Advanced Transition Metal Organometallic Chemistry
Prof. Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology-Bombay

Lecture – 12
Transition Metal Cyclopentadiene Complexes: Molecular Orbital Diagram

Welcome to this lecture on, Advanced Transition Metal Organometallic Chemistry. We have been discussing a very important topic in the last two lectures and this is about structure and bonding in transition metal cyclopentadienyl complexes. Now, cyclopentadienyl ligand had been an important ligand, in the realm of organometallic chemistry, particularly for their stabilization of many types of transition metal complexes.

Also, but they are known for their reactivity and their properties. Now as a measure to understand, the exceptional or unique reactivity of this transition metal cyclopentadienyl comp, complexes, one need to look at its structure and bonding, and that is what we have been doing in the last two lectures. Now the approach had been to build a molecular orbital diagram for this particular transition metal cyclopentadienyl ligand interaction, which work on which are constructed from the various atomic orbitals of the ligand and the metal.

Now, we had looked into interactions of metal orbitals, with various ligand orbitals, which are mainly P type orbitals, and what we had seen that the cyclopentadienyl ligand has primarily 5 P orbitals, whichforms various kind of fragment molecular orbitals through symmetry combinations of atomic orbitals, and what in the gist it turns out, that these ligand orbitals, can interact with the metal in 3 type of interactions.

These can be this conventional, sigma, pi, and delta type interaction, which is sort of same as, another complete other transition metal ligand interactions, but the unique thing about this particular interaction, is in this case, the PI interaction is predominant whereas the Sigma interaction, which in almost all of the cases are according to conventional wisdom always had been the predominant, but in this particular , in transition metal cyclopentadienyl complexes, these Sigma interactions are nonbonding.

As well asthe Delta interactions are weakly bonding, so which sort of makes that ligand to metal PI interaction in metal cyclopentadienyl complexes to be the predominant and that sort of makes these complexes, not only unique, with respect to their metal ligand interactions but also unique to various kind of properties they exhibit. Now, continuing further along this line, we are going to today, look into, the quantitative aspect of the molecular orbital generated as a result of interactions between the two cyclopentadienyl ligand and the metal orbital in a metallocene type of complexes.

To, start with staggered geometry which is supposedly the most stable conformation for better loosing type complexes.

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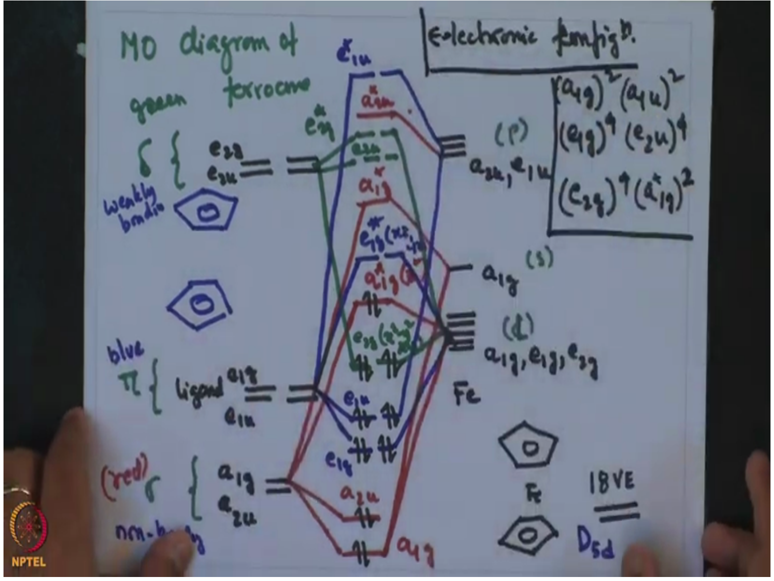

And then one can start with a staggered geometry of the type. Nowwhat we had said, that,this is the ligand. So, the ligand orbitals would be somewhere over here, the metal, let us say, we assumed iron being the metal, so the ligand orbitals would be, this is, a1g and e2u, then there are two sets of degenerate e type orbitals, which are, e1g and e1u and there are two high energy e2 type orbitals, e2g, e2u.

Now this, a1, is supposedly involved in Sigma type interactions, e2, supposedly involved in PI type interactions, u1g and u1u and e2g and e2u involves in Delta type interactions, with the metal. Now what are the orbitals of the metal? As for the metal orbitals, there will be five D orbitals and they would be of a1g, e1g, e2g, so 2 + 2 + 1, 5, then 1 s orbital will be there. So, there a1g, so this is a metal d orbital, this is metal s orbital, and then there will be metal p orbital, they will be a2u, and e1u, so this ismetal p orbital, ok. Now the interaction occurs, as such that, the a1g of the ligand,interacts with a1g d type of the metal, ok. As well as with a1g, s type of themetal, is type of the metal, resulting in, a1g star which is orbital somewhere over here.

So, this is a1g, a1g star, ok, as well as with this, it gives a1g, a1g star, and this is mainly dz square, okay, soone a1g interacts with 2 ligand a1g ligand orbital, giving three orbitals 1 2 3 1 is a1g, a1g star and a1g star, so this primarily it looks like, nonbonding in nature, okay, then a2u remains pretty much nonbonding, does not find any interacting partner with any of the metal orbitals, in the sense that, in the P, has a, a2u component.

But this energy difference between a2u of the ligand, and a2u of the metal, is so high that the ligand a2u, primarily remains nonbonding or does not interact, as a result the same thing happens over, a2u of the P, that also does notformally sort of react or does not have any component of interaction,but slightly anti-bonding, so maybe having very weak interaction of a2u, and this one may have a very weak interaction from the P, and this is called a star 2u.

Okay, so now all the ligand, a1g, a2u, who have gotten engaged with a2u, a1g, a1g of the metal, the next comes these e1g interaction, e1g interacts with e1g of the ligand from the d orbitals, and that interaction is given as and it will also have a anti-bonding component which is somewhere here. So, this is e1g Star and the metal all involves a xz and yz, ok so now e1u, that remains over here that interacts with e1u P of the metal.

And so this gives u1u, this is e1g, and this is e1u, and one would then have, e1u, anti-bonding which is way up in the top, a star 1u, which is over here, so that leaves us with the, e2u and e2g orbitals. So, e2g interacts with e2g of the d, here to here, giving two sets of orbitals. This is e2g and this is x 2 - y 2 , and xy. Similarly there will be e2g star, which will be somewhere over here.

This is e2g star, and thatsort of engage is that so that leaves with, e2u as the nonbonding orbital, e2u, as the nonbonding orbital, which does notfind any takers over here. Now this sort of gives the overall the molecular orbital diagram, now for ferrocene, for ferrocene so the overall it is 18 valence electron compound, so that means, that this is fully occupied, 2, 4, 6, 8, 10, 12, 14, 16 and this is 18 so 18 valence electrons are over here.

And these sort of represent the various form of sigma, PI, delta interaction. Now remember we had a discussion, as to saying that why the Sigma interaction is sort of nonbonding and that can be explained by two explanation, one was just a visual explanation, which I had discussed in the earlier class saying that the ligand orbitals around the periphery of the cone, a cone or plan whereas the middle orbitals are at the center of the cone.

So, the overlapof that being almost minimal and that isthe reasonwhy this interaction does not happen and the other explanation is this, that one can see that nonbonding nature, even from the quantitative molecular orbital diagram, that is shown over here, and which sort of sees which sort of says that if one looks at thisbonding and anti-bonding orbital of a1 and a2 one sees thata2 is nonbondingwhich is sort ofnot interacting and a1 is sort offilledin the bonding and the anti-bonding as well resulting in the overall bond order of zero.

So, that is a very important observationwhich sort of says that even in the quantitative treatment of the CP star molecular orbital diagram, thattheseSigma interaction is almost zero ornonbonding in nature. So, Sigma is nonbonding and Sigma interactions over here, are these, Delta interaction is weakly bonding, so this is a delta interaction, so this is Delta weakly bonding, why it is weakly bonding? Because this represents the Delta interaction so it is weakly bonding.

Sigma is nonbonding because a1g and a1g star, they are both equally populated, so it does not, it sort of cuts off, and the predominant interaction thus are these PI interactions which are sort of the major interactions. So, let me just reiterate that, Sigma interactions are shown in red, PI interactions areshown in blue, andDelta interactions are shown in grey, green, and these provides very importanttreatment of these orbital interactionin ferrocenyl complexes.

Now I would also suggest the people taking this course to construct this molecular orbital from scratch because while constructing one can sort of get a real feel of how these orbitals are really interacting, to give the molecular orbital of the ferrocene, and of course there is this additional joy in being able to construct this molecular orbital of such complexity by followingcertain principles and then matching them up with the proper symmetry related orbitals of the ligands and metals and then coming up with such a complex construction.

Nowthese orbitals is sort of the DNAof ferrocene reactivity, because most of the reactivity that isobserved or seen in not only ferrocene but other metallocene complexes, in fact should be explained by the electronic structure as is constructed in this orbital, and hence these orbital becomesvery important and relevant. Now with these, let me just go even further, and said that even though this orbital diagram is shown for ferrocene complexes.

But they can equally applicable to other metallocenescomplexes where metal will change as a function instead of iron, and also, the other important aspect is that these orbital diagram is also varied for various rotomers, so that the orbital energies would not really much change and going from eclipsed to staggered conformations they would vary slightly, the bond energy would not change.

Now mm, proceeding further along the line, based on this diagram then one has to also take a look at various other metallocenes, and one sort of sees that by looking at the filling of molecular orbitals in this metallocene, one can sort of explain the para magnetism what seen in other metallocene complexes and the electronic configuration and so on and so forth.

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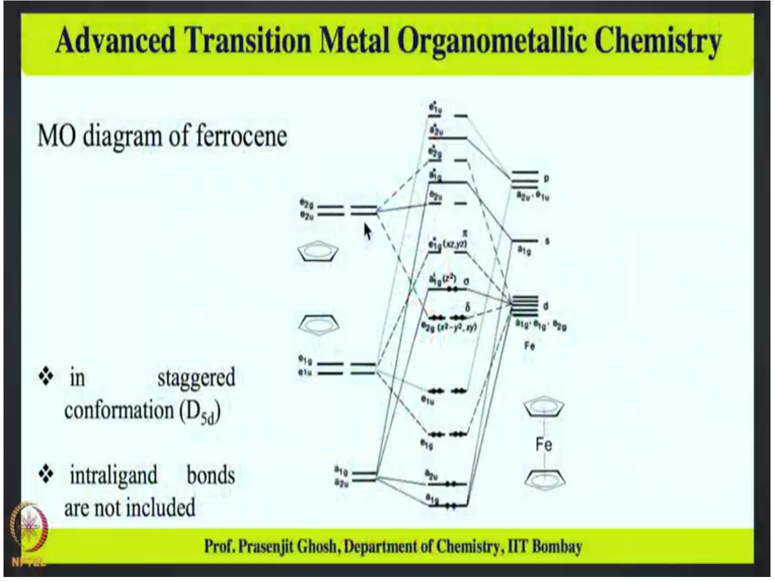

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MO diagram of ferrocene

- in staggered conformation (D_{5d})
- intraligand bonds are not included

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So, we are going to discuss that subsequently in this lecture. So these are ferrocenestaggeredconformations for d5, 5d and also would be valid for da 5, 8.

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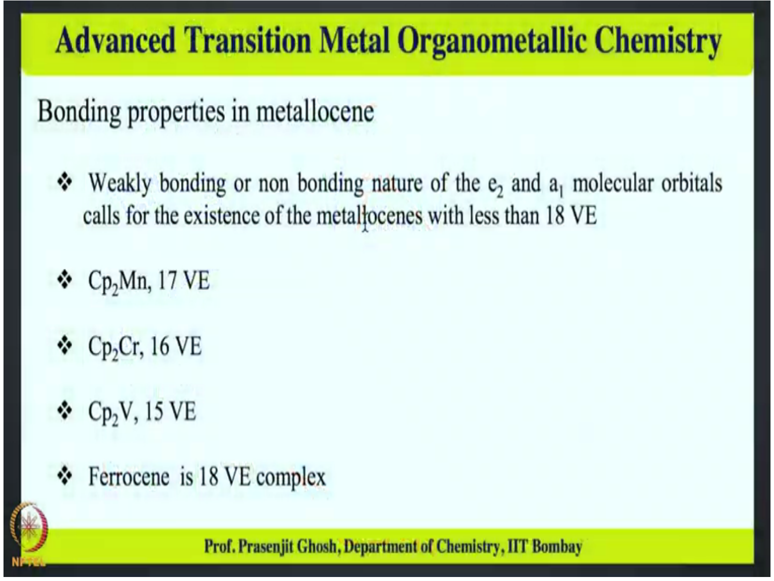

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Bonding properties in metallocene

- Weakly bonding or non bonding nature of the e_2 and a_1 molecular orbitals calls for the existence of the metallocenes with less than 18 VE
- Cp_2Mn, 17 VE
- Cp_2Cr, 16 VE
- Cp_2V, 15 VE
- Ferrocene is 18 VE complex

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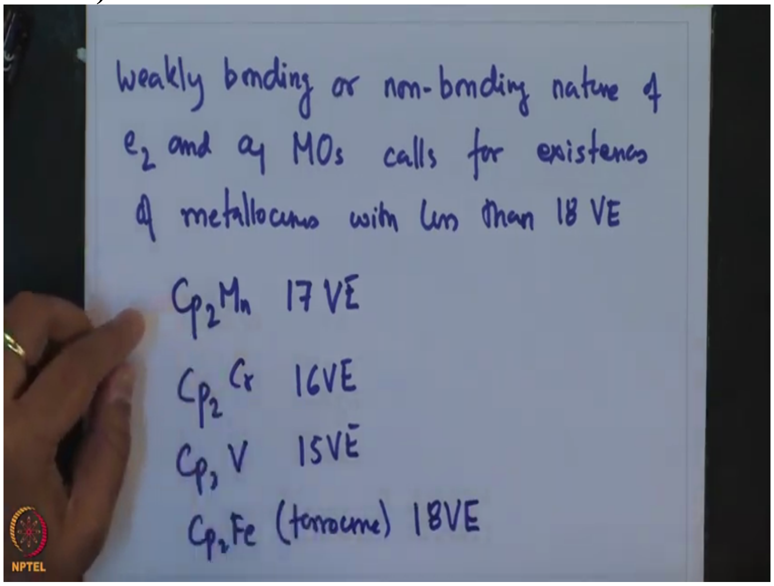

Weakly bonding or non-bonding nature of e_2 and a_1 MOs calls for existence of metallocenes with less than 18 VE

Cp_2Mn 17 VE

Cp_2Cr 16VE

Cp_2V 15VE

Cp_2Fe (ferrocene) 18VE

So, now moving further weekly bonding, or nonbonding nature of bonding or nonbonding nature of e2 and a1 molecular orbitals call for existence of of metallocenes, with less than 18 valence electrons. For example, BCP manganese is 17 valence electrons,for example BCP chromium having 16 valence electrons, BCP vanadium having 15, valence electron, BCP iron which is ferrocene, which we have already seen, has 18, valence electron.

So, these treatment provide quantitative answer to vandalism observed for these other metallocenes, which are paramagnetic in nature and also explainedand their magnetic property which is kind of very useful. Also it is to be noted that these orbital diagrams which was shown for the ferrocene isdifferent than the normaloctahedral symmetry treatment, which is given to transition metal complexes in the sense that thethe orbital splitting's in ferrocenyl systems are different from that the regular octahedral or tetrahedralenvironment that students are often used to.

So these molecular, this particular molecular orbital diagram, explains the magnetic and the electronic properties of these complexes, andwe are going tosort of take a look at it in bit more details. For example we go back to theseorbital and let us take a look at this ferrocenic,ferrocene electron configuration,which can thus be eh, written as a1g, for these, the electronic configuration is a1g, then a1u2, then e1g4, and e2u4, then e2e2g, eg4 and extra 1g, 1ga a2 - extra bond ga2.

So, this is the electronic configuration of ferrocene now having said that,one canlook at the electronic configuration of various transition metals.

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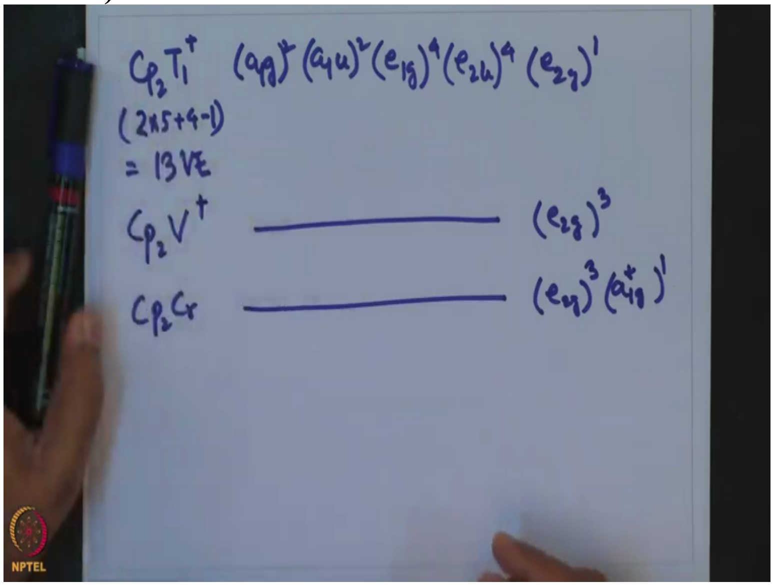

Cp_2Ti^+ $(a_{1g})^2(a_{1u})^2(e_{1g})^4(e_{2u})^4(e_{2g})^1$

$(2\times5+4-1)$

$= 13$ VE

Cp_2V^+ ——— $(e_{2g})^3$

Cp_2Cr ——— $(e_{2g})^3(a^{+}_{1g})^1$

For example,CP2 titanium plus, does the electronic configuration would be a1g2, a1u2, e1g4, e2u4 and then e2g1. Now, titaniumwill havethis is a 13 valence electron so 2 * 5 + 4 - 1 because so it is a13 valence electron. So, this is4, 8, 12 + 1, 13. Similarly if onelooks atCP2vanadium plus then all this remains same and it becomes e2g3, okay,if it isCP, CP2 chromium, then all of it remains same and then e2g, e2g3 and a1, extra 1g, 1, ok. So, like thatone can sort ofexplain the electronic configuration for much of the compound.

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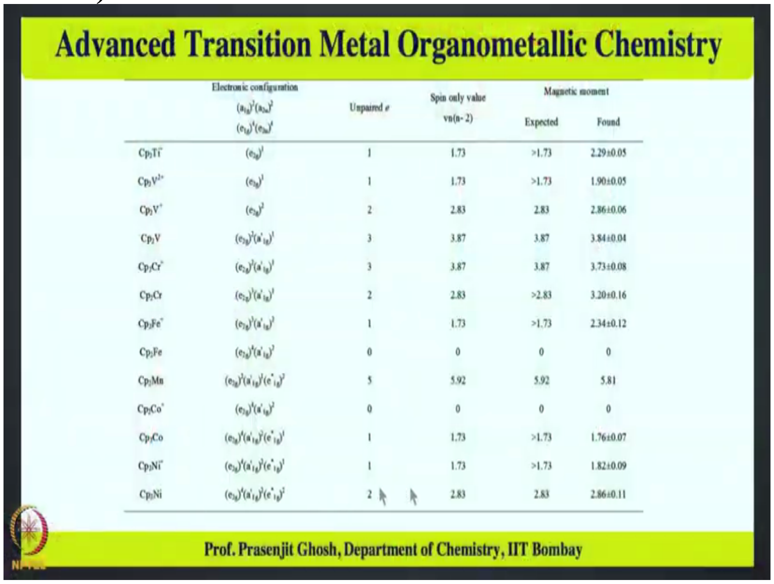

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	Electronic configuration $(a_{1g})^2(a_{2u})^2$ $(e_{1g})^4(e_{2u})^4$	Unpaired *e*	Spin only value $\sqrt{n(n- 2)}$	Magnetic moment	
				Expected	Found
Cp_2Ti^+	$(e_{2g})^1$	1	1.73	>1.73	2.29±0.05
Cp_2V^{2+}	$(e_{2g})^1$	1	1.73	>1.73	1.90±0.05
Cp_2V^+	$(e_{2g})^2$	2	2.83	2.83	2.86±0.06
Cp_2V	$(e_{2g})^2(a'_{1g})^1$	3	3.87	3.87	3.84±0.04
Cp_2Cr^+	$(e_{2g})^2(a'_{1g})^1$	3	3.87	3.87	3.73±0.08
Cp_2Cr	$(e_{2g})^3(a'_{1g})^1$	2	2.83	>2.83	3.20±0.16
Cp_2Fe^+	$(e_{2g})^3(a'_{1g})^2$	1	1.73	>1.73	2.34±0.12
Cp_2Fe	$(e_{2g})^4(a'_{1g})^2$	0	0	0	0
Cp_2Mn	$(e_{2g})^2(a'_{1g})^1(e^*_{1g})^2$	5	5.92	5.92	5.81
Cp_2Co^+	$(e_{2g})^4(a'_{1g})^2$	0	0	0	0
Cp_2Co	$(e_{2g})^4(a'_{1g})^2(e^*_{1g})^1$	1	1.73	>1.73	1.76±0.07
Cp_2Ni^+	$(e_{2g})^4(a'_{1g})^2(e^*_{1g})^1$	1	1.73	>1.73	1.82±0.09
Cp_2Ni	$(e_{2g})^4(a'_{1g})^2(e^*_{1g})^2$	2	2.83	2.83	2.86±0.11

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And the detailed variation of this is shown, in the table for, various electronic, various electronic configuration of, various types of metallocene compounds and their species the corresponding unpaired electrons their spin only values then calculated and expected to provide value for that.

Now with these, I would like to conclude today's lecture, which involved our detailed quantitative treatment of transition metal ferrocenyl complexes, we have looked into the construction of the molecular orbital diagram, using the interaction between the ligand orbital and the metal orbitals.

And we have not only seen that how does it exist, what is thisinteraction about, but we will also see how the inter orbital diagram can be translated to explain the magnetic property of various types of metallocenes andcomplexes, particularly their magnetic behaviorand so on and so forth.So, with this I conclude today's lecture andmm, I am going to take up on the reactivity and the property of these types of complexes in the next lecture, till then goodbye and thank you.