Advanced Transition Metal Organometallic Chemistry
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Lecture – 11
Transition Metal Cyclopentadiene Complexes: Bonding Properties

Welcome to this eleventh lecture of this Organometallic Course entitled and once Transition Metal Organometallic Chemistry. We have been discussing and very interesting topic over the last two lectures and these are about transition metal cyclopentadienyl complexes particularly with respect to their synthesis and more importantly in the last lecture we have looked into their structure and bonding.

By structure and bonding, I mean we looked into atomic orbitals as well as the molecular orbitals who formed from the atomic orbitals of the cyclo pentadienyl decant, and then their subsequent interaction with the transition metal orbitals. Now in this discussion let me just recapitulate what we had spoken about in the last class, so that we can build on it in this class and take it further. In the previous class we had looked into the atomic P orbitals of the CP ligands and based on their symmetry based combinations.

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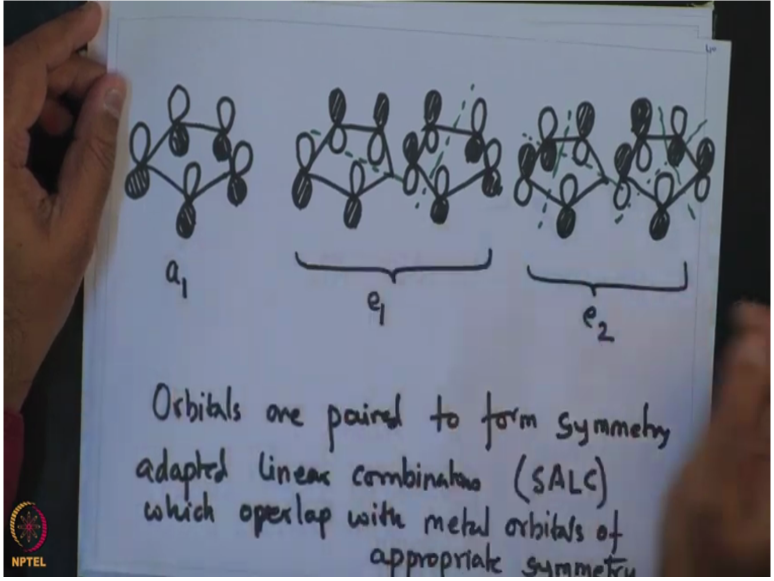

Orbitals are paired to form symmetry adapted linear combinations (SALC) which overlap with metal orbitals of appropriate symmetry

There are five P orbital's resulting in 5 molecular orbital's, and of these 5 molecular orbital's they fall into 3 classes. One is a1 molecular orbital, which is fully bonding in nature versus e1, these are degenerate set of orbitals, with having one nodal plane, and then subsequently e2, they are again degenerate set of orbitals, having two model planes, so a1 having zero nodal plane lowest in energy followed by e1 followed by e2 having two nodal planes and these are also degenerate two orbitals.

So, these orbitals are formed from linear combination of atomic orbital based on symmetry. Now when one looks into the metallocene transition metal orbital interaction, then one has to consider, 2 CP’s in eclipsed are in staggered conformations and that is illustrate over here. So in this case what we had shown is there are 2 CP in staggered form the reason the staggered form is chosen because between eclipsed.

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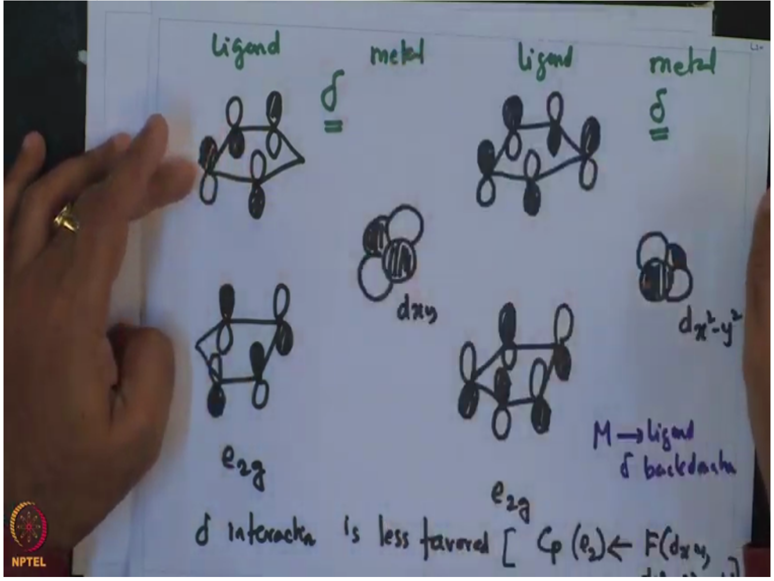

And staggered form for ferrocene the staggered form was found to be more stable. Having considered these staggered form were 2 CPS are mutually facing each other in opposite direction so as to get a staggered conformation, we looking into the various metal orbital’s that would get involved or yet get interact individually with a1 e1 and e2 type ligand orbital’s. In our last class we have also looked into this interaction starting with e2, where the metal orbitals of different symmetry, reacted with e2.

Now these metal orbital reacting with the ligand orbitals, these interactions is of delta type. The delta type means that these are face-on interactions, where one phase of the D orbital, reacts with the face of the CP ligand, and what we had seen that there are two possible combinations of these interaction, one is e2g with the dxy orbital.

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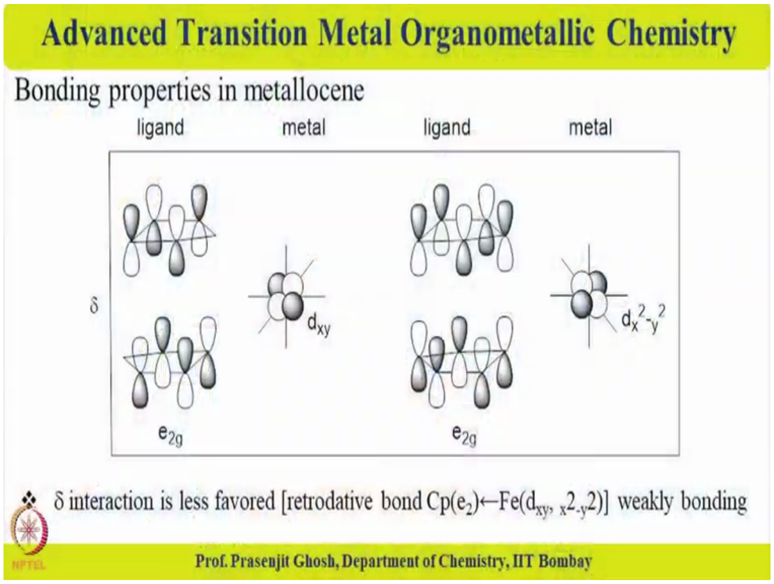

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Bonding properties in metallocene

- δ interaction is less favored [retrodative bond $Cp(e_2) \leftarrow Fe(d_{xy}, {}_{x^2-y^2})$] weakly bonding

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G is the gerade symmetry likewise, one can have a opposite symmetry of U type and then the metal orbitals reacting for this is dx square - y square. These delta interactions are weaker in nature compared to Sigma and PI interactions and then we are going to discuss that in bit more details.

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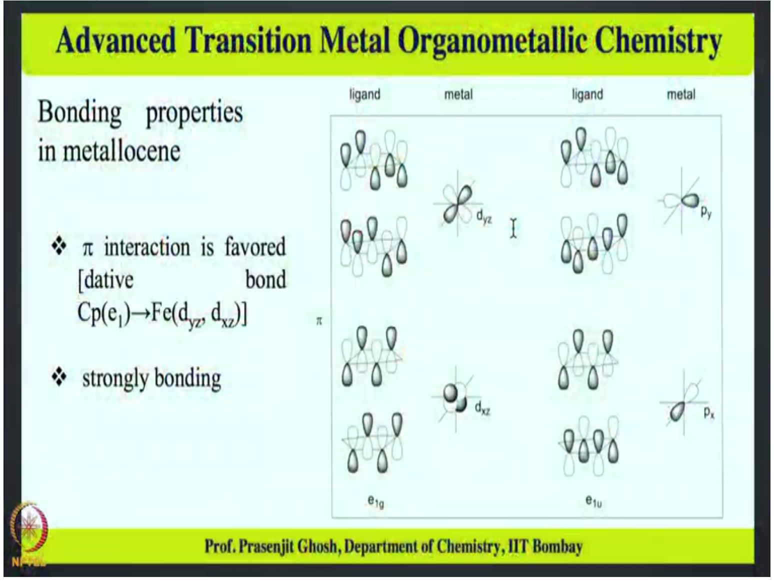

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Bonding properties in metallocene

- π interaction is favored [dative bond $Cp(e_1) \rightarrow Fe(d_{yz}, d_{xz})$]
- strongly bonding

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After the delta interaction, the next interaction is about the PI interaction.

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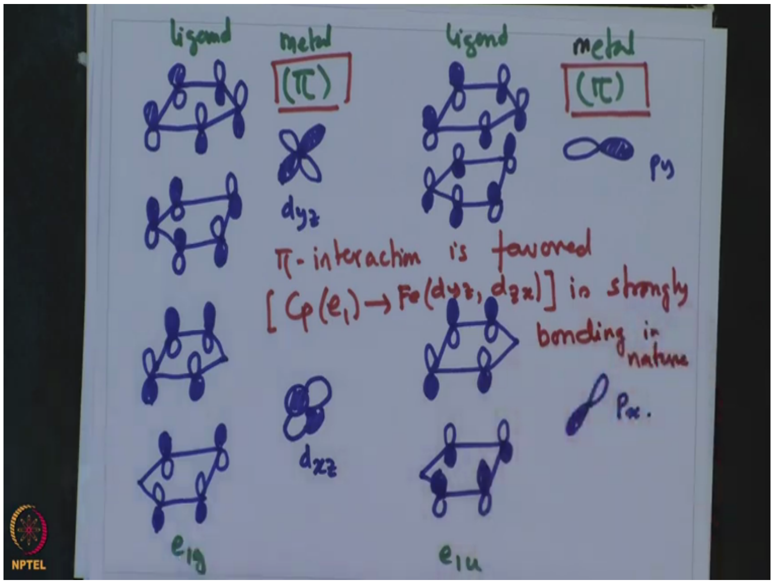

And the ligand PI orbitals, are of this type, and the metal orbital interacting with it dyz, and this is a PI type interaction. Now these are set of degenerate orbitals and similarly the opposite combination and that reacts with py of the metal. This also is a PI type interaction. So, these are e1g orbital, and also involves a PI type interaction, the orbital involved is the dxz, similarly the other combination is as shown over here and this is called e1u, and the corresponding P orbital of the ligand is Px. Now these PI interactions are of the ligand to the metal.

These is the most important of the three interactions that CP has with the metal, these three types of interactions being delta, which we had discussed in the earlier class, and these two kinds of PI type interaction followed by the Sigma interaction that we would be discussing subsequently. So of the three types of interaction, that a CP ligand makes with the transition metal these all these 4 PI kind of interaction is by far the most important and the most favoured one.

So, the take-home message is PI interaction is favoured dative bond between CPe1 to Fe dyz dzx is strongly bonding in nature. So this is a kind of unique thing about metal cyclo pentadienyl interaction, let me just reiterate the metal cyclo pentadienyl interaction can be of three type, first is delta which is weaker, followed by this PI which is strongly bonding, which comprises of the maximum extent of bonding, followed by Sigma. Now usually, the convention is that PI bond or PI interactions always weaker than Sigma.

So, the conventional wisdom is that Sigma is the most single strongest component of bonding followed by PI followed by Delta, but here we would see something more, something unique, happening here, we see that Sigma is almost nonbonding, so Sigma is almost zero PI is the most strongest component followed by delta which is weaker.

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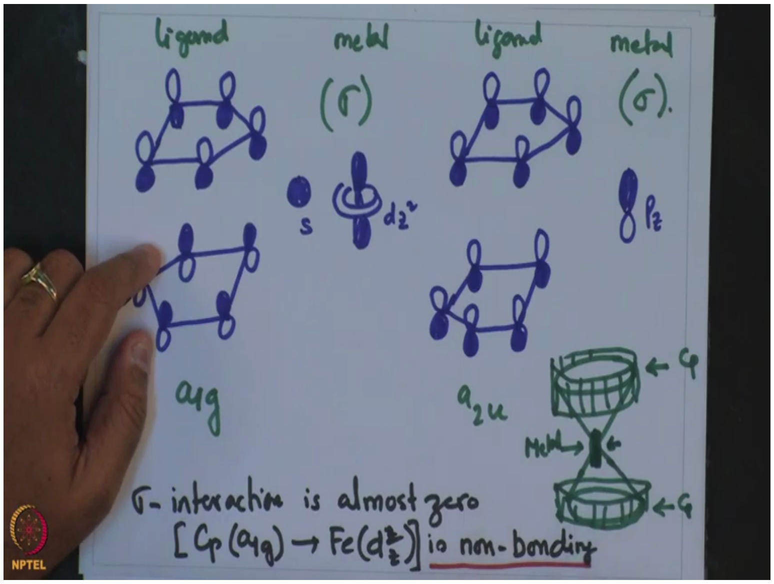

σ- interaction is almost zero

[Cp (a1g) → Fe(d_{z^2})] is non-bonding

One can draw the Sigma orbitals. So, these are ligand fragment molecular FMOs, and metal the metal actually can interact with two orbitals one is the S type, as well as the dz square, okay and this is called a1g, and this is a Sigma type interaction. Similarly the other combination is, this is called a2u, corresponding metal orbital is PZ, and this also is a sigma type interaction. Now this Sigma interaction in metal is almost zero, so CP a1g Fe pdz square is nonbonding.

So, this is a very important take home message from this discussion that usually Sigma bonding interaction always are the most strongest form of interaction and beyond Sigma, then the PI interaction happens by interaction never most of the cases is a standalone interaction because Sigma involves head-on overlap, whereas PI involves, sidewise overlap. So it has always been the case that PI interaction always occurs over and above us influencing the interaction.

But here in this transition metal cyclopentadienyl interaction, in what we find that Sigma interaction is almost nonbonding, so nonexistent, and the predominant nature or standalone form of bonding, is indeed the PI interaction followed by a very weaker Delta direct interaction.

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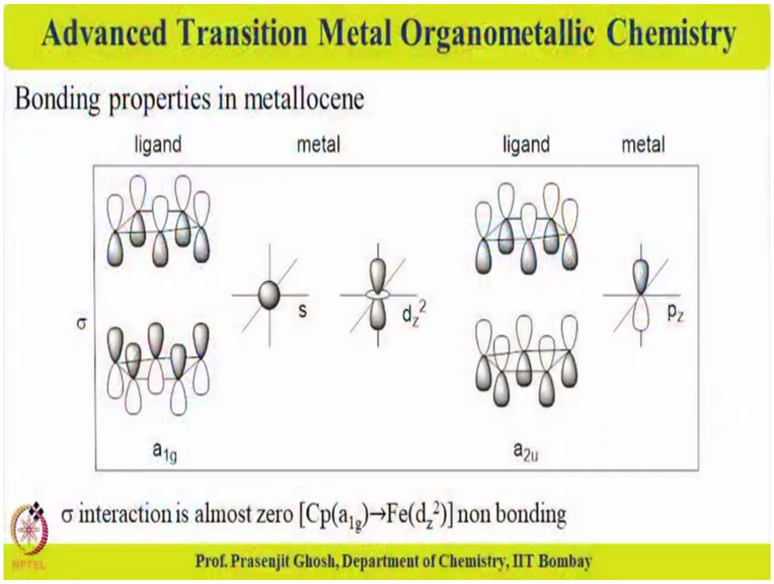

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Bonding properties in metallocene

σ interaction is almost zero $[Cp(a_{1g}) \rightarrow Fe(d_{z^2})]$ non bonding

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As for this nonbonding Sigma interaction is in concerned. Let me explain this through a simple drawing, now if one are to look at this orientation of CP as well as the metal, so these sort of can be represented by conical diagram like this well these faces represents the CP rings and the metal represents this point.

Now if one were to look at these ligand orbitals the law or the CP orbitals the CP orbitals would be along the periphery of the ring, somewhere over here, same thing over here whereas the metal orbitals, will be in the core will be somewhere over here. So, actually in principle the match of overlap between this peripheral orbital to that of the metal orbitals which directed at the center physically would be almost none and that that is why it explains the nonbonding nature of the Sigma interaction.

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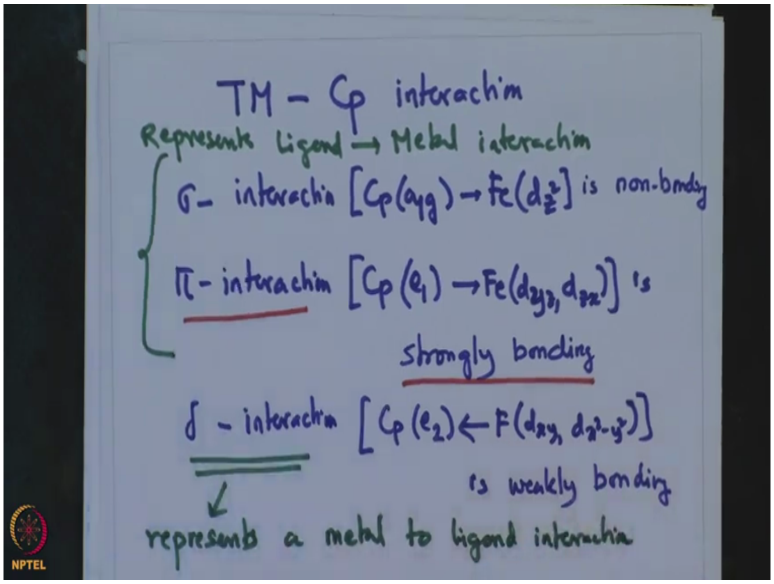

TM – Cp interaction

Represents Ligand → Metal interaction

σ- interaction [$Cp(a_{1g}) \rightarrow Fe(d_{z^2})$] is non-bonding

π- interaction [$Cp(e_1) \rightarrow Fe(d_{yz}, d_{xz})$] is strongly bonding

δ - interaction [$Cp(e_2) \leftarrow F(d_{xy}, d_{x^2-y^2})$] is weakly bonding

↓ represents a metal to ligand interaction

For transition metal CP interaction, Sigma is nonbonding by interaction, is strongly bonding Delta interaction of this type CPe2 is weakly bonding. Both Sigma and PI represents ligand to metal interaction whereas the Delta interaction represents metal to ligand interaction.

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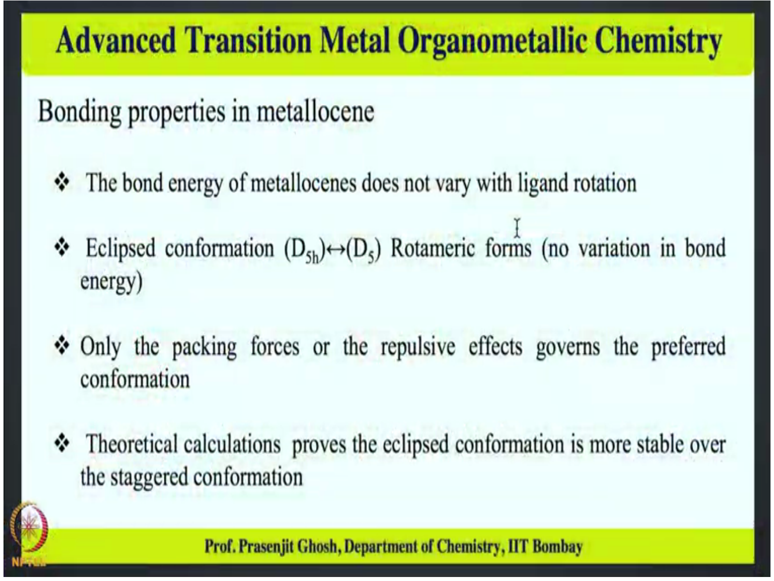

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Bonding properties in metallocene

- The bond energy of metallocenes does not vary with ligand rotation
- Eclipsed conformation (D_{5h})↔(D_5) Rotameric forms (no variation in bond energy)
- Only the packing forces or the repulsive effects governs the preferred conformation
- Theoretical calculations proves the eclipsed conformation is more stable over the staggered conformation

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Another important aspect is that metallocene complexes can exist in two symmetrical forms.

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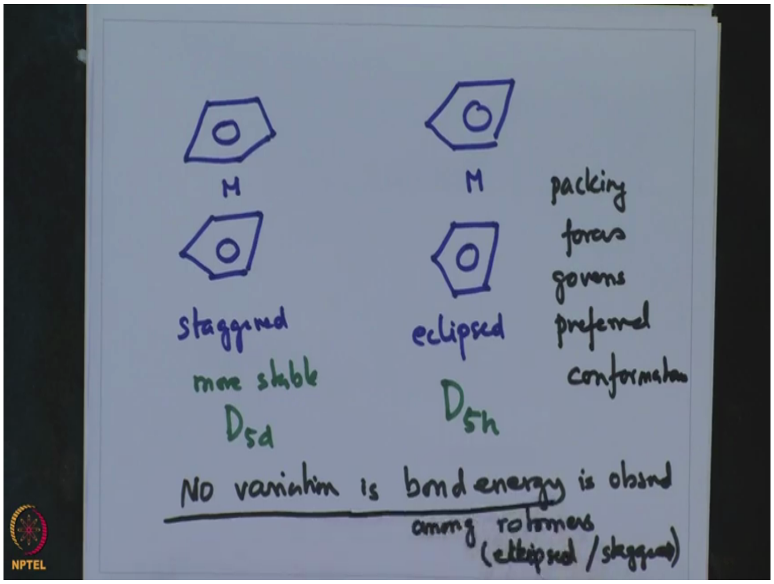

One is the staggered form staggered and the other one is the eclipsed. The staggered form is more stable and its point group is 5d where as the eclipsed form is d-5h. Now the important thing is that the orbital energy, does not change our bond energy does not change in going from the staggered to the eclipsed forms, bond no variation, in bond, energy is observed among robomers, eclipsed or staggered, okay.

Now also the second important point is packing forces, forces governs preferred conformations. So with this I would like to conclude today's discussion in which we have really looked into this cyclopentadienyl transition metal interaction right from the scratch and then looked into how the orbitals interact with the transition metal and we came up with the conclusion, that this is any kind of interaction, where the PI interaction is predominant Sigma and Delta components are negligible or non-existent.

And also we have looked into the variation of these orbital energies as a result of change from one conformation to other. So, based on these, we are going to do some more detailed molecular orbital treatment on this transition metal cyclo pentadienyl interaction and now that would continue in the next lecture and looking forward to taking up this topic in more detail in the next lecture, thank you.