Advanced Transition Metal Chemistry – 18-Electron Rule
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Lecture – 21
18 Electron Rule and Effective Atomic Number (EAN)

I welcome you once again to MSB lecture series on advanced transition metal chemistry. In my previous lecture, I had initiated discussion on 18 electron rule and I hope I made you familiar with this method of electron counting and using both ionic method as well as covalent or neutral method. Let me continue from where I had stopped by giving more interesting examples here.

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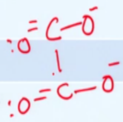
	Ionic method	Covalent method	
$[ClMn(CO)_5]$	6,2, 10 = 18	7,1, 10 = 18	7+1+10=18
$[(\eta^5\text{-}C_5H_5)_2Fe]$	8,10	6,12	8+10=18
$[Re(CO)_5PF_3]^+$	7, 10, 2, -1	6, 10, 2	7+10+2-1=18
$[HFe(CO)_4]^-$	8, 1, 8, 1	8, 2, 8	8+1+8+1=18
$[Ir(CO)(PPh_3)_3(Cl)(NO)]^+$	9,2,6,1,1,-1	6,2,6,2,2	9+2+6+1+3-1=
$[Mn_2(CO)_{10}]$	7,10,1	7,10,1	1=20
$[CpFe(CO)_2]_2$	8,4,6,1	7,6,4,1	14+20=34 (17)
$[(C_2H_4)Re(CH_3)(CO)_2(PR_3)_2$	7,2,1,4,4	6,2,2,4,4	34
$W(CN)_8^{3-}$	6,8,3	1,16	6+8+3=17
$Mn(acac)_3$	7,9	4,12	7+9=16
$Fe_2(CO)_9$	16,18, 2(=)	16,18,2	16+18=34
$V(C_2O_4)_3^{3-}$	5,6,3	2,12	5+9+3=17



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So, now, I have given several complexes in this table and I hope you should be able to do it. Let me do one or two examples to make you familiar once again and let me start with covalent method. So, manganese has 7 electrons and then chlorine is giving 1 electron and then carbon monoxides are giving 10 electrons. So 18, fantastic, 18 electrons are there. So, now if you take ferrocene, here it is 8 electrons and then 10 electrons because covalent method it is 18 electrons, so it obeys.

And if you take rhenium, rhenium comes below manganese. So, we have in the same group, so we have again here 7 electrons, and then we have 10 electrons and then we have 2 electrons and one positive charge is there, so you should subtract one, so it becomes 18 electrons, so 18 electrons. So, now let us look into $[HFeCO_4]^-$ and here 8 electrons; one electron is coming here from H and then again 8 electrons are coming and negative charges is there add +1, so we have 18 electrons.

In covalent method, when you are considering a cation, depending upon how much the charge is there, that many electrons have to be subtracted. When you are considering anion depending upon what is the charge, that many electrons, if one negative charge is there one electron has to be added, only in case of positive charge electrons have to be subtracted. And if you continue that, of course once when you go for ionic method, it is already accounted there is no need to add or subtract an electron due to the charge present on the complex.

Now, let us consider the Iridium complex. So, Iridium 9, and then we have CO, 2 and 3 triphenylphosphines are there 6, and 1 chloride is there 1, and then NO is there 3 and then one positive charge is there. So, now if you count this one, if you have given three electrons, there is a problem. So, basically if this goes what you have is it becomes 20 electrons, so it is not true. So, that means here it is giving only one electron.

So, now you get some confusion here, let us try to address that one when you go to ionic method. I deliberately put this one here, so just remember this. Now, let us go to $Mn_2(CO)_{10}$. In case of $Mn_2(CO)_{10}$ you have 14 electrons and then we have 20 electrons = 34, you need a metal-metal bond. You need a metal-metal bond here, this is 17 electron system. And now of course, this already I showed you, so this has no issues.

This also needs a metal-metal bond, a 13 electron species. In the same way ethylene will be giving 2 electrons and rhenium we have 7 electrons and this isone electron and this is 4 electrons and this is 4 electrons and in this case charges is 3. So, let us do it now. Let us consider this one as 6, in this case 6, covalent method cyanides are giving 8 electrons and plus you add 3 negative charges. So, what we have is here 17 electrons.

Let us verify that one here because 6 electrons taken away from metal and three charges are there. And then look into acac and again here 7 electrons are there and acac will give 3 electrons each, so we have 9 electrons, so then you can have 16 electrons here. And now if you consider this one here: 2Fe, 16 electrons are there and 18 electrons, this is 34 electrons here.

And here oxalate, oxalate can give you 4 electrons. So, you can consider 3 electrons here, 5 + (3 x 3 = 9) + 3. So, it will be 17 electrons. So, this is how it is covalent method. Now let us look into it. Now, you can see here yes this is fine. And here again no issues, ionic method and covalent both account for 18 electrons here. In this case also no issues, 18 electrons are there. In this one also no issues. And here if you see in ionic method when you count 9 electrons are coming, it should have been not ionic method.

Ionic method should be here and covalent method should be here, if you just look into this one, this will give you precisely. If it is 9 electrons and then 2 electrons from here, 6 electrons are there, 1, 1 and 1. So, it gives you precisely, so it cancels the 18 electrons. So, this is correct. So, here this should have been here and this should have been here, so 18 electrons are there. So, correction has to be made, so it is not 3, it is 1 electron.

Now, you go to this one, again this is an 18 electron species, here because one covalent bond will be there 7 + 10 and 1, metal-metal bond will be there. So, it will become 18 electron species here. And then in this one also metal-metal bond is added here, so it becomes 18 electron species and here no issues. And here also it is 18 electron species. And then if you consider here, it is a 17 electron species. It is a 17 electron species you can see.

And here it is 16 electron species and here it is 34 electron species. And here it is 12 electron species. Vanadium has 5 electrons, 6 electrons are coming from this one and plus negative charge it becomes 14 electron species. So, it is 17, is incorrect, you should remember. Of course, oxalate when you write here this is something here and of course the electrons will also be coming from this one, you have to consider that.

You should be able to write in this fashion and sometime of course, so these two electrons will be coming here. So, it becomes essentially what happens 2 + 2, 4 + 4, 8 electron species it becomes.

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The 18 electron rule can also be used to help identify an unknown transition metal in a compound

	Ionic method	Covalent method
$[M(CO)_7]^+$	18-14=4+1 =5, V	
$[M(CO)_6]^-$	18-1-12 = 5, V	
$[M(CO)_5]^X$ What is x = M =?	18-10 = 8 X = 0, Fe X =+1, Co X =-1, Mn	

Now, another interesting thing is you can also use this 18-electron rule to identify an unknown transition metal in a given compound provided we say that the compounds obey 18 electron rule. If I say this compound obeys 18 electron rule and you have to identify the metal I have given here. What you should do is first you write 18 electrons and start subtracting the number of electrons coming from the ligands and also add or subtract depending upon what kind of charge you have.

Then you will end up with electrons that electrons add to a d-orbital and then count; what is that metal atom or ion in this case. So, here 18 electrons are there and 14 you subtract, 4, 4+1 charge you subtract and then you have 5, so this $3d^2 4s^2$ vanadium, so vanadium is in +2 state in this case, so you can simply write. And now you go to this one, so have a negative charge. So, write 18 electrons, subtract 1 electron for charge, subtract 12 electrons for ligands, you will be left with 5.

So, again it is vanadium here. It is a cationic complex with more electrons, is anion complex one electron less, in both the cases. That means vanadium carbonyl you can make $V(CO)_7^+$ or $V(CO)_6^-$ both will obey 18 electrons rule. And here if the metal is not given and also the charge is also not given, then you may have several options. For example, you take 18 electrons and subtract 10 electrons you will be left with the 8 electrons, 8 electrons you can do it.

And here we do not know what is the charge here and if you assume this the neutral compound such as the $Fe(CO)_5$ then this is 0, then iron is 0 valence state and if it is in +1 then it will be cobalt, and if it is –1 this will be manganese. So, that means both the entities are unknown, then arriving at the exact structure is difficult, at least one of the entities should be defined here.

So, otherwise what happens one should be able to write all possibilities precisely. Sometimes in challenging exams they may ask you, then you should not end up saying question is wrong or anything, you should make an attempt to identify all these species. Sometimes they give this type of questions deliberately.

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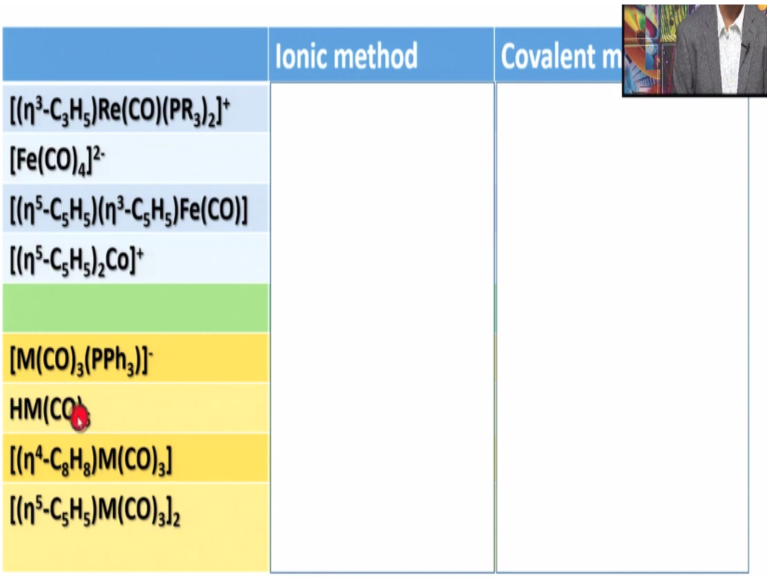

Similarly, what you can do is you can work out electron counting using both ionic method and covalent method. If you have any problems, let us know, I shall tell you more details about those things. And of course, only thing is here we have an allyl group there, so allyl group you should remember as a neutral ligand is a three electrons donor, as an anion ligand is four electron donor that you should know.

And of course, here it is a cationic and if you consider here we have 8 electrons are there and 8 electrons are there, two charges gives 2 so it becomes 18. For example, $Na_2[Fe(CO)_4]$ is an example. And similarly, you can see here one is 5 electron donor, one is a 3 electron donor, 5+3, 8 +2, 10, 10+8 18 using covalent method. In ionic method, so this will be 6 electrons, this will be 4 and iron is 6 electrons, so 6+4 10, 10+6+2 =18. You should be able to write in the same fashion.

Now, this will become 18-electron complex because if you just look into this one charge is there, so 6, 6+, 12, so 12 + 7, 19; 19 – 1 it will be 18 electrons species, so now this is stable. Why cobaltocene is unstable and cobaltocene cation is stable is for the same reason. So, that means 18 electron count can also tell you about relative stability of different complexes. And here if you have a negative charge you have to identify M here, if it obeys 18 electron rule. Similarly, you can look into this one, try to work out these examples here.

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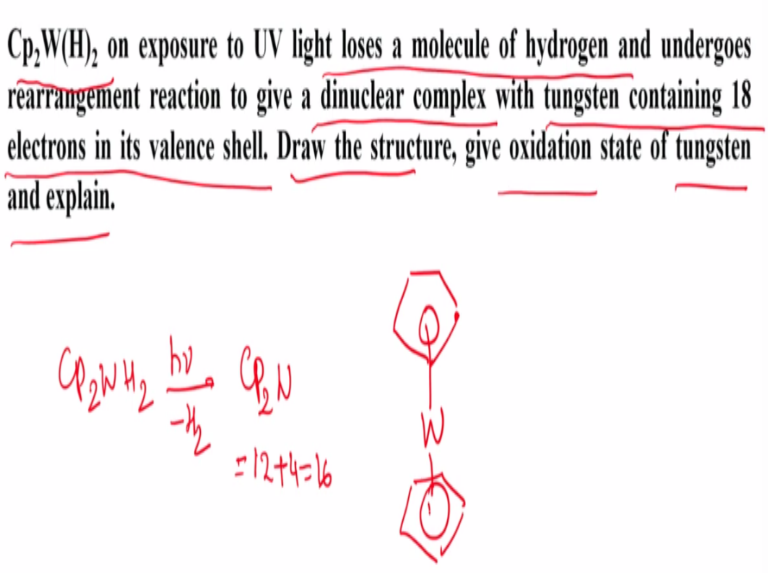

Now, I have given an interesting question here. $Cp_2W(H)_2$ on exposure to UV light loses a molecule of hydrogen and undergoes rearrangement reaction to give a dinuclear complex, this is very important, with the tungsten containing 18 electrons in its valence shell. That means when it undergoes dimerization, tungsten obeys 18 electron rule or it satisfies 18 electron rule. That means it has 18 electrons in its valence shell.

Draw the structure, give oxidation state of tungsten and explain. So, you have to do it. Now, first thing you should remember is we are considering this molecule here on UV light what happens it loses a molecule of hydrogen. So, you take $Cp_2W(H)_2$ you shine UV light $–H_2$ comes out and we will be left with this fragment here. Now, this fragment undergoes dimerization. If undergoes dimerization as of now let us see how many electrons are in this one.

So, if you take it is like tungsten you have seen this we have is 12 electrons + 4 electrons, so 16 electrons are there. If 16 electrons are there you should not think that there are two metal-metal bonds are between tungsten, in this case the compound may not be stabilized it because you do not have any bridging ligands to stabilize two tungsten units. Just in absence of any bridging ligand probably this dimeric structure having two double bonds may not be stabilized.

So, then you should look for alternate methods. What are alternate methods, you have to use some of your chemistry knowledge to see what would happen to Cp group is already present on it. Whether something else happen to Cp groups? Let me write something like this. So, yes, is there any activation of this one CH bond activation. If CH bond activation happens, what would happen? One hydrogen can come out; in that case other one may remain something like this.

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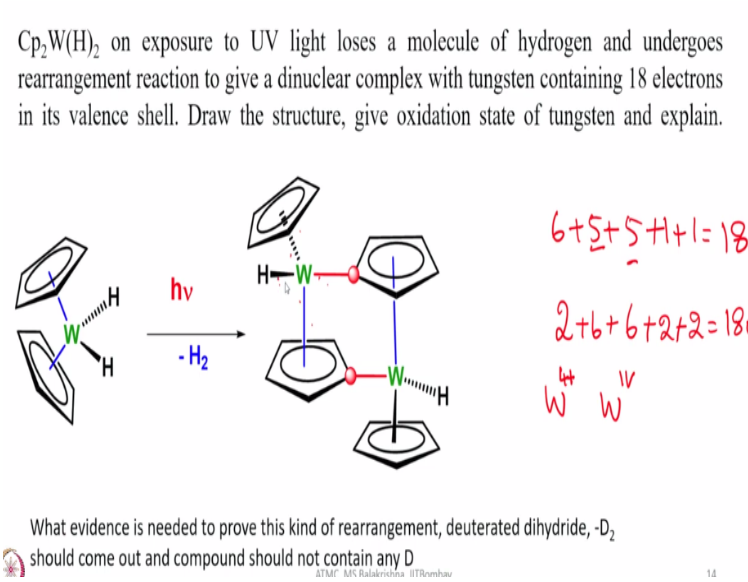

So, now let me show you what would exactly happens to this one here. Can you see here? CH bond activation happens. When the CH bond activation happens, one of the CH bond on one of the Cp groups is activated and then the tungsten is added oxidatively to the CH bond. And then same thing is true on either side. That means we have a fragment, one is η^5, one is η^1 and then this will add up. That means at the end what happens?

Both of them are η^6 in case of both of them, but here it acts as η^1 and in this case it acts as an η^1. So additional η^6, you have η^1 and then two electrons are there. So, now let us try to write electron count for this one, it becomes very clear here. For example, if you take this tungsten here and if you see tungsten, we have charges, let us count here. So this is also negative, this also negative and this also negative.

So in covalent method it should be 6 electrons + 5 + 5 these two and then this carbon is giving 1 electron and this hydrogen is giving 1 electron. So, then it becomes the 18 electrons. That means there is 2 in case of both, here also same thing, so it is a symmetric molecule with central symmetry. And now let us look into ionic method. Ionic method if you consider if you see 1, 2, 3, 4. So, all are anionic ligand, so tungsten should be in +4 state.

If it is in +4 state we will be left with only 2 electrons and then this is 6 electron donor and this is 6 electron donor and now this H is 2 electron donor and now this is carbon minus charge, it is a 2 electron donor. So, it is 18 electron species. So, you should be able to write here 18 electron species and now the structure is drawn and oxidation state is +4 we know, +4 and state of tungsten is 4+ or one can also write like this.

So, this is how you can write and you can also explain very easily. Sometime it may appear like challenging, but if you just start thinking about this one what are the possibilities and if you have some coupling reactions in your mind, already know about coupling reactions where CH activation all those things takes place, you can apply that one and you should be able to write conveniently the structure of this molecule here. And next is what evidence is needed to prove this kind of rearrangement.

So, that means basically you start with the deuterated one and then when you shine UV light, D_2 will come out, and of course once the D_2 come out if you monitor that reaction using ^{1}H-NMR, you should be able to see disappearance of these two, indicates that these two goes and then we have a series and actual CH activation takes place and this hydrogen is not coming from here before the formation of this kind of bond through CH activation, this also eliminated and it is not coming back into reaction scheme again.

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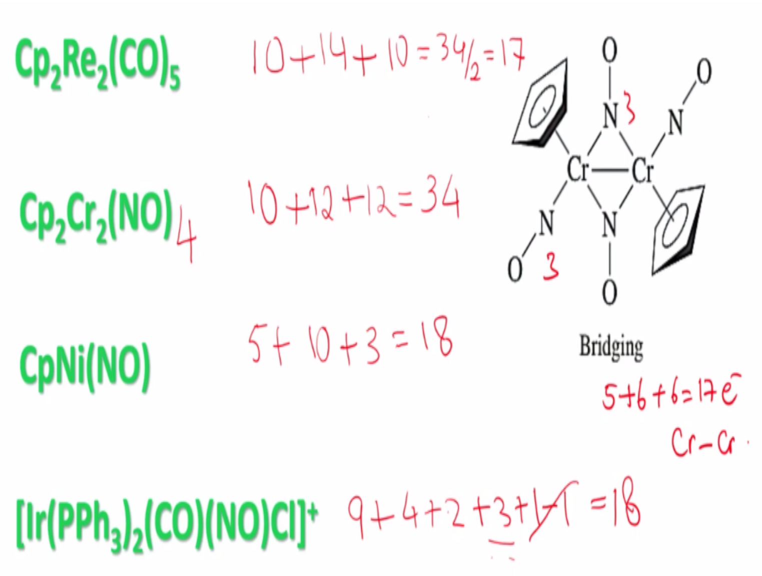

So, now some more electron counting to make you familiar here. I have shown here you can see the 17-electron species and you have to put a metal-metal bond here. And in this case, the number is missing here. And if we say that there is metal-metal bond between chromium and then give the number of nitrosyl ligands present and one should be able to write in this fashion NO is four here, you can count and you can tell.

And then in this one 5 are coming from Cp and 10 electrons from the system, nickel $3d^8 4s^2$ and then it is giving 3 electron it becomes 18 electron species. And similarly, if you go for this one, it is again 18 electron species. So, keep calculating for molecules you come across while studying coordination chemistry so that you become familiar and you will not do any mistakes and if you take this one to be able to write again. And if you see 4 nitrosyl groups are there.

And you can confine to a nitrosyl group completely contributing to one chromium, and here it is Cr 5, we will take 5 electrons and here we have 6, 11. So, 6 + 6 6 one, so 12 + 6 18. And there is one metal-metal bond. So, that means here what you have is the 17 electron species because this one is giving 5 electrons and then this has 6 electrons and this is 3 and this is 3, 6 electrons, we have 17 electrons there, you need one chromium to chromium metal-metal bond. So that explains why we have a bond here.

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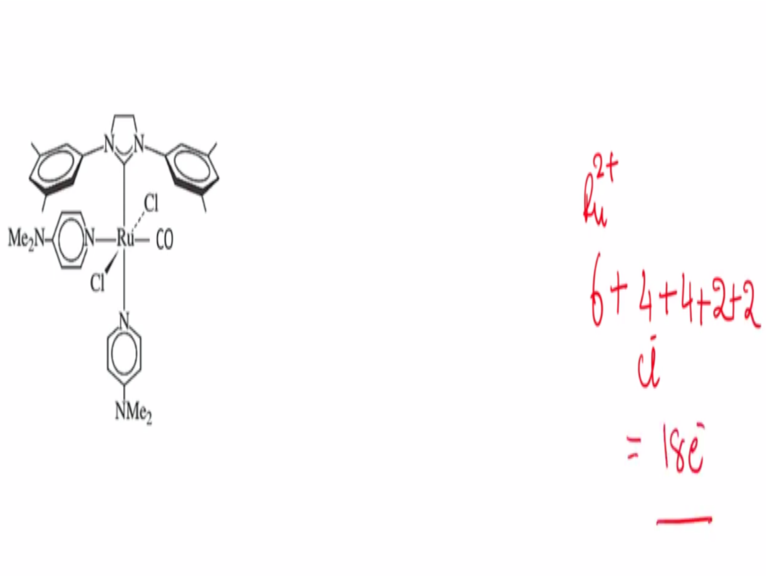

Now, we have another interesting ligand here. We have an N-heterocyclic carbene that is also a neutral ligand and it is a 2 electron donor. Now, ruthenium is there and ruthenium is attached to chlorides. We can go directly to ionic method. We know that ruthenium is in +2 oxidation state. Ruthenium is 2+ so that we have 6 electrons. They are coming from ruthenium and then 4 electrons are coming from chloride ions and then from substituted pyridines we are getting 4 electrons. And then CO is giving 2 electrons and then N heterocyclic is giving 2 electrons. So, we have 18 electrons.

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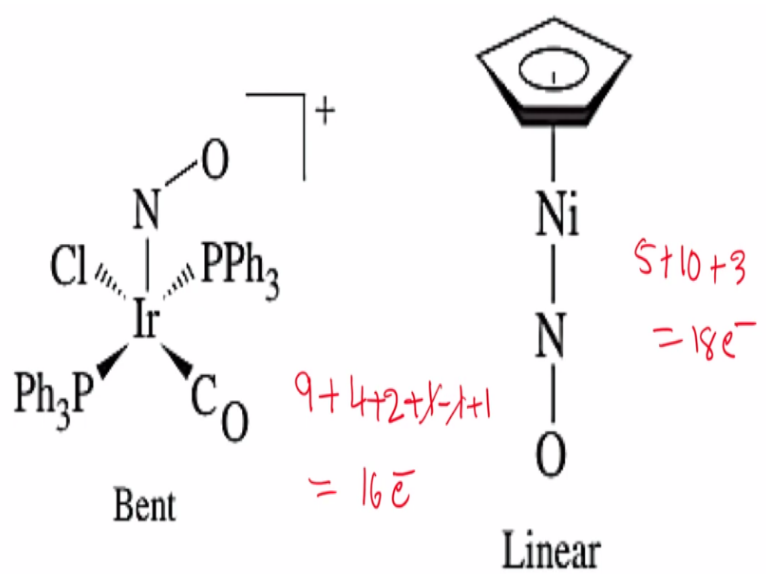

Now, look into one more, of course this I already showed you. So, a linear geometry is there and this one is a 3 electron donor. So, if you take 5 + 10 + 3 = 18 electron species. Now if you consider this one, the bent one is there, in this case what you can do is you can take iridium is 9 and 4 and CO, 2 and Cl, 1 and charge –1 and then how many? we have, +1 electron donor, bent, so it becomes 16 electron species. So, you should be able to write. So again, you know when bent is a 1 electron donor, when it is linear, is 3 electron donor, so that is also verified in this example.

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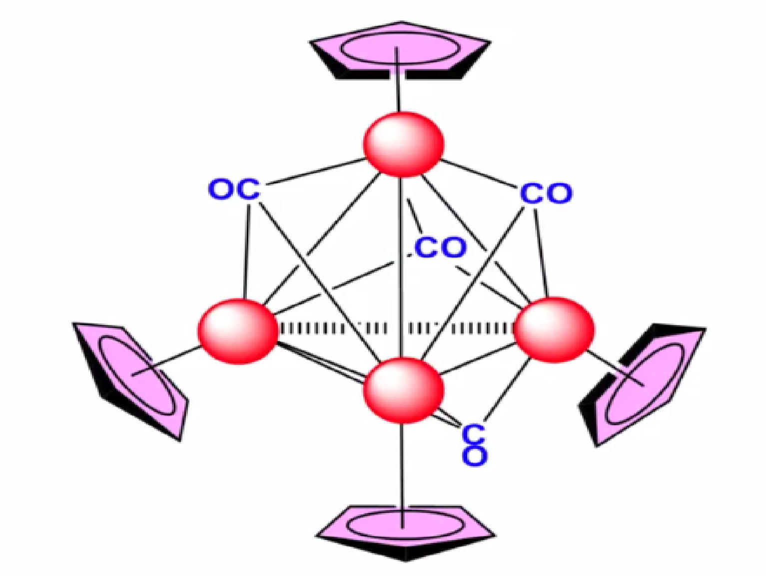

Now, I have given a system here and in this one you have to identify the metal species. Just try to work out about this one. In my next lecture, I shall tell you about how to identify in this kind of interesting 18 electron puzzles in the metal ion.