Transition Metal Organometallic Chemistry: Principles to Applications

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Lecture - 06
Week - 02
18 Valence Electron Rule and Classification

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. In the previous lecture, we were looking at the very famous 18 valence electron rules, and the classification of organic organometallic compounds based on 18 VE rule. In that regard what we saw that there are three classes of compounds. Class one which does not obey the 18 valence electron rule; class two does not exceed 18 valence electron rule; and class three which obeys 18 valence electron rule. Of this three classes that we had discussed we had looked at the molecular orbital picture of the metal interacting with the ligand and tried to explain what was the reason for various classes of compounds. In class one, what we saw was the metal orbitals interacting with sigma six sigma ligand orbitals.

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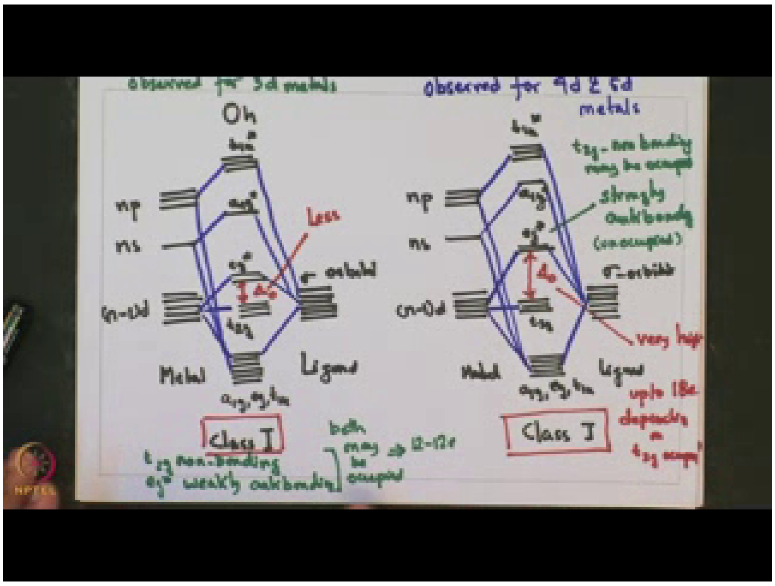

This metal orbital involve 5 n minus 1 d of metal 1 s and 3 n p orbital interacting with 6 ligand sigma orbital of ligand in a octahedral environment. So, what we had seen that as a result of the sigma interactions, there are 6 ligand orbital interacting with 2 d orbital 1 s orbital 3 p orbital resulting in 6 bonding orbitals. These are a 1 g, e g, t 1 u and that giving rise to 2 e g star antibonding orbital. And there are 3 ligand d orbitals which are non bonding, they are t 2 g; and 1 antibonding p orbital a 1 g star, and 3 antibonding t 1 u star. So, this is what we had seen in class one compounds.

And what is the term which is of foremost interest is this difference in energy between t 2 g and e g star referred to as delta 0. And what it says that this t 2 g was non-bonding, and e g s star weakly antibonding which implies that both can be populated implying further that it can have about 12 to 22 electrons. And hence the class one type of complexes do not obey the 18 valence electron rule.

With that in mind, now let us take a look at class two type of complexes. Here also metal has similar 5 n minus 1 d orbital 1 n s orbital and 3 n p orbital. In this case also, it interacts with 6 sigma orbitals of the ligands. Giving 6 bonding orbitals and that leaves with 3 non bonding e 2 g levels, which are basically d orbitals of the metal; and these 6 bonding orbital would result in 6 antibonding orbital. And similar to what has been encountered in the class one ligand, what we have over here is a similar diagram with the subtle difference. The subtle difference being that this delta 0 is much higher than the delta 0 over here. This delta 0 is a much higher in energy than this, which makes this e g star this e g star strongly antibonding.

So, as a result e g star is unoccupied, and the t 2 g non bonding may be occupied, so that is the important difference between class one and class two type of complex. So, in class one, this octahedral delta z value is very less; in class two, this delta o value is very high. As a result the total occupancy over here can be up to 6 plus orbital plus 9, so it can be anywhere up to 18 electrons depending on t 2 g occupancy. So, the metals which are responsible or metals which belong to class two compounds are generally 4 d and 5 d metals observed mainly for 4 d and 5 d metals, whereas class one is observed mainly for 3 d metals.

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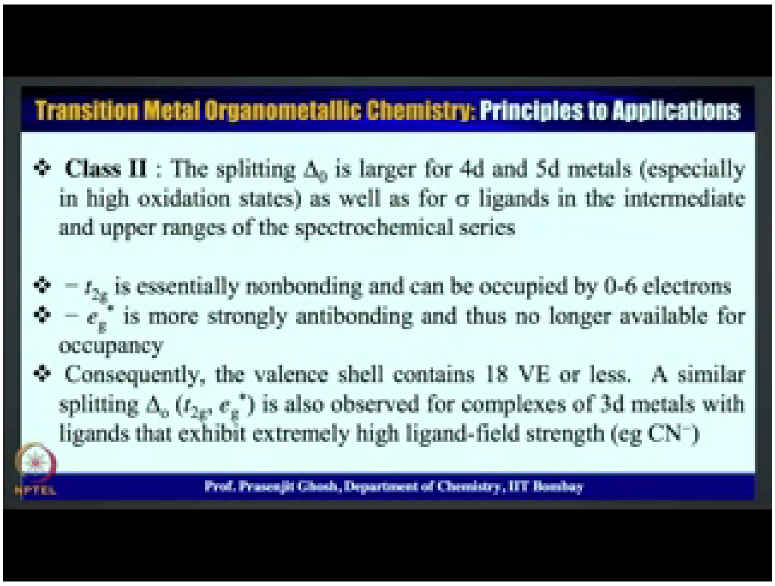

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- **Class II** : The splitting Δ_0 is larger for 4d and 5d metals (especially in high oxidation states) as well as for σ ligands in the intermediate and upper ranges of the spectrochemical series
- – t_{2g} is essentially nonbonding and can be occupied by 0-6 electrons
- – e_g^* is more strongly antibonding and thus no longer available for occupancy
- Consequently, the valence shell contains 18 VE or less. A similar splitting Δ_o (t_{2g}, e_g^*) is also observed for complexes of 3d metals with ligands that exhibit extremely high ligand-field strength (eg CN^-)

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So, it is very common for a 3 d metal complex to have electrons even more than 18 valence electron rule. And for the 4 d and 5 d metals which constitute class two, they may have valence electrons which may not exceed the 18 valence electron count. And that being the case that cf is splitting delta z 0 for the 4 d and 5 d metals are eminently larger than the c f is splitting for the 3 d metals and that is why this difference is observed. So, after looking at class one and class two, we come up on a very interesting class of compounds, which are class three types.

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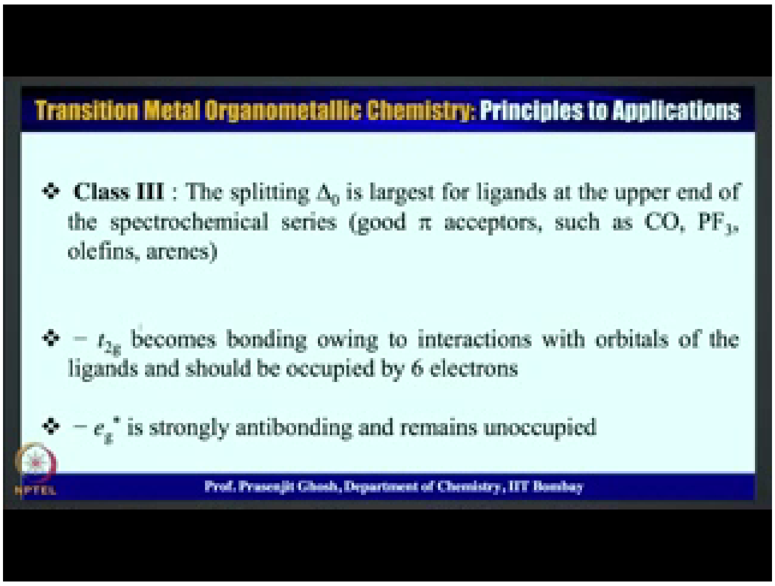

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- **Class III** : The splitting Δ_0 is largest for ligands at the upper end of the spectrochemical series (good π acceptors, such as CO, PF_3, olefins, arenes)
- – t_{2g} becomes bonding owing to interactions with orbitals of the ligands and should be occupied by 6 electrons
- – e_g^* is strongly antibonding and remains unoccupied

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Class three types are very interesting.

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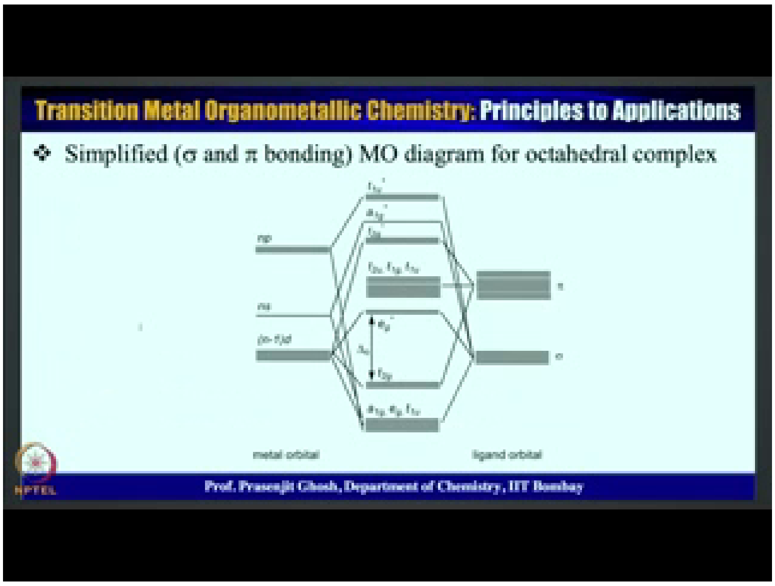

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- Simplified (σ and π bonding) MO diagram for octahedral complex

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So, are slightly different type of interaction pattern. Let us take a look at class three type of complexes under octahedral symmetry.

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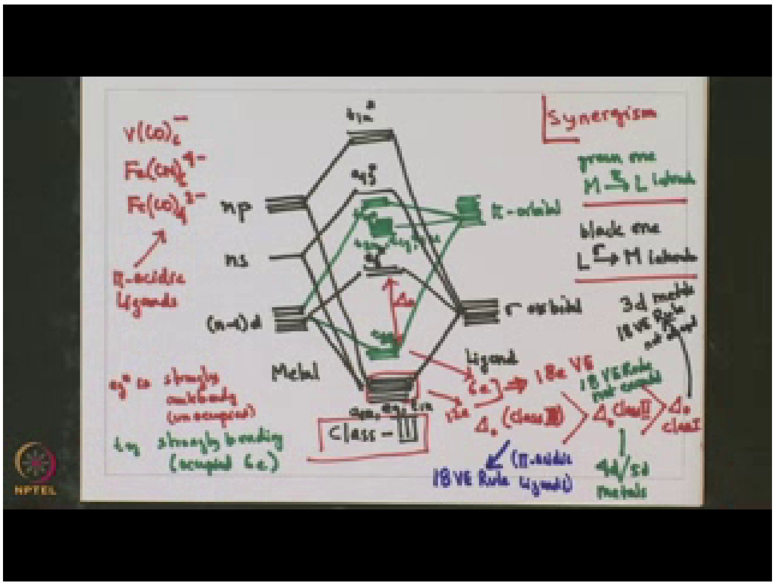

In this case also the metal has 5 n minus 1 d orbitals 1 n s and 3 n p orbitals. These interact with 6 sigma orbitals of the ligand. So, as had been seen earlier six of sigma orbital would interact with 2 of the d orbital, 1 of the n s orbital and 3 of the n p orbital giving 6 antibonding orbital, and 6 bonding orbital. These are a 1 g e g t 1 u, and 6 antibonding orbital e g star a 1 g star t 1 u star. Till this part, it is similar to what we are observed for the class one and class two type of complexes, but from here something more interesting happen. These compounds which are of class two type they have pi orbitals - high energy pi orbitals which can engage in bonding with three of the non bonding d orbitals which does not interact with the sigma orbitals in a pi fashion with the pi orbitals.

So, these high energy pi orbitals, pi type orbitals are usually unoccupied. And as a result this non-bonding d orbitals of the metal, which would be filled, they would engage in pi type interaction with this unoccupied pi type interaction of the ligand. To illustrate this point in addition to the six ligand orbital let say that there are pi type orbitals which are unoccupied in the ligand. And each of the sigma orbital is accompanied by 2 of pi type orbital resulting in 12 pi type orbital over here. So, of this 12 pi type orbital, 3 of this pi type orbital interact remaining 3 of the d orbital which has not taken part in sigma interaction and engage in pi type bonding giving 3 pi bonding orbital which is t 2 g and 3 pi antibonding orbital which is t 2 g star, so that leaves with 9. So, out of 12, if 3 gets involving bonding, so 9 non-bonding pi type orbital of the ligand and these are t 2 u t 1 g and t 1 u from the ligand side.

So, what emerges out is a two way interaction, first one the black one, black one represents ligand to metal sigma interaction and the green one represents metal to ligand pi interaction. What is the important over here is again the difference in energy between t 2 g and e g star, which is represented by this delta 0. Now, what we see that delta 0 class three is much greater than delta 0 class two, which is greater than delta 0 class one, because of this pi engagement with the non-bonding d, the delta zero has increased substantially.

As a result e g star is strongly antibonding and unoccupied whereas, t 2 g is strongly bonding and always occupied with 6 electrons. So, overall for this class three type of complexes, the t 2 g always have 6 electrons and all these bonding this has 12 electrons; as a total all of it has 18 electrons. So, class three always obeys the 18-electron rule. Now, an important attribute of class three is the presence of synergism between ligand to metal sigma interaction and the metal to ligand pi interaction. This is a hallmark of class three type of complexes which always obey 18-electron rule and that the ligand has to have pi type orbital to interact with metal orbital.

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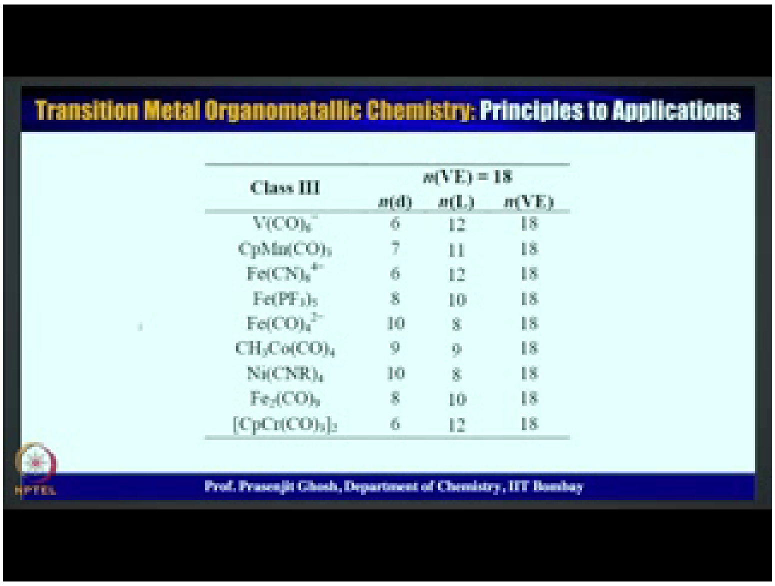

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Class III	$n(VE) = 18$		
	$n(d)$	$n(L)$	$n(VE)$
$V(CO)_6^-$	6	12	18
$CpMn(CO)_3$	7	11	18
$Fe(CN)_6^{4-}$	6	12	18
$Fe(PF_3)_5$	8	10	18
$Fe(CO)_4^{2-}$	10	8	18
$CH_3Co(CO)_4$	9	9	18
$Ni(CNR)_4$	10	8	18
$Fe_2(CO)_9$	8	10	18
$[CpCr(CO)_3]_2$	6	12	18

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Let us take a look at some of the examples of class three type complexes for example, v 0 6 minus this has 6 d electrons and 18 valence electrons, Fe CN 6 4 minus Fe CO 4 2 minus and so and on and so forth. And all of these complexes have pi acidic ligands. So, this is a hallmark of this class three type of ligand. Now, let us compare across the classes of three different types of compounds. And what we saw is that class three has higher delta z 0 value and they always obey 18 electron rule, and they have pi acidic ligands for class two the deltas 0 value is somewhat lesser than class three. And they are for 4 d and 5 d metals. In this case, the 18 VE rule is not exceeded.

And lastly for class one type of compounds this is mainly observed for 3 d metals and 18-electron rule is not followed. So, in this way, I converse upon completion of various classes of organometallic compounds and the underlying molecular orbital diagram responsible for it. I have shown the diagram and I feel that you really seen how the picture evolves from the molecular orbital interaction. And with this, we come to an end of today’s lecture. And we will take up some another interesting topic in the next lecture, which we will look at complexes which do not obey 18 electron rule, and the kind of geometries they execute.

So, with that thank you for being in this class and I look forward to the next lecture looking at different aspects of organometallic chemistry.

Thank you.