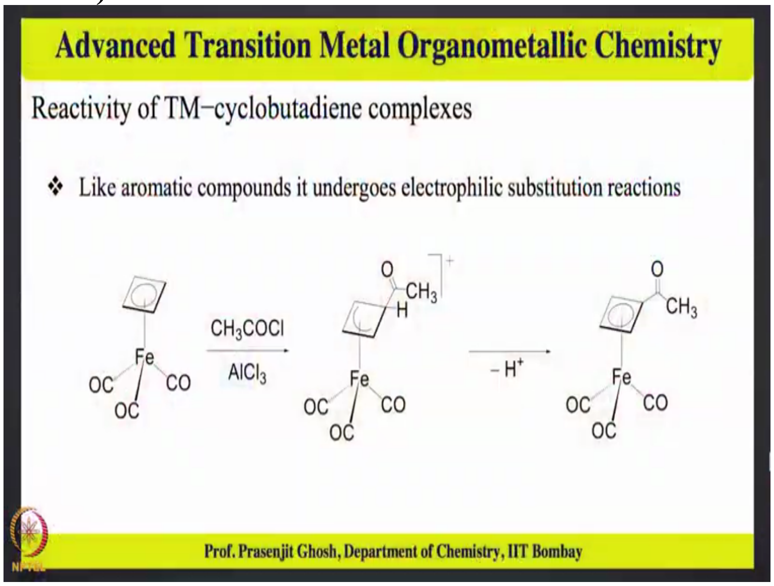

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Reactivity of TM−cyclobutadiene complexes

❖ Like aromatic compounds it undergoes electrophilic substitution reactions

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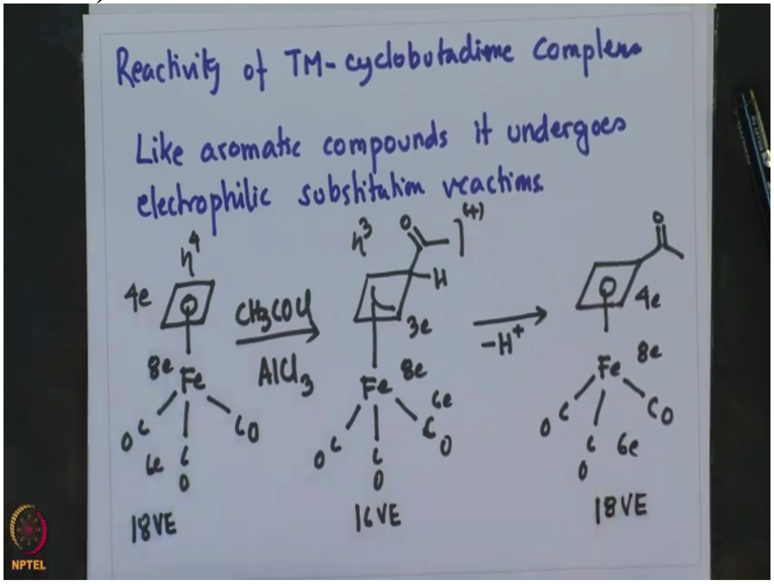

Reactivity of TM-cyclobutadiene complexes

Like aromatic compounds it undergoes electrophilic substitution reactions.

So, like aromatic compounds it undergoes electrophilic substitution reactions, for example the reaction of these half-sandwich compound, cyclo butadiene iron with CH3 CO Cl in presence of Al Cl3 like any standard oscillation reaction, the eta 4 bound cyclo pentadiene converts to eta 3 bound allylic ligand similar to one shown over here and the electrophilic substitution occurs at the ring needless to say that both of these are 18 electron compounds.

For example 4 from cyclobutadiene, then 8 trait overall making 12 and 6 electrons from C, 3 COs so 12 plus 6 18, this is the 18 valence electron compound and upon reaction with acetyl chloride this eta 4, bound cyclobutadiene ligand transforms to eta 3 bound allyl ligand, and here too, the the complex become 3 from the ligand 8 from the metal so and 6 so this is 17 electron with a cationic charge.

So, overall it becomes a 16 valence electron compound which sort of is not too stable loses back its proton to give the isolated cyclobutadiene compound Biron bound to iron tricarbonal. So, now this again attains the 18 valence electron compound structures. So what we see that similar to what a normal aromatic compounds exhibit that they undergo electrophilic substitution reaction here also we saw that these hydrogen of cyclo one of the hydrogen of the ring hydrogen's of cyclo butadiene can be made to substitute with, as acetyl chloride giving CH3 CO bound cyclobutadiene ring.

And that reaction is very much similar to what is observed for aromatic electrophilic substitution reaction, in the process, the hapticity of cyclo butadiene changes from eta 4 are in the reactant to eta 3 allyl type in an intermediate compound back to eta 4 in the substituted oscillator cyclobutadiene and ring and as far as the total valence electron of the complex is concerned, it goes from 18 valence electron to 16 valence electron in this cationic compound to back to 18 valence electron in the isolated cyclobutadiene and ring compound. Cyclo butadiene ring having CH2 X substituent's are very easy to solvolyse are readily undergoes solvolysis and here is an example.

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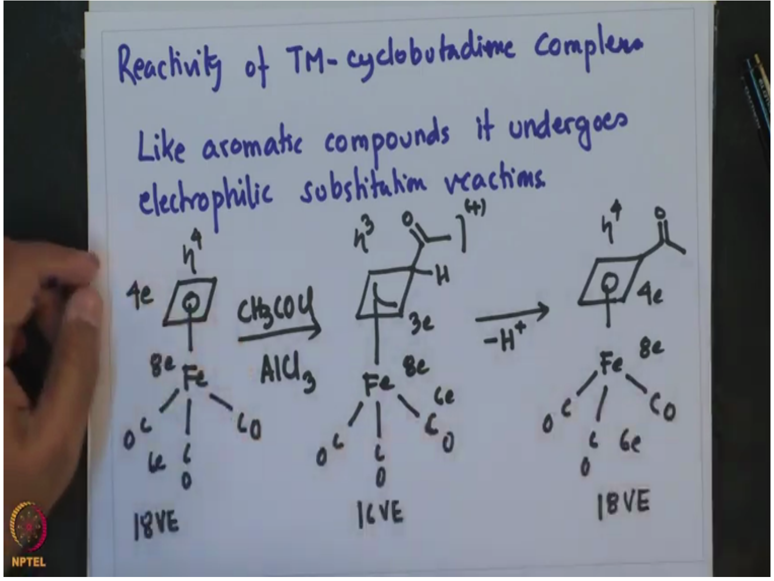

Reactivity of TM-cyclobutadiene Complexes

Like aromatic compounds it undergoes electrophilic substitution reactions.

or example, cyclobutadiene CH2 Cl with Fe CO3 in presence of Sb Cl5 a halide abstraction occurs resulting in elimination of Sb Cl6$^-$ and generation of these compound which is cyclo butadiene CH 2 + Fe CO3 now these charge CH2 plus charge as adjacent to the cyclobutadiene ring is resonance stabilized, resulting in an exocyclic double bond and eta 3 allyl compound where the net positive charge is now delocalized in the ring, bound to Fe CO3 compound and that then reacts with OH$^-$ giving these CH to OH, Fe CO3 compound.

So, this is an interesting reaction where we saw that CH2 halide moiety on the substituent of the cyclo butadiene ring is prone to solvolysis and the reason is because of the stabilization of the charge that is generated upon the leading of the halide group and subsequent attack of the OH$^-$ results in the formation of the alcohol. Likewise one can go reverse by having a proton which will protonate this alcohol and then eliminating water one can also generate these cyclo butadienyl stabilized cation which can then fire further undergo or solve Elise's reaction.

Another very important aspect of cyclobutadiene transitional compound is the fact that they are source of free butadiene for various organic transformations.

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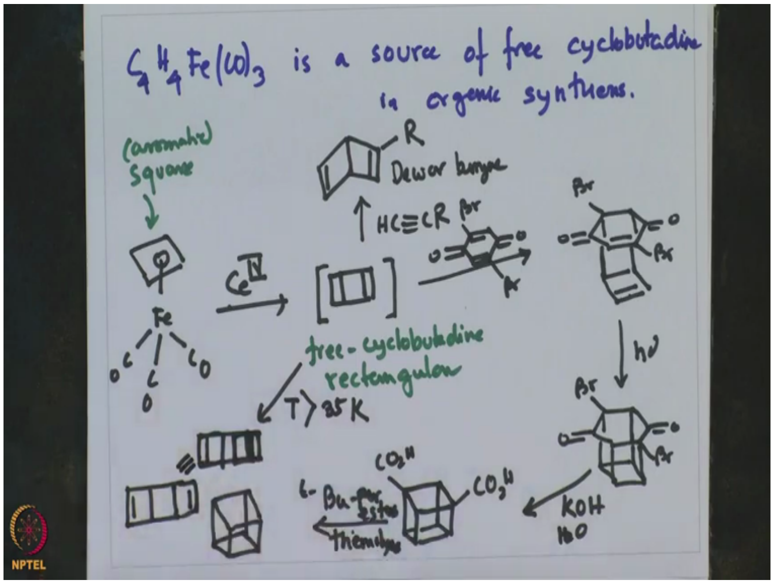

$C_4H_4Fe(CO)_3$ is a source of free cyclobutadine in organic synthens.

For example C4 H4 Fe CO3 is source of free cyclobutadiene in organic synthesis. So this I will explain with an extremely intriguing source of reactions which will show that they can be effectively used for synthesizing many different kinds of organic compounds where C4 cyclobutadiene Fe CO3 is a source for free cyclo butadiene, for example, the compound C4 H4, CO, FeCO3 a in presence of an oxidant, cerium 4, produces cyclo butadiene.

Ok now please note the structure which is written over here is of free cyclo free cyclo butadiene and hence rectangular, whereas this one is symmetrical and bound to aromatic and hence square. So, upon D complexation cyclobutane ring changes from square geometry to a rectangular geometry, which can react with acetylene, terminal acetylenes, giving these debar benzene compounds.

So, this is just 2 + 2 cycloaddition of one of these double bond with that of the olefinic link resulting in these dewar benzene compounds, it can also react with quinine's to give this cycloaddition product so here one of these undergoes 2+2 cycloaddition with the quinine which in presence of light and further undergo 2+2 cycloaddition reaction leading to the formation of cubic compound of the typeface that in presence of KOH, water keeps this compound of cubic structure.

And that in presence of t-butyl part esters and thermolysis gives d carboxylates and gives this perfect cube ends. And also for this free cyclo butadiene at temperature is the kind of unstable at

35 degree Kelvin undergoes reaction to give this, so this is undergo dimerization, so as if two of the cyclo butadiene unit, two of these unit, has dimerizes to give this compound. So we have two of this cyclo butadiene with two double bonds in the end.

So, what this provides is a rich chemistry that transition metal cyclo butadiene complex can give that can give rise to plethora of compounds very difficult to synthesize otherwise, and that can all arise from this simple precursor of cyclo butadiene iron tricarbonal, so with that I will conclude today's lecture hopefully yeah I think he will go home with appreciation for various kinds of different and intriguing chemistry exhibited by cyclo butadiene iron tricarbonal compounds.

As well as other cyclo butadiene transition metal compounds and with that we conclude our discussion on cyclo butadiene complex and then we will take it up further in the next class where not only we will just look a little bit more up on these cyclobutadiene transitional complexes but also on cyclopentadienyl complexes which form substantial body of literature in transition metal organometallic chemistry. So with that thank you and I look forward to being with you in the next lecture.