Transition Metal Organometallic Chemistry: Principles to Applications
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Lecture - 45
Transition Metal Carbonyls: Bonding properties

Welcome to this lecture, on transition metal organometallic chemistry from principles to applications. We have been discussing a very important topic in the last lecture and this is about transition metal carbonyl it is bonding properties.

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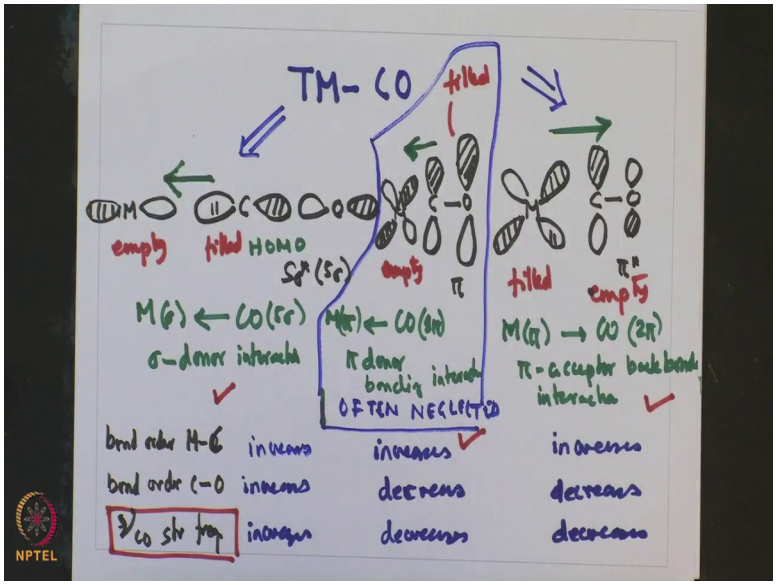

In transition metal carbonyl bonding properties that, we have been studying what we saw is that, in order to understand metal carbonyl transition metal carbonyl bond, we need to first understand carbon CO bond or carbon monoxide bond and to understand this. We have treated this metal carbonyl interaction with regard to molecular orbital theory particularly constructing all molecular orbitals of carbon monoxide, and this we have done by looking at how the atomic orbital of carbon and atomic orbital of oxygen combine to give the carbon monoxide molecular orbital.

Now, having done this construction of molecular orbital in the previous lecture, what we have discussed upon is frontier molecular orbitals of the carbon monoxide which interact with the frontier atomic orbitals of the metal. And what we have seen that, frontier

molecular orbitals of the carbon monoxide consist of sigma orbital on carbon, which contains the lone pair and that can be given something like this and it has the lone pair.

So, this is sigma star or 5 sigma orbital. So, this is a field orbital which is sort of the HOMO of carbon monoxide and we had also seen the lumo contains 2 degenerate orbital, which is a p type and contains interaction like this.

So, this is a pi star orbital and similarly, there can be CO pi orbital corresponding to that, similarly a pi orbital which is CO pi. Now, this what is interest, what we are right now focusing on this lecture is this how this orbitals 1 sigma and 1 pi orbitals CO pi and CO pi star, these orbitals how does interact with the metal orbitals.

So, for example, as for the CO sigma star, which interacting containing a lone pair like to in the metal orbital interaction. So, this is empty and this is filled and this is often referred it refer to as metal sigma CO2, metal sigma or this is called sigma donor interaction where, interaction is happening over here.

Now, the other important interaction which will happen is that, this empty pi star will interact with filled metal orbital as shown over here, and this is called metal pi to CO2 pi or pi acceptor back bonding interaction.

Now, apart from these 2 interaction this one and this one which has been discussed here, there is another interaction which is often neglected, but nonetheless I would like to show it in this discussion is that, this CO pi orbital donating electron to metal pi orbital, which is empty and this is filled and this is called CO 1 pi to M pi, pi donor bonding interaction.

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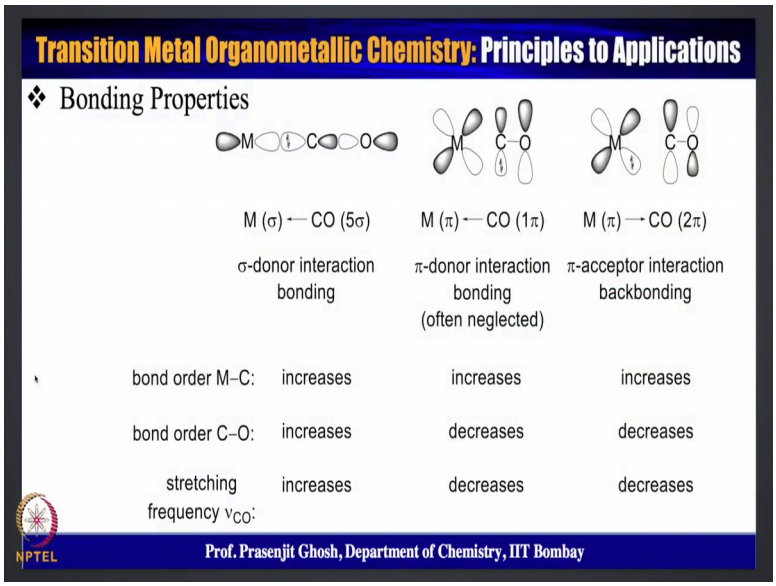

But these interaction pi donor bonding interaction, which is depicted over here is often neglected mainly, when people talk about metal CO interaction, they talk about of the 2 interactions one is this CO to metal sigma interaction and the other is metal to CO pi back interaction these 2 interactions are often spoken about and this interaction of CO field to metal pi vacant is often neglected, but nonetheless this is an important interaction and is being discussed in this current topic.

Now, what is important that each of these interaction effects the metal CO bond order, also bond order of and CO and new CO stretching frequency. So, as this forward sigma do donation or backward pi do donation forward pi do donation affect, then it affects the metal CO bond order, as well as CO bond order and as a result the CO stretching frequency increases or decreases they get affected.

Now, what has been observed is that as the metal C bond order increases because, of sigma do donation of the carbonyl if this the sigma do donation increases then, metal C bond order increases similarly, if this interaction this do donation pi to the metal vacant increases, then again the metal C bond order increases, because now a bond is being formed and if the metal to pi back bonding interaction also increases, that also leads to increase in metal C bond order.

So, what we see is that the interaction between CO and transition metal, in forward sigma donation forward pi donation or backward pi donation increases the bond order of

metal C; however, the forward sigma donation forward pi donation backward pi donation affects the CO bond order differently.

For example, in the forward sigma donation metal CO sigma donation the CO bond order also increases and that is because, when the electron density is moved from carbon onto the bonding region carbon develop positively charged, and that the CO bond now is more tightly held as a result the CO bond order increases and stretching frequency of CO also increases; however, when the CO 2 metal forward pi donation increases, then the CO pi bond weakens because of this pi donation and as a result CO bond order decreases and if because, of the pi electron now being donated to the metal CO bond order decreases.

Then CO stretching frequency also decreases and lastly when metal to CO pi back bonding increases, there to since the electron is being dumped on the anti bonding orbital. So, the CO bond order again decreases and correspondingly CO stretching frequency decreases.

Now, what we come to see is that, this CO stretching frequency is an important experimental marker, that can reflect on these 3 interaction this one forward sigma donation, forward pi donation, as well as backward pi donation and from the increase or decrease variation of the CO stretching frequency one can have an insight into the extent of forward donation, that is CO is undergoing with the metal orbital or the extent of backward donation, that the metal orbital is undergoing with the CO.

Now, as I said in the beginning of the discussion, that the forward sigma donation and backward pi donation are the ones which are mostly spoken about and this forward pi donation the one that is shown over here, is less prominent or more often neglected, but these are more important when it comes to sigma pi kind of bridging modes where, the pi or orbital gets engaged with the metal pi type empty orbital and donate it is pi electron cloud onto the metal pi vacant pi orbital as a result since, the electron density on the bonding pi orbital is given to the vacant metal d orbital of appropriate symmetry the pi bond weakens and as the pi bond weakens the CO bond order decreases and CO stretching frequency decreases.

Now, as for the metal to carbon pi star pi back donation the electron donates on to the pi star orbital now, pi start orbital get strengthen; that means, the CO bond order decreases and as a result the CO stretching frequency decreases. So, this is a very important slide

which gives a total perspective of on how CO interacts with the metal? And how this interaction may affect CO stretching frequencies?

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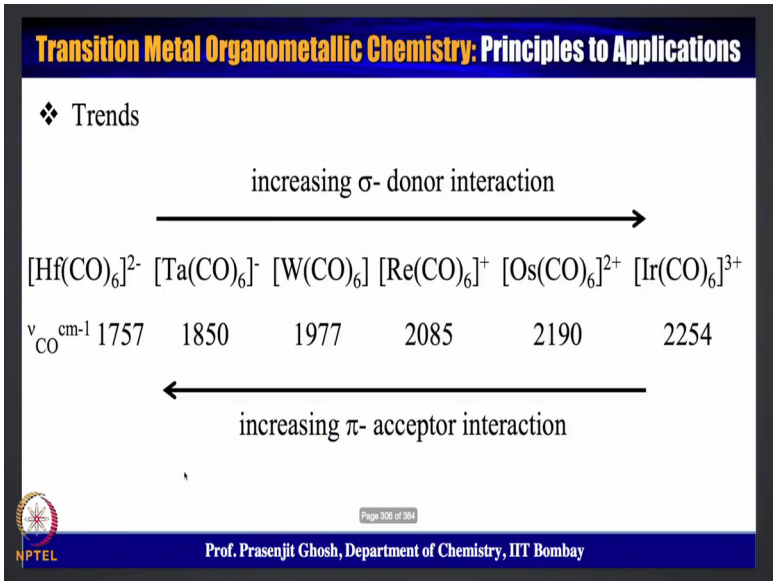

We are going to deal these in more details for example, we are going to take a look at series of complexes these are all d 6 type complexes.

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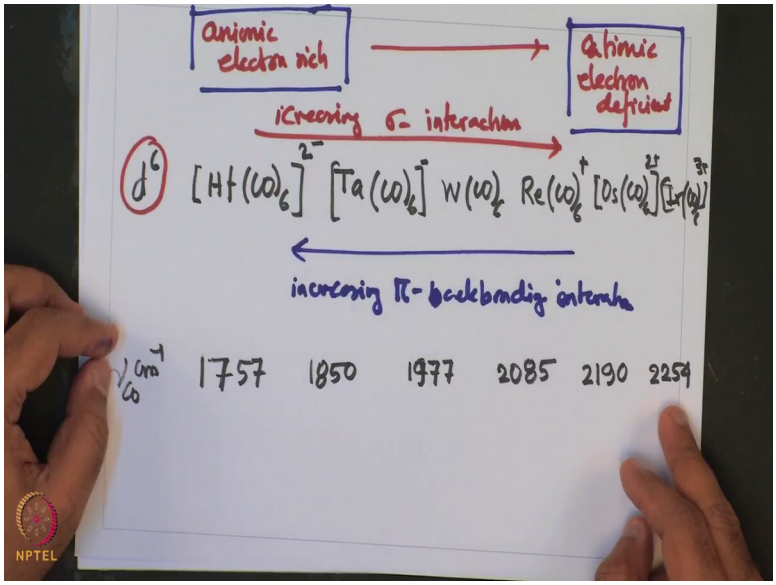

For example, between hafnium CO 6 2 minus this is a metalate this has d 6 electron, then let say tantalum CO 6 minus comes tungs10 CO 6 which is the neutral, then comes rhenium CO6 plus followed by osmium CO 6 2 plus finally, iridium CO 6 3 plus. All of

these are d 6 systems; that means, it has d 6 systems, but it goes from anionic electron rich metal centre to cationic electron deficient metal centre, as a result the backward now, the backward pi donation decreases or sigma interaction increases this way.

So, for this kind of complexes. So, more on the right-hand side places the back donation and more is the sigma interaction and on going from right to the left increasing the left one being more electron rich it has, it undergoes increasing pi acceptor interact or pi back bonding interaction.

So, on one side on the left-hand side we have anionic electron rich complexes on the right-hand side, we have cationic electron deficient complexes which will not undergo pi back donation. The ones which it will not undergo pi back donation for them the nu CO stretching frequency will be the highest, and that is exactly what we see centimetre onwards for example, for hafnium which is highly electron rich can undergo significant amount of hafnium CO back bonding has very low stretching frequency of 1757, then tantalum which is slightly lesser electron rich has 1850, tungsten 1977, rhenium 2085, osmium 2190 and iridium 2254.

So, this is the nice example where we the metal ligand, metal CO sigma, as well as metal CO back interaction, that we have studied how they can be explained, then we used to explain the variation of nu CO stretching on going from very electron rich metal centre to a very electron deficient metal centre and what it is observed, that the more electron deficient metal centre cannot undergo pi back donation as a result the CO stretching frequency is the maximum and a electron rich metal centre which can undergo pi back donation will lead to weakening of the CO bond order, and that would be followed by lower ring of CO stretching frequency.

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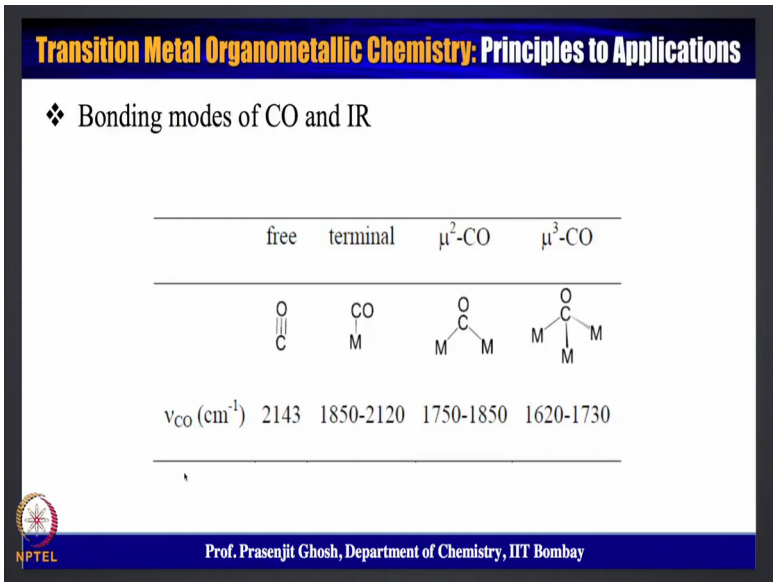

We will take a look at few more of the type of binding modes of CO and how that correlates with the CO stretching frequencies, that will also give us insight as to how the bind on modes affect the metal carbonyl stretching frequency.

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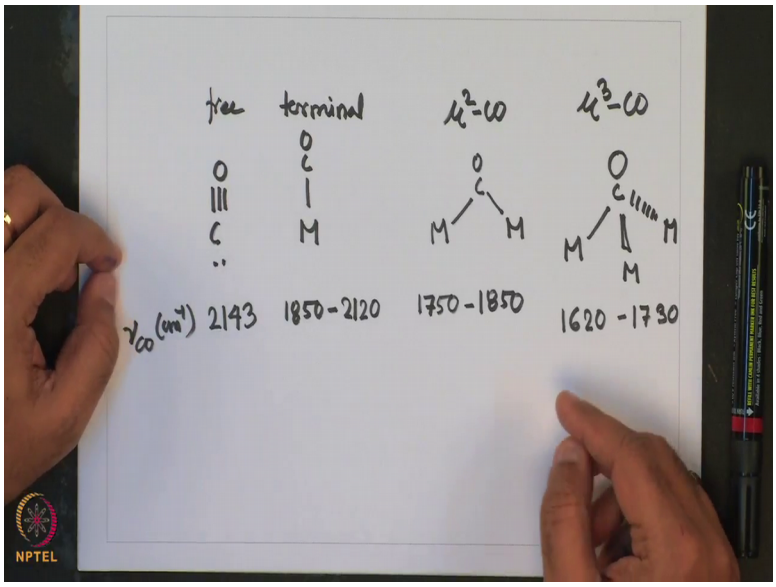

For example for free CO the nu CO stretch is 2143, for terminal CO nu CO stretch has reduced now, as opposed to free CO the metal can undergo pi back donation to the extent of is electron richness and one can observe a range where, it has gone down to 1850 where, significant amount of back donation has happened 2120 which is very high and

close to 2143 where, minimal amount of back donation has happened to mu 2 CO where, CO can bridge between 2 metal.

Now, bridging COs there is significant amount of interaction or back donation from the metal, and the bond order right now has moved from 3 to 2 and that is reflected in the CO stretching frequency where, it has even further fall into 1752-1852 something like mu 3 CO where now, CO is bridging between 3 metal centres and for that this has also fallen substantially from 1620-1730.

So, what we see is that there is ah huge amount of correlation happening between the binding modes of CO and the corresponding switching frequencies and what one see is that, if one goes from free carbonyl on the way to terminal metal carbonyl where, carbonyl is bond to one metal to the mu 2 bridging type where, carbonyl is bond to 2 metals to mu 3 bridging type where, carbonyl is bond to 3 metals in all of the cases the stretching frequency decreases on going from 2143 to 1850 to 2120 to 1750 to 1850 to 1620 to 1730.

Now, electron density of metal which is reflected or astride by the charge in the metal leads to variation in electron density, and that can be seen for this following kind of complexes these are all d 10 complexes.

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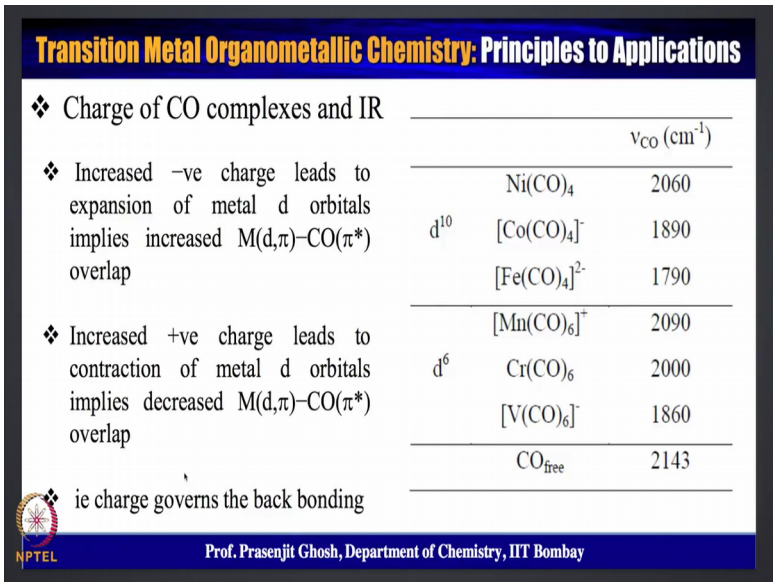

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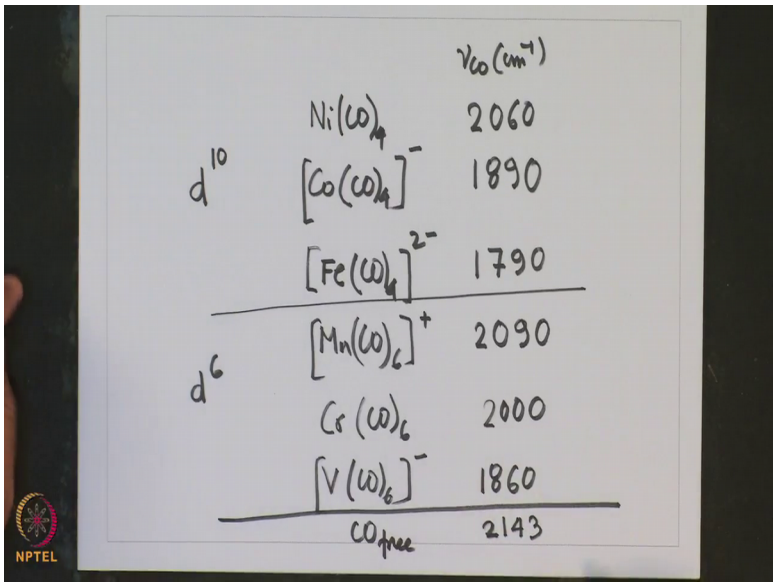

Let us say nickel tetracarbonyl which has a nu CO of 2060 now, when it becomes to cobalt tetracarbonyl this is also a d 10 system now this being mono anionic. So, metal is more electron rich and now, the nu CO has further decreased because of it is extensive backbone donation to 1890, then to iron tetracarbonyl 4 2 minus which again is a d 10 system now, it is dianoinic it even goes further to 1790.

So, what we see is as the metal centre is more electron rich, then the metal to CO pi star back donation increases as a result the CO stretching frequency decreases. The same is observed in another set of d 6 systems for example, Mn CO 6 plus which is a d 6 system now, this being a cationic complex has cannot undergo too much of back donation and hence now, the CO stretching frequency is quite high because, there is a little back donation happening from cationic manganese onto the CO pi star as a result leading to very high CO stretching frequency.

Then another chromium CO 6 this is the neutral this is compound were related to manganese cationic compound significant amount of back donation happens and now 2090 has reduced to 2000 centimetre inverse to finally, going to anionic VCO 6 minus where, metal is more electron rich back donation is permitted, and then this has even gone further to 1860.

So, just to give you a feel for free CO where, there is no back donation opening the stretching frequency is very high because, of the triple bonded nature of the CO bond

and that arise at 2143. So, with these let me summarise the development which has been spoken about in today's lecture, we have looked at various kinds of binding modes of carbonyls to begin with metals and what we saw that, the interaction of the frontier atomic orbital of the metal plays a key role in understanding the metal carbonyl binding, and that can happen through sigma donation from the carbon lone pair on to empty metal orbital or the pi orbital of the CO donating on to the empty metal orbital this is pi forward donation this usually is kind of neglected or not. So, common and the last kind of interaction that may happen is from filled metal orbital on to vacant CO pi star orbital.

Now, we had seen that how each of this interaction would affect the CO and metal carbon bond orders and which would can be reflected in the CO stretching frequencies on that, in mind we have taken a look at some of the examples where we saw that, variation of metal electron richness of the metal for a particular valance orbital let us say for d 6 or d 10 systems that, we have looked at that we saw that, as one goes from electron rich to electron deficient metal centre we see that, with the decrease in the back donation the CO stretching frequency increases for electron deficient metal centre.

So, we have also discussed about the correlation of types of bridging is sort of bigger to terminal or mu 2 CO or mu 3 CO of carbonyl with the metal centre with respect to how they affect the stretching frequencies of the CO bond. So, with that let me conclude today's lecture where, we have given a brief as well as very detailed discussion on how the CO stretching frequencies can be actively used in understanding the type of interaction that, may happen between those frontier orbitals of CO with that, of the frontier atomic orbitals of the metal and how these interaction will help detect or determine the kind of stretching frequencies or variation in stretching frequencies that one observed.

So, with that I would like to thank you for being with me in this lecture and I am going to take up more detail reactivity studies another properties of metal carbonyl complexes, which will crucial to understanding this important class of compounds in the next lecture, till that time goodbye and I look forward to being with you in the subsequent lecture.

Thank you.