Transition Metal Organometallic Chemistry
Principles to Applications

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Lecture – 05
Week - 01
18 Valence Electron Rule and Classification

Welcome to this lecture in organometallic chemistry, in our previous lecture we have looked into an important concept which is sigma donation and pi back donation that occurs between the ligand and the metal in organometallic compounds and that results I in a unique kind of reactivity for this transition metal compounds. This transition metal organometallic compounds thus show variety of reactions which are unique to them, and we are at a point where we are trying to understand why does it happen or why is it so. And what we saw that it is the partial occupancy of the valence orbital, which can lead to their acceptance of electrons or as well as back donation of electrons leading to this unique sense of the activity.

And hence we came into a very important rule which is called 18 valence electron rule. This is the rule sort of used for guiding the stability of transition metal organometallic comp complexes, and that is often used as a definition of a stable organometallic transition metal organometallic compounds. And later we came to know that there are a quite large number of transition metal organometallic compounds which may obey this 18 valence electron rule as well as some may veiled the same.

And in this lecture we try to understands the reason for compounds for doing so. And our approach in this discussion would been at looking at closely at this 18 valence electron rule, and also try to look at the metal ligand interaction from a molecular orbital stand point trying to see how does the metal orbitals really interact with the ligand orbitals in manifesting, in the valence reactivity. So, with this you are going to start today’s lecture on 18 valence electron rule and its and the classification of organometallic compounds.

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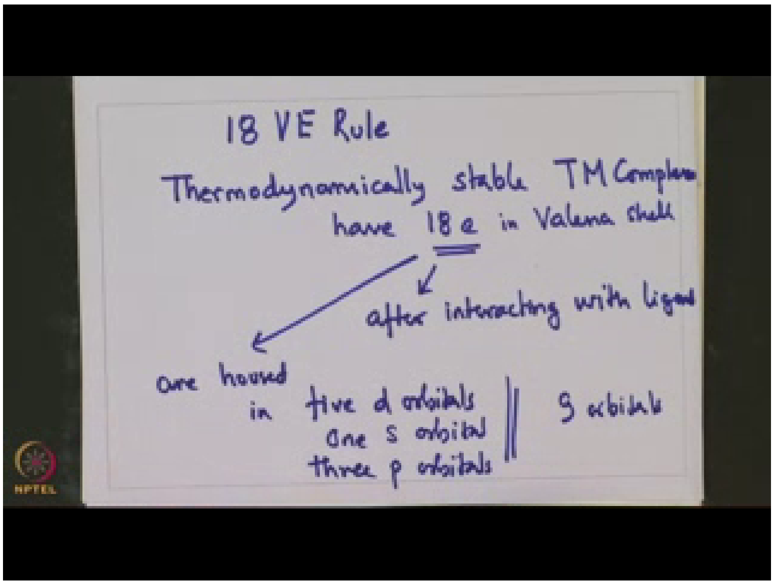

18 VE Rule

Thermodynamically stable TM Comple
have 18 e in Valence shell

after interacting with ligan

are housed in five d orbitals
one s orbital
three p orbitals || 9 orbitals

Now, usually it is said that thermodynamically stable transition metal complexes has 18 valence electrons.

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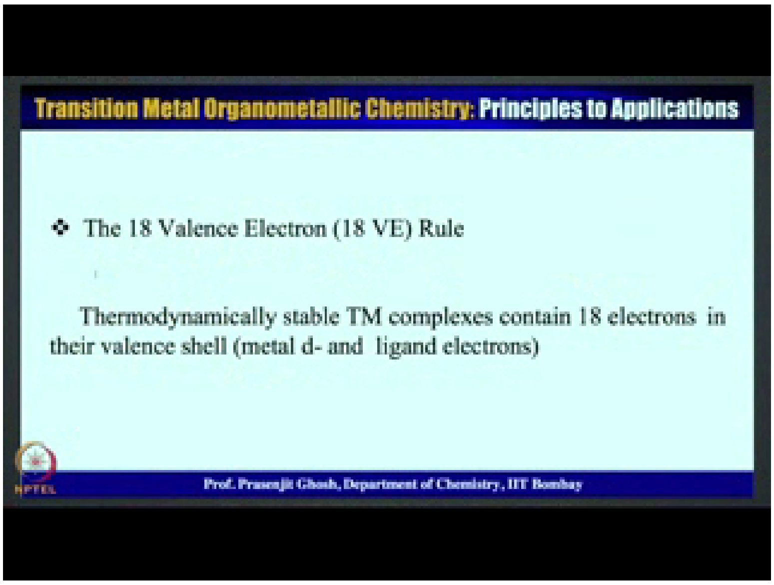

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- The 18 Valence Electron (18 VE) Rule

Thermodynamically stable TM complexes contain 18 electrons in their valence shell (metal d- and ligand electrons)

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Stable transition metal complexes has 18 electron in valence shell. This complexes attend their 18 electron after combining them with ligands, and these 18 electrons are housed in 5 d orbitals one s orbital and 3 p orbital, overall this leads to 9 orbitals having 18 valence electrons.

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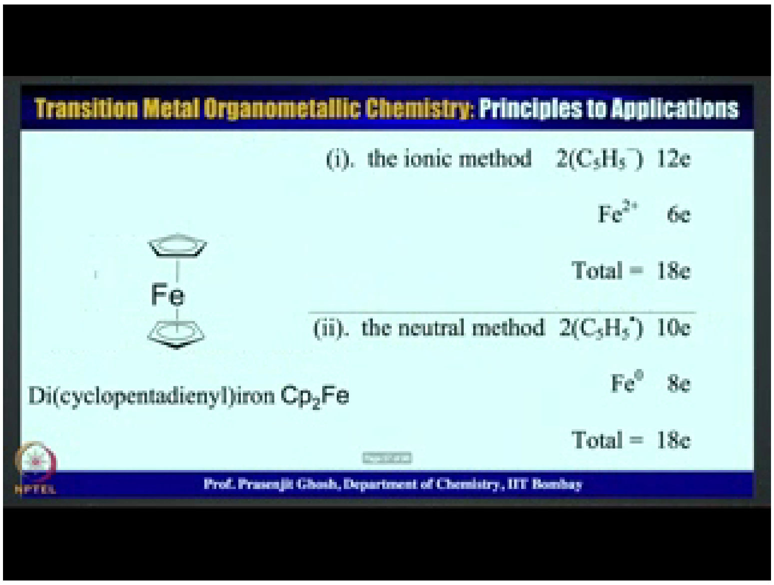

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Di(cyclopentadienyl)iron Cp_2Fe

(i). the ionic method $2(C_5H_5^-)$ 12e

Fe^{2+} 6e

Total = 18e

(ii). the neutral method $2(C_5H_5^\bullet)$ 10e

Fe^0 8e

Total = 18e

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Indeed 18 valence electron compounds are extremely stable and they are sort of inner towards many reactivity; with that in mind let us look at a various stable compound which is ferrocene is the stable compound it is open referred to as dicyclopentadienyl iron.

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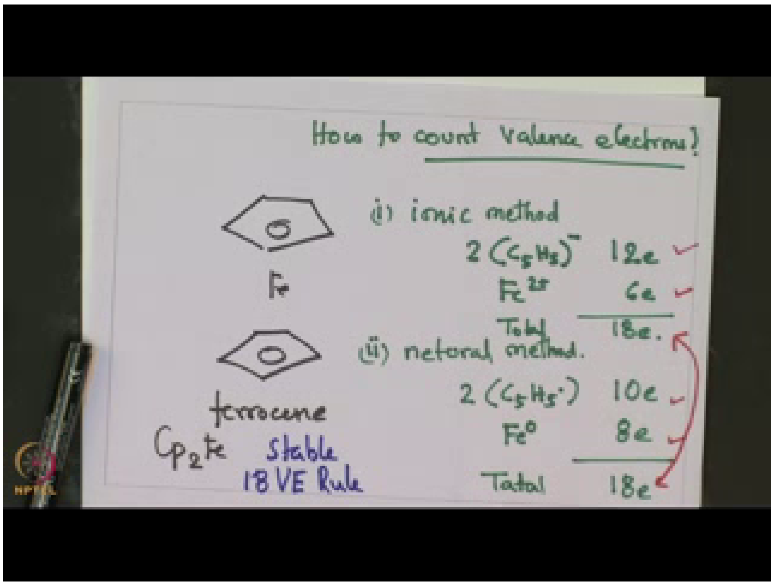

How to count Valence electrons?

ferrocene

Cp_2Fe Stable

18 VE Rule

(i) ionic method

$2(C_5H_5)^-$ 12e ✓

Fe^{2+} 6e ✓

Total 18e.

(ii) neutral method.

$2(C_5H_5^\bullet)$ 10e ✓

Fe^0 8e ✓

Total 18e

And it should have 18 valence electrons in its outer orbital. So, this leads to very important aspect of counting electron count or counting valence electrons. Electron counting is an important concept or a important way of ascertaining the stability of complexes and we should know how one can count its valence electrons. There are 2 methods, one is a ionic method of counting valence electron and the other one is a neutral method. In ionic method it is define it is thought that this cyclopentadienyl iron is in composed of 2 kinds of interaction, where you have 2 cyclopentadienyl anion each having 6 electrons. So, giving to 12 electron interacting with a iron 2 plus which is 6 electron leading to a total of 18 electron.

Now, the other way of counting this is by the neutral method. In the neutral method these 2 cyclopentadienyl ring is thought of as a 2 cyclopentadienyl radical, and they would bring about 10 valence electron, and iron is taken to be iron 0 hence 8 electron and that gives a total of 18 electron. So, what is note worthy over here that, in material of the method of counting the total valence electron they sort of match, independent of which method is used for counting the electrons.

But one must be aware that if one uses ionic method, they should use ionic method all the way through or if one uses neutral method they should uses neutral method all the way through, but the cannot half way use a ionic method and then a neutral method and arrive at a right answer. So, you have to adopt to one formalism either the ionic method or a neutral method in counting electrons. As far as I am concerned I find neutral method to be a more convenient to use, but that was that is simply just my personal preference.

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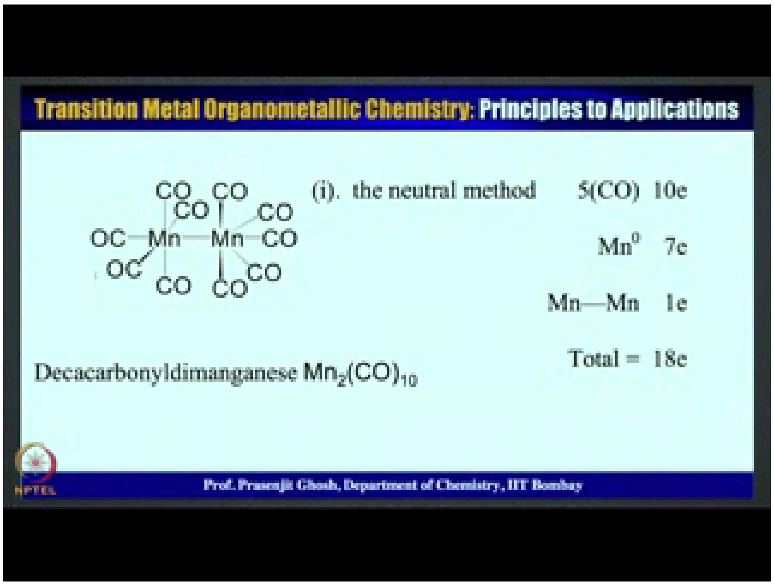

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(i). the neutral method

$5(CO)$ 10e

Mn^0 7e

Mn—Mn 1e

Total = 18e

Decacarbonyldimanganese $Mn_2(CO)_{10}$

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So, let us take a look at few other examples here is de Decacarbonyl manganese. So, we have Mn 2 CO 10.

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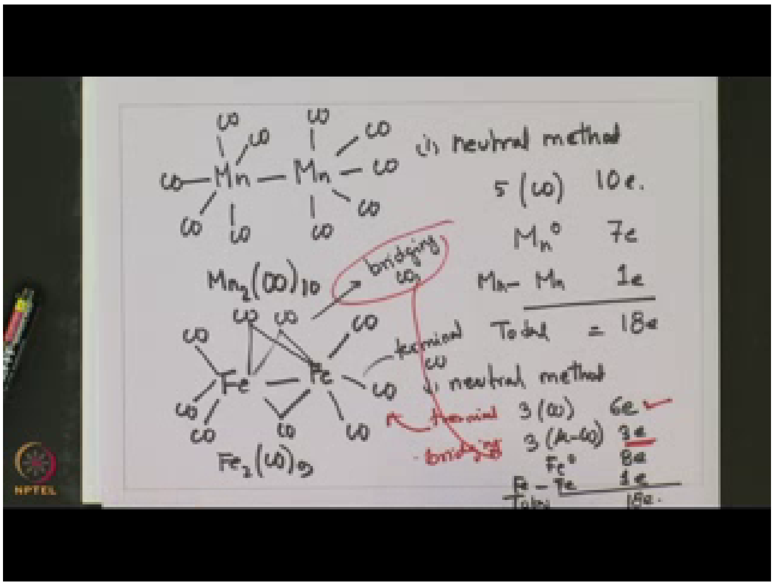

The structure of this compound is with each manganese having 5 carbonyls and there is a one manganese manganese bond. So, a neutral method 5 carbonyl will give 10 electron, manganese 0 7 electron, one manganese manganese bond giving one electron and total of 18 electron. So, these obeys 18 electron count.

Similarly, if we take a diironyl nonacarbonyl the formula is, and the structure of this compound is. So, what we have here is 2 iron atoms, 3 carbonyls which are at the side these are called terminal carbonyls, and 3 bridging carbonyls these are called bridging carbonyls. So, again let us do the counting by neutral method, 3 carbonyls, terminal carbonyls, 6 electrons, 3 bridging carbonyls, 3 electrons Fe 0 8 electron, F e F e 1 electron, these gives a total of 18 electron per iron centre. So, what we see is that ligands contribute differently as they bind for example, when the CO is terminal like situation like this they contributes 2 electrons 3 of them providing 6 electron, and when CO is bridging as in the case over here, they provides a single electron. So, depending on how carbonyl binds to the metal there the number of electron it donates to the metal changes.

Now, that is bring backs to a important topic of ligand classifications. So, how does ligands classify in transition metal organometallic chemistry. So, one think a one is to know that certain ligands can have both neutral positive and negative charges.

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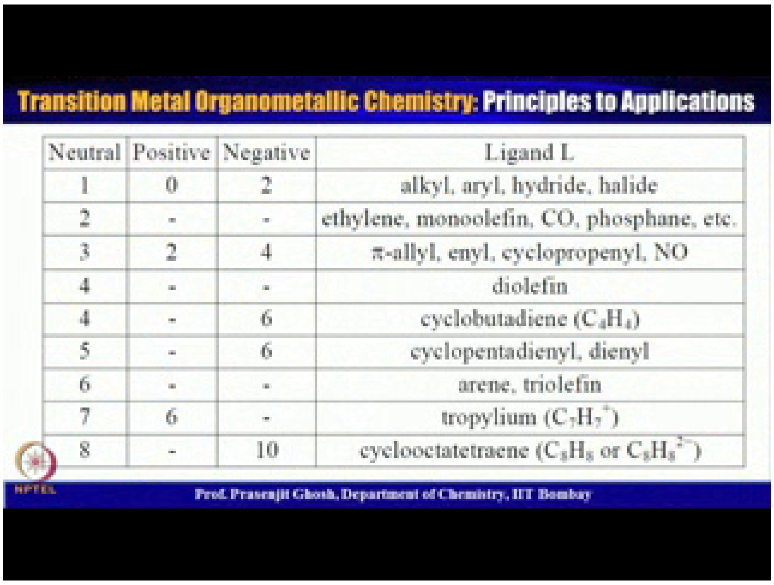

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Neutral	Positive	Negative	Ligand L
1	0	2	alkyl, aryl, hydride, halide
2	-	-	ethylene, monoolefin, CO, phosphane, etc.
3	2	4	π-allyl, enyl, cyclopropenyl, NO
4	-	-	diolefin
4	-	6	cyclobutadiene (C_4H_4)
5	-	6	cyclopentadienyl, dienyl
6	-	-	arene, triolefin
7	6	-	tropylium ($C_7H_7^+$)
8	-	10	cyclooctatetraene (C_8H_8 or $C_8H_8^{2-}$)

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And they may contribute electrons accordingly. For example, if we have metal alkyl when the ligand is Alkyl, aryl, halide you know or in the neutral form, it contributes one electron in the positive form, they do not really bind and in the negative anion form it contributes 2 electrons.

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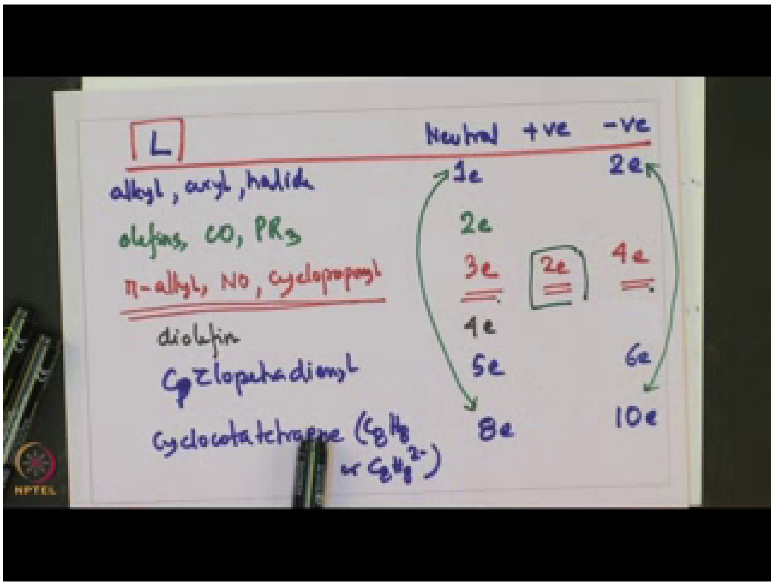

L	Neutral	+ve	-ve
alkyl, aryl, halide	1e		2e
olefins, CO, PR_3	2e		
π-allyl, NO, cyclopropenyl	3e	2e	4e
diolefin	4e		
Cyclopentadienyl	5e		6e
Cyclooctatetraene (C_8H_8 or $C_8H_8^{2-}$)	8e		10e

Let say if we look at other ligands for example, olefins carbon monoxide phosphines; in the neutral form they provide 2 electrons, they do not bind in the cationic and the ionic form. If there are ligands like pi allyl type, NO, then in the neutral form they provide 3 electrons, in the positive form 2 electrons, in the negative form 4 electrons. So, this is unique ligands which binds to the metal not only as a neutral entity, a positive entity and or negative entity and provide different electrons. If there is di olefin, then in the neutral form it provides 4 electron there are similar examples of this and I am going to just take some few representative anions.

Let us say we have Cyclopentadienyl, then in the neutral form 5 electrons and in the negative form 6 electron. LOet us go to an extreme example of cyclooctatetraene which is C 8 H 8 or C 8 H 8 2 minus. So, in the neutral form it provides 8 electron in anionic form it provides 10 electron.

Now, let us look at the different electron donating abilities of this ligands that, bind to transition metal. So, what we see these ligands they pro can provide electrons all the way from 1 to 8 or even 2 to 10. So, that is a huge diversity in terms of the ligand being able to provide elections to the metal, and also another important thing is that the ligand not only bind in the neutral or the negative state, but it also binds in a positive state or can bind in a positive state to the metal. Now that is very counterintuitive because metal itself usually are cationic in nature. So, a cationic metal interacting with cationic a ligand is something which one would not initially sort of think right about. So, it is counterintuitive, but we have ligands in organometallic chemistry, that can bind to the metal in all forms of states, and that is why it gives rise to some very important piece of chemistry.

Now, let us take a look at the task various classes of transition metal organometallic compounds.

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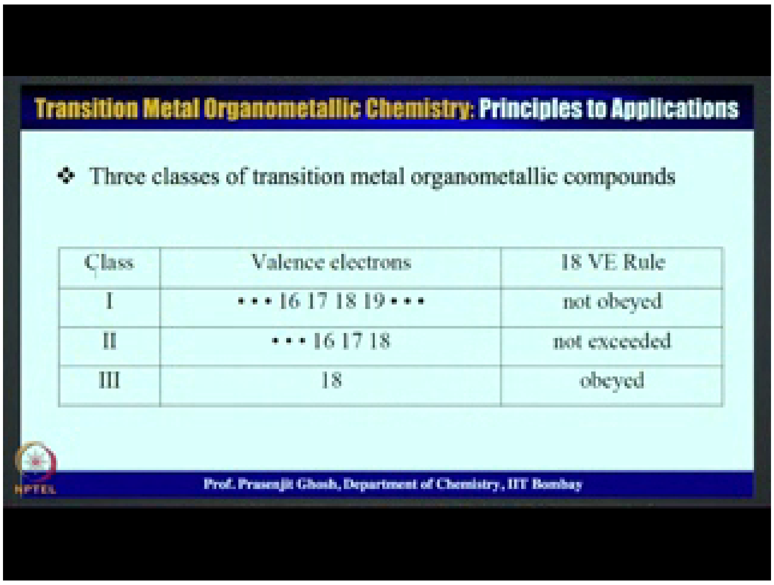

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- Three classes of transition metal organometallic compounds

Class	Valence electrons	18 VE Rule
I	• • • 16 17 18 19 • • •	not obeyed
II	• • • 16 17 18	not exceeded
III	18	obeyed

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And this condition metal organometallic compounds are of 3 classes.

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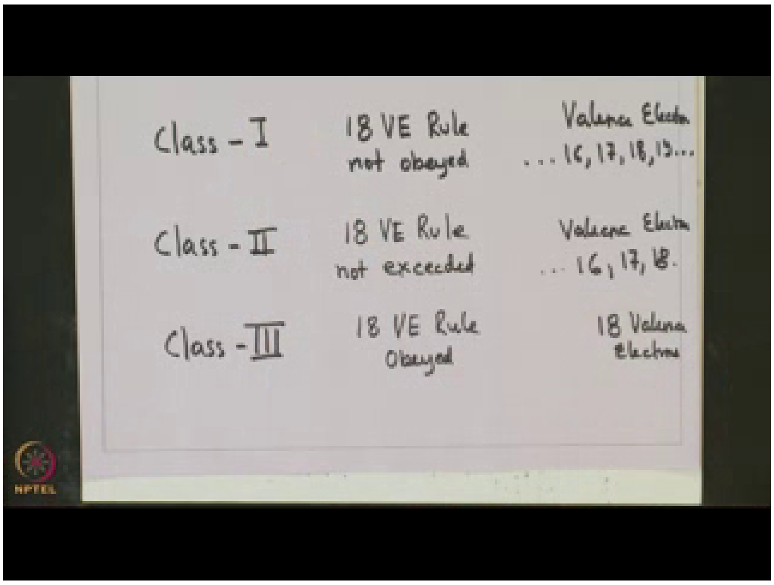

Class - I	18 VE Rule not obeyed	Valence Electn ...16, 17, 18, 19...
Class - II	18 VE Rule not exceeded	Valence Electn ... 16, 17, 18.
Class - III	18 VE Rule Obeyed	18 Valence electrons

Class 1 has 18 electron ruled not obeyed; that means, they have valence electrons from 16, 17, 18, 19 and more. Now we have class 2 where 18 valence electron rule not exceeded, and then their valence electron can have all numbers till up to 18, and last type are the class 3 types which obey 18 valence electron rule, and they have only 18 valence electrons.

So, what we see this is class 2 where 18 valence electron rules are not exceeded, in their valence orbitals they have electron they can have electrons which is 18 as well as they may have a number which is even lower than 18 like 16, 17, 18. Now we have class 3 which has 18 valence electron rule obeyed this for this class of compounds, and they have exactly 18 electrons in the valence shell. What is noteworthy is that our initial belief of 18 valence electron being the governing rule for transition metal organometallic chemistry, is only one type of subset of the complex is that of total realm of organometallic compounds. There are 2 other classes equally existent equally valid by their own written merit beyond ,they 18 valence electron rules and these were classes 2 and classes 1.

Now, let us take a look and trying to understand how this classification are happen or what is the molecular level interaction happening between the metal and the ligand in forming this class 1, class 2, class 3 type complexes.

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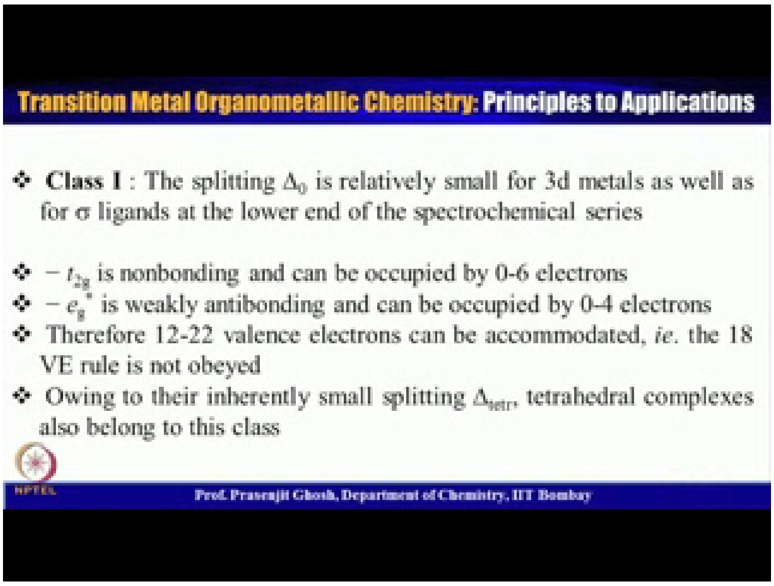

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- **Class I** : The splitting Δ_0 is relatively small for 3d metals as well as for σ ligands at the lower end of the spectrochemical series

- $-\ t_{2g}$ is nonbonding and can be occupied by 0-6 electrons
- $-\ e_g^*$ is weakly antibonding and can be occupied by 0-4 electrons
- Therefore 12-22 valence electrons can be accommodated, *ie*. the 18 VE rule is not obeyed
- Owing to their inherently small splitting Δ_{tetr}, tetrahedral complexes also belong to this class

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So, in class one what we know that 18 electron rule is not valid. So, what is important to us is in trying to understand that how this 18 electron rule is not valid, but the compound can still be formed as come count and still exist.

So, let us take a look at the interaction between ligand and metal for class one type of complexes, in these transition metal organometallic compounds.

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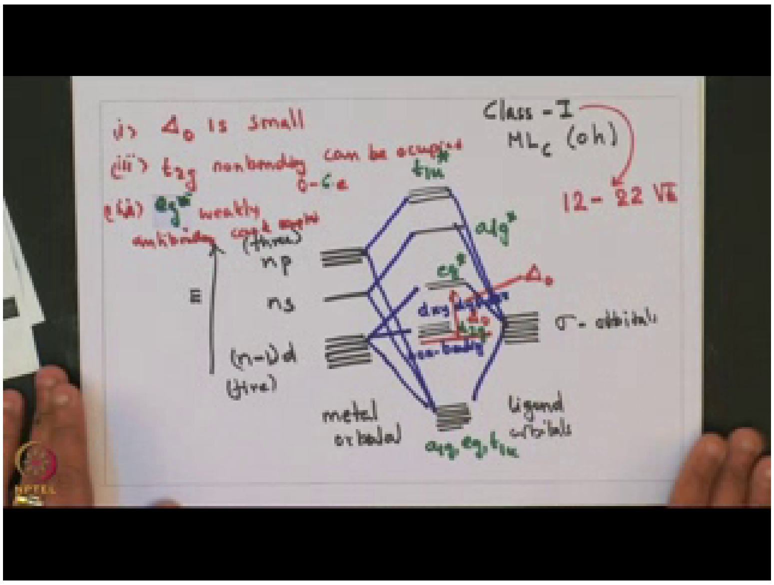

So, for class one let us say we have metal orbital, and we have now for the metal orbital there are let us say n minus 1 d levels d orbitals and this is the energy. So, there are 5 d orbitals, now above d will be the n s orbital, and above s there will be 3 n p orbital. Now these 9 orbital 5 plus 1 plus 3 would interact with ligand orbitals. Let us assume that this ligands orbitals are all sigma interacting; that means, that this ligand orbitals will point towards the metal orbital along the axis inter nuclear axis, and let us take a look at the a simple octahedral complexes, where we are looking at metal l 6 octahedral kind of interaction. So, in such scenario there would be 6 ligand orbitals interacting with the sigma ligand orbitals, interacting with this 9 metal orbital.

Now, of these if there are 6 sigma orbital, then the ligand orbital should interacting with si only 6 of the 9 metal orbitals so; that means, 3 of the 9 metal orbitals would not be interacting with this 6 sigma orbital. So, these 3 orbitals which do not interact are the ones which are not along the inturn nu nuclear axis, but they are in between and the axis and these are d x, d y and d z. So, 3 of the 6 orbitals would sort of not interact with this 6 of the ligand in orbitals and these are d x y, d y z, d z x. So, they sort of stay as nonbonding

So, that leaves us with 3 it two of the d orbital, one of the s and 3 of the p orbitals interacting with 6 of the ligand orbitals. So, this they would interact 2 of these, one of that and 3 of that interact would give 6 bonding orbitals, and these are called a 1 g, e g, t

1 u. And this 3 d x y, d y z, d z x which does not interact are called t 2 g orbital now the way there are 6 bonding orbitals formed that would result in 6 anti bonding orbitals 2 of the anti bonding would be from d type, and these would be a the e g star. So, e g it is over here the bonding one the end bonding is e g star, then the n s will give one orbital which is anti bonding orbital called a 1 g star, and lastly 3 of the p orbitals would interact to give 3 sigma anti bonding p orbitals called t 1 u star.

Now, what we see over here is that t 2 g is non bonding, this is non bonding and e g star is the empty anti bonding or the lowest empty anti bonding orbital. Now looking at this one can arrive at the conditions for which the type one would be valid, and these difference in the energy is called delta 0 or the splitting energy. So, it says for class 1 type of complexes delta 0 splitting is small and t 2 g is non bonding can be occupied 0 to 6 electron, and third e g star weekly anti bonding and can be occupied.

So, what it says that electrons can be over here, over here as well as over there. Now if all of it is full then how total you would get about 12 plus 6 18 plus 4 22 electrons, and if these are empty and these are full then we should get about 20 12 6 into 2. So, overall what it means that for class one complexes there can be 12 to 22 valence electrons. And hence what we see that this explains why that class one type do not obey 18 valence electron rule, and for class one type there can be a valid 22 valence electron compound and still be stable. So, with that I will conclude today's lecture what is interesting about today's lecture is we have deconstructed a molecular orbital correlation diagram, looking at the orbital interaction of a metal centre with that of a ligand centre, how they come along, and how they interact how can how they give rise to the bonding and anti bonding orbitals, and how the bonding and anti bonding orbitals explain the total valence electron count and the stability of this complexes.

So, we are going through a very exciting series of concepts, we are developing and in the next lecture what we are going to look in more detail about con construction of molecular orbital diagrams for the class 2 and class 3 types of complexes, and understand how the result in stability. So, with that I thank you for being with me in this class, and I look forward to being with you in the next class where we take a much deeper look at this molecular orbital interaction for class 2 and class 3 type of complexes. I hope to look forward to being with you in the next class till then good goodbye and.

Thank you.