Advanced Transition Metal Chemistry – Metal-Metal Multiple Bonding
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Lecture – 24
Metal-Metal Multiple Bonds
(Quadruple and Quintuple Theory)

Hello everyone. Once again, I welcome you all to MSB lecture series on transition metal chemistry. In my previous lecture, I was discussing about metal-metal multiple bonding. While describing the reason for metal-metal multiple bonding, I also showed you how one can use effectively the molecular orbital concept to understand the significance of metal-metal bond and also to understand the magnitude of the metal-metal bond. Let us continue from where I had stopped. Today, we shall look into more quadruple bond and quintuple bonding we come across among coordination compounds.

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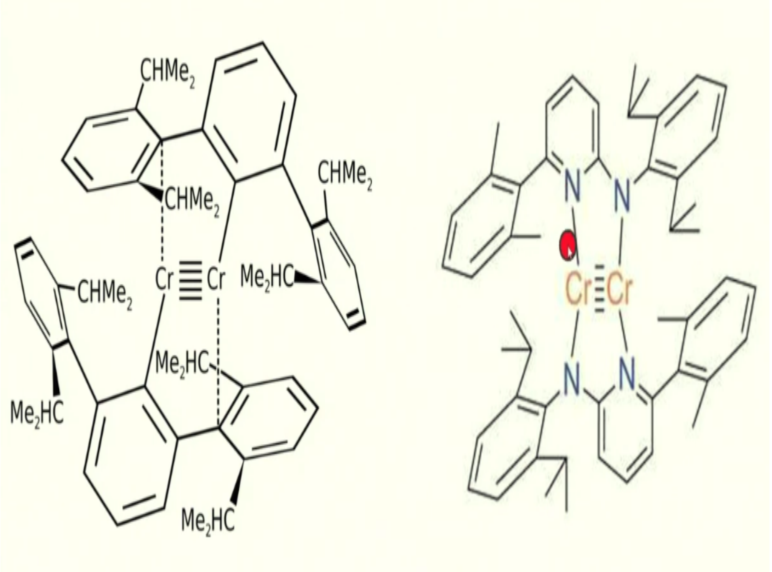

I have given here are two examples. Look into it carefully, one is a chromium complex and another one is also a chromium complex but ligands are very different. And you can see in the first one, you can see ortho-methylation is there on opposite sides and you see weak interaction with this phenyl group carbon atom. So, you are having some sort of interaction here and same thing is true here. So, that means essentially chromium has one ligand that is a very bulky ligand.

And one should remember, if you want to stabilize any metal in its low valence state which is coordinatively unsaturated, only way is you have to do it kinetically. How to do it? You have to go for a very bulky ligand so that it will give umbrella protection surrounding the metal atom so that it does not give scope for other bigger ligands to enter. So, in this context, initially this monoligated chromium compound was made and then this interacts to such monocoordinated chromium species.

They interact with this ortho substituted carbon here: you can see and as a result what happens? It appears to be having two coordination with almost linear geometry. And in this case, if you carefully count here, we have 5 bonds here and if 5 bonds are there how to explain that, same thing is true in this case also, whereas here nitrogen is there central pyridine that one is coordinating and also the nitrogen lone pair is coming here.

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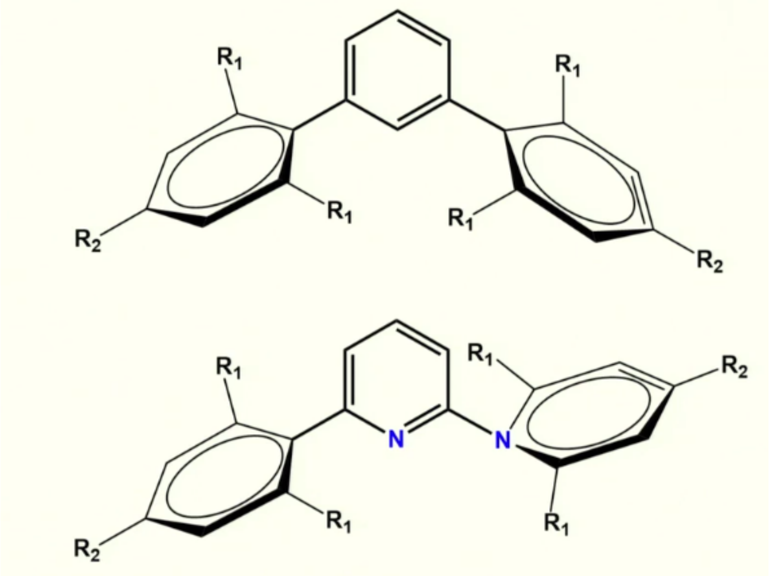

See, this is a ligand used in case of the first one and in the second case we have used this ligand. And you can see here first it binds here and you will be having almost 1:1 metal to ligand ratio. And then since this side is open, what happens 2 such molecules will arrange in such a way that something like this. They establish di-metallic core. Now we have to explain the origin of 5 bonds in this one, how to do that one?

Again, we have to go to the same concept that we used earlier to explain multiple bonding like single bond, double bond, triple bond and are up to four bonds or quadruple bond, same analogy we should use here. One interesting thing is here; in previous case we were just confined to four orbitals that is d_{z^2} forming a sigma bond, and then we had d_{xz} and d_{yz} forming two pi-bonds and then we had d_{xy} forming delta bond.

Four orbitals we used. So, four orbitals means if the capacity is 8, then you can have bond order 4, but if we want to have bond order of 5, in order to see the formation of quintuple bond, we need 5 electrons on each metal d-orbitals that means d^5 configuration we have to take in. But in earlier case when we took d^5, what happened was 2 electrons were going to delta (δ), 2 to delta star (δ*), as a result what happens, bond order was reducing from 4 to 3.

But in this case what happens since it is using *sp* hybridization, we are left with all the 5d orbitals for bonding purpose. In square planar complexes, we are using $d_{x^2-y^2}$ for making metal to ligand bond. You just recall valence bond theory where we are using a *dsp*^{2} hybridization that d orbital is $d_{x^2-y^2}$, whereas in this case it undergoes sp hybridization to accommodate 2 ligands surrounding chromium atom.

As a result what happens all the d orbitals are left unutilized and chromium electronic configuration if you see d^4s^2 or d^5s^1 and this ligand if you see the top one if it is monoanionic here through CH activation it forms, so then it is a monoanionic means oxidation state should be +1 and as a result what happens chromium will be left with 5 electrons. So, 5 electrons are there and five d-orbitals are there. Now that means along with d_{xy}, $d_{x^2-y^2}$ also participates in delta bond formation.

So, that means now we have one sigma bond, two pi bonds are there and then we have overlapping of d_{xy} and $d_{x^2-y^2}$ from two Cr^I to form two delta bonds. That means 10 electrons are there in the bonding, 10 divided by 2 = 5, so bond order is 5, this is how you can visualize quintuple bonding in these kinds of compounds, that will become clear when we go to the next one. So, I again just I have shown here how it happens. So, next, you can see here.

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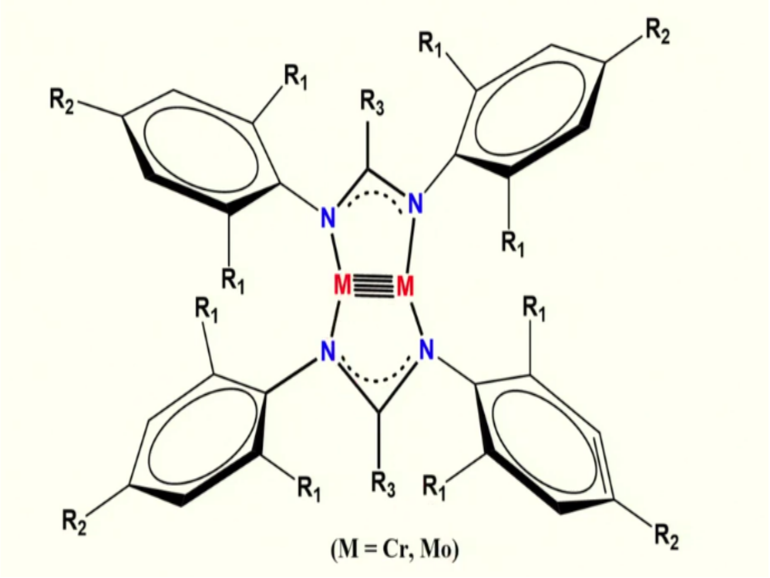

This is another compound here. Of course, here you can see, you just go back to this one and here if delocalization happens here, of course this is anionic should we say here nitrogens are coordinated. So N^- this is. So here almost is similar to NH_2^- I would say NR_2^-. So, now what happened this is delocalized as a result becomes monoanionic very similar to a couple of ligands I showed you in my earlier lecture, you can see now anionic it is, so chromium or molybdenum they are in +1 state. So, d^5 electronic configuration.

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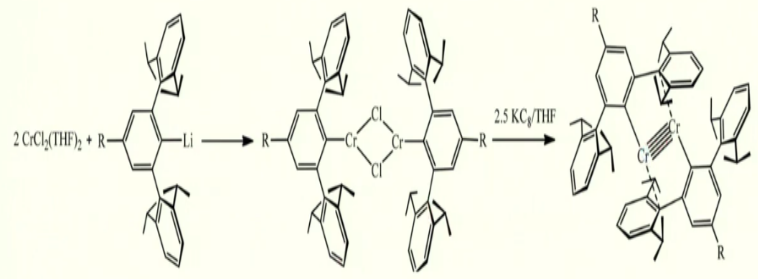

Dalton Trans., 2014, 43, 5618-5638

And how this compound is made, I have given the method here. First to take this compound where chromium is in +2 state $CrCl_2$ coordinated to two neutral ligands such as THF. You take this one and treat this one with lithiated aromatic group , LiCl comes out and you left with one Chloride here. As a result, what happens it forms a dimeric structure having to chloro bridges here.

And now, this one needs reduction for that one KC_8 potassium or graphite is taken slight excess and THF, then it will abstract the chlorides to generate chromium+1 species from chromium +2 and then now chromium+1 species is coordinatively unsaturated, it interacts with this carbon here and then establishes a bidentate mode of coordination having this kind of structure and you should remember that here we have 5 electrons in the d orbital. So, this was reported in 2014 in Dalton Transactions.

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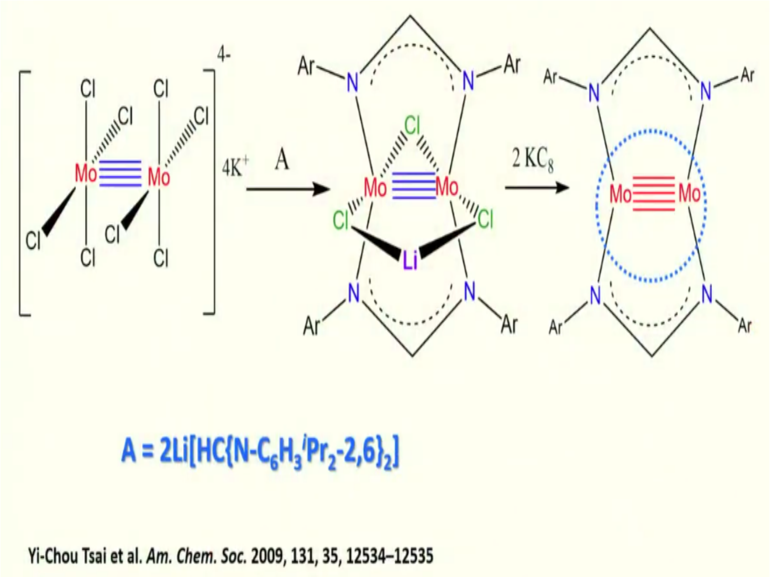

A = 2Li[HC{N-$C_6H_3{}^iPr_2$-2,6}$_2$]

Yi-Chou Tsai et al. *Am. Chem. Soc.* 2009, 131, 35, 12534–12535

So, another compound is there. I will give you the preparation of this compound also before I proceed to show the MO diagram to confirm the presence of 5 bonds. So, in this one you know this is a quadruply bonded compound very similar to rhenium dimer $[Re_2Cl_8]^{2-}$. So, just look into this one. So, this is a potassium salt and because tetra anionic so what one should do is add a ligand.

That ligand I will show you, what it is and then you can make a compound of this type here. I will show you what is A and then again you use the reduction process using potassium or graphite that leads to the formation of a quintuply bonded compound like this. So, you may be wondering what is A, so A is this one here lithiated this bulky aromatic compound here, this the lithiated one and then if you just see here two two lithiums are there.

That means when you are using two equivalent one lithium is coming out as Li Cl, so you can see the missing of one chlorine here and then another one will remain here coordinated two lone pairs of chlorine here. And then of course, once when you reduce with KC_8 everything is gone and you simply ended up with Molybdenum+1 compound having this monoanionic ligands bridging in this fashion. I am sure it is clear about preparatory methods. So, this came in 2009 **(()) (09:12)**.

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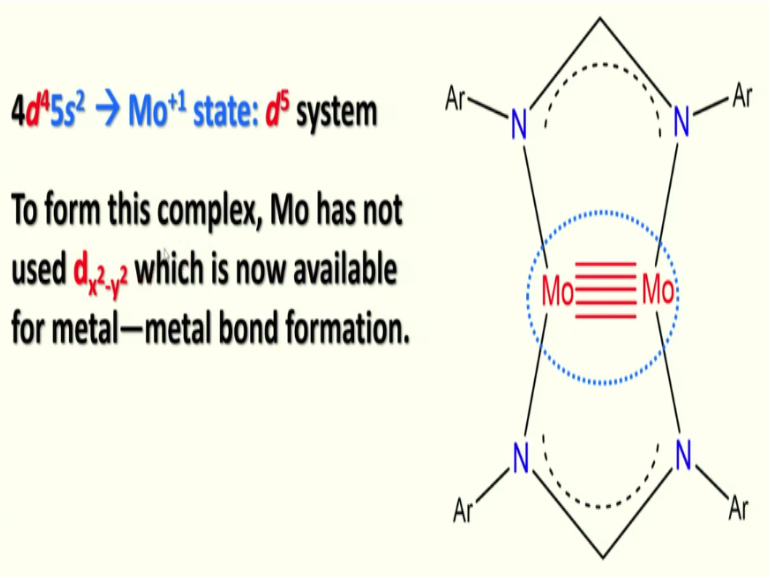

$4d^45s^2 \rightarrow Mo^{+1}$ state: d^5 system

To form this complex, Mo has not used $d_{x^2-y^2}$ which is now available for metal–metal bond formation.

So, now just see here Molybdenum is +1 state d^5 system to form this complex. As I mentioned earlier, Molybdenum has not used $d_x{}^2 - {}_y{}^2$, otherwise it would have used if it had square planar geometry. So now this is also available along with the d_{xy} oriented in this fashion, something like this one is like this and another one is at 45 degrees. Both of them can only overlap in this fashion when they stacked in along the z axis.

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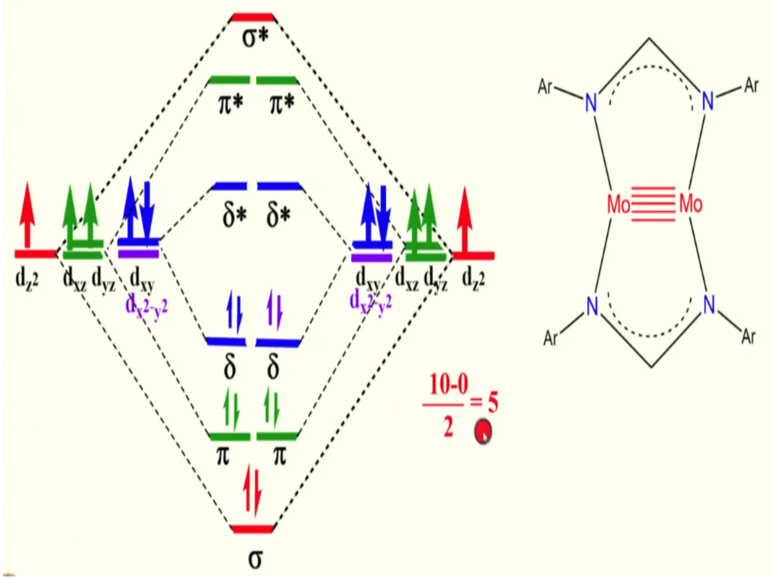

You can see here five are there. Now just see I have added $d_x{}^2 - {}_y{}^2$ also for this bonding scheme here. We have total 5 electrons, whether you take chromium or molybdenum, first to establish a sigma bond by utilizing 2 electrons and now pi bond, we are using these two, these two, 4 electrons, so two pi bonds are there.

And now we are using now 2 electrons here, one each from d_{xy} and $d_{x^2-y^2}$ from both the metal centres and then we established two delta bonds. So, then the bond order is 5. So, this is how you can explain quintuple bonding among coordination compounds having d^5 electronic configuration with $d_{x^2-y^2}$ available for metal-metal bonding.

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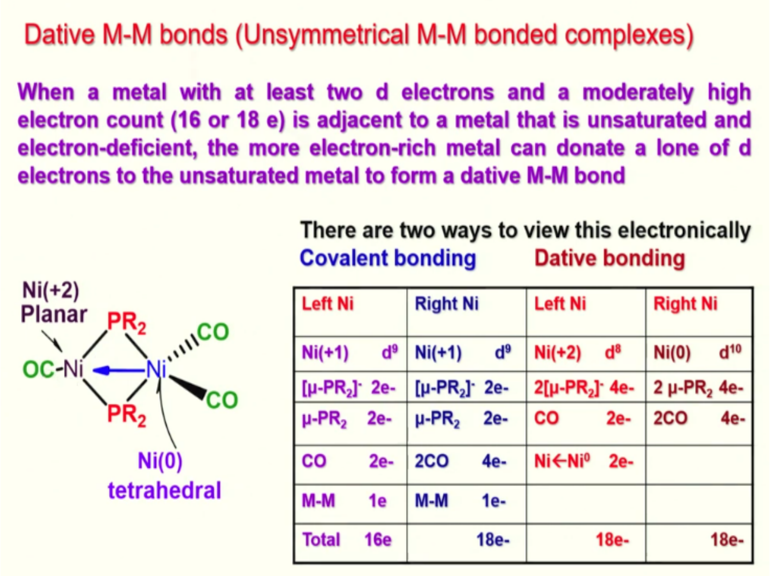

Dative M-M bonds (Unsymmetrical M-M bonded complexes)

When a metal with at least two d electrons and a moderately high electron count (16 or 18 e) is adjacent to a metal that is unsaturated and electron-deficient, the more electron-rich metal can donate a lone of d electrons to the unsaturated metal to form a dative M-M bond

There are two ways to view this electronically

Covalent bonding Dative bonding

Left Ni	Right Ni	Left Ni	Right Ni
Ni(+1) d^9	Ni(+1) d^9	Ni(+2) d^8	Ni(0) d^{10}
$[\mu\text{-}PR_2]^-$ 2e-	$[\mu\text{-}PR_2]^-$ 2e-	$2[\mu\text{-}PR_2]^-$ 4e-	2 $\mu\text{-}PR_2$ 4e-
$\mu\text{-}PR_2$ 2e-	$\mu\text{-}PR_2$ 2e-	CO 2e-	2CO 4e-
CO 2e-	2CO 4e-	$Ni \leftarrow Ni^0$ 2e-	
M-M 1e	M-M 1e-		
Total 16e	18e-	18e-	18e-

Now, let us go to another interesting component here. If you recall my previous lecture, where I classified metal-metal bonding compounds into covalent bonds and dative bonds and symmetric metal-metal bonding. So, now let us look into dative bond scheme. So, when a metal with at least two d electrons and a moderately high electron count is adjacent to a metal that is coordinatively unsaturated and electron deficient.

In that case what happens, both of them can have some sort of Lewis acid base interaction, the one metal that is electron rich can give a pair of electrons to the one which is electron deficient, provided it has empty orbital of suitable symmetry to take those electrons. In that case what happens? You can establish a dative metal-metal bond or you can call it as adduct of two metal centres. So, I have given one ideal example here.

And it is very interesting to analyse this one and there are several ways one can analyse this compound. This is a phosphide ligand here you can see PR_2^- and this is also PR_2^- and we have 3 carbonyl groups altogether. And if you just look into this one, well of course this can be +2 state. Nickel can be +2 state provided anionic establishes a bond with nickel, in that case what happens this will be +2 state that means d^8 system, d 8 + 4 is 12 and plus 14, so this becomes a 14 electron species.

On the other hand, this one is Ni^o, now PR_2^- acting as a neutral ligand towards this nickel. So, d10 + 8 is 18 electron system. That means it is very similar to $Ni(CO)_4$ or $Ni(PPh_3)_4$. Now, this is 18 and this is 14, so these electrons can go here, so that it becomes a 16 electron species and to an extent electron deficiency can be removed here. So, you can see how dative bond is directed from this coordinatively saturated and electronically rich nickel to this 14-electron species.

That means what are the other alternates? For example, we can have phosphide one each on these two metals, in that case what happens both of them will be nickel +1 state. If they are in nickel +1 state what happens the d^9 system, both of them become d^9 system and then we have anionic on both sides. So, 2 electrons are coming here and bridging one neutral also 2 electrons are coming. Whereas in this case 1 carbon monoxide is there and of course there is one metal-metal bond you can think of d^9 system.

So, 16 electrons will be there for this one. And then here in +1 state and then you have electrons, this will be 8 electrons. But here if it is 16, many d^8 systems are stable with 16 electron species, you cannot think of a dative bond. So, since it is an example that is proved through experiments and also x-ray structure, so this kind of analysis is incorrect. So, nickel +1 is not correct, instead what I said earlier, so this is in 0 state and this is in +2 state is the correct analysis and nickel with the 18 electron is donating 2 electrons to this one.

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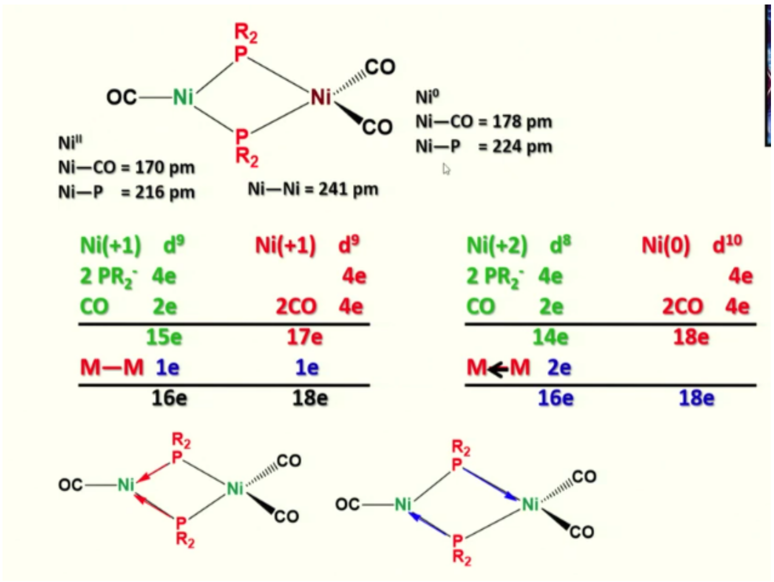

Ni^{II}
Ni—CO = 170 pm
Ni—P = 216 pm

Ni—Ni = 241 pm

Ni^0
Ni—CO = 178 pm
Ni—P = 224 pm

Ni(+1) d^9	Ni(+1) d^9	Ni(+2) d^8	Ni(0) d^{10}
2 PR_2^- 4e	4e	2 PR_2^- 4e	4e
CO 2e	2CO 4e	CO 2e	2CO 4e
15e	17e	14e	18e
M—M 1e	1e	M←M 2e	
16e	18e	16e	18e

So, let us analyze for better understanding. So, now you can see here two options. I have shown both atoms here. I have shown here nickel, this is binding to four neutral ligands with 18 electrons with d^{10} system that is 0 and now this is going this way. That means now this is a nickel +2 because here we are talking about phosphide anionic. So, this is a covalent bond and this coordinate bond.

Now, this is in nickel+2 and 16 electrons species and this will nickel^o. So, this also becomes 10 plus 16 electron species, both are 16 electron species. In that case what happens, none of them can give electrons to this. On the other hand, other alternative is as I mentioned nickel 1, nickel+1 can be there; again we overruled from my previous discussion and argument. And then what would happen here 17 and 18. And now here is 16 and 18.

But when we looked into the x-ray data what it shows is Ni—CO =170 picometre and Ni—P = 216 picometre. Now let us look into the bond parameter for this one nickel^o, Ni—CO = 178 picometre. That means it is longer. Why is it longer because it is taking some back bonding and is electron rich. With the back bonding is more to CO, what happens Ni-CO bond shrinks and CO bond distance increases.

So here this electron deficient is not readily donate electrons to pi star of CO. As a result, what happens Ni-CO bond is little longer as a result CO bond still has a triple bond character, so it is slightly shorter. So, that means this proves that this is in +2 state and this is in 0 valence state. And again, that is also reflected from Ni-P = 224 picometre. This is a coordinate bond, whereas here we have a covalent bond because it is an anionic Ph_2P^- so 216, this is shorter.

Always covalent bonds are shorter compared to coordinate bond. So, this is another proof to say that this has a dative bond with nickel°, 18 electron species and nickel+2 a 14 electron species. So, this proves beyond any doubt that there is a dative bond between two nickels and this is Ni° donating a pair of electrons to this one to overcome its electron deficiency. This is how one should analyze carefully by looking to all parameters. The Ni-Ni distances to 241 picometre or 2.41 angstrom units.

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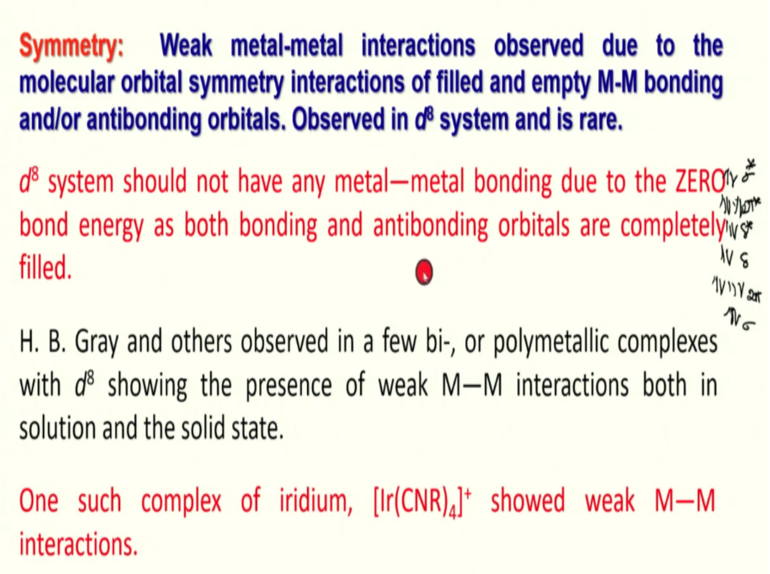

Symmetry: Weak metal-metal interactions observed due to the molecular orbital symmetry interactions of filled and empty M-M bonding and/or antibonding orbitals. Observed in d^8 system and is rare.

d^8 system should not have any metal—metal bonding due to the ZERO bond energy as both bonding and antibonding orbitals are completely filled.

H. B. Gray and others observed in a few bi-, or polymetallic complexes with d^8 showing the presence of weak M—M interactions both in solution and the solid state.

One such complex of iridium, $[Ir(CNR)_4]^+$ showed weak M—M interactions.

So now let us come to the last one. I did mention about symmetry metal-metal bonding. So, what will happen here is weak metal-metal interactions observed due to the molecular orbital symmetry interactions of filled and empty metal-metal bonding orbitals and or antibonding orbitals observed in d^8 system and is very rare. The d8 system should not have any metal-metal bonding due to the zero bond energy as both bonding and antibonding orbitals are completely filled.

That means you can see here for example if you recall the MO diagram, just I am writing here, 2 electrons sigma, 2 pi here and 2 delta and then again delta is filled and pi is filled and then sigma is filled. So, this is sigma, 2 pi and then delta, delta star, 2 pi star and sigma star. So, all 10 electrons are there, so bond order is 0. So, that means you do not expect any metal-metal bonding in a square planar complex having d^8 system.

But H. B. Gray and others observed in a few bi or polymetallic complexes having d^8 electronic configuration and showed the presence of weak metal-metal interactions both in solution and in solid state. That means if you observe in solution, these molecules retaining weak interactions and stacking along the axial position, probably there is bonding that has to be explained. So, one such complex of iridium with isocyanate showed weak metal-metal interactions and that gave enough proof to go further.

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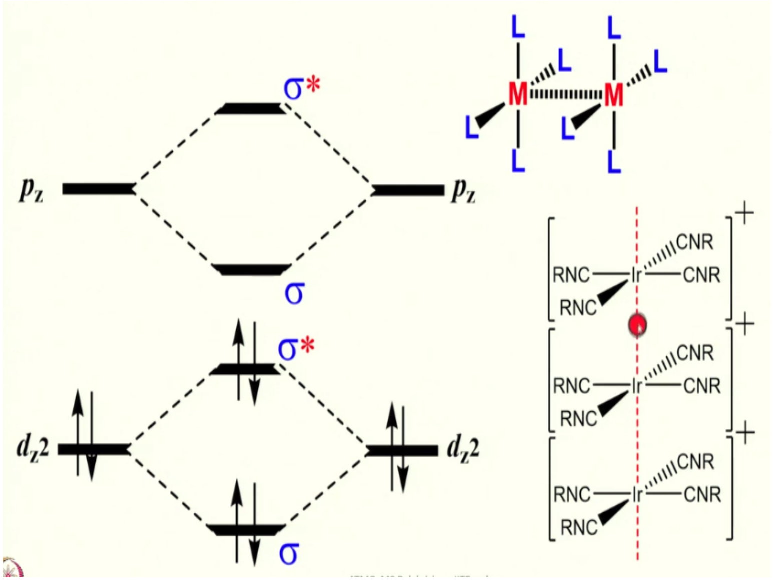

You can see here. It is iridium complex here, Ir^I compound, d^8 system having neutral isocyanate ligands, stacked up in this fashion having unusually shorter iridium-iridium bond despite we overruled any metal-metal bonding as bond order comes to 0, then how to explain this one? So, Gray proposed in 1974 that these weak metal-metal interactions were caused by a molecular orbital symmetry interaction between the field σ metal-metal bonding and σ* antibonding orbitals with the empty p_z σ and σ* orbitals.

You should remember, when we think of valence bond theory to explain the square planar complex geometries, we are using *dsp*^{2}. That means the orbital is $d_{x^2-y^2}$ and then we are using s orbital along with p_x and p_y orbitals and p_z orbital is unutilized in a square planar complex along with four other orbitals, but in d^8 what happens everything is filled.

That means now the interaction between d_{z^2}, where we have σ, σ*, filled and unfilled, they interact with empty σ and σ* of p_z orbitals. That means take p_z orbitals from two metal centres and try to establish a molecular orbital σ p_z and σ*p_z and then they are empty and whereas this is filled. That means there is some interaction happens between these two pair of molecular orbitals, the filled d_{z}^{2} bonding and antibonding orbitals with empty p_z.

Due to these kinds of interactions, the empty orbitals are pushed up in energy and the filled orbitals pushed down in energy by the symmetry interaction. So due to this kind of arrangement, this generates a weak metal-metal bond strong enough to allow these complexes to form M-M bonds and retain them even in solution. So, this was observed in many complexes of iridium and even palladium and platinum compounds with the d^8 electronic configuration.

Probably if you look into literature and work by Gray, you will come across more examples. With this, I am completing the discussion on metal-metal multiple bonding. So, once this is done, you should remember one thing, when we predict metal-metal bonding in these cases, where you can have single bond, double bond, triple bond, quadruple bond or quintuple bonding, the concept usually is very different compared to what we come across in predicting metal-metal bonding while using the 18 electron rule.

Some time, there may be in some cases, it does not apply, do not try to mix up, they are different entities and different type of compounds we come across of these things. There may be some examples where we can see both merging to give a correct explanation about 18 electron rule, nevertheless they are different entities but beautiful concepts and without any problem one can explain using simple molecular orbital concept.

What one should remember is again, in case of square planter complexes we have 4d orbitals are there, d_{z}^{2}, d_{xy}, d_{xz} and d_{yz}, and d_{xz} and d_{yz} generate two pi bonds, d_{z}^{2} generates one sigma bond and because of their orientation d_{xy} will overlap only like this and they generate delta bonding. And then we have 8 electrons in the bonding and if bond order is nothing but number of electrons present in bonding orbitals minus number of electrons present in the antibonding divided by 2.

So, this gives the bond magnitude of 4, to have 4 bonds or a quadruple bond, though a square planar metal complex should have d^4 electronic configuration or they should have 4 electrons in their d orbitals. And if we have unutilized $d_{z}^{2}{-}_{y}^{2}$ also with lower symmetry or *sp* hybridization for example, in that case what happens $d_{z}^{2}{-}_{y}^{2}$ is also made available for bonding. In that case, all 5d orbitals are available for bonding you can imagine or you can explain and quintuple bonding.

There may be more examples. Of course, if you are more interested you can always go to literature and look into more examples. In my next lecture, I shall discuss about the preparation of some of the important coordination compounds and organometallic compounds keeping their utility in further reactions and then making ideal compounds for homogeneous catalysis. Until then have an excellent time reading chemistry.