Transition Metal Organometallic Chemistry: Principles to Applications
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Week - 09
Lecture - 44
Transition Metal Carbonyls: Bonding properties

Welcome to this lecture on transition metal organometallic chemistry from principles to applications. We have been looking at very important class of compounds particularly the transition metal carbonyl compounds in the last few lectures. This compounds, as mentioned that these are very long lone in the field of organometallic a compounds unlike the carbene complexes which were discovered recently transition metal carbonyl have been known for more than a century in the area of transition metal organometallic complexes.

However, what is interesting about this transition metal carbonyl compounds is the fact that even though they have been long discovered for over a century their bonding properties have only been recently studied and understood. So, this transition metal carbonyl compounds even though they have been discovered for over a century their bonding properties are only being recently understood.

So, in the last lecture, what we have discussed was the type of bonding mounds of these transition metal carbonyl complexes.

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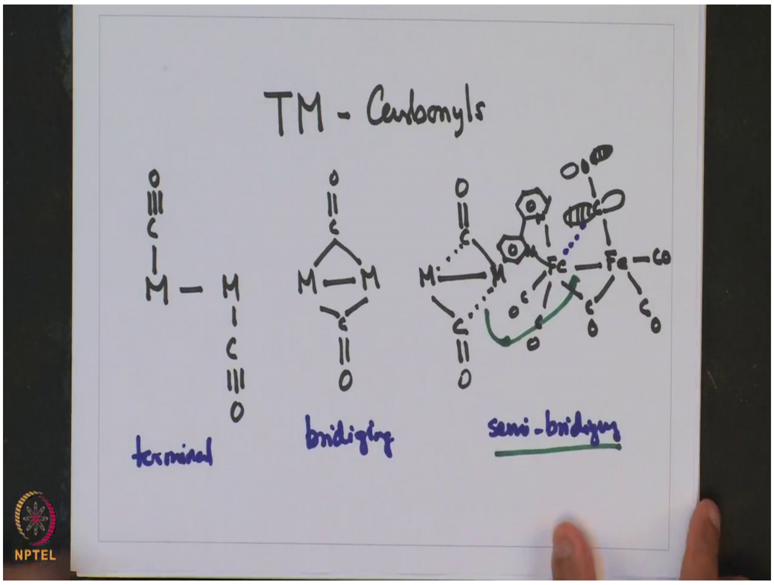

And what we had seen the transition metal carbonyls can be the terminal ones of the ones which is shown; which is the terminal carbonyl. It can also be a bridging type or can be semi bridging as one can see from here of the type this and very nice example of this semi bridging complex was achieved by binding to bipyridine ligand in a iron carbonyl compound where it was found that the same bridging reaction occurs when this bipyridine ligand which makes the iron more electron rich interact with the pi star orbital of this carbon monoxide ligand and leading to this semi bridging bonding that we had seen.

And this semi bridging arises because of disproportionate electron density between the 2 iron centres and that arises because of replacement of carbonyl by the strong electron sigma donor bipyridine ligand. Now, continuing further on this discussion, we are going to look at various kinds of unsymmetrical sigma pi bridging in metal carbonyls.

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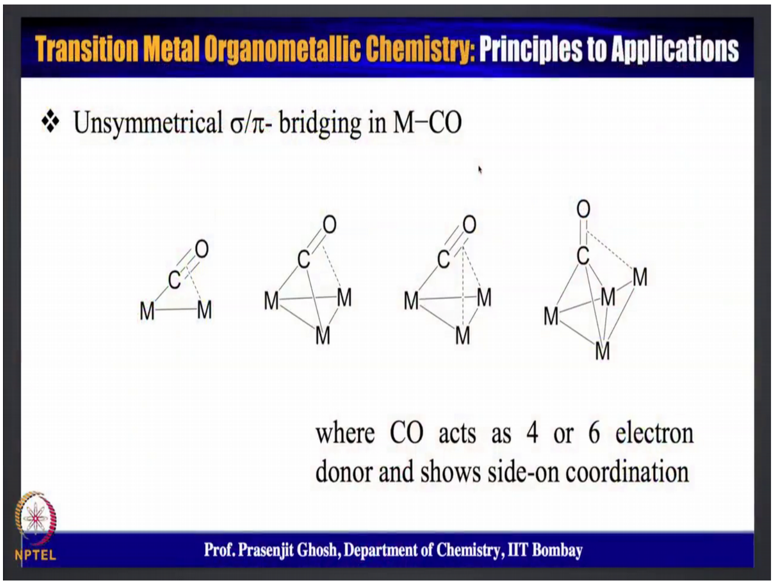

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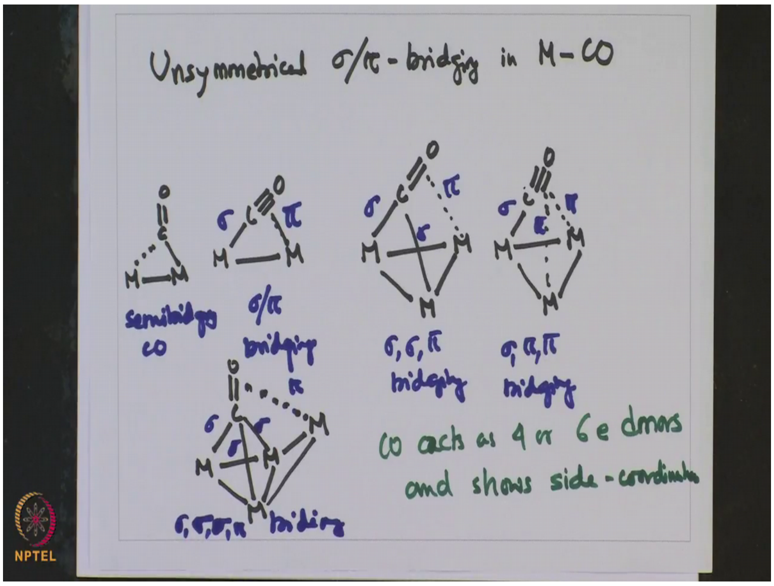

And this is gained by metal carbonyls and one can see that apart from the semi bridging which we had just discussed there can be unsymmetrical sigma pi kind of bridging which is shown over here.

So, here it is pi type interaction from the carbonyl and here, it is sigma type, on the other hand, the semi bridging ones that we had just now seen that was slightly different from this in the sense that this metal was interacting with the CO carbon whereas, the second metal is interacting with the CO pi cloud. So, this is pi type and this is sigma type and this is how, this kind of bonding is different from semi bridging and this is sigma pi type pi nuclear bridging, there other variants of this sigma pi bridging which can extend from one metal centre to another metal centre as can be seen over here.

Now, in this case, this is pi this is sigma and this is sigma is also bridging now bridging over 3 metal centres there is a variation of this where this is sigma; sigma pi 1 can have slightly different. So, in this case this is sigma pi-pi bridging.

And another very interesting example involved this is sigma pi type; so, bridging; now as one can say that carbon monoxide can act as 4 or 6 electron donors and shows side on coordination. Now in order to understand; how does this carbon monoxide unit interacts with the metal frontier orbital one needs to look at what is the bonding scenario of CO or carbon monoxide before that we are going to take a look at some of the examples of sigma pi bridging carbonyls which have been structurally characterised.

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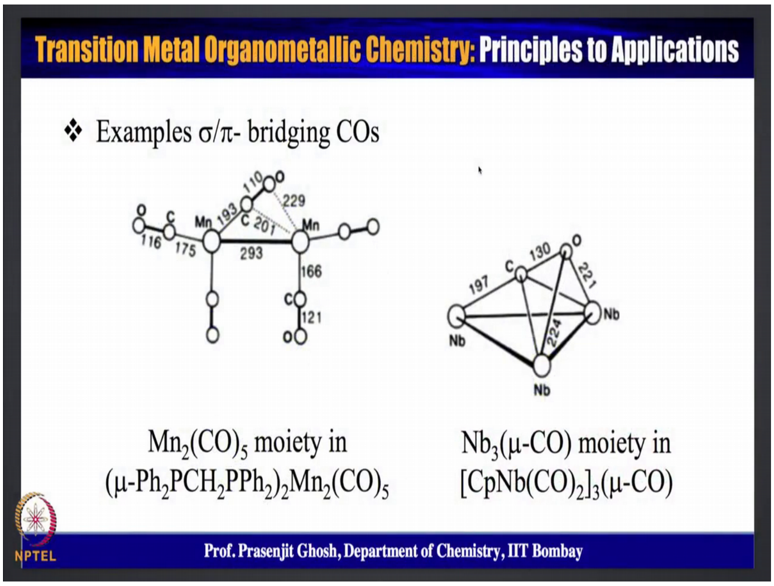

One such example is this manganese complex which is this Mn 2 CO 5 moiety in mu Ph 2 P CH 2 PPh 2 whole 2 Mn 2 CO 5.

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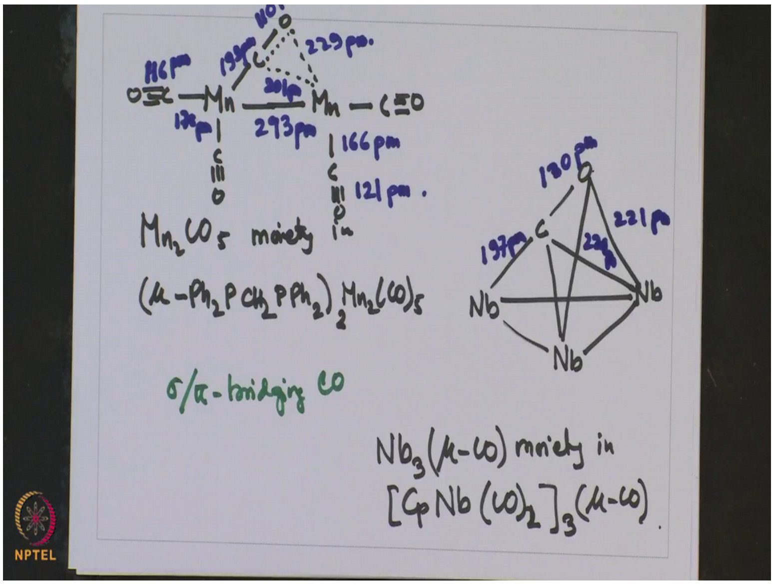

For clarity purpose this mu Ph 2 C Ph 2 moiety is vomited for sake of clarity of the drawing and this sigma pi bridging example of manganese can be seen over here for example, it is Mn CO.

Now, manganese distance is 293 picometer, manganese carbon distance is 166 picometer terminal carbonyl and CO distance is 121 picometer in this terminal carbonyl. This distance; it was 166, this is 175 picometer and this carbon monoxide is 116 picometer.

Now, this is a bridging carbonyl. So, this has a greater manganese carbon distance of 193 picometer and this pi interaction is 201 picometer and 229 picometer and this CO is 110 picometer. Similarly another example is this bridging sigma pi bridging carbonyl is found in is found in Nb 3 mu CO unit moiety in CpNb CO 2, whole 3 mu CO here to see similar sigma pi bridging happening. So, we have Nb, Nb, Nb; 3 of them, then CO; this is bonded to this is sigma pi. So, this CO is bonded to 1 Nb another, then same series bonded to another niobium and this NbC bridging distances 197 picometer the CO is 130 picometer and NbO is 224 picometer and NbO is 221 picometer.

So, what we see by comparing these 2 structures that this sigma pi bridging compounds are present in big cluster compounds with having bulky ligands and what also we see that the bridging carbonyl metal carbonyl distances around 200 picometer; 193 picometer for manganese and 197 for picometer for niobium and also the CO metal interaction on the side on overlap is around 221 to 229 picometer and same it to see in case of the niobium.

So, what we see is that this bridging sigma pi carbonyl compounds exhibit longer the metal carbonyl distance as is expected and also the pi interaction to the metal is even weaker and that even gives even longer distances. So, these 2 are pi bridging. So, pi electron interaction with the metal and they are the longest and this is the sigma interaction in the metal and so, hence, this has the shorter bond and same thing, we see for the manganese complex as well as for the niobium complex in both of this complex is this bulky ligand mu Ph 2 P CH 2 Ph or in the niobium case Cp niobium CO 2, those bulky ligands has been Cp and CO 2 have been nominated for sake of clarity.

So, with these as I said that to understand the sigma pi bridging nature one has to look at the molecular orbital diagram of the carbonyl to get a clear picture of how the carbonyl or by frontier orbitals interacts with this metal.

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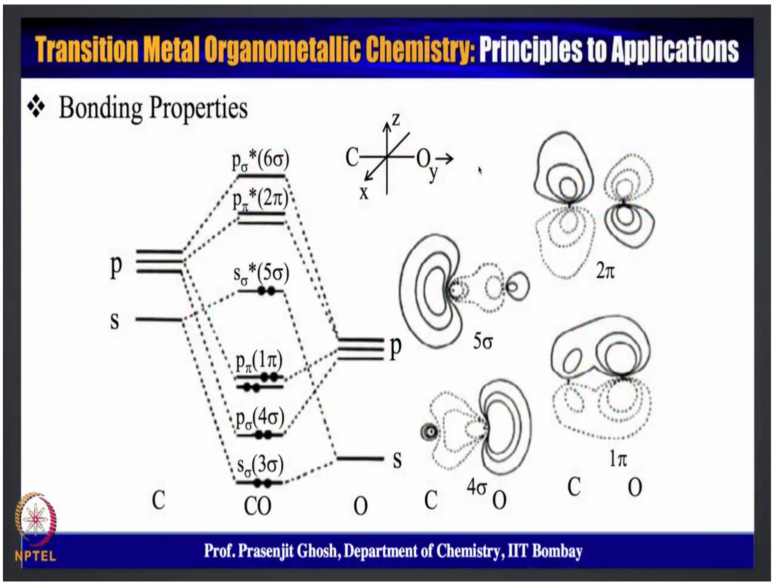

Frontier orbital; so, to understand this, let us surround take a look at the frontier molecular orbital of CO. So, we have carbon monoxide we have oxygen.

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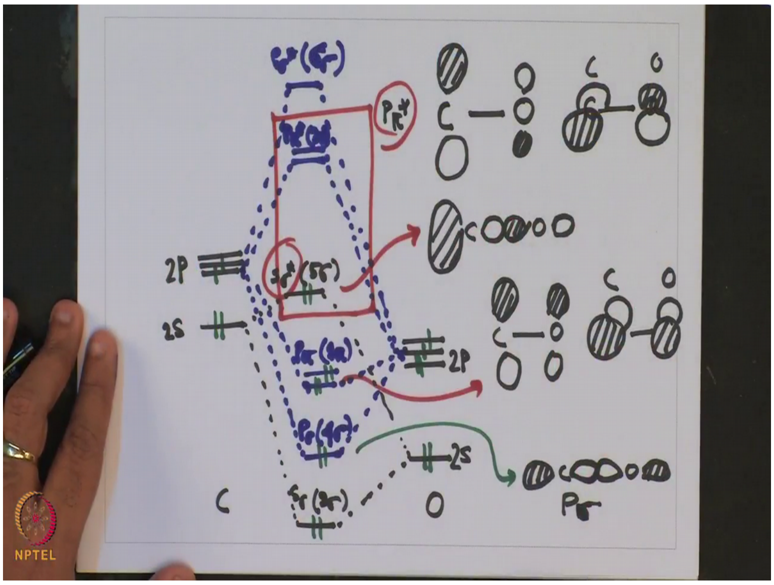

Carbon has S and P has the valance electron. So, this is the S orbital and then this is the P orbital to S to P a and oxygen is also has S and P orbital, but oxygen being more electronegative; these orbital are more closely held to the oxygen. So, this becomes S and this become P orbitals for oxygen carbon has P 2 configuration. So, there are 2 on the P and this is full oxygen has P 6. So, so there are 4 in the P and 2 on the oxygen and the S of carbon interact with the S of oxygen and to give sigma bonding interaction as well as sigma star interaction.

So, this is sigma or S sigma 3 sigma and this is S sigma star, this is pi sigma orbital. Now as for the P orbitals are concerned there is 1 S and 2 P interactions. So, first is the P z interacting with P z? So, giving P sigma orbital this is P sigma or 4 sigma orbital and that gives a P sigma star or 6 sigma orbital. So, that interacts with one of the P orbital of oxygen given P orbital of carbon giving the corresponding sigma star and that leaves with to P y orbitals which P pi type and these are degenerate and then these are P pi star 2 pi type.

Now, with these there are ten electrons 4 plus 6. So, 2, 4, 8 and 10, all of these are occupied. So, what is important over here is this frontier orbitals vital frontier orbital is pi sigma star is the frontier orbitals. Now pi sigma star sort of looks like something like this something. So, you have this something like this and this is the front frontier orbital and then this pi star is the empty CO orbital. So, the pi star would look like. This is P pi star. So, one orbital would look something like this is degenerate. So, it has 2 orbitals. So, this is also a pi star orbital and similarly the sigma orbital would look like this is P sigma orbital and the corresponding the P pi orbital would look like and so, this is the corresponding pi orbital. Now if you look at it.

So, this gives us a fair amount of idea about how this C orbitals looks like what we see is that the carbon mono CO interaction consist of S and P orbitals of the carbon interacting with S and P orbitals of the oxygen the oxygen or molecular orbitals are low in energy and as a result, there are 3 sigma bonds this is the sigma between the S this is the sigma between the pi orbital which is shown over here and this is the pi star orbital sigma will be pi this is the py orbitals bonding 2 of them degenerate in perpendicular plane of each other now this is the sigma star orbital which is over here and then the pi star orbital comes around over here.

Now, these are the say 5 sigma star and P pi star are the frontier molecular orbitals and these frontier molecular orbitals interact with the metal orbitals and then corresponding the binding modes of how these frontier molecular orbital interacts the metal come into picture so that thing that we should focus. Now these 4 orbitals. So, this is the homo and these are the lumos; where these are pi star orbitals and the homo is the sigma star orbital which interact with the metal when it comes to the metal carbonyl interaction.

So, with these let me conclude what we have discussed in today's lecture; today's lecture covers the very important topic which is very fundamental and needs to be elaborated with proper understanding and what we have discussed today is about the binding modes of metal. Particularly, in this lecture we have started with semi bridging modes of metal carbonyl complexes in which metal bridges with the carbonyl complexes.

Then we have looked at various possible examples that may arise out of sigma and pi bridging type of carbonyl complexes these are different from the semi bridging ones and we have elaborated that with examples we have seen in sigma pi bridging kind of complexes carbon mono CO can donate as a as many as of to 4 or 6 pi electrons and this may lead to sidewise overlap which is new kind of bridge binding mode of carbon monoxide.

We have looked into specific examples where like Mn 2 CO 5 in a particular complex where you can see the sigma pi bridging type of carbon monoxides this examples have been structurally characterised and then we have looked into the metal carbonyl interactions particular with respect to this bridging sigma and pi type and for that reason we have constructed this mo molecular orbital correlation diagram between the CO unit between the S and the P orbitals of the carbon monoxide and we have seen how these orbitals are found by mutual interaction and we have identified, this 5 sigma as the homo which is the lone pair on the carbon monoxide the orbital is very close to the carbonyl energy that is why this homo represents more of more is more on carbon which binds the metal.

And then we also have identified degenerate P pi type pi star type orbitals which are empty a and they can accept electrons when they interact with the metals we looked at the corresponding molecular orbital diagrams of this orbitals constructed from atomic orbitals of this carbon and oxygen fragments.

So, with these I would like to conclude today's discussions. On this bridging mode of carbon monoxide and we are going to take this discussion bit more detail in the subsequent lecture, whereby, we will see that how this molecular CO molecular orbital constructed in this lecture, help us understand and realise the subsequent contraction of this metal carbonyl with metal fragment molecular orbitals.

So, of these will throw some insight as to how carbon monoxide binds and bridges with a metal in a terminal or bridging fashion. So, with this I would like to conclude today's lecture and thank you for being with me, till the next lecture which will be on more of binding modes of carbon monoxide and then understanding atom molecular orbital level; so, till then goodbye and.

Thank you.