Advanced Transition Metal Organometallic Chemistry
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Lecture – 23
Transition Metal Arene Complexes: Structure and Bonding

Welcome to this course on advanced transition metal ornamental chemistry we have been talking about transition metal arene complexes its structure and bonding over the last few lectures. In the past lecture we had seen in this regard that how the P orbitals of arene's particularly in benzene stack up using this linear combination of each other to form a various fragment molecular orbital. So, what we have seen that 6 P orbitals in benzene they align itself to form 4 sets of orbitals.

These are particularly a 2u which is the bonding orbital having no nodes followed by e 1g there are 2 W degenerate two sets of orbitals having one nodal plane then comes e 2u which is again W degenerate set of two orbitals having two nodal planes and lastly it comes to b 2g which is anti-bonding orbital having three nodal planes. Now these orbital the stack up in 4 sets of our set suborbital energy carry and the division is 1:2, 2:1 and now it is important to construct molecular orbital in this arene complex using these 4 sets of energetically a different molecular orbital.

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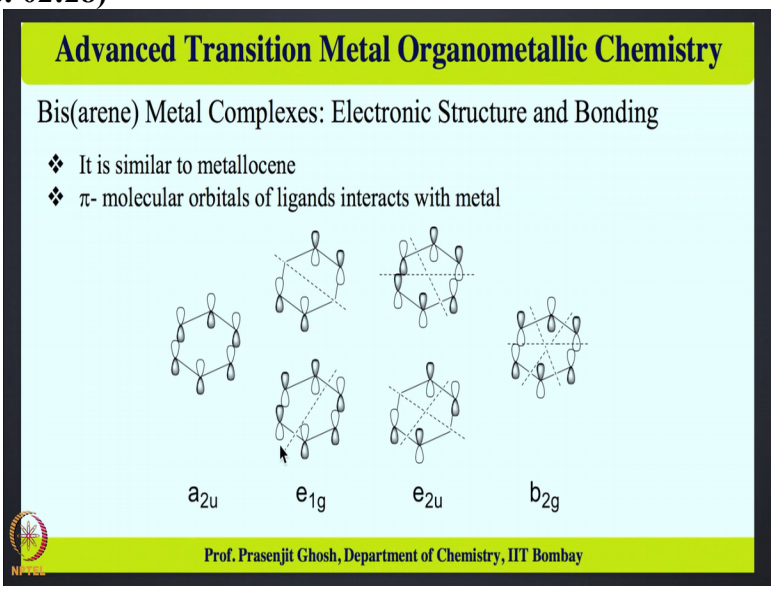

Now before we do that it is sort of see how these 6 orbitals a 2j e 1g e 2u and b 2g a sort of align themselves you have to interact with various possible metal orbitals. So, we start off with the Sigma interaction which is shown over here. For example for the a 1g orbital this is a Bis-arene

metal complexes where we have 2 benzene rings of 6 P orbitals H, so a 1g combination is something like this.

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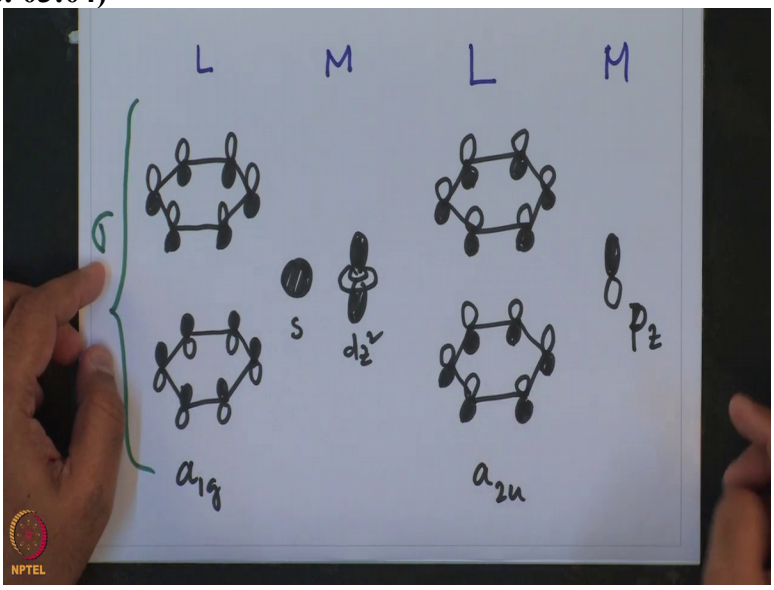

So, this is a 1g and it can interact this was a 1g ligand orbital and the following metal orbital that it can interact with are s and dz 2. Similarly the other combination would be e 2u where they would just flip over to give a combination of something like this. So, in this alignment the dark shapes around the bottom and the top of the ring but in this alignment a 2u the dark shapes are both at the bottom of the ring and the corresponding metal orbital that would be interacting with it would be Pz.

The interesting thing about these interactions are that all of these interactions are Sigma type interaction we are like you know the electron density is maximum the inter interacting inter nuclear access okay. So, oh these a 1d orbital of benzene in Bis-arene complex would thus interact in a sigma fashion with s and dz 2 as well as a 2u would interact in a sigma fashion with Pz orbital.

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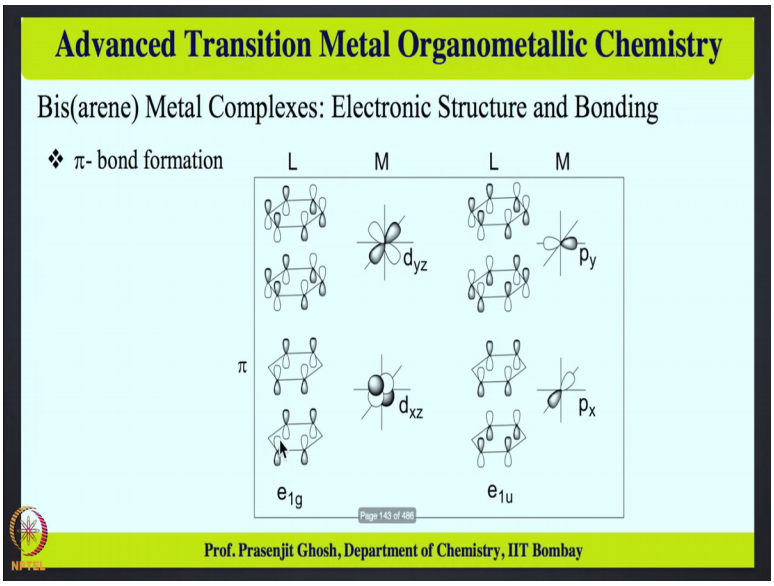

Now let us take a look at orbitals which would be interacting in a PI fashion.

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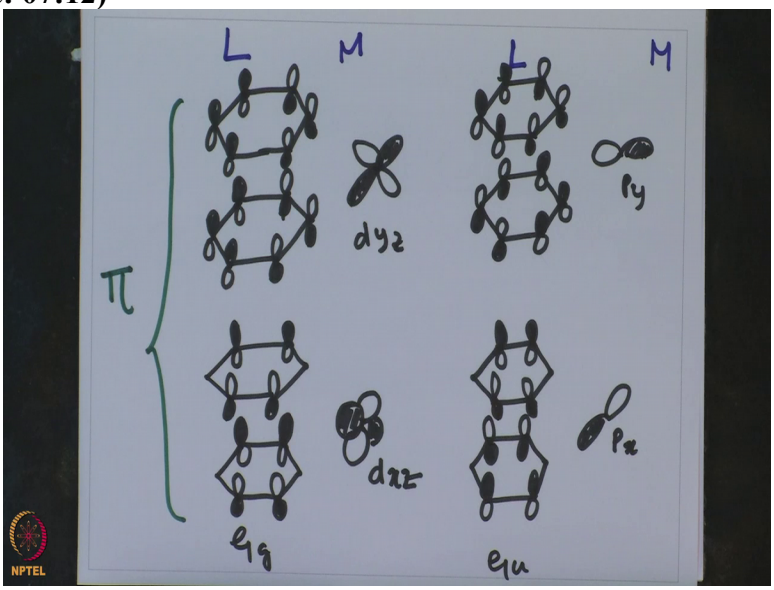

And these are e 1g for the ligand so I am going to show it over here the corresponding orbitals over here would does be and the metal orbital would be the dxz the other the other combination is e 1u, so this is the metal orbital the other ligand orbital combination would be e1 u which would again have the following combinations of orbital's. In this case it is; and the orbital which of the metal would be Px.

Similarly the for the other e 1d orbital the combinations are which is of this combination and the metal orbital involves or accordingly dyz and similarly the combination over here would be something like this and the corresponding metal orbital would be a Py. Now these 4 sets of

orbital this is of gerade symmetry and this is slipped over here ungerade symmetry this also is a gerade asymmetry that flipped over here is ungerade symmetry.

So, they would combine with a dyz, dxz Py and Px and all of these reflects PI type interaction all of these reflects PI type interaction with the ligand interaction with the metal.

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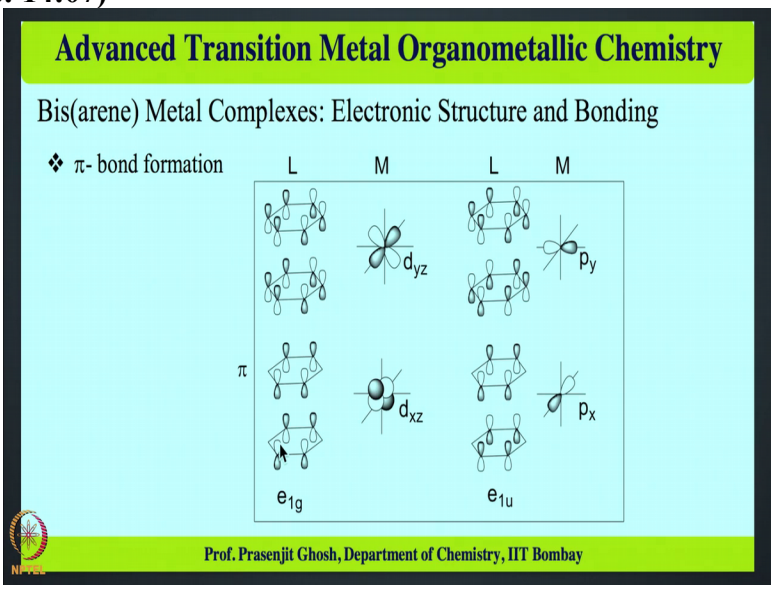

So, now the last, set of orbitals are that involved in Delta type interactions are shown over here.

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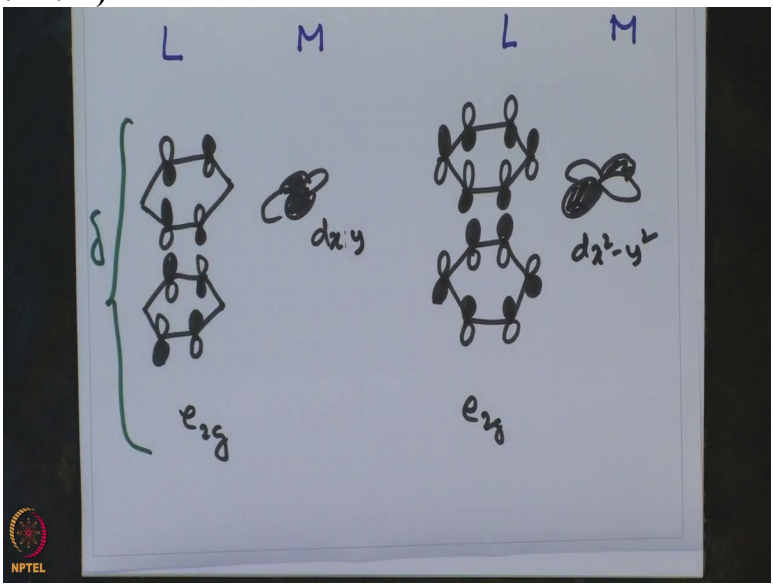

So, here this involves e 2g orbital of this combination that would be interacting with dxy and the other that involves is this combination and this dx 2 - y 2 and these orbitals are involved in Delta type of interaction.

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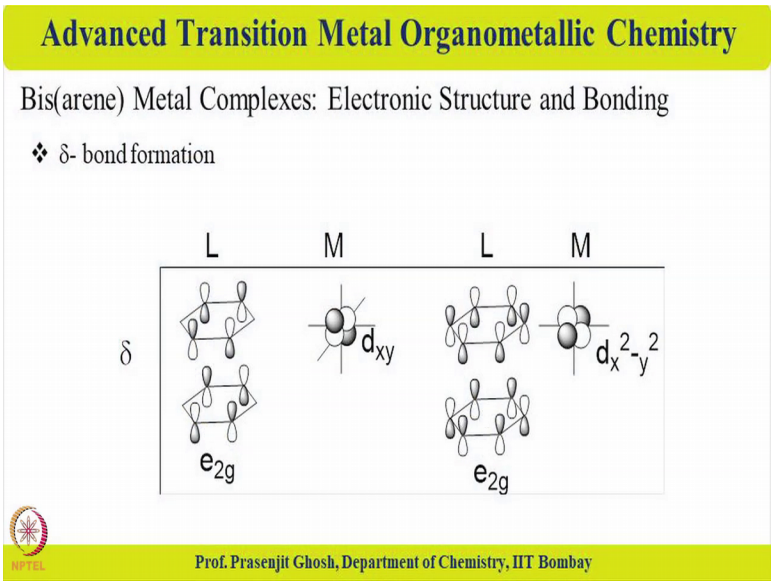

So, we had seen that how these 6 orbitals benzene orbitals you know combined with the metal orbitals resulting in three kinds of interaction sigma, Pi and delta types and the corresponding ligand orbitals which are involved in such interaction is shown over here. So, now we are going to move on to the most important aspect of it which involves this construction of the molecular orbital correlation diagram.

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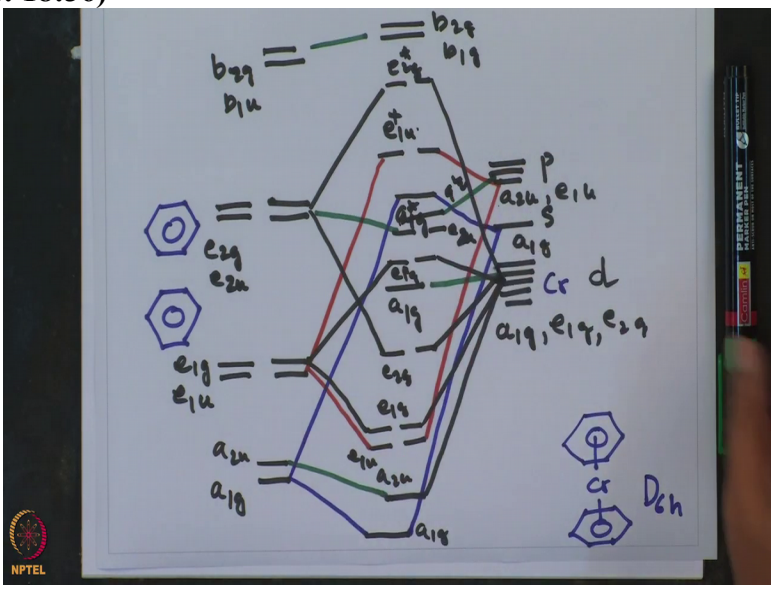

And this is done for the eclipsed conformation of this benzene chromium complex as an example of case study the symmetry is d68 and we are going to construct this molecular orbital. Now as far as the; this benzene is concerned in the least conformation its ligand orbitals are a 1g and a 2u similarly e 1g and e 1u this will be e 2g and E 2u and finally b 2g and b 1u so 6 yeah each 6 having a 12 set of orbital 2, 4, 6, 8, 10, 12 of gerade symmetry.

Similarly as far as the chromium is concerned there are five d orbitals these are d orbitals and they are off a 1g, e 1g and e 2g symmetry then there is one s orbital which is a 1g and then there are 3 P orbitals and this is a 2u and e1u symmetry. Now let us see how these orbital interacts with each other the for example a 2, a 2u is kind of nonbonding in nature and what remains by itself this is a 2u ok.

Now a 1g a 1g interacts with a 1g of the metal which is a 1gs of the metal giving bonding a 1d orbital and over here a 1g star orbitals. So, the correlation diagram is somewhat over here so this a 1g now is occupied as a result the a 1g of the symmetry of the metal orbital remains nonbonding a 1g remains nonbonding. All the nonbonding orbitals are shown in green and e 1g interacts with e 1g of d orbitals e1 g of d orbitals.

And then correspondingly it is e 1g star somewhere over here and that is e 1g star and e 1u of the beneze interacts with e 1u of the p orbital e 1u and the corresponding e 1u of the p orbitals e star 1u and that is shown over here e 1u, so this is now fully engaged one with this none of this, this one is also engaged one is nonbonding. Now we come to this e 2u is a nonbonding orbital e 2u is a nonbonding orbital and e 2g interacts with e 2g of this.

So that is shown over here e 2g and e 2g interacts giving e 2g star and as a result so one of these is nonbonding the other one interaction well here. Similarly for this e 2, e 1g is interacting and e2 e2 u is a nonbonding somewhere here a 2u that is a nonbonding orbital which is somewhere here and these orbitals b 2g and b 1g remains b 1g remains unaffected. So, what sort of comes out over here that between the 2 ag combination one is nonbonding in nature whereas between b 2u both are engaged and one is nonbonding for this, and similarly for the p orbital one remains nonbonding.

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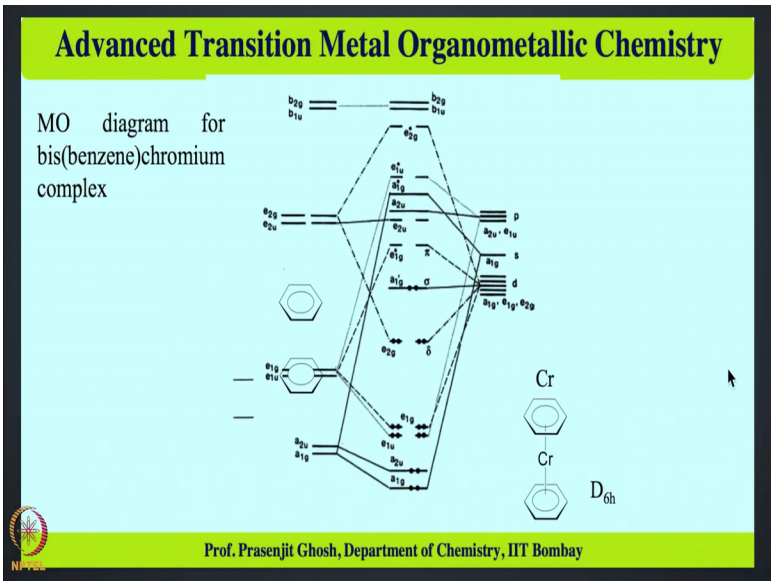

Now these is done in a qualitative way the most quantitative picture obviously is given in the screen it is important that one sort of constructs at this molecular orbital just to give get a feel for all the bonding and the non bonding orbitals and how they interact. So, with this I come to the conclusion of today's lecture where we have seen the construction of the molecular orbital for Bis-arene complexes.

How they interact and which remains's bonding anti bonding and non-bonding and that sort of explains the electronic structure of these compounds. So, with this I conclude today's lecture and we are going to be taking up the structure and bonding in bit more detail and followed by the reactivity of these arene complexes in the next class till then, good bye and thank you