Advanced Transition Metal Chemistry – Ligand Field Theory

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Lecture – 20
Ligand Field Theory (LFT)

Hello everyone. I once again welcome you all to MSB lecture series on transition elements. Today, let me discuss about the 18 electron rule and also the effective atomic number. In my previous lecture, I informed about ligand field theory is important and how ligand field theory effectively explains bonding in coordination chemistry and also it is capable of explaining almost all properties related to transition metal compounds and also organometallic compounds.

Today, let me introduce another important topic that is 18 electron rule. That means electron counting and what are its significances? What we should follow while counting electrons. What does it mean to coordination compounds or organometallic compounds: stability and their application? All those things let us study in detail. I shall give you numerous examples so that you will become familiar in electron counting.

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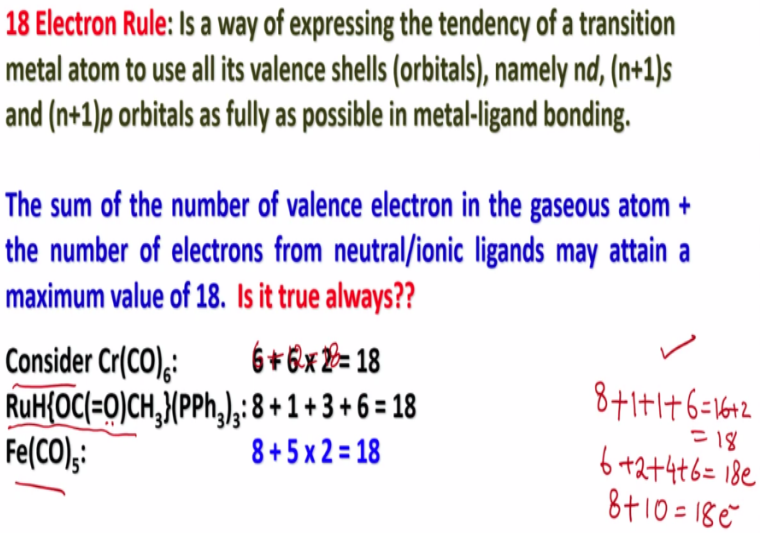

First of all, let us try to look into what is 18 electron rule. It is a way of expressing the tendency of a transition metal atom to use all its valence shell. When we talk about the transition elements, we have three valence orbitals that is nd orbitals and (n+1) s orbital and

the (n+1) p orbitals. That means we have a total of 5+1+3, 9 orbitals with a capacity of 2 electron each means 18 electrons.

So, these metals have a tendency to have as many electrons as possible into their valence shell so that it will be having 18 electrons at the end and that is called the 18-electron rule. Just recall about the octet rule we used in main group compounds, especially for p-block elements introduced by Gilbert N. Lewis. What it says is, we have p block elements having $s^2 p^1$ to s^2p^6 electronic configuration.

That means, we start with one electron in the p orbital starting from boron group to end with 8 electrons in the valence shell, along with s^2 electrons, that is, inert gases. That means most of these p block elements have a tendency to have as many as 8 electrons to have stability and attain the next inert gas configuration. And if you just look into any ion, whether it is a cation or anion, they always make an attempt to have next inert gas configuration.

If it is not possible, they lose some electrons to become positively charged one to attain previous elements or previous inert gas configuration. For example, if you take N^{3-} it has s^2p^3 and with another three electrons, will become s^2p^6 so that it becomes an inert gas configuration. Similarly, oxygen with the s^2p^4, it will take 2 more electrons to become $O^{2-}$and similarly if you go for chlorine, bromine, iodine or fluorine they have 7 electrons.

They need one electron that is the reason they form mono anions. That means whenever you look into a stable cation or anion, it must satisfy inert gas configuration whether the next one or the previous one. In the same way, if we extend the same octet rule to transition elements here, instead of having 4 orbitals with capacity of 8 electrons, we have 9 orbitals with a capacity of 18 electrons, as a result we call it as 18 electron rule.

The sum of the number of valence electrons in the gaseous atom plus the number of electrons from neutral or ionic ligands may attain a maximum value of 18. That means is it really true that 18 electron rule must be obeyed by all transition elements? Before I answer that question, let us look into simple examples here. So, I have given here chromium hexacarbonyl. You know, chromium electronic configuration is $3d^44s^2$ or $3d^54s^1$, does not matter.

So, it has 6 electrons and plus 6 carbonyl groups are giving 12 electrons here, so it becomes 18. So it obeys 18 electron rule. Now let us look into this one here and in this one, let us assume H is giving one electron. There are two methods to count electrons, one is called ionic method, other one is called neutral method or covalent method. In ionic method, we are defining the actual state of the metal depending upon how many anionic ligands are present.

In the neutral or covalent method, we are ignoring and we are just counting all electrons from the metal before its oxidation and then we are giving one electron for chloride or one electron for hydrogen, so it goes that way. In the next slide, I will make you familiar with counting electrons and make you familiar with different ligands can give how many electrons in both ionic method as well as in covalent method.

So, now if you consider let us consider here using neutral method, so here we have $4d^6 5s^2$, so 8 electrons are there and then this hydrogen is giving 1 electron and then this acetate is giving 1 electron and then they are giving 6 electrons. It becomes 16 electrons, but in this acetate what happens, this also giving 2 electrons, as a result to add another 2 it becomes 18 electrons. So, now let us go for other method.

So, now we know that oxidation state of ruthenium is +2 here because one is H^- one is acetate CH_3COO^-, therefore here we have 6 electrons. And now H^- is a 2 electron donor and acetate is 4 electrons donor now and + 6, so this is 18 electrons. So, this is how you can count. And in this case, it is very straightforward, iron has 8 electrons $3d^6 4s^2$, so we have 8 electrons. And then in this case, carbon monoxide is 5 x 2 = 10, it is 18 electrons. So, whatever the complex I have shown here, all of them obey 18 electron rule. So, same thing I have shown here.

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Effective atomic number (EAN) (Sidgwick): Electron pairs from the ligands are added until the central metal atom is surrounded by the same number of electrons as the next noble gas. It is not must for complexes to have stability. Metals with odd no. of electrons can never attain noble gas configuration, if the electrons are added in pairs. It is necessary to produce a symmetric structure irrespective of number of electrons involved.

Atom	At. No.	Complex	e⁻ lost in ion formation	e⁻ gained by coordination	EAN
Cr	24	$Cr(CO)_6$	0	12	36
Fe	26	$[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$	2 3	12 12	36 35
Fe	26	$Fe(CO)_5$	0	10	36
Cu	29	$[Cu(CN)_4]^{3-}$	1	8	36
Ni	28	$[Ni(NH_3)_6]^{2+}$ $[Ni(en)_2(NH_3)_2]^{2+}$	2	12	38
Ru	44	$[CpRuCl(NCMe)(PPh_3)$	2	12	54

Now, I will introduce another term called effective atomic number. This was introduced by Sidgwick. So, electron pairs from the ligands are added until the central atom is surrounded by the same number of electrons as the next noble gas. It is essentially the same. What in 18 electron all we did was: we counted only valence electrons, if you count all the electrons including those coming from ligands in a metal complex that is essentially called as effective atomic number, EAN.

Metals with odd number of electrons can never attain noble gas configuration. That means there are some exceptions, if the electrons are added in pairs, metals with odd number of electrons can never attain noble gas configuration. It is necessary to produce a symmetric structure irrespective of number of electrons involved. That means always when we do not know the structure when we make an attempt, and try to write a symmetric structure to a given complex.

Now, I have given more examples here. Let us look into these examples to calculate the effective atomic number in each case. And you consider chromium here, atomic number is 24. Chromium as I mentioned electron lost during the formation of this one is 0 because the 0 oxidation state and electron gain is 12. So, what we have is here 24 + 12 it is 36, so it attains, this is the effective atomic number for chromium hexacarbonyl.

Similarly, if you take iron the first one here in this one, so here iron is in +2 state. Iron is +2 state, 2 electrons are lost here. So, we will be left with 24 electrons and then six cyanides are giving 12 electrons, this is also 36. Now if you take this one, so electron lost are 3 here, so we

will be left with 25 and now 12 electrons are coming here, then it would be 35. So, one electron less than next inert gas atomic number.

Let us look into iron pentacarbonyl. Here electrons lost are 0 and then 10 electrons are coming, 26 + 10 = 36, yes, this also attains effective atomic number. Now, if you look into copper, so 1 one electron is lost here, copper is in +1 state and then ligands are donating 8 electrons, so it becomes 36. So, it follows. Nickel if you consider, nickel has 8 electrons, 2 electrons are lost and 12 electrons are coming.

So that means 26 +12 = 38. It does not obey, we have 2 electrons excess. So, next same thing is 2 in this case also, instead of 6 ammonia we have 2 ammonia and the 2 bidentate ligands ethylenediamine. The total number of electrons coming are again 12. So here again 38, it does not obey. And if you consider this compound here electron lost are because Cp cyclopentadienyl anion 1 electron is going from ruthenium, 1 electron is going towards chloride.

So, ruthenium is having 6 electrons and now what we have is this is 6, 6 electrons are there, 42 + 12 = 54 we have. So, this satisfies effective atomic number. This is how you can calculate. I have shown here. We can verify whether it is correct or not. Yes, so this is how you can count the electrons and also you can write the effective atomic number and also you will be knowing whether a given complex satisfies 18 electron rule or not.

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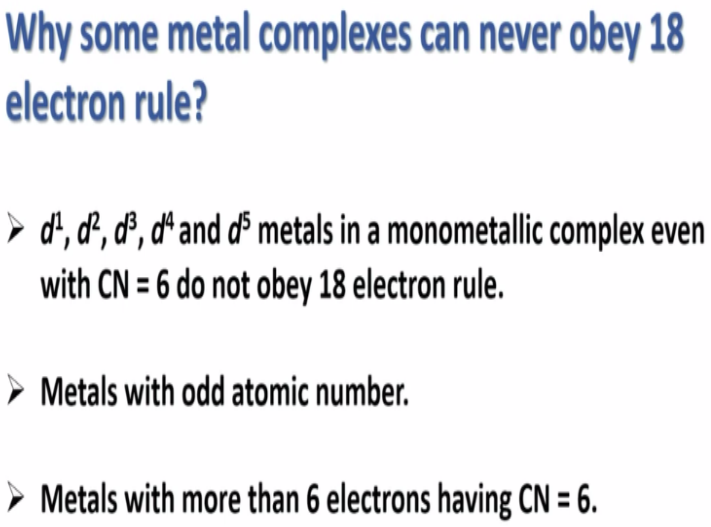

Now, the question is why some metal complexes can never obey 18 electron rule? Is it true? If you look into 3d metals, 3d metals can have a maximum coordination number of 6 within octahedral geometry. So, that means 12 electrons are guaranteed when it forms an octahedral complex with coordination number 6 then if total of 12 electrons are coming from ligands, metal should possess at least 6 electrons.

In order to satisfy 18 electron rule, but by virtue of being an early metal does not have more than 6 electrons in their d orbital, then it can never obey 18 electron rule despite having coordinates number 6 and 6 ligands surrounding it. That means the metals having an electronic configuration of d^1, d^2, d^3, d^4, and d^5 with monometallic complex formation even with coordination number 6, they can never obey 18 electron rule, because they will be having less electrons within the metal itself prior to that complex formation.

And again, metal with oddl atomic number can never obey 18 electron rule. On the other hand, if metals have more than 6 electrons with coordination number 6, they also do not obey 18 electron rule because they will be having excess electrons that we saw in case of hexamine nickel 2+ complex. That means outer orbital complexes always have slightly excess electrons than the next inert gas, as a result they are unstable and they do not obey 18 electron rule.

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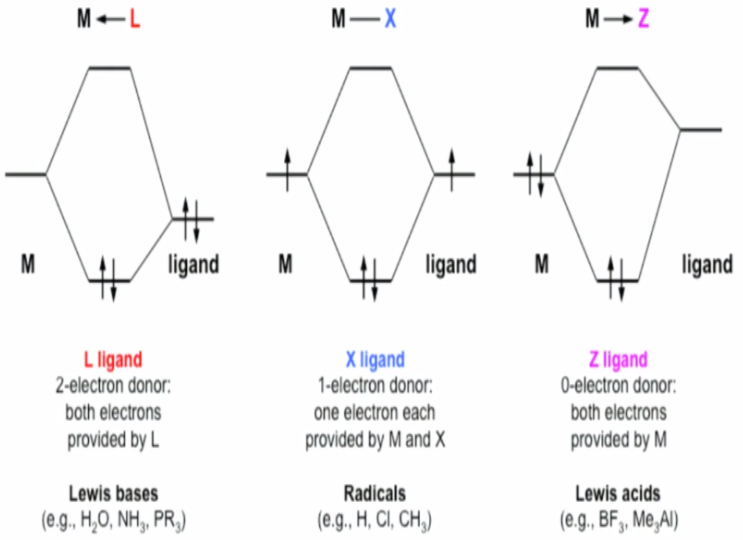

So, now again to make you familiar with electron counting, I am just showing you here three different types of ligands we come across. One is the 2 electrons donor. And here in the neutral method, there are one electron donors. And here of course, this does not come into picture, here we have Lewis acids, and of course in case if you come across, then you have to

subtract 2 electrons for Lewis acids if they are present on a metal centre while electron counting.

(Refer Slide Time: 13:27)

Electron Counting Schemes for Common Ligands

Ligand	Method A ionic	Method B covalent	Ligand	Method A	Method B
H	2 (:H⁻)	1	NO (linear, M-N-O)	2 (:NO⁺)	3
F, Cl, Br, I	2 (:X⁻)	1	η^3-C_3H_5	2 ($C_3H_5^+$)	3
OH	2 (:OH⁻)	1	≡CR	3	3
CN	2 (:CN⁻)	1	≡N	6 (N^{3-})	3
CH_3	2 (:CH_3^-)	1	Butadiene	4	4
NO (bent)	2 (:N=O)	1	η^5-C_5H_5	6($C_5H_5^-$)	5
CO, PR_3	2	2	η^6-C_6H_6	6	6
=CR'R"	2	2	η^7-C_7H_7	6 ($C_7H_7^+$)	7
CH_2=CH_2	2	2			
=O, =S	2 (:O_2^-; :S_2^-)	2			

Now I shall make you familiar with the different ligands we come across and how many electrons they will contribute in ionic method and covalent method. H, what happens, it has 1 electron. So covalent method it is a 1 electron contributor, but when you take one electron from the metal, metal oxidation state increases by +1 and hence that electron will come and it becomes H–, now we have 2 electrons, so it becomes 2 electrons donor.

In the same, way if you take halides, they are all 1 electron donors in covalent method, but they are 2 electrons donor in ionic method because they have this pair of electrons that can go to the metal. Same thing is true in case of hydroxide, cyanide and also methyl. So, in all these cases, in covalent method always you consider one electron, when you are using ionic method, you are considering 2 electrons.

And this extra electron you should remember that is coming from the metal accordingly metal oxidation state increases and number of d electrons decreases. In case of NO, if it is bent it is a 1 electron donor, but in ionic method it is also 2 electron donor. And carbon monoxide and tertiary phosphines, whether you consider ionic method or covenant method, they are 2 electron donors. And then this is ethylene, olefins, they are 2 electron donors both in ionic method and covalent method.

And with all neutral ligands if you consider irrespective of method a or method B, they are always 2 electrons donors. So, if you consider this π-bonding, then they are 2 electrons donors. If you consider oxide O^{2-}, then they are 2 electrons donors or they are 4 electrons donor. Similarly, if you consider NO with linear they are 2 electrons donor in method A and 3 electrons donor in method B.

And allyl, again 2 electrons donor in ionic method and covalent method they are 3 electrons donor. And with ionic method they are actually 4 electron donors. In case of alkyne they are 3 electrons donor here and here it will be 6 electrons donor. In ionic method, they are 6 electrons donor whereas here they are 3 electrons donor. And butadiene 4 electrons, 4 electrons donor.

Cp^- it is 6 electrons donor, when I consider Cp it is a 5 electron donor. η^6-benzene for example is a 6 electrons donor, here also 6 electrons donor. And if you consider tropylium ion it is a 6 electrons donor cation, otherwise it is 7 electrons donor. So, now you are familiar with assigning the electrons that are coming towards the metal from these ligands in both ionic method and covalent method, now let us look into more examples.

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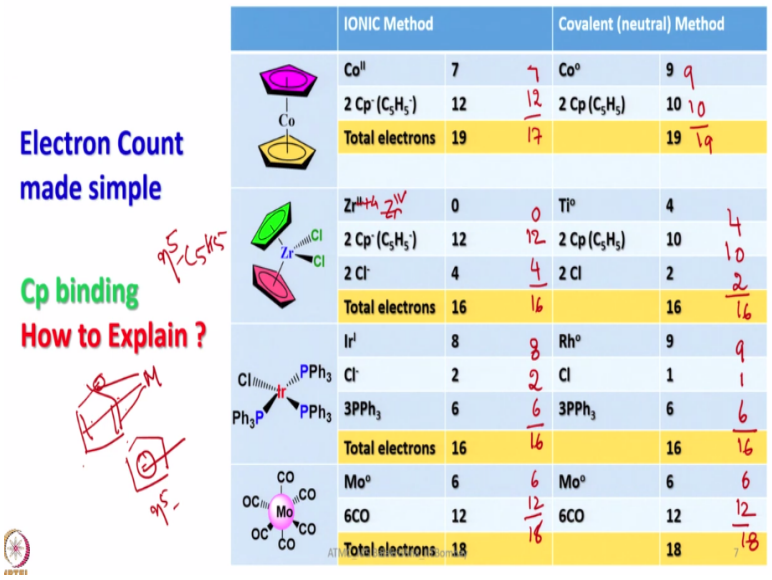

	IONIC Method			Covalent (neutral) Method		
	Co^{II}	7	7	Co^0	9	9
	2 Cp^- ($C_5H_5^-$)	12	12	2 Cp (C_5H_5)	10	10
	Total electrons	19	17		19	19
	Zr^{IV}	0	0	Ti^0	4	4
	2 Cp^- ($C_5H_5^-$)	12	12	2 Cp (C_5H_5)	10	10
	2 Cl^-	4	4	2 Cl	2	2
	Total electrons	16	16		16	16
	Ir^I	8	8	Rh^0	9	9
	Cl^-	2	2	Cl	1	1
	$3PPh_3$	6	6	$3PPh_3$	6	6
	Total electrons	16	16		16	16
	Mo^0	6	6	Mo^0	6	6
	6CO	12	12	6CO	12	12
	Total electrons	18	18		18	18

So, now I have given several examples here. Let us try to use both ionic method and covalent method. In case, if you do not know the oxidation state, there is no need to worry, first let us make an attempt to write electron count using covalent method and then if any anion is there, we will add one electron depending upon whether a monoanion, dianion, trianion accordingly and then count how many electrons are left on metal.

You will end up with knowing the precise oxidation state of the metal centre in that particular complex. And if you consider here, let us start with covalent method. Covalent method this is $3d^74s^2$. So, we have 9 electrons here, 9 electrons are there and two Cp they are giving 10 electrons. So, this becomes 19 electron species. Let us check now in ionic method. So, ionic method it is 7 electrons are coming and Cp they are giving total electron because Cp^- will be 6 electrons. So, this is 19 electrons.

And zirconium this is $4d^25s^2$. So, this is in +2 state here, whether it is +2, four are there, so it cannot be +2 state, it has to be +4 state, that is zirconium +4 state. So, in this case if you go for covalent method, we have 4 electrons here and 10 electrons are coming here and 2 electrons are coming here. So, this is 16 electron species, but if you go with ionic method, here 0 electrons are there and they are giving 12 electrons and they are giving 4 electrons. So, it becomes 16 electrons, so it is matching now.

Now if I add 2 electrons here and 2 electrons here, obviously you will be knowing the actual state of zirconium is +4. Now, let us go to iridium. Iridium is; cobalt, rhodium, iridium $5d^76s^2$ and 1 chloride is there, so let us not worry about that one. First let us write here 9 electrons and 1 electron is coming here and then 6 electrons are coming from three triphenylphosphine.

So, 16 electrons are there. And similarly, now we know the actual state, it is giving 8 electrons and chloride is giving 2 electrons and 6 electrons. This is a sixteen 16 electrons species. The 16 electrons species having d^8 electronic configuration play a prominent role in homogeneous catalysis for a variety of organic transformations, I shall tell you more details about the catalytic properties and how to use them in catalysis when I go to oxidative addition and elimination reactions at some point of this course.

So, now let us look into molybdenum hexacarbonyl, 0 that means 6 electrons are there and 12 electrons are coming here, 18 electrons. And same thing is true here 6+12 = 18 electrons. So, now I believe you are familiar with electron counting using both ionic method as well as neutral or covalent method. Let us look into it, so 19, yes prediction is correct. This is correct. And this is 16 electron species and this is also 16 electron species, so correct.

So tally works well. So that now you know the oxidation state of zirconium is +4, here is not titanium, you correct it as zirconium. Of course, titanium and zirconium have similar

properties when it comes to electron counting. Chemistry may be a little bit different because one is 3d series, other one is 4d series, 16 electrons, 16 electrons, 18, 18. So, electron count made simple. So, one should be able to use both ionic method and covalent method.

What you should do is whenever you come across any metal complex, try to do electron counting to make yourself familiar with this process of electron counting. Now, Cp binding. The Cp binding why we call it as η^5 hapticity 5, I shall show you. So, we always make it like this C_5H_5, then where this 5 hapticity is coming for this one. Let me write something like this. So, we are removing one electron, so we have a negative charge here and we have two bonds here.

Now, first this one makes a bond to the metal through covalent bonding sharing electrons. Now, what happens? This also a 2 electrons donor, this can also go to the metal and this can also go to the metal and then this one you can start writing resonance texture. This negative charge can keep on coming here, coming here, coming here, accordingly double bonds will be moving; as a result what happens?

It looks like delocalization occurs and when delocalization occurs, we write simply something like this a negative charge and we show here. So, that means here this is for two electron η^2, two electron $\eta^2 = \eta^4$ and then one electron and now this is considered as η^5. So, this is how one can explain bonding in case of Cp having hapticity of 5.

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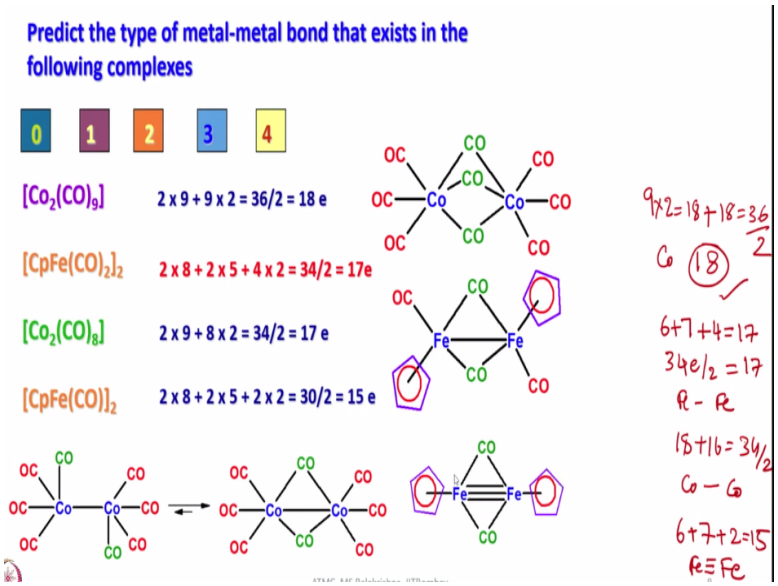

Now, I have four interesting dimeric species. By simple electron counting, you should be able to tell whether a metal-metal bond exists or not. If it exists, what is its nature, whether single bond is there, two bonds are there or three bonds are there. Let us begin with a simple example of $Co_2(CO)_9$. Of course, cobalt has 9 electrons in its valence shell, 9 means each one, so 9 x 2 = 18, 18 is there and another 18 electrons are coming from 9 carbon monoxide, 18, so 36 are there divided by 2.

So, each cobalt has 18 electrons. So, it obeys 18 electron rule and there is no need to include any metal-metal bond between two cobalt atoms. I will show you at the end its structure. So, it follows 18 electron rule. Now, let us look into the second one cyclopentadienyliron dicarbonyl dimer. So here we know the iron is in +1 state. So let us write directly here per iron I am writing.

So 6 electrons are coming and then what we have is iron has $3d^6 4s^2$ one electron is gone, so we have 7 electrons. And then we have four carbon monoxides there and that means two carbon monoxide will contribute 4 electrons, so we have 17 electrons there. That means it is a 34 electrons species and if it is 2, it is 17 electrons each. That means each iron cation has 17 electrons, in order to satisfy 18 electron rule, you have to establish a metal-metal bond, that means there will be one Fe-Fe bond will be there in it.

Now let us look into $Co_2(CO)_8$. $Co_2(CO)_8$ it is again 18 + 16 electrons are there now. So that means again 34 are there, divided by 2, again you need a cobalt-cobalt single bond. Then look into the last case here. In this case, what we have is again 6 electrons are there and 7 are there, but 1 carbon monoxide per, so two are there. So that means 15 are there, so 15 means you need 3 more electrons, so that probably there is a triple bond between two metal atoms.

So, this is how you can predict. And also, you should remember, when you make an attempt to write the structure, you should try to make it as symmetric as possible. You can see here. Yes, it is 18 electrons, it does not need any. So, this is how the structure looks like. As I mentioned, you have to try to write a symmetric structure. This is the only way you can write symmetric structure.

Each cobalt has three terminal and three carbon monoxide as bridging, it is a very symmetric molecule and does not have any metal-metal bond. It does not need because both of them

have 18 electron each. Now you consider this one. As I said one electron is needed, again it is very symmetric and also it has a central symmetry. So, you have to put a metal-metal bond. And you should remember by adding a metal-metal bond, the number of electrons does not become 36.

You should remember, it remains 34 only, at a given time you can satisfy 18 electron rule for each one. When you are satisfying 18 electron rule for this one, this one will be having only 16 electron, you should remember. And when you are satisfying this one, this will be having 16 electrons. This is very similar to octet rule. Recall octet rule when I wrote for carbon monoxide, I kept six electrons between two carbon monoxide and a pair of electron and carbon and oxygen.

If you count simultaneously, you can never obey 18 electron rule, but on the other hand when you count for oxygen, it has 8 electrons and carbon has only 4 electrons. But on the other hand, when you count for carbon, it has 8 electrons and oxygen has 2 electrons. So, this is how it is, so you should remember that one. Simply by adding a metal-metal bond you should not make it instead of 34 to 36, number of electrons remain same.

Lot of students, they do these kinds of mistakes while counting electrons, you should not do it. Electrons are not coming from anywhere, within what we do is in order to satisfy its octet rule to make it stable, we are making a metal-metal bond. Now let us look into this example where we need one cobalt-cobalt bond and that is the reason cobalt octacarbonyl it undergoes dimerization, $CO(CO)_4$, if you make it immediately dimerizes in order to satisfy the electron rule and structure looks like this.

Of course, it can have both the structures and this is more stable, but one can also see this one and of course you can analyse whether we have this structure or this one by just simply looking to IR spectroscopy where carbon monoxide stretching frequency can precisely tell you whether you have this one or this one or a mixture of both. So, here we have 30 electrons there, we need 3 more bonds. So, this is how it is.

For example, when I am counting electrons for this one, you should remember it has 18 electrons, but this will be having only 12 electrons, you should remember that one. Let me stop here and continue discussing 18 electron rule with more interesting molecules in my next

lecture. Until then, keep calculating this 18 electron rule and try to make yourself familiar with it.