Advanced Transition Metal Chemistry – 18-Electron Rule
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Lecture – 22
18 Electron Rule and Effective Atomic Number (EAN)

Hello everyone, I welcome you once again to MSB lecture series on advanced transition metal chemistry. In my previous lecture, after giving introduction to 18 electron rule, I showed you several examples with interesting properties and how you can assess and count and show whether they have 18 electrons or not in their valence shell and also whether they satisfy effective atomic number or not. Today, let me continue with few more interesting examples to make you familiar with the electron counting process,

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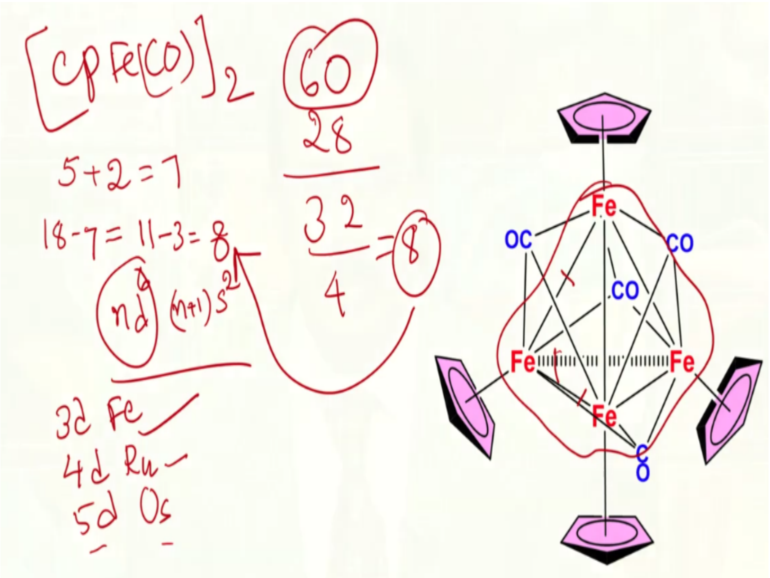

I have shown here a structure where four atoms are hidden behind this orange spheres and you can see the rest everything is clear. There are quite a few things one can give as hint. If no hints are given and from this one you can see through metal-metal bonds, you should be able to identify the metal, despite the total valence electrons present in this cluster, is not given. So, to begin with, let me not give the total valence electrons present in this cluster.

But however, I say that this cluster satisfies 18 electron rule, then what is that metal atom present in this cluster? So, it is very simple. Except for metal atom, rest is known and if you simply start using neutral method or covalent method you should be able to arrive at the answer to identify the metal atom here. So, let us begin. Here let us start with covalent method. According to covalent method C_5H_5 is giving 5 electrons.

So, let us begin with one metal centre 5 and we have 2 carbon monoxide per metal here because we have 4 carbon monoxides there, totally 8 electron donors, but each one should have 2 electrons to share in that case, so this one. Now, we have a total of 7 electrons there and if we believe that this satisfies 18 electron rule then $18 - 7 = 11$, now 11 and if it is satisfying 18 electron rule, let us detect 3 electrons for each one then it will be 8.

So, then metal should have 8 electrons. If the metal should have 8 electrons, first we should put into s^2, i.e $(n+1)s^2$ and remaining nd, now we can put d electrons easily. So, that means the metal ion we are talking about should have, of course, if it is a 3d series, it should be $3d^6$ and $4s^2$ or if it is 4d it should be the other way around, okay it is $4d^6 5s^2$ or it goes on, does not matter. So, this is the one and if this is the one means 8 electrons in the valence shell means it goes to iron group.

If it is 3d, it should be iron. If it is 4d it should be ruthenium. If it is 5d it should be osmium. If it is 3d iron, 4d ruthenium and 5d osmium. So, we can check whether the metal atom is iron or not if it is 3d. On the other hand, if I say this cluster has a total of 60 electrons, identify the metal centre, so in this case, what we should do is we have to take 7, 7 we have, each one 7 is there, 7 into 4 is 28, 28 goes, then we have 32, 32 by 4 equal 8.

So we are also coming here only. So that means already here, that total number of valence electrons present in this cluster is also known, given 60, in that case it is 8. So, in both ways you should be able to tell, but provided, if we say that this cluster satisfies 18 electron rule. Let us look into it. Iron atom, you can see these bonds are there, one bond here and two bond here, another bond here, so each one is coming. So that means each one has 15 electrons and in order to satisfy 18 electrons, they established 3 Fe—Fe bonds.

And you recall when I gave this example here a dimer, in this case we established a triple bond between them because here only 2 iron atoms and since we have 4 iron atoms there it will be establishing single bond each because each iron atom is making 3 bonds with neighbouring iron atoms, which are arranged in a tetrahedral fashion here. You can see this is arranged in tetrahedral fashion. So, this is how 18 electron problems can be solved almost like mathematical puzzles. Then let us go to one more example.

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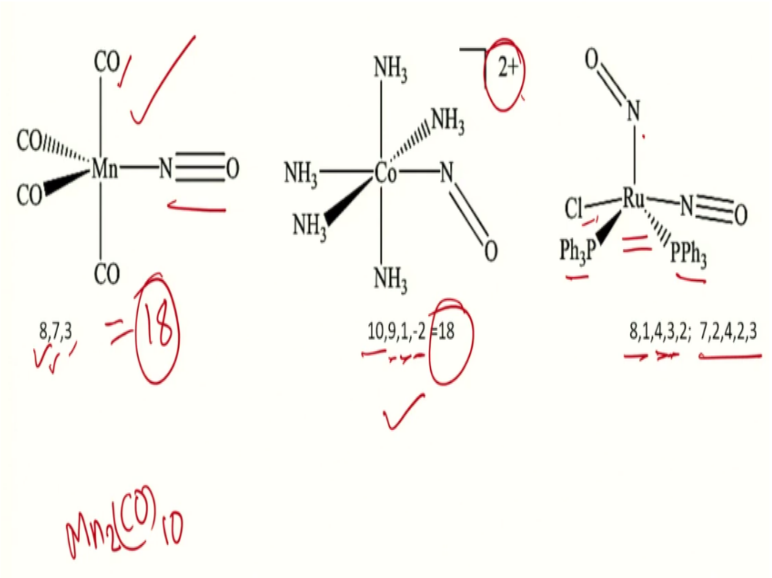

Of course, here you just recall $Mn(CO)_5$. If you make that exists as a dimer having this kind of composition, the reason why? It will be answered by this example here. Just look into this one. We have four carbonyls there, 8 are there, and of course this is $3d^5 4s^2 = 7$ and then this is linear 3 electrons are there. So, this is 18 electrons. Since here in case of carbon monoxide we have NO, instead of 2 electron donor, let us say CO, is a 3 electron donor, now it satisfies 18 electron rule, that is the reason, it does not undergo dimerization.

So, this is an 18-electron complex. Now, let us look into this one here. We have 10 electrons coming from 5 ammonia molecules, by covalent method cobalt has 9 electrons and then N is bent so 1 electron is giving and two charges are there, subtract 2, so you get 18. So, it satisfies 18 electron rule.

And now, let us look into this molecule here, again go with covalent method. So, 8 electrons are coming from ruthenium and then 1 is coming from chlorine. And then 2 each coming from two triphenylphosphine and one is linear 3 electrons are coming, one is bent 2 electrons are coming. So, we have a total of 18 electron. You go to ionic method, same thing happens here also. So, eventually you can use both the methods and you can decide. In some cases, like here, even if the mode of coordination of NO is not given, you should be able to tell after electron count, that one is linear, one has to be bent, so that 8 electron rule is satisfied.

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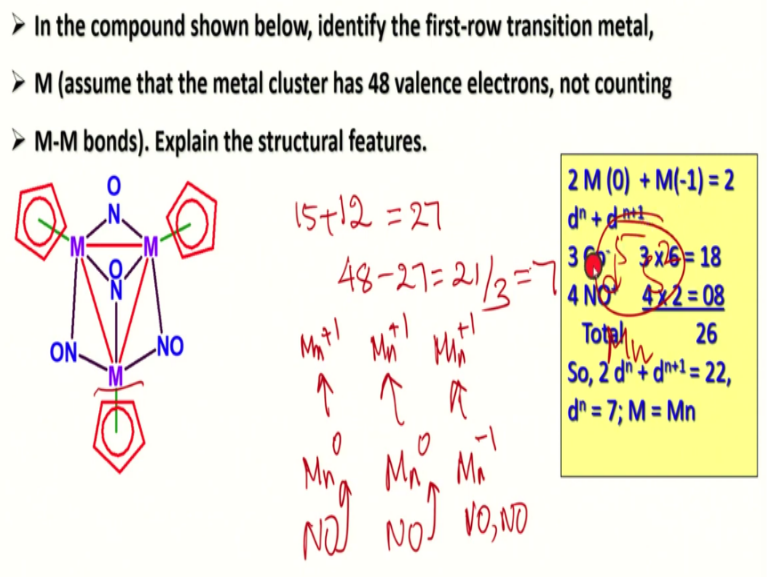

- In the compound shown below, identify the first-row transition metal,
- M (assume that the metal cluster has 48 valence electrons, not counting
- M-M bonds). Explain the structural features.

$15+12=27$

$48-27=21/3=7$

Mn^{+1} Mn^{+1} Mn^{+1}

Mn^{0} Mn^{0} Mn^{-1}

NO NO NO, NO

2 M (0) + M(-1) = 2 $d^n + d^{n+1}$

3 Cp^- 3 x 6 = 18

4 NO^+ 4 x 2 = 08

Total 26

So, 2 $d^n + d^{n+1} = 22$,

$d^n = 7$; M = Mn

Now, I have given another similar example here. In the compound shown below identify the first row transition metal. That means, you have to identify which 3d metal is there in place of M here in this case. And then here the total valence electrons are given. And of course, when total valence electrons are given, you have to keep in mind that you should not count metal-metal bond. Metal-metal bond will not give you extra electrons.

You have to manage with the electrons by taking from neighbouring atoms so that at a given time each metal centre satisfies 18 electron rule, that is what I told you. I am again stressing upon that one, you should remember when we add metal-metal bond, we will be managing within the electrons present in the valence shell, we are not taking extra electrons from anywhere. So, now if this cluster contains 48 electrons, we have to identify the metal.

And now NO, let us assume four NO's are there, four NO will be giving 12 electrons and then we have three Cp groups are there, they are giving 15 electrons. So, it 27 and what we have is 48, 48 – 27 of course 21. Because 3 metal centres are there equals 7, if I put s^2 here, I have to put d^5, so it is d^5s^2, d^5s^2 means it has to be manganese. Now if I ask you to state the oxidation state of each metal, it is bit tricky here.

And NO comes as NO^+ so that basically what happens, whatever the electrons they are giving for Cp to make it Cp– so assume each one will be (Mn) in +1 state. So, four NO's are there, one will give one electron here, another one give another electron here and then the two NO's will give 2 electrons to one of the manganese. As a result what happens it becomes Mn^0, this becomes Mn^0 and then it becomes Mn^{-1}.

So, now we know that you can do by ionic method to identify the metal here. You should remember if you consider Cp, Cp to become Cp– manganese has to give an electron, it is given here, so all manganese are in +1 state because each one is making a bond with Cp group. And now, four NO's are there, out of four NO's two NO's have to give 2 electrons to one of the metal centres.

In that case let us assume two NO's are giving here; NO, NO and here one NO is giving 1 electron and one NO is giving 1 electron. So, it becomes 0, 0 and it becomes –1. So, this is how you can also identify the oxidation state by doing a proper counting and through the electron counting the way I described using both ionic method as well as covalent method. You can see here, I showed, whatever I described is here. So, two metals have 0 oxidation state and whereas one has "–1" oxidation state.

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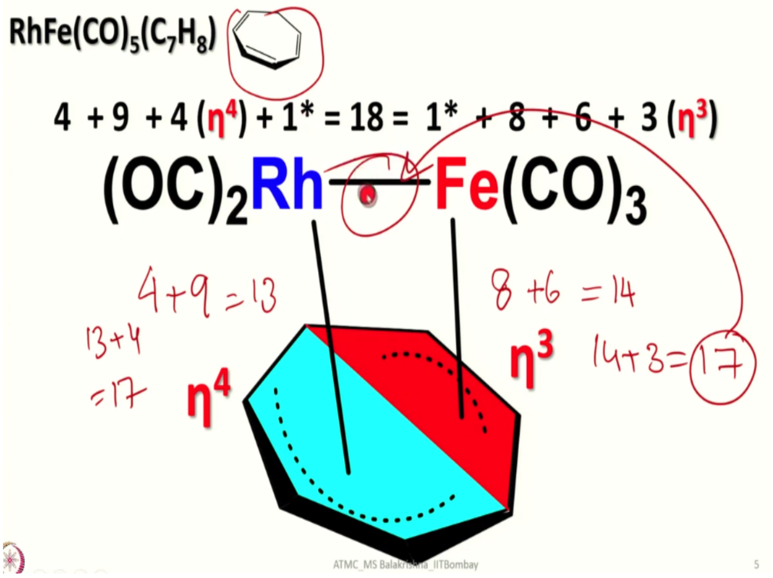

$RhFe(CO)_5(C_7H_8)$

$4 + 9 + 4 (\eta^4) + 1^* = 18 = 1^* + 8 + 6 + 3 (\eta^3)$

$(OC)_2Rh — Fe(CO)_3$

$4 + 9 = 13$

$13 + 4 = 17$

η^4

$8 + 6 = 14$

η^3

$14 + 3 = 17$

Now, another interesting one is there, $RhFe(CO)_5(C_7H_8)$. And what is C_7H_8 as I have shown here, cycloheptatriene. Now, if a system like this is there, you should assume that there is a metal-metal bond and now one metal-metal bond is there, but what is interesting is this group is sharing its electrons with both rhodium as well as iron depending upon how many electrons are needed for each one.

So, it is very interesting structure, I should show you here. So, this is how first you should write. You should ask me why I have put two carbon monoxide on rhodium and three carbon monoxide on iron, you should know that iron has lesser number of electrons compared to rhodium in its valence shell, to begin with because iron has $3d^6 4s^2$, whereas rhodium has $4d^7 5s^2$, so already it has excess electrons, it needs very few electrons to satisfy its octet.

As a result, you have to add more ligands to those which have less electrons in their valence shell. Now, if you start counting here by neutral method 4 electrons are there and 9 ($4d^7 5s^2$), and here we have 6 electrons, +6 we have 9 electrons are there and here 13 electrons are there. So, 13 electrons are there, one bond is coming let us say from covalent bond, then we have to see how many electrons are needed now, 8 electrons are there here.

So, 8 + 6 = 14 electrons are there. So, now let us put it here in such a way that it can bind to both the rhodium and iron atoms now. So what does it show now? You can see one is η^4, one is η^3. Now η^4 means 4 electrons are coming, so 13 + 4 is 17 and 1 is coming from this bond and here 3 are there, 14 + 3 is 17, so another is coming from this one. So, now you can see very nicely.

So that means in order to satisfy the 18-electron rule in this dimeric, in this heterodimetallic complex, cycloheptatriene binds in this fashion having η^4 towards rhodium and η^3 towards iron. So, this explains are very nicely and you can see now both that metal atoms are obeying 18 electron rule and this whatever I showed with star this represents metal-metal bond.

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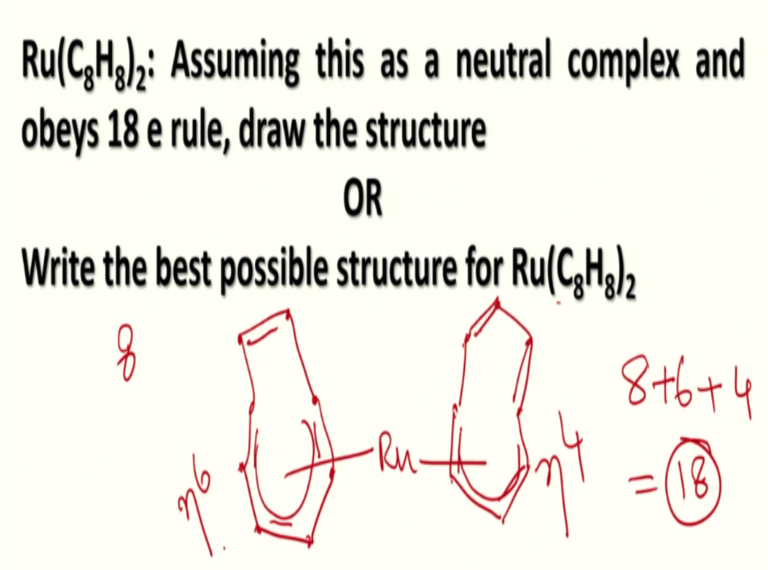

$Ru(C_8H_8)_2$: Assuming this as a neutral complex and obeys 18 e rule, draw the structure

OR

Write the best possible structure for $Ru(C_8H_8)_2$

So, now I have one more interesting molecule there. Assuming this complex as a neutral one and obeys 18-electron, draw the structure. Write the best possible structure for ruthenium C_8H_8, that means cyclooctatetraene, here we are talking about. If you are taking a cyclooctatetraene and both of them should satisfy and of course ruthenium has 8 electrons there. Ruthenium has 8 electrons, what you need is now 10 electrons are needed. If 10 electrons are needed, how one can write? So, it is 1, 2, 3, 4, 5, 6, 7, 8 are there.

If the 8 are there, let me see whether I can put bonds like this. And also let me write one more 1, 2, 3, 4, 5, 6, 7 something like this. If I put something like this, if I take this one, and if I take this one, it becomes sort of 3 electrons, recall it is like a benzene and it is ethylene. So, now, let me try to put in this fashion, and this will be η^6 and this will be η^4. So, that means this is giving 6 electrons, this is giving 4 electrons. We already have 8 electrons and 6 electrons are there and 4 electrons are there.

So, it satisfies 18 electrons that means you should remember. You may ask me why it should not be η^8 and η^2. If you see the structure of cyclooctatetraene, it is very difficult to take all the four to ruthenium because of the orientation of this molecule here. So, it is very difficult. As a result, what happens you cannot bind all four double bonds to a single metal, but this is the most appropriate, metal prefers to bind having it η^6 and η^4 coordination.

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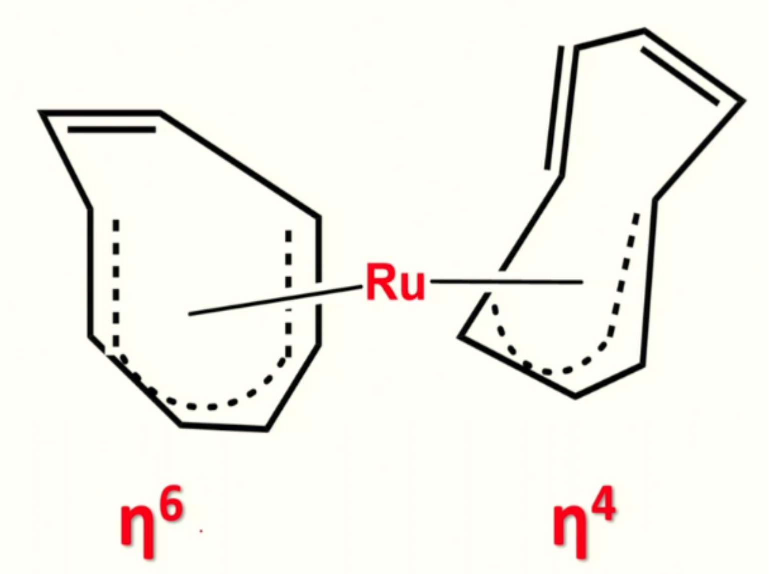

So, that means one should give some thought and analytically one should try to analyse how one can write a structure without much stress on the molecule, but it satisfies 18 electron rule. This completes the discussion about electron counting and the 18-electron rule and effective atomic number. I believe now if any metal complex is given, you should be able to solve it without any difficulty.

Now, let us move on to another interesting topic called metal-metal multiple bonding and I shall tell you, in this one that type of metal-metal bonds we come across among coordination components as well as organometallic compounds. And also, I shall tell you more about quadruple and quintuple bonding. That means, according to the convention, we cannot have more than three bonds between two metal centres.

But due to the painstaking work from Cotton's group, we came to know that yes metals can have more than four bonds or even five bonds between two metal centres that we call it as quadruple bonding and quintuple bonding. And if these bonds are there, whether we can use molecular orbital theory to explain this bonding is what interesting. I shall tell you in detail to make you very familiar with identifying some of these multiple bonds between two metal centres when you come across in coordination chemistry. Let us start discussion.

What is you know about meta-metal multiple bonding? So, metal complexes with metal-metal multiple bonds have been known for decades, even while doing electron count also I showed you the existence of metal-metal double bond, triple bond. Bonds formed by the overlap of valence d-orbitals of transition meal ions received greatest attention after the discovery of quadruple metal-metal bonds by FA Cotton in 1960s.

Cotton's group at MIT, earlier he was a professor at MIT and later he moved to Texas A and M. So, during that time, he was interested in rhenium chemistry for which he started working on rhenium salts such as K_2ReCl_4 and one of the Russian scientists earlier, that means, in 1950s, had characterized this compound and composition and he called this one as K_2ReCl_4 salt.

Cotton was purchasing rhenium salts from one mining company called Coors in Colorado, in USA, where the metal was obtained as a side product while mining molybdenum. One such sample having K_2ReCl_4 obtained from Coors group was found to have several crystals suitable for single crystal x-ray structure determination. As a result, what happened? Cotton performed the structure and he determined the structure of the so called, K_2ReCl_4.

To his surprise and his group's surprise, the sample was shown to have a stoichiometry of $KReCl_4$ but not K_2ReCl_4 what it was thought earlier, and it was found to be a dianion with two $ReCl_4$ moieties connected together with a metal-metal bond. So, then curiosity was there to think about that one.

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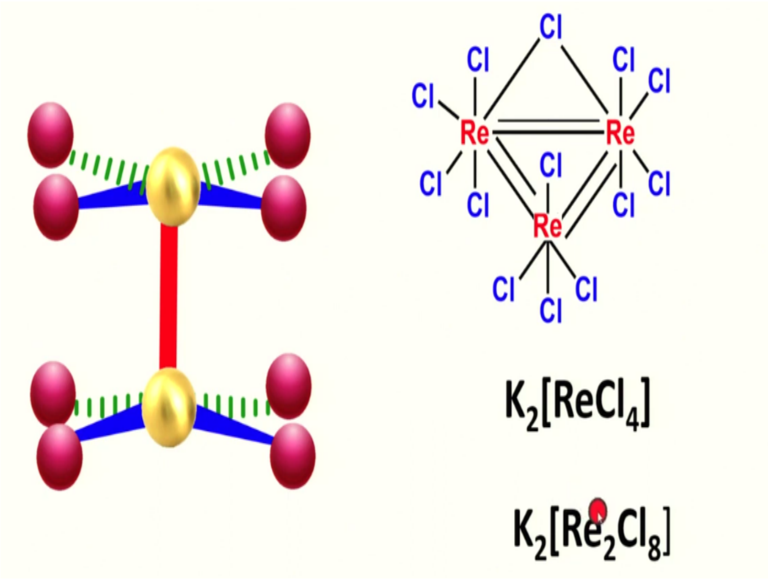

$K_2[ReCl_4]$

$K_2[Re_2Cl_8]$

Before looking into those things while working with rhenium salts, Cotton has solved the structure of the trimeric molecule Re_3Cl_{12} and he found they have double bonds between the metals in this fashion. So, he had prior knowledge of this one. However, a Russian group predicted this to be having this kind of composition, but later when they found they found it as a dianion connected through these rhenium atoms.

This is how the structure was formed after establishing through single crystal X-ray analysis. It was thought to be monoanionic and then the dimer was dianionic. So, dianion was found to have D_4 symmetry, you can see from what I showed with the eclipsed tetragonal $ReCl_4$ planes, something like this. **(Video Starts: 20:18)** They are eclipsed and with a very short rhenium-rhenium distance of 2.2 Angstrom units.

To support the short rhenium-rhenium bond and the eclipsed structure, the chlorine atoms were formed to be bent away from bond with an angle of 104. That means they will not exactly like this, what happens in order to prevent this kind, these four went up a little bit and then went down like this, in this fashion. So, something like this, establishing bonding of 104 degrees between the metals, something like this.

So clearly, the eclipsed structure appeared to be due to the electronic effects, but if you consider steric consideration, staggered would have been much more stable. So, a graduate student of Cotton named Charles Harris presented theoretical arguments for a quadruple bond between rhenium atoms. So, that means, now they went for bonding concepts: how to explain this bonding or short bond between the rhenium atoms using some bonding concepts. **(Video Ends: 21:29)**

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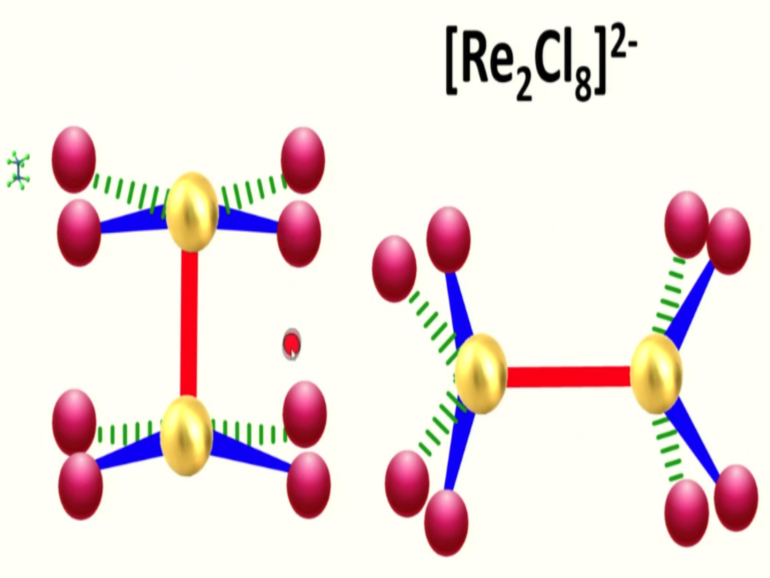

So, this is how it was appearing. As I mentioned, they went up a little bit, these four, to minimize repulsion, you should remember the fact that each chlorine has three lone pairs and they will be having some repulsive forces, to keep them away from this one. In the eclipsed configuration, they were slightly pulled up, and they were slightly pulled down, in that structure. Now let us look into the orbital interactions.

The orbital interactions between the rhenium centres included a sigma-bond followed by overlapping of $d_z{}^2$ orbitals from two rhenium atoms and then there were two degenerate π-bonds having the similar or same energy due to the overlapping of d_{xz} and d_{yz} orbitals of two rhenium atoms and a δ-bond was established through weak overlapping of d_{xy} from two metal atoms, rhenium atoms, in particular positive overlap of the adjacent d_{xy} orbitals request that the tetragonal $ReCl_4$ planes adopt eclipsed structure.

So, that means I will show you in a couple of minutes or maybe in my next lecture why the square planar units should have an eclipsed configuration, not the staggered one. So $d_x{}^2$-$_y{}^2$ orbital remains involved with ReCl bond formation and hence it does not participate in ruthenium-rhenium bonding. Since rhenium 3+ ion has d^4 electronic configuration, if you consider 4 electrons from each d orbital, we have a total of 8 electrons.

These 8 electrons would be occupied in a fashion such as σ^2, π^4 and δ^2, so that bond order will be 4. So, I shall give you a clear MO diagram and explain step by step to make you familiar with the understanding of this quadruple bonding concept and also predicting the nature of the metal-metal bond in molecules, where we have different electronic configurations. Until then have an excellent time reading chemistry.