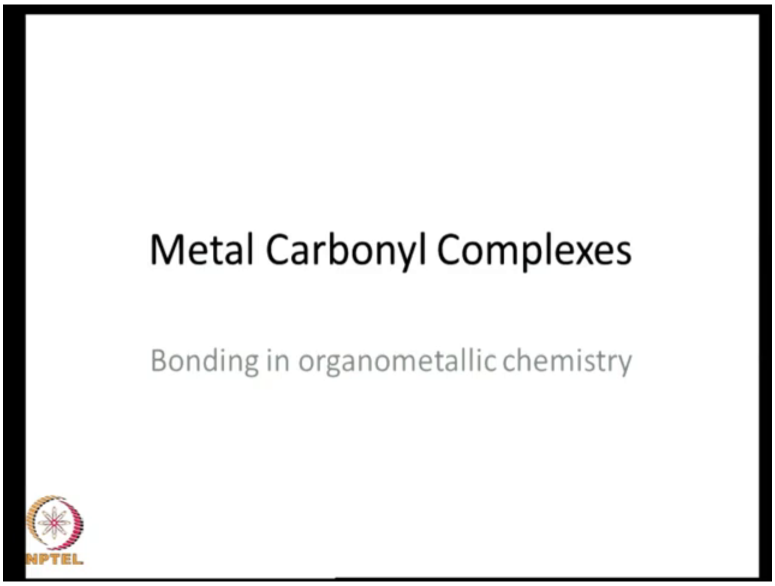
# Introduction to Organometallic Chemistry

**Prof. A. G. Samuelson**
**Department of Inorganic and Physical Chemistry**
**Indian Institute of Science, Bangalore**

## Lecture - 3
## Metal Carbonyls –Part II

Today, we will continue our discussion on metal carbonyl compounds.

(Refer Slide Time: 00:21)



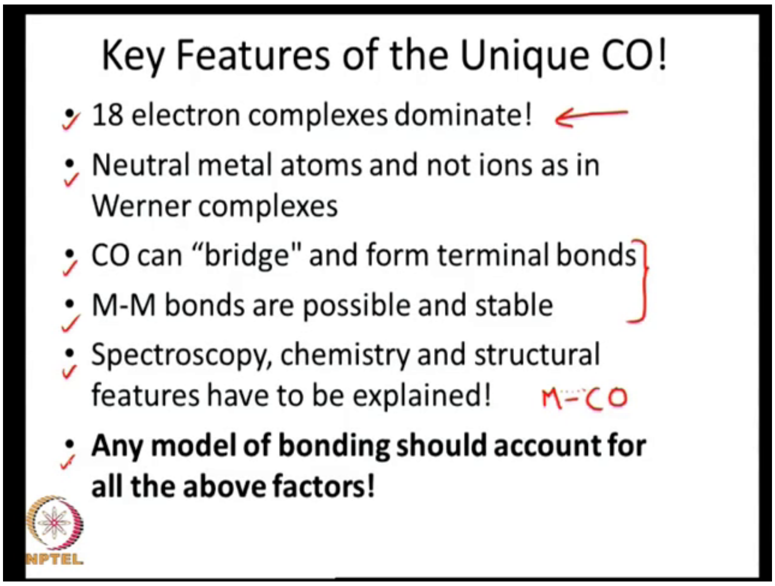
Metal Carbonyl Complexes

Bonding in organometallic chemistry

As I had mentioned earlier, metal carbonyls are one of the most important class of compound in organometallic chemistry. That is because carbon monoxide is like the R group in organic chemistry. Whenever you want a group to be placed in a position on the metal where there is some unsaturation, the carbon monoxide can be used just like the R group can be used anywhere in organic chemistry to plug in an unsaturated position.

So, today we will talk about some bonding aspects and metal carbonyl complexes. This is extremely important because as an archetypical ligand, carbon monoxide typifies several interactions that are present in organometallic compounds. Once we understand the interactions in organometallic compounds containing carbonyl groups, most of the interactions can be understood very easily. So, let us take a look at the bonding in metal carbonyl complexes.

(Refer Slide Time: 01:23)



## Key Features of the Unique CO!

- 18 electron complexes dominate!
- Neutral metal atoms and not ions as in Werner complexes
- CO can "bridge" and form terminal bonds
- M-M bonds are possible and stable
- Spectroscopy, chemistry and structural features have to be explained! M–CO
- **Any model of bonding should account for all the above factors!**

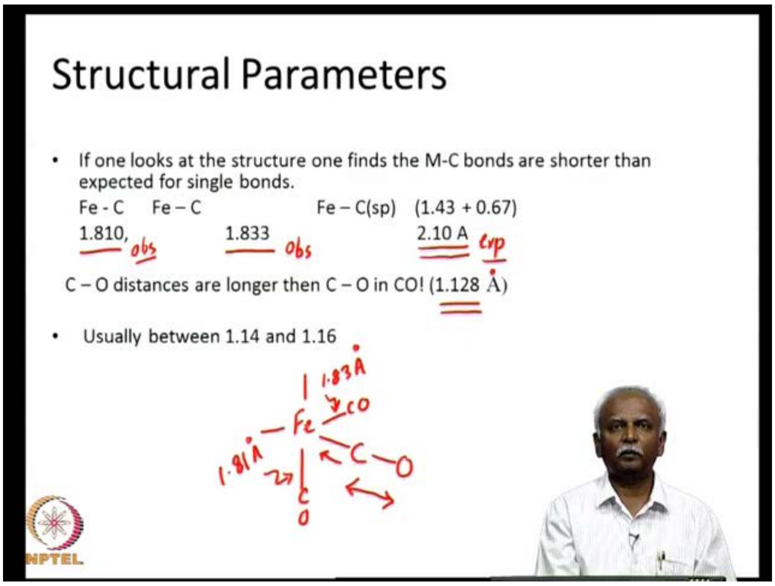
We should look at some of the key features which characterise metal carbonyl compounds. Since, the chemistry is extensive; we had to split this into 2 lectures. In the first lecture, we covered the fact that most metal carbonyl compounds are in fact most metal carbonyl compounds are in fact typically 18 electron systems.

So, they tend to be 18 electron complexes. They also are characterised by the fact that they are metals in zero oxidation state. When they are on the zero oxidation state or in the negative oxidation state, they apparently do not have this electrostatic component. They must be having a strong covalent interaction to stabilise the system. It will also note that there are two other factors, which distinguish them from Werner complexes. These two factors are, one is the fact that carbon monoxide can bridge many metal centres very easily. The bridging form and the terminal form are almost iso energetic, which means that they can shift one to the other very easily.

It is also interesting that metal metal bonds are facile even when there are no bridging ligands. So, organometallic compounds are distinguished, especially carbon monoxide based compounds are distinguished by these strange factors. In the last lecture, we covered the fact that both spectroscopic chemistry and structural features in the metal carbonyl chemistry is unique. So, MCO or metal carbonyl compounds are unique.

This is because they have this multiple bonding or the hint of a multiple bond between metal and carbon monoxide. Any bonding model that we propose should account for all these above factors. All the factors that we have looked at in the previous lecture namely in terms of the bonding aspects had to explain the factor they are neutral systems. They are metals. They can contain metal metal bonds. They have spectroscopic features, which are unique. They have structural features, which indicate the formation of a double bond.

(Refer Slide Time: 03:55)



Structural Parameters

- If one looks at the structure one finds the M-C bonds are shorter than expected for single bonds.

Fe - C    Fe – C    Fe – C(sp)  (1.43 + 0.67)

1.810, obs    1.833 obs    2.10 A exp

C – O distances are longer then C – O in CO! (1.128 Å)

- Usually between 1.14 and 1.16

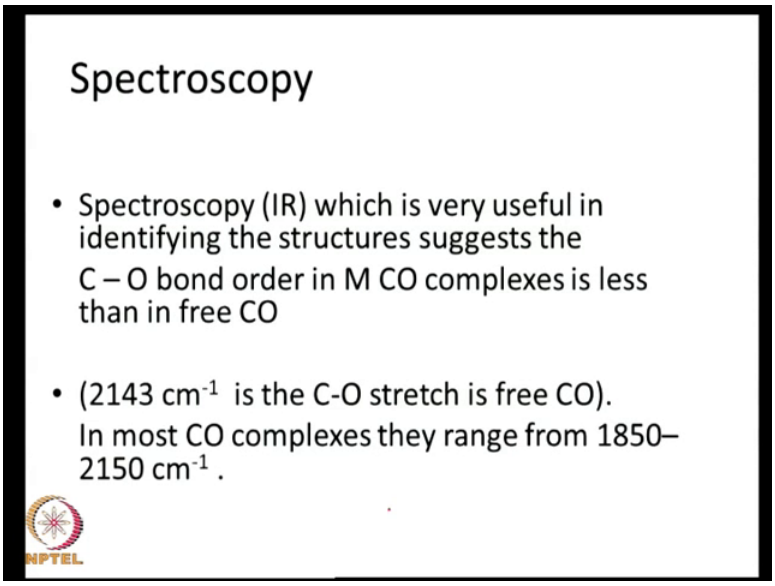
So, let us proceed further. Let us look at just and revise some of the structural parameters that characterised the metal carbonyl compound. If one looks at the iron carbon bond in an iron carbonyl complex, we noted the fact that the bond distances should have been approximately 2.10 Angstroms. This is the expected value. What we observe this is the observed value. So, very clearly, the observed value is much shorter, either it is 1.833 or it is 1.810. These are two observed values in a complex.

We have two values because we have an unsymmetrical complex. We have a trigonal bi pyramidal system where we have equatorial bonds and we have axial bonds. Surprisingly, the axial bond is the one that is shorter, this is 1.81 and this is 1.83 Angstroms. So, this is a very interesting observation the fact that you have shorter bonds and the fact that you have shorter axial bonds comparatively equatorial bonds.

If you look at the carbon oxygen bond distance, the carbon oxygen bond distance should have been 1.12. Heat it if it is unaffected from the starting bond distance observed in neutral carbon monoxide. So, neutral carbon monoxide has a bond distance of 1.13 Angstroms. We can ignore this third decimal place.

Let us just round it off to 1.13 Angstroms. In the complexes, it usually ranges between 1.14 and 1.16. In other words, this bond distance has been elongated. This bond distance has been shortened. This is what we suspect is coming from the fact that they have multiple bonds between iron and carbon. You have a weakening of the carbon oxygen bond distance.

(Refer Slide Time: 06:21)



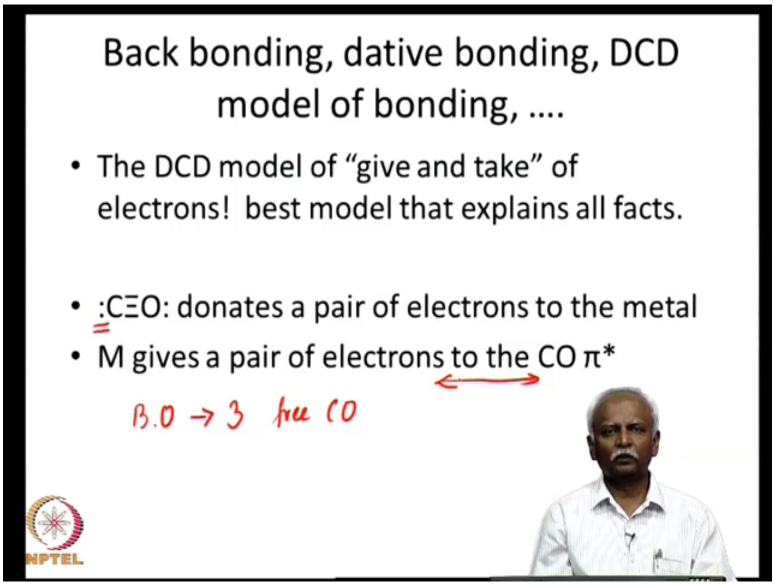
Spectroscopy

- Spectroscopy (IR) which is very useful in identifying the structures suggests the C – O bond order in M CO complexes is less than in free CO
- (2143 $cm^{-1}$ is the C-O stretch is free CO). In most CO complexes they range from 1850–2150 $cm^{-1}$ .

So, this is also reflected in the spectroscopic features of metal carbonyl complexes. In metal carbonyl compounds, the stretching frequency ranges from 1850 centimetre minus 1 from 1850 centimetre minus 1 to 2150 centimetre to minus 1. That is approximately to a 100 to almost 300 centimetres minus 1 lower than what you have trouble free carbon monoxide.

If you have this reduction in stretching frequency, it is indicative of the fact that is easier to stretch carbon monoxide in the complex compared to stretching carbon monoxide in the Free State. So, clearly the bond order between carbon and oxygen has been reduced. This is identical to the result we have observed from the bond distances. So, these 2 factors point to a single event. That is the reduction in the stretching frequency reduction in the bond between carbon and oxygen.

(Refer Slide Time: 07:24)



Back bonding, dative bonding, DCD model of bonding, ….

- The DCD model of “give and take” of electrons! best model that explains all facts.
- :C≡O: donates a pair of electrons to the metal
- M gives a pair of electrons to the CO $\pi^*$

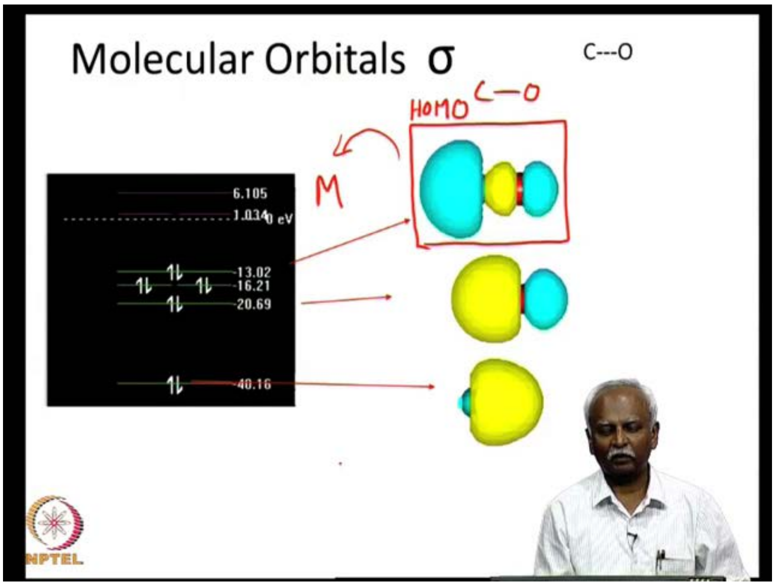
B.O → 3 free CO

So, in general, this reduction in the bond order between carbon and oxygen has been explained using what we call is back bonding, dative bonding or the DCD modular bonding. DCD comes from a Dewar-chat-Duncan son, the 3 people who extensively talked about the multiple bonds between the metal and the carbon and the reduction in the bond order in multiple bonded systems, which are bonded to the metal. In this case, carbon monoxide initially has a formal bond order of 3. The bond order between carbon and oxygen is actually 3 to start with in free carbon monoxide.

So, this bond order is reduced when you have coordination to the metal. As we have seen in many complexes, it is the carbon end, which is donating the pair of electrons. It is this pair of electrons on the carbon, which is being donated to the metal. In the reverse fashion, in the reverse direction we have donation of electron density from the metal into the carbon monoxide pi star orbital.

So, this is a phenomenon, the second phenomenon. The first phenomenon is very similar to what we have observed in Werner complexes. In Werner complexes, we would expect donation of a pair of electrons from the ligand to the metal. This is exactly what is happening in the case of carbonyl complexes also, but in addition to that, we have donation of a pair of electrons from the metal to the carbon monoxide pi star orbitals. In the previous lecture, we just briefly reviewed the orbitals of free carbon monoxide.

(Refer Slide Time: 09:15)



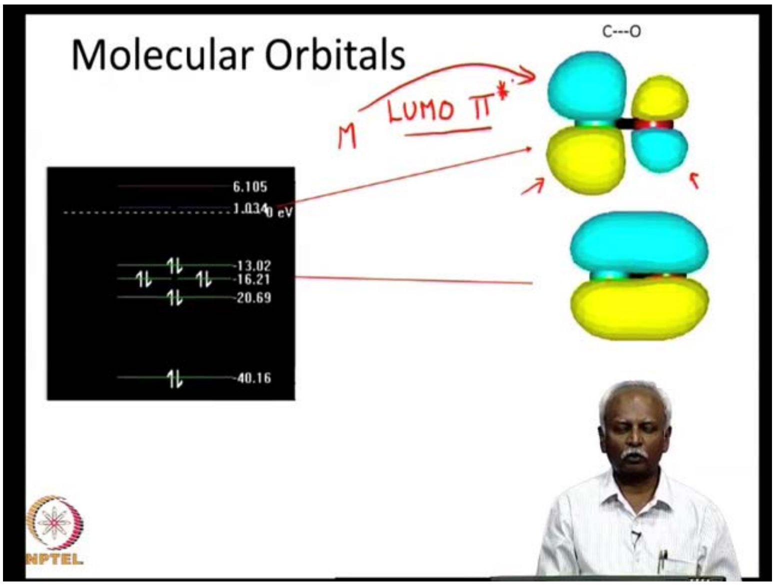
Molecular Orbitals σ

Let us just take a quick look at that once again before we proceed further. Let us look at the sigma orbitals in carbon monoxide first. We have a very low-lying sigma orbital on carbon monoxide, a second and a third sigma orbitals, which are in fact more interesting ones. The carbon monoxide orbital, which is the most important one, the sigma orbital which is the most important one is this one. This is the highest occupied molecular orbital. This is the highest occupied molecular orbital on carbon monoxide. It is primarily concentrated. The lone are primarily on the carbon side.

So, you have this is the carbon side and this is the oxygen side. You can see that the carbon side has got a very large lone. This lone is now pointed towards the metal atom. So, this is the homo, which means the electrons will flow out from the homo onto the metal.

So, this is the primary interaction that we are talking about when you have a lone pair on carbon and on oxygen. The lone pair on carbon is more easily donated and that is pumped into the metal vacant orbitals of metal. So, that is lying at minus 13.02 electron volts that are indicated here. So, the highest occupied molecular orbital is the one, which donates a pair of electrons to the metal.

(Refer Slide Time: 10:52)



Molecular Orbitals

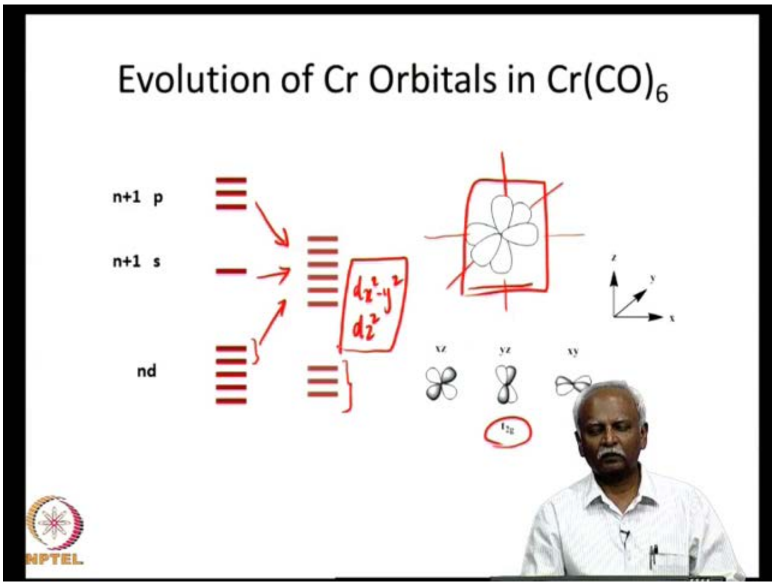
Let us now look at the pi orbitals. The pi orbitals are two of them are there, which are pictured here. They are totally 4. We will come to that in a moment. The pi orbital or the bonding molecular orbital is the one, which has got more concentration from oxygen and less from carbon.

The pi star orbital, which is the lumo, is the lowest unoccupied molecular orbital. The lumo has got a large contribution on carbon and a smaller contribution on oxygen. So, you can see that very easily in this picture here. This is a large contribution on the carbon and a small contribution on the oxygen, whereas the pi or the bonding molecule orbital has got more contribution from the oxygen side.

So, this particular combination of the donor orbital being concentrated on carbon and the donor, the acceptor orbital on carbon monoxide concentrated on carbon is a major incentive for carbon monoxide to bond through the carbon end to the metal. You will notice since the pi star orbital is vacant, you can now pump electron density from a filled orbital on a metal into this pi star orbital.

If you occupy the pi star orbital, if you populate the pi orbital with electron density, then you will reduce the bond order between carbon and oxygen. It would become easier to pull the carbon monoxide apart. So, the stretching frequency is in fact reduced. So, that is how we understand the fact that carbon monoxide has got lower stretching frequency when it is bonded to a metal complex.

(Refer Slide Time: 12:46)



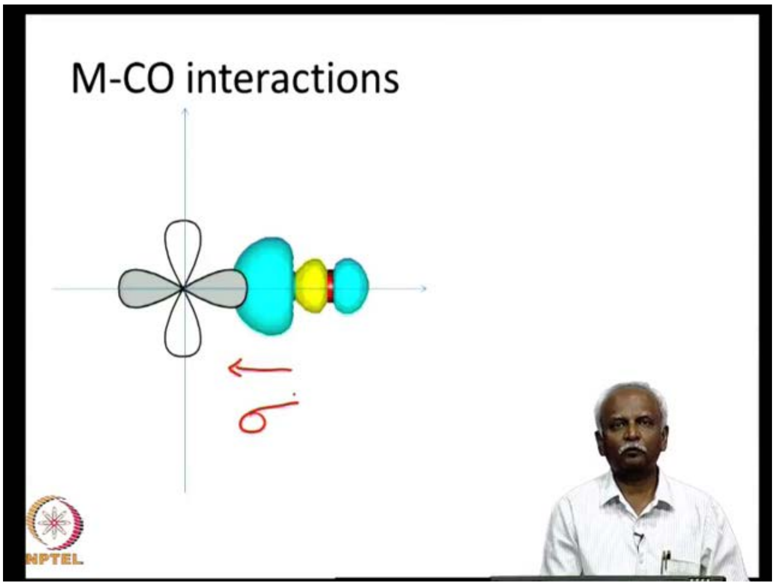
Evolution of Cr Orbitals in $Cr(CO)_6$

Let us take a brief look on the metal side. Let us understand the metal first. If you take a molecule like hexa carbonyl chromium, you will notice that we need 6 vacant orbitals where we can accommodate lone pairs on carbon monoxide. So, if you want to generate 6 vacant orbitals, we have to generate a set of orbitals that can be formed from s p 3 d 2. That is the hybridisation scheme that we have learnt from v r c p r theory, which will lead to 6 orbitals. They are pointed in the octa heading direction.

So, here I have pictured 6 orbitals. The 6 orbitals are coming from 3 p orbitals 1 s orbital and 2 p orbitals. So, this is the s p 3 d 2 hybrid. The d orbitals that are contributing to this hybrid are the d x square minus y square and the d z square. So, these 2 orbitals are the ones, which are coming from the d. However, the s and the p are completely involved in the hybridisation scheme, so that you generate 6 vacant orbitals on metals. These 6 vacant metals are pictured here. Notice that 3 orbitals are left without any interaction when you do this hybridisation. If I have 6 ligands, which are coming along the x y and z axis that is this axis pictured here.

If I have all of these axis having 1 carbon monoxide each, then the 3 orbitals that will be left behind without much interaction with ligand would be what we call as a t2 g set or the d x f d y z and the d x y orbitals. This is also pictured here. So, this hybridisation scheme is very useful in understanding how we will be involving only the d x square minus y square and the d z square orbital in the d. Let us now proceed to make what we learn from carbon monoxide and use what, we have learnt from the metal side and try to form a combination that will be establishing.

(Refer Slide Time: 15:14)

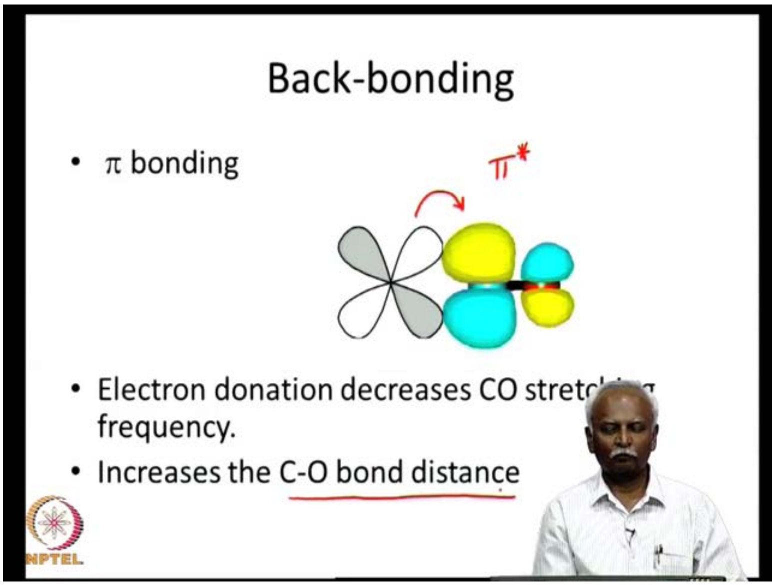


M-CO interactions

So, the first important combination is donation of electron density from the carbon monoxide. So, carbon monoxide gives a pair of electrons to the metal. As I mentioned before for convenience, we have only pictured the d x square minus y square orbital. But, it is actually a hybrid of the d s and 3 p orbitals. So, this hybrid accepts electron density from the carbon monoxide.

So, it is like a sigma bond that can be formed. This is because any amount of rotation around this axis, which we have between carbon and oxygen, will lead to no change in the bonding at all. So, that is the sigma interaction. So, that is very important for us to understand this is a sigma interaction.

(Refer Slide Time: 16:04)



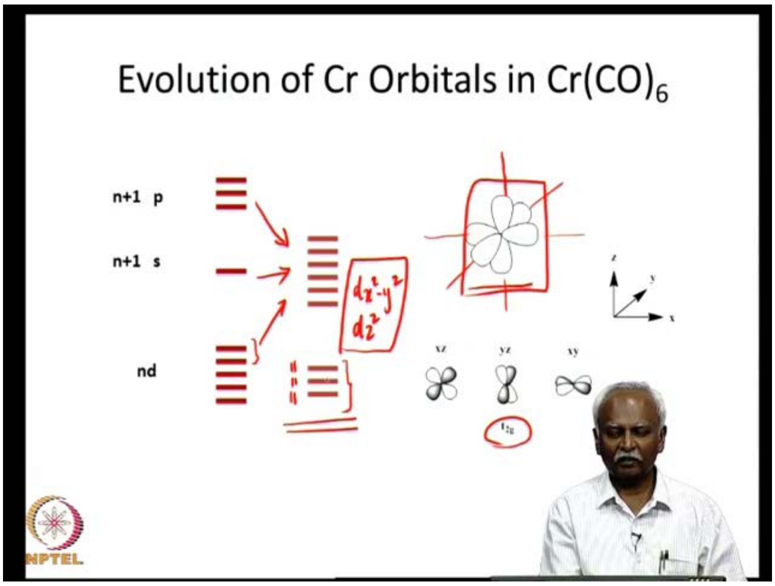
### Back-bonding

- $\pi$ bonding
- Electron donation decreases CO stretc frequency.
- Increases the C-O bond distance

In the next case, we talk about pi interaction. The pi interaction is the one, which decreases the carbon monoxide stretching frequency. As I mentioned earlier, it is the pi star orbital on the pi star orbital on the carbon monoxide. It is capable of accepting electron density from the filled metal orbitals onto the carbon monoxide entry orbitals.

This will clearly make the carbon oxygen bond weaker because it is a pi star orbital or an anti-bonding orbital. It will also increase the CO bond. So, if we increase the CO bond distance, it will decrease the CO stretching frequency for the sake of completeness.

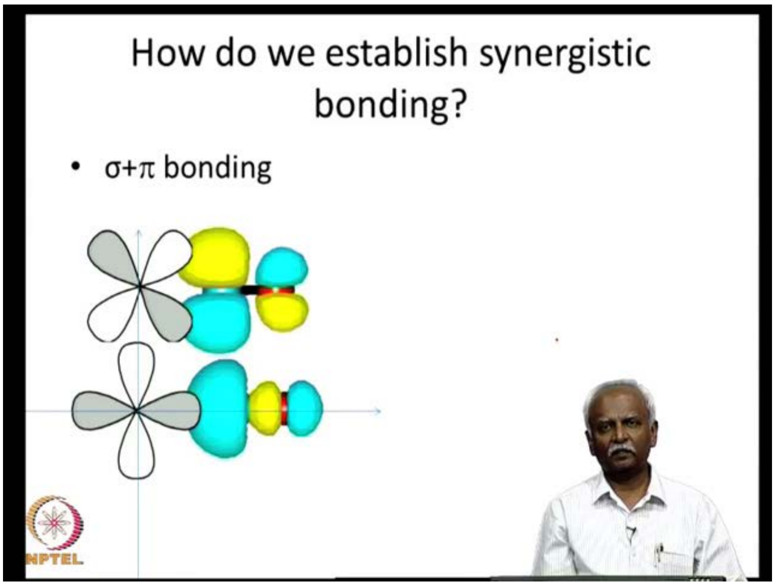
(Refer Slide Time: 16:53)



### Evolution of Cr Orbitals in $Cr(CO)_6$

Let us take a look at the metal orbitals. In the case of chromium, we have a total of 6 electrons. So, these 6 electrons will be populating the 3 orbitals, which are here in the t2 g set. If this is now filled, you will notice that they are completely ready to donate a pair of electrons into from here into the pi star orbitals of carbon monoxide. So, we have in fact a very nice complimentary or a synergistic interaction. The carbon monoxide gives a pair of electrons. It also gives a pair of electrons from the metal into the carbon monoxide. This leads to a very stable situation.

(Refer Slide Time: 17:43)

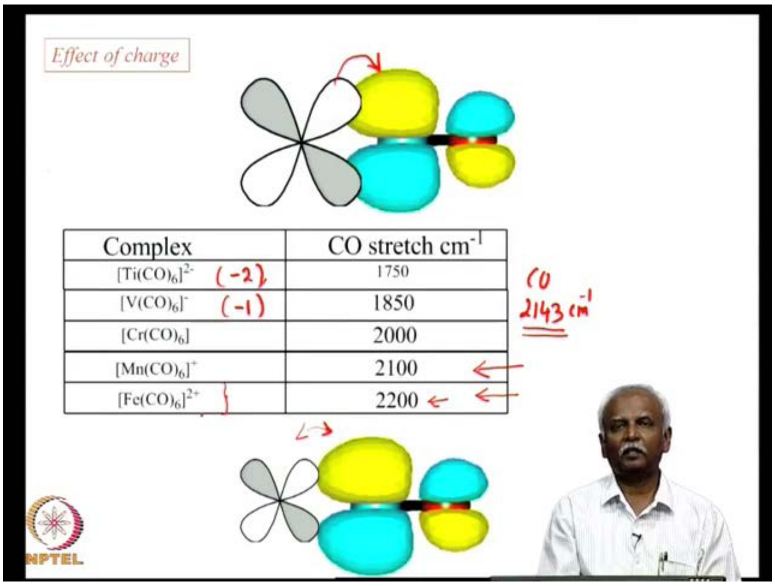


How do we establish synergistic bonding?

- $\sigma+\pi$ bonding

So, as I mentioned, we have synergistic bonding. The sigma bond and the pi bond are operational here in the same system. Since, these two electron density flows on an opposite direction, we can have a metal, which is neutral or even negatively charged and still form a very nice complex with the two species that is carbon monoxide and a metal.

(Refer Slide Time: 18:15)



*Effect of charge*

| Complex | CO stretch $cm^{-1}$ |
|---|---|
| $[Ti(CO)_6]^{2-}$ (-2) | 1750 |
| $[V(CO)_6]^{-}$ (-1) | 1850 |
| $[Cr(CO)_6]$ | 2000 |
| $[Mn(CO)_6]^{+}$ | 2100 |
| $[Fe(CO)_6]^{2+}$ | 2200 |

CO
2143 $cm^{-1}$

Now, how to be sure that these factors that we have been talking about are indeed happening in metal carbonyl chemistry. Let us just take a look at the effect of charge since we have mentioned that we can have neutral and negatively charged complexes. Let us just take a look at what happens when you have a negative charge on a metal.

So, these complexes unlike the Werner complexes have got excess electron density on the vanadium. So, vanadium is in the minus 1 oxidation state in this case and titanium is in the minus 2 oxidation state in this case. We will notice that the stretching frequency, the average stretching frequency of carbon monoxide in these octahedral compounds are significantly reduced from what we observe in hexa carbonyl chromium. Free carbon monoxide has got a stretching frequency of 2143 centimetre minus 1.

Let us just recollect what we discussed in the previous lecture. Now, it is decreased significantly in chromium hexa carbonyl and even further when you add a negative charge. So, as the metal has more and more negative charge, it will pump in more electron density into the carbon monoxide pi star orbitals.

So, it is natural that we have this greater reduction in the stretching frequency. So, if you want to put it in orbital terms, the overlap between the metal d orbital and the carbon monoxide pi star orbitals will be much better when you have a negative charge on a metal. That is because the greater electron density will increase the size of the metal orbital. It will try to expand because of the repulsion between the electrons is much greater and the new compare to the nuclear charge, which is holding this electrons.

So, negative charge tends to increase the size of this electron cloud. Better overlap means more electron density can flow from the metal into the carbon monoxide pi star orbitals. So, that explains what happens in these negatively charged systems.

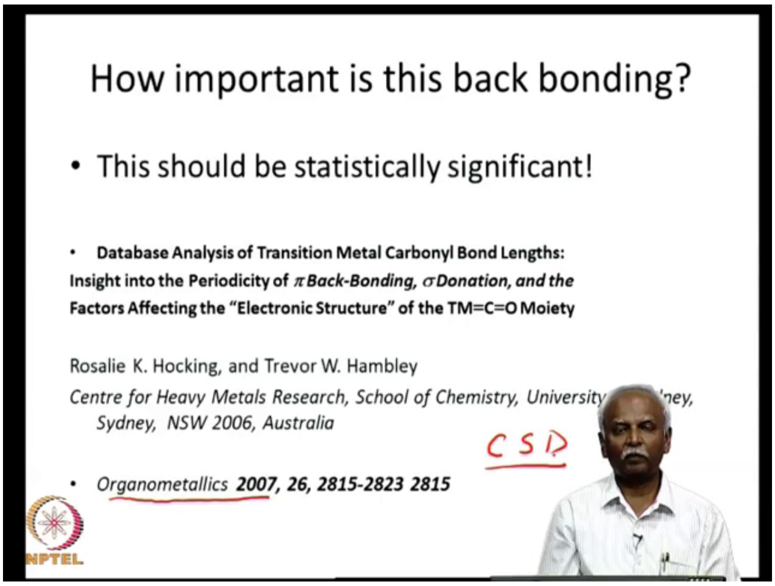
If you look at a few complexes, which have been synthesised recently by Strauss and co-workers, you will find that the carbon monoxide stretch frequency can be close to the free carbon monoxide stretching frequency as in this M n CO6 complex where you have a positive charge on the metal. It can even be higher than the stretching frequency that you observe in free carbon monoxide. So, here we have an increase in the stretching frequency. Nearly, 57 centimetre minus 1 increase is observed in the case of Fe CO 6 2 plus.

So, how do we explain this one factor that readily comes to mind? This is a fact that because the orbitals are now contracted with an increased positive charge on a metal, the 2 orbitals contract in size. So, when they contract in size, they overlap between the carbon monoxide pi star orbital and the filled orbitals on the metal. They will decrease. The decrease in size results in poorer electron density transfer from the metal to the carbon monoxide.

So, if there is no pi star population, the frequency obviously cannot go down below the value of 2143 centimetre minus 1. We still have a problem. We have to explain why the frequency has increased in this complex to 2200 centimetre minus 1. This is a strange factor that has been observed only recently because these complexes have been characterised fairly recently by Strauss and co-workers through some very careful chemistry.

This is because these complexes are extremely moisture sensitive and are not very stable. Still, they have managed to characterise them crystallographically and show spectroscopic ally that indeed it is possible to have a positive metal ion interacting with the carbon monoxide.

(Refer Slide Time: 22:40)



## How important is this back bonding?

- This should be statistically significant!

- **Database Analysis of Transition Metal Carbonyl Bond Lengths: Insight into the Periodicity of $\pi$ *Back-Bonding*, $\sigma$ *Donation, and the* Factors Affecting the "Electronic Structure" of the TM=C=O Moiety**

Rosalie K. Hocking, and Trevor W. Hambley

*Centre for Heavy Metals Research, School of Chemistry, University ney, Sydney, NSW 2006, Australia*

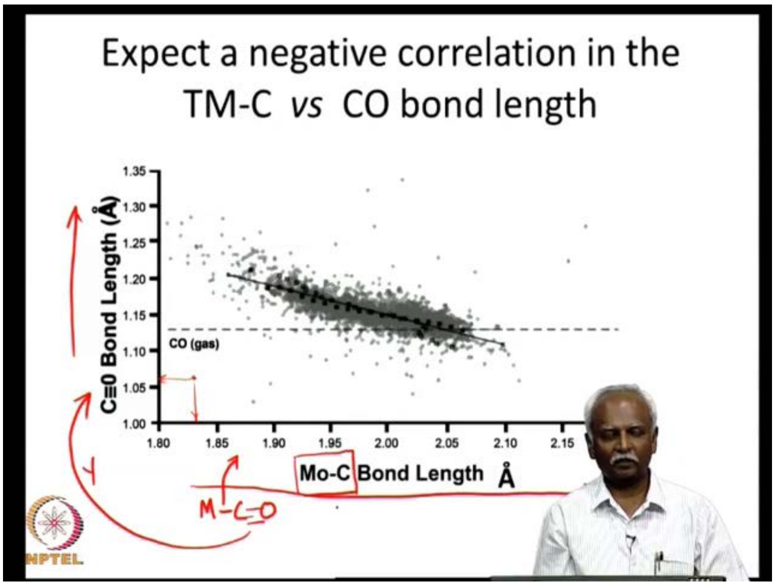
CSD

- *Organometallics* ***2007*, *26*, *2815-2823 2815***

So, let us take a look at this a little more closely before we proceed to the positively charged compounds. Let us just take a look at a fairly recent paper that has appeared in the journal of organometallic. This paper deals with the generality of back bonding or this pi bonding that feel synergistic bonding. We just referred that the ligand gives electron density to the metal. The metal in turn, populates the ligands anti bonding or empty orbitals, so that we can have synergistic interaction.

So, they have looked at a large number of transition metal compounds, which have got carbon monoxide as a ligand. When they examine all the bond distances that are available in this crystal structure database that is a crystal structure database analysis CSD, crystal structure database; when they did that, they found some very interesting trends. I would like to briefly mention that because this tells you how important back bonding is in organometallic chemistry in metal carbonyl chemistry in particular.

(Refer Slide Time: 23:55)



Expect a negative correlation in the TM-C *vs* CO bond length

So, what they carried out is a database analysis. Let me explain to you what this figure means. If you take a metal carbonyl complex, in the same complex, if I measure the metal carbon bond length and that is plotted on the x axis, so the x axis is actually the metal carbon bond length. If this metal carbon bond length is combined with the carbon oxygen bond lengths for the same system, so if you have a metal CO, this bond length goes on the y axis. So, this goes on the y axis. The metal carbon bond length goes on the x axis.

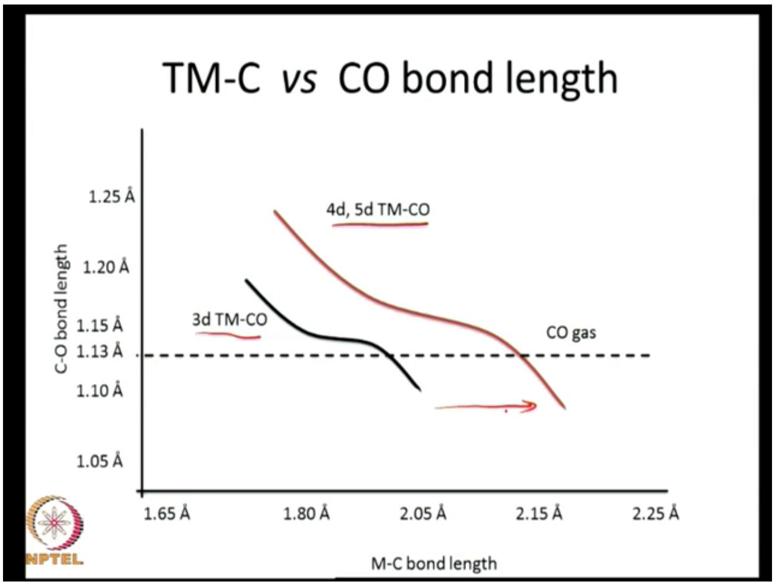
So, for each metal carbonyl complex, you will have 2 points of reference. If I take this, it indicates that for the particular system that I am talking about, I have a bond distance approximately 1.2, 1.825 Angstroms and a carbon oxygen bond length of 1.06 Angstroms if you this graph.

If you plot this particular graph with all the metal carbonyl bond distances, you observe for the sets that you have for molybdenum complexes. You have a variation in this particular fashion. All the bond lengths seem to fall in approximately clustered around a straight line, but you have a negative correlation. In other words, as you shorten the molybdenum carbon bond length, as you shorten it, the carbon oxygen bond length seems to increase. So, the carbon oxygen bond length increases as you shorten the metal carbon bond length.

This is in fact what you have observed for a synergistic interaction because if the metal pumps in more electron density into the carbonyl group, then the metal carbon bond length should decrease. This is because pi bonding is better. If this happens, then the pi star orbital is occupied. The carbon oxygen bond length should increase.

So, these 2 are negatively correlated. So, you would expect a straight line with a negative slope. That is what we have observed. So, this is very comforting because it is supporting just a few complexes that we have looked at the previous light, but in a wide range of complexes in the database that is available now.

(Refer Slide Time: 26:38)

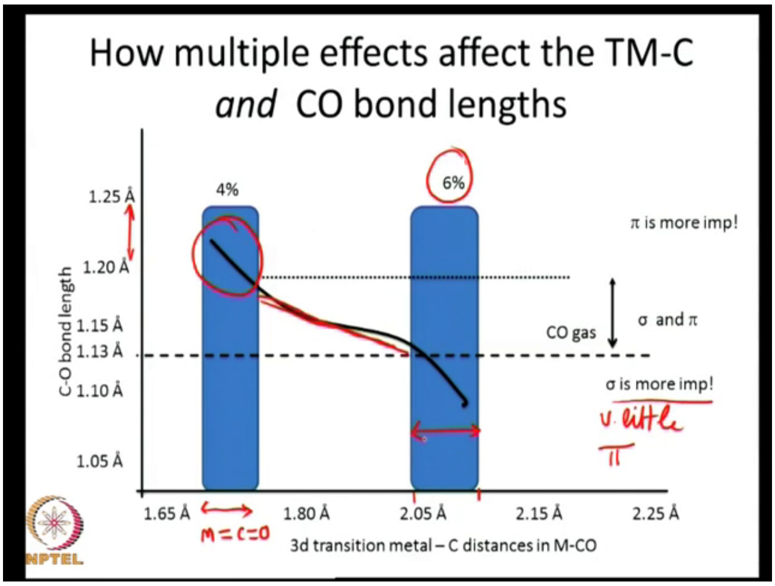

TM-C *vs* CO bond length

What is even more interesting is the fact that if you take a series of compounds 3 d transition metal carbonyl complexes, you have trend, which is indicated in this graph right here. You can plot the same type of analysis, same type of a plot, a scatter graph. We call it this scatter graph. It can be done for 4 d or 5 d transition metals.

Then, you find that graph is very similar. It has got a sigmoid nature. You can notice this by the fact that there is an s shaped graph here. The graph is similar for both 3 d and 4 d metal ends. The only thing that has happened is that the 4 d graph is shifted along the x axis and this shifting along the x axis happens.

This is because 4 d and 5 d transition metals are much larger than 3 d transition metals. This larger size of 4 d and 5 d is responsible for this horizontal shift of this graph, but otherwise, all the other factors appear to be the same. So, let us take a look at what would be the factors, which are responsible for making a sigmoid graph when you look at all the complexes put together.

(Refer Slide Time: 28:02)



How multiple effects affect the TM-C *and* CO bond lengths

So, here is the same graph. Now, I have redrawn it in such a way that will mark the 3 regions, which deviate from the linear portion of graph. This is the linear portion of the graph, which had a negative correlation between carbon oxygen and the metal carbon distances.

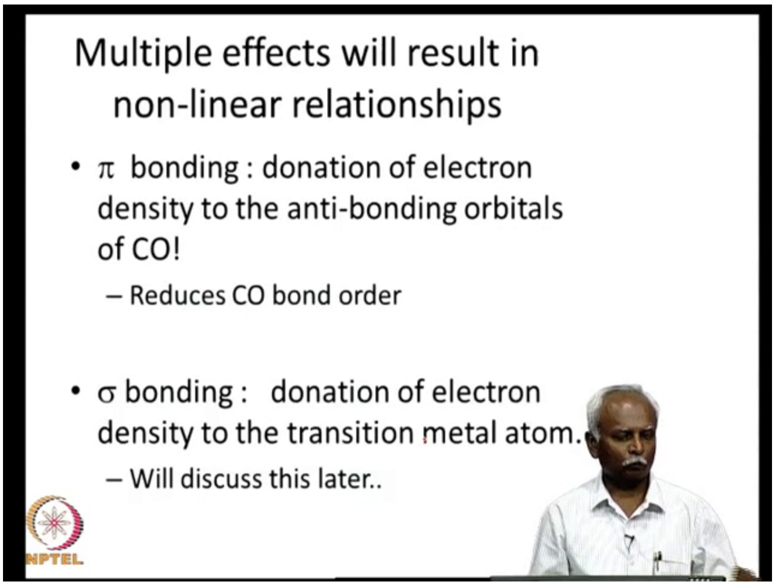
So, this linear portion of the graph is what we looked at initially. Then, we looked at all the distances together. We realise that in several systems, there is a slight deviation from linearity of the 2 extremes when you have very large metal carbonyl distances. That is pictured here towards the end. These are the systems, which have got very weak interactions between the carbon monoxide and the metal. That is a very small fraction of total number. Approximately 6 percent of the metal carbonyl complexes have got this weak interaction between carbon monoxide in the metal.

You will find that in these cases, the sigma bonding is probably more important. There is very little pi bonding, very little pi interaction, whereas in the other extreme, you have a small group of complexes. These are pictured here. This small group of complexes have got very short metal carbon distances. So, they have a strong double bond character between the metal and the carbon monoxide. So, one can almost draw this balanced bond structure.

So, you have a short distance. This has led to an increase in the carbon oxygen bond length. So, the carbon oxygen bond length is significantly elongated. This is also a small fraction of the metal complexes that we have. This is approximately 4 percent.

90 percent of complexes are the ones, which have a negative correlated, negative linear correlation between the metal carbon and the carbon oxygen bond length. So, when we have multiple effects like this, you have a sigma bond and you have a pi bond. Then, you have 2 different effects operating. Then, only one is operating. Obviously, the slope of this graph would change. That is indicated in the 2 extremes of this scatter graph.So, this is a very indirect, but very clear evidence of the fact that you have 2 effects operating here.

(Refer Slide Time: 30:41)



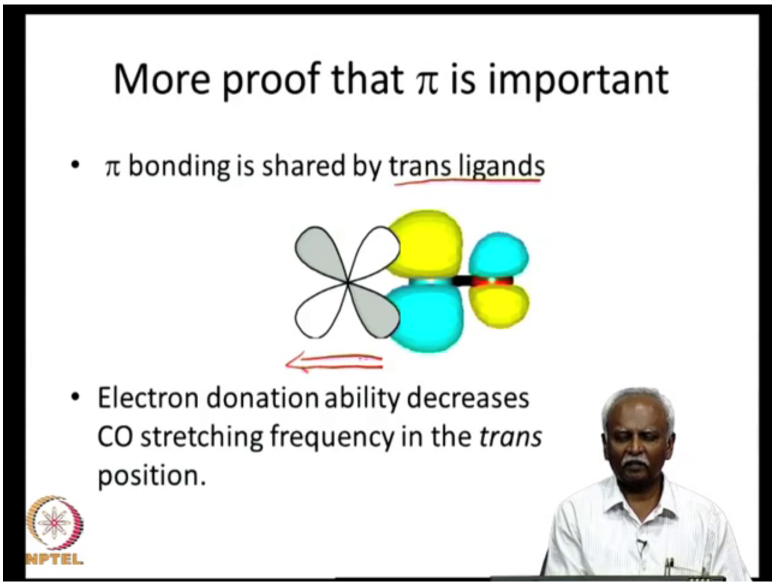
Multiple effects will result in non-linear relationships

- $\pi$ bonding : donation of electron density to the anti-bonding orbitals of CO!
  - Reduces CO bond order
- $\sigma$ bonding : donation of electron density to the transition metal atom.
  - Will discuss this later..

In chemistry, whenever you have multiple effects on a particular relationship. Then, you will have non linear behaviour. So, this is a clear case where you have 2 different effects. That is pi bonding, which is leading to population of the anti bonding orbital of carbon monoxide and reduction in the carbon oxygen bond order.

You have another effect, which is a sigma bonding. This results in reduction in the electron density on carbon monoxide. It is coming from this 3 sigma orbital on carbon monoxide, which we mentioned earlier, mostly populated on carbon. This electron density is something that we will have to discuss later in greater detail during the course of this lecture.

(Refer Slide Time: 31:33)



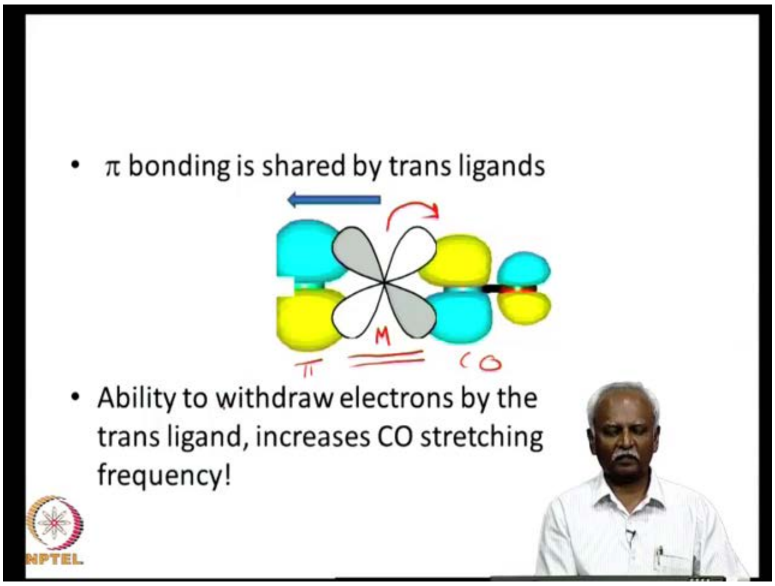
More proof that π is important

- π bonding is shared by trans ligands
- Electron donation ability decreases CO stretching frequency in the *trans* position.

So, we provided very important proof that the pi bonding is important. You have a strong metal carbon double bond that is formed. As we use the electron density on the metal to populate the pi star orbitals, this will reduce the CO stretching frequency. This CO stretching frequency is reduced and carbon monoxide is significantly affected by the Trans ligand. I want to tell you that the Trans ligand plays a more important role than the other ligands, which are present in the metal complex.

So, let us take a look at the reasons why the Trans ligand is so important. Let us consider octahedral complex again or square planer complex. In these complexes, the t2 g set or the d x y d x z orbital are the ones, which are involved in pi bonding. This is pictured here. You will notice that the d xy or the d x z orbital that we are talking about is pointing towards the carbon dioxide. That half of the orbital is in fact pointed in the other direction also.

(Refer Slide Time: 32:52)



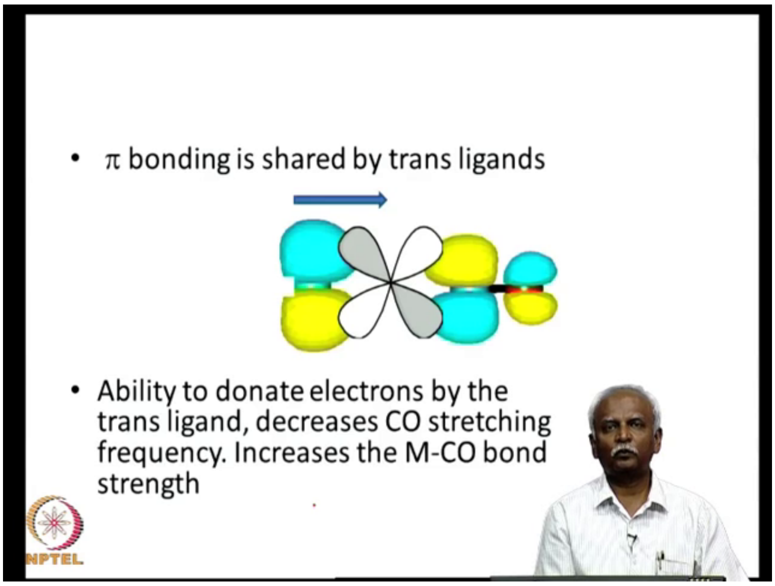
- π bonding is shared by trans ligands

- Ability to withdraw electrons by the trans ligand, increases CO stretching frequency!

So, if you have another ligand in the transposition, which is also capable of interacting with the high orbital on the transition metals, so this is the metal. So, here is the metal. Here is the ligand, which can interact in the pi fashion. The Trans ligand in fact, shares the same orbital for pi interactions. So, you had a carbon monoxide in one side and another ligand in the transposition, which is capable of interacting in a pi fashion.

So, what will happen is either you will have a competition for the electron density that is there on the metal. The electron density that is there on the metal has now to be shared between the carbon monoxide on one side and the other pi ligand on the opposite side, on the client side. So, it is the same because the same orbital is shared between 2 different ligands. You tend to have very significant effect due to the Trans ligand.

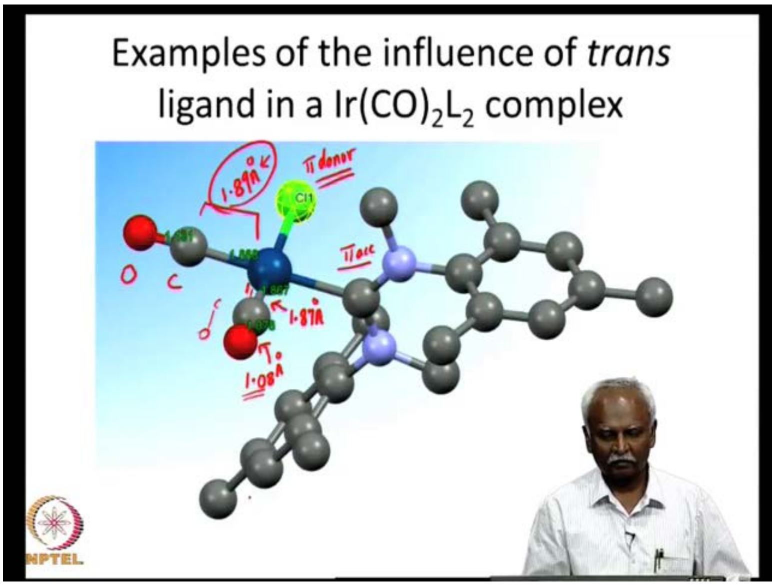
(Refer Slide Time: 33:55)



- π bonding is shared by trans ligands
- Ability to donate electrons by the trans ligand, decreases CO stretching frequency. Increases the M-CO bond strength

So, let us take a look at some of the effects of this. It not only changes the CO stretching frequency, it also changes the metal bond order and hence, the bond distances. We will be able to see such effects very clearly in the crystal structure.

(Refer Slide Time: 34:15)



Examples of the influence of *trans* ligand in a $Ir(CO)_2L_2$ complex

So, I have given you. I am going to show you 2 examples now where you have carbon monoxide attached to the metal. Here is iridium complex. In this iridium complex, you have 2 carbon monoxides. This is a carbon, which is black and oxygen is pictured in red. So, there are 2 carbon monoxide ligands. You will notice that these 2 carbon monoxide ligands have got 2 different Trans ligands. When you have a chloride as Trans ligand, the metal carbon bond distance is 1.87 Angstroms. So, this bond distance is 1.87 Angstroms. This carbon oxygen bond distance, which is shown in green, is not very clear. So, I am writing it again. It is approximately 1.08 Angstroms.

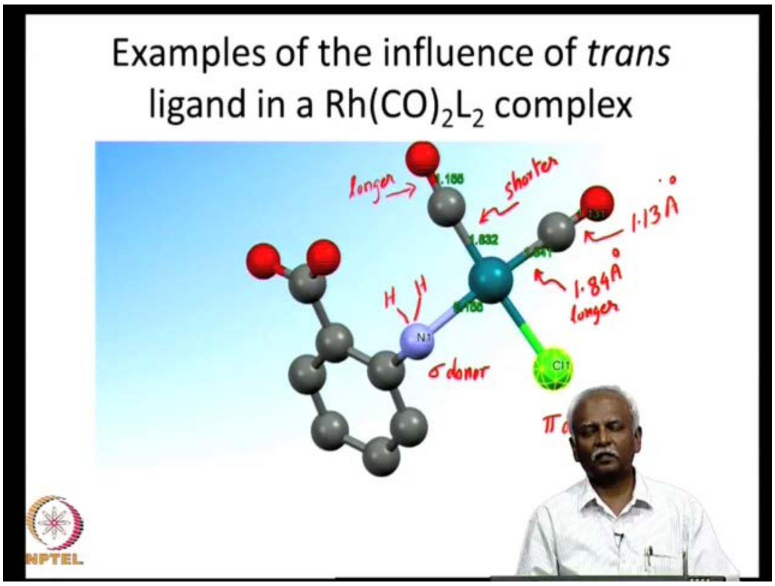
So, you will notice that in this particular system, you have an iridium complex. When the chlorine is in the transposition, what happens is that chloride ligand can have a filled pi orbital. So, the filled pi orbital will not compete with the carbon monoxide for pi bonding. So, what happens is it is at this distance that becomes very short. So, this distance is in fact, if you compare the 2 carbon metal carbon bonds, this distance is short.

This carbon metal distance, which is pictured here, is close to 1.89 Angstroms. So, the ligand on the other side is in fact the ligand, in which we have partial double bond character. This is also a pi acceptor ligand. So, this is a pi acceptor ligand in the transposition. So, this metal carbon bond is elongated. This metal carbon bond is shortened compared to what you would expect for carbon monoxide in a simple system without pi interacting ligand.

So, this is a pi donor. The chlorine is a pi donor and will not compete with carbon monoxide for pi accepting. So, this bond becomes very strong. This becomes very strong and this becomes very weak. The carbon oxygen becomes very weak. So, this double bond is weakened. So, you have a bond distance of 1.08 Angstrom.

In the other case, where you have a carbene ligand, which is on the transposition, this bond distance is increased. The metal carbon bond distance is increased to 1.89 angstrom. So, that is elongated and this is in fact the distance, which is in fact weak. This is because you have competing. This metal carbon bond distances are longer. It is weak because you are competing pi acceptor ligand. So, let us take a look at another system where you have different types of pi interactions.

(Refer Slide Time: 37:38)



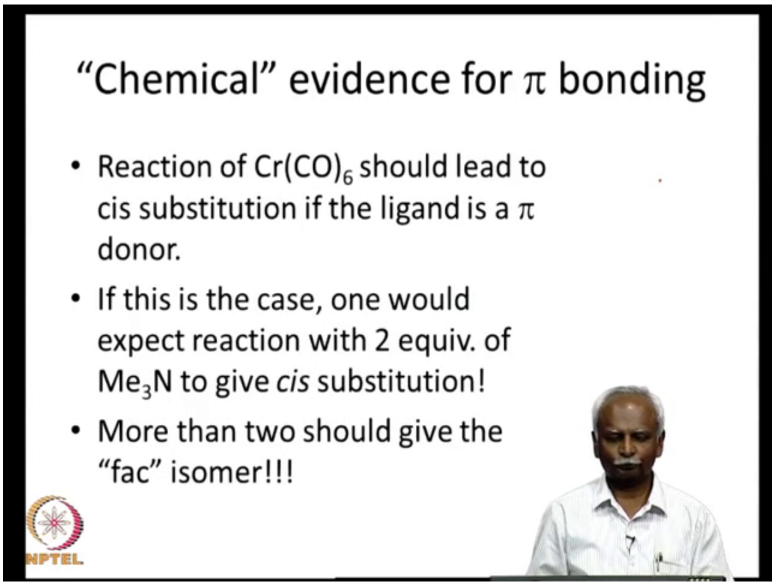
Examples of the influence of *trans* ligand in a $Rh(CO)_2L_2$ complex

Here is amino benzoic acid. This is amino benzoic acid, which is coordinated to a rhodium compound. In this particular instance, you have again chlorine, which is a pi donor. This is a sigma donation, sigma donor ligand. Once again, you will find that when you have a sigma donor ligand, this bond length is 1.841 Angstroms.

It is shorter when you have a pi donor ligand on the transposition. So, this is shorter. This is longer. That is because this is a sigma donor ligand. This is a pi donor ligand. So, this pi donation has a significant effect on the transposition. You have a shorter metal carbon bond. You have elongation of this carbon oxygen bond. This becomes longer. We will see that this distance, which is again in green. I have written it out for you. It will want small; 1.13 angstrom is a bond distance in the transposition.

So, you can see that the Trans ligand has a significant influence on the carbon monoxide bonding. This is because they have to share the same orbital, several same orbitals when you have a metal carbonyl bond. The sigma and the pi interactions are complimentary. They are in fact synergistic. So, you have significant interactions, significant changes when you either have a sigma donor or a pi donor or a pi acceptor.

(Refer Slide Time: 39:43)



## "Chemical" evidence for $\pi$ bonding

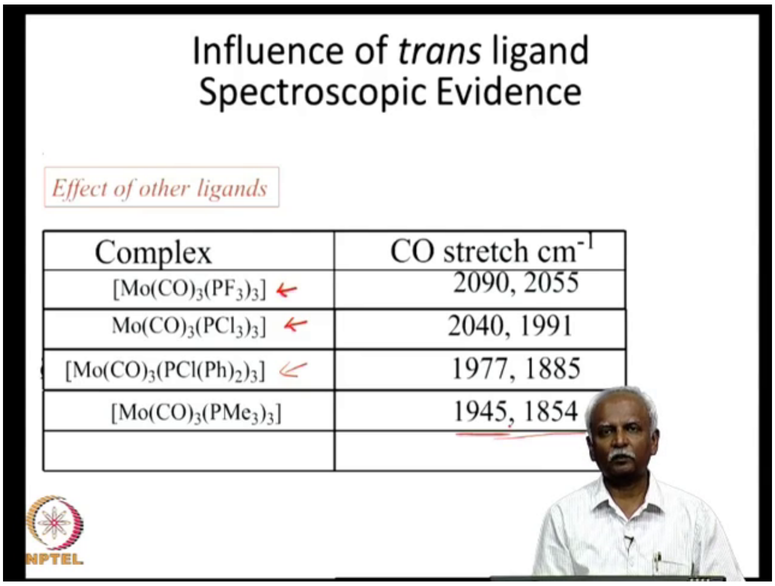
- Reaction of $Cr(CO)_6$ should lead to cis substitution if the ligand is a $\pi$ donor.
- If this is the case, one would expect reaction with 2 equiv. of $Me_3N$ to give *cis* substitution!
- More than two should give the "fac" isomer!!!

So far, we have been looking at structural evidence. We have also been looking at some spectroscopic evidence for the fact that there is very significant pi bonding in the metal carbonyl complexes. In fact, there is also some chemical evidence for pi bonding. By chemical evidence, what I mean to say is that if you react chromium hexa carbonyl in principle, if I have 2 ligands coming in, I should be able to form both the cis complex and the Trans complex.

So, if I treat Cr CO6 with 2equivalents of Me3 N, I should get both cis and trans. If I have more than 2 ligands that are if I get treated with 3 ligands, then I should have both the fact isomer and the mer isomer. But, surprisingly from the reactivity of chromium hexa carbonyl, we can see that the cis complex is the only one which is formed when there is a di substitution. It is only the fact isomer, which is formed when you have a tri substitution.

This is because you would rather have a ligand and the transposition, which is not pi acceptor ligand. If you have a sigma donation ligand and sigma donor ligand as trimipramine, then it would be better to have it in the transposition metal where it will push electron density into the metal and lead to better carbon monoxide metal binding.

(Refer Slide Time: 41:23)



## Influence of *trans* ligand Spectroscopic Evidence

*Effect of other ligands*

| Complex | CO stretch $cm^{-1}$ |
|---|---|
| $[Mo(CO)_3(PF_3)_3]$ | 2090, 2055 |
| $Mo(CO)_3(PCl_3)_3]$ | 2040, 1991 |
| $[Mo(CO)_3(PCl(Ph)_2)_3]$ | 1977, 1885 |
| $[Mo(CO)_3(PMe_3)_3]$ | 1945, 1854 |
| | |

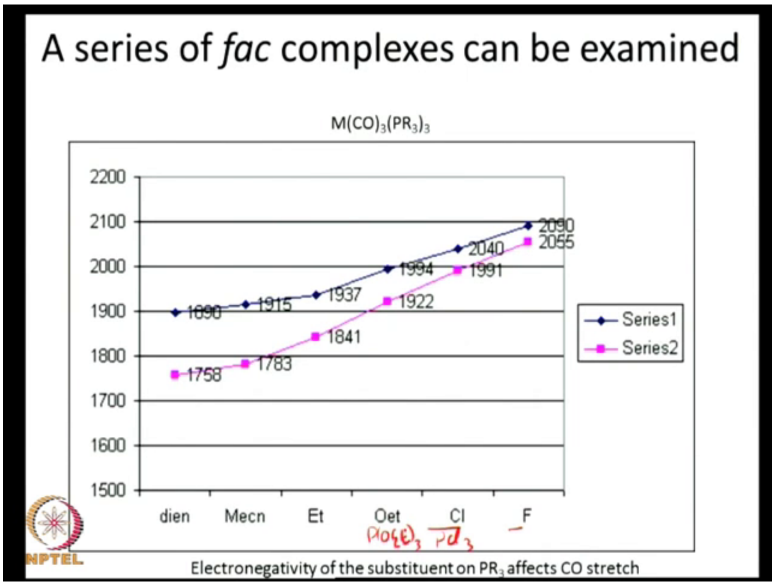
So, this is Trans ligand. In the case of the cis complexes where you have the substitution of 3 ligands, it has got very nice relationship with the carbon monoxide stretching. So, I am going to show you this relationship once more in a graphical form. What I have pictured here is a set of complexes where you have PR3 or 3R, groups which are attached to the phosphorus because of the electron withdrawing nature of fluorine or chlorine.

Here, I have fluorine on the phosphorus. Here, I have chlorine on the phosphorus. So, PCl3 and PF3 will have difference in the ability to donate or remove electrons from the molybdenum. So, if you have PF3, then you have less electron donation into the molybdenum. If you have less electron donation to the molybdenum, then the carbon monoxide will have higher stretching frequency.

That is exactly what we see here. We substitute each one of these chlorines with R groups. Here, I have shown you an example where 2 of the chlorines have been substituted by phenyl groups. I tend to have smaller stretching frequency. That is because chlorine withdraws electron density more than a phenyl group.

So, by virtue of the electron density withdrawn from the molybdenum or the poor electron molybdenum, you have changes in the CO stretching frequency of the Trans ligand PMe3. You have very strong electron donor. So, you have smaller or a weaker stretching frequency for a 3 carbon monoxide in the transposition.

(Refer Slide Time: 43:15)

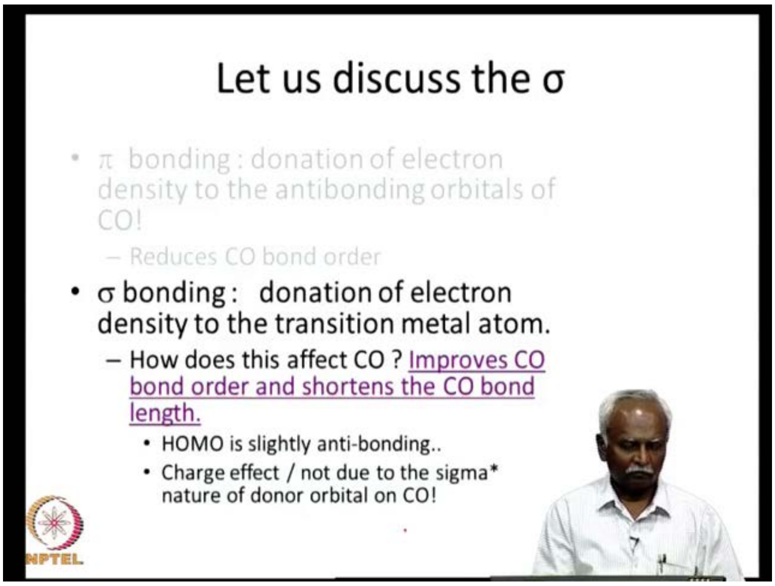


A series of *fac* complexes can be examined

Electronegativity of the substituent on $PR_3$ affects CO stretch

So, you can in fact plot this. Again, you will see a linear relationship in a small region where you have only one of the effects dominating. That is in this particular case. It is mostly the pi effect, which is being observed. So, you have the effect of the Trans ligand. You have PF3. This is PF3 on the right side and PCl3. This is PCl3 ligand. If you look at the stretching frequency of all these or of all these compounds, then you tend to have a linear relationship in the stretching frequency of the carbon monoxide, which is present in the transposition.

(Refer Slide Time: 43:59)



Let us discuss the σ

- π bonding : donation of electron density to the antibonding orbitals of CO!
  - Reduces CO bond order
- σ bonding : donation of electron density to the transition metal atom.
  - How does this affect CO ? Improves CO bond order and shortens the CO bond length.
    - HOMO is slightly anti-bonding..
    - Charge effect / not due to the sigma* nature of donor orbital on CO!

So, let us now discuss the importance of the sigma bonding orbital. Earlier, we have discussed extensively what pi donation does in terms of spectroscopy. What it does in terms of the bond distances? Now, I want to briefly mention what exactly happens when you donate electron density from the carbon monoxide in the sigma orbital. Let me just briefly change over to remind you of what we have discussed earlier. The effect of charge under effect of sigma under pi bonding is twofold.

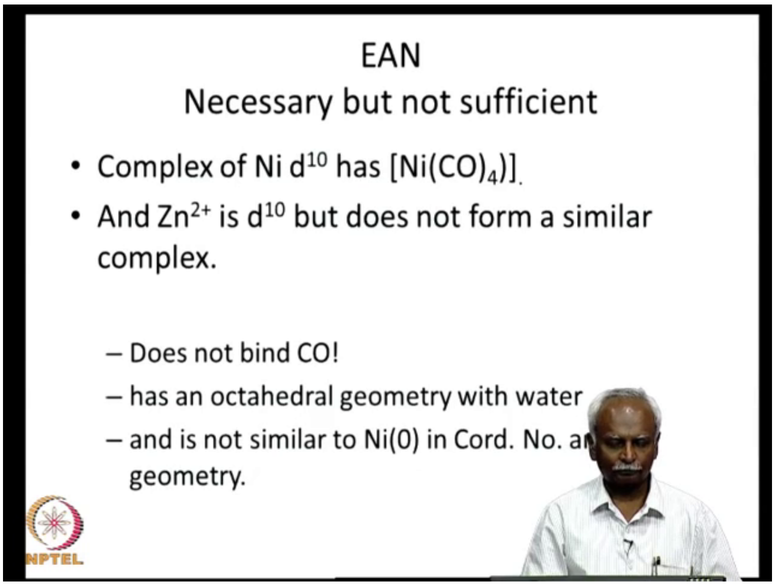
One is the fact that you have electron density donated into an empty orbital on the d orbital on the metal from the carbon monoxide, which is in a linear. This is shown here along say the x-axis. It is donating electron density into d x square minus y square orbital. So, what we have is in fact an effect due to mostly the sigma bond. When you have a charge on a positively charged metal atom, the positively charged metal atoms will have a smaller d orbital. This is because of contraction d orbitals. So, the pi bonding becomes insignificant. So, the pi interactions become even become insignificant when you have a positive charge on a metal.

So, the primary interaction when you have a positively charged metal atom is due to sigma bonding. How does this affect the CO stretching frequency? How does it affect bond length? First of all, because pi affect is an additional effect, you tend to have weaker carbon monoxide metal interactions. You have longer metal carbon bonds, but it seems to be having a strange effect on the carbon monoxide stretching frequency.

So, the charge effect that has recently been discussed about is a fact that when you have a positive charge next to the carbon on the carbon monoxide, then it tends to have an influence, which increases the carbon oxygen bond order. So, we will discuss this in the subsequent slides. There is also another rationale that has been given. That is the fact that the highest occupied molecule orbital on carbon monoxide is in fact slightly anti-bonding in nature. Because it is anti bonding, you tend to have the reduction in the electron density on this homo, which is slightly anti bonding.

You tend to have stronger co interaction once you remove electron density, but compelling evidences have come to indicate that it is primarily a charge effect. If you place a positive charge next to the carbon monoxide in the carbon end, then you tend to have a stronger stretching frequency for carbon monoxide. This is primarily because the electron withdrawing nature of carbon is enhanced by the positive charge close to the carbon monoxide.

(Refer Slide Time: 47:29)

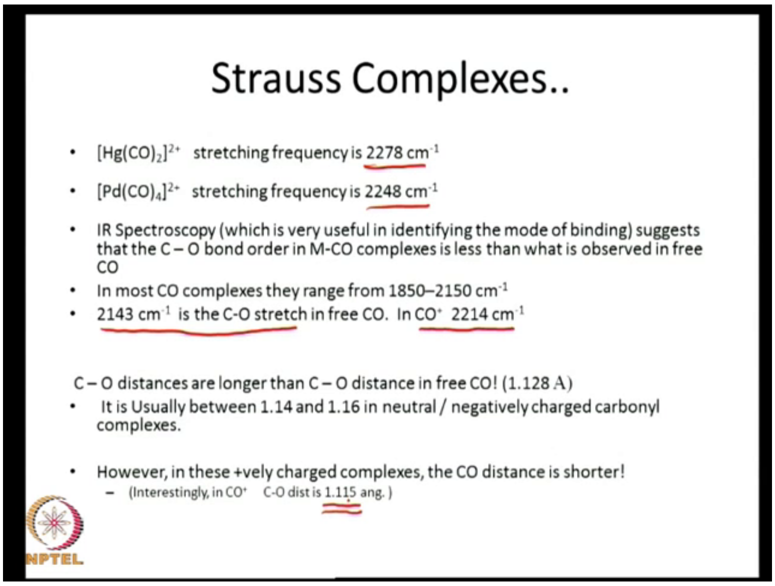


EAN
Necessary but not sufficient

- Complex of Ni $d^{10}$ has $[Ni(CO)_4)]$.
- And $Zn^{2+}$ is $d^{10}$ but does not form a similar complex.
  - Does not bind CO!
  - has an octahedral geometry with water
  - and is not similar to Ni(0) in Cord. No. a geometry.

So, let us first look at some of the first positively complexes. It is not easy to make positively charged metal carbonyl complexes. Here, I have shown you nickel tetra carbonyl. Zinc 2 plus is an iso electronic system, but it does not form a similar complex, at least not easily. You will remember that nickel carbonyl was very easily generated by passing carbon monoxide at 1 atmospheric pressure. Zinc 2 plus on the other hand does not form a simpler complex at all. It will form a very nice Werner complex with compounds like water.

(Refer Slide Time: 48:11)



## Strauss Complexes..

- $[Hg(CO)_2]^{2+}$ stretching frequency is 2278 $cm^{-1}$
- $[Pd(CO)_4]^{2+}$ stretching frequency is 2248 $cm^{-1}$
- IR Spectroscopy (which is very useful in identifying the mode of binding) suggests that the C – O bond order in M-CO complexes is less than what is observed in free CO
- In most CO complexes they range from 1850–2150 $cm^{-1}$
- 2143 $cm^{-1}$ is the C-O stretch in free CO. In $CO^+$ 2214 $cm^{-1}$

C – O distances are longer than C – O distance in free CO! (1.128 A)

- It is Usually between 1.14 and 1.16 in neutral / negatively charged carbonyl complexes.
- However, in these +vely charged complexes, the CO distance is shorter!
  - (Interestingly, in $CO^+$ C-O dist is 1.115 ang. )

As I told you, Strauss generated or synthesised a wide range of complexes with positively charged metal ions. Interestingly, the stretching frequency in all these cases ranges is in the higher side compared to 2143 centimetre minus 1, which is a free carbon monoxide stretching frequency which is indicated here. The free carbon monoxide switching frequencies indicated here as 2143 centimetre minus 1.

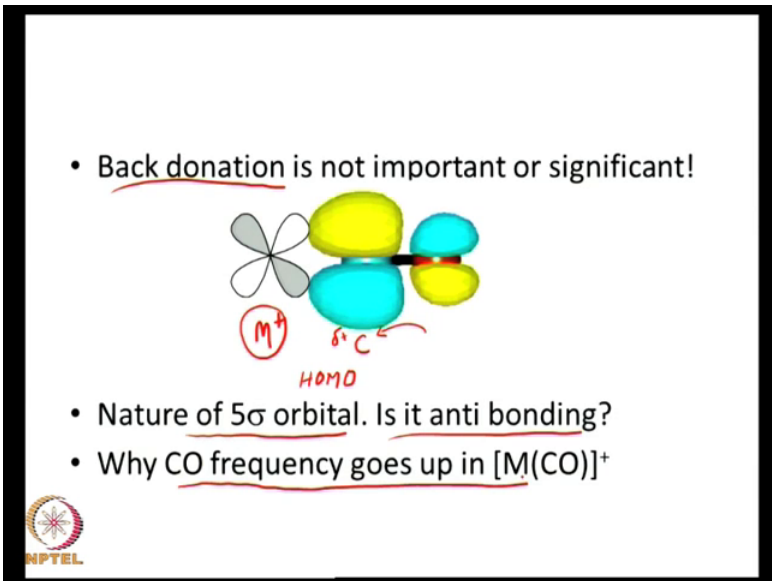
In the positively charge metal complexes, the frequency is significantly enhanced to 2248. As I mentioned to you, there are 2 factors that we have to know. One is a fact that if you remove an electron from carbon monoxide, it generates you a pass. The stretching frequency goes up. This appears to indicate that removal of electrons from the highest occupied molecular orbital tends to have a strengthening effect for the carbon monoxide bond.

So, the bond now becomes stronger. Now, 2 explanations were given. One is a charge effect. That seemed to indicate that if you place a positive charge next to the carbon, the electron withdrawing capacity of carbon is increased. So, it will have greater pulling power of the electron density towards itself. It will behave more like nitrogen. If it does that, then the bond order between carbon and oxygen increases significantly. That is why, the stretching frequency goes up.

So, CO distances are in fact in the case of positively charged complexes. It is in fact 1.115 angstrom. This is in fact shorter than what you would expect. We had earlier mentioned that the pi affect increases this carbon oxygen bond length, whereas the sigma effect shortens the carbon oxygen bond length. As I told you in the graph, there are hardly 4 percent of the complexes, where there is a delta plus or a slight positive charge on the metal atom.

So, in most complexes, the range is on the lower end. The frequency of carbon monoxide is on lower end. It is reduced from 2143 centimetre minus 1, but in a few complexes, it is in fact enhanced. That is because of the positive charge on a metal. When you have a very strong positive charge as in these 2 cases, which are shown here, then the frequency is about 100 centimetres minus 1 more than what you expect for free carbon monoxide.

(Refer Slide Time: 51:04)



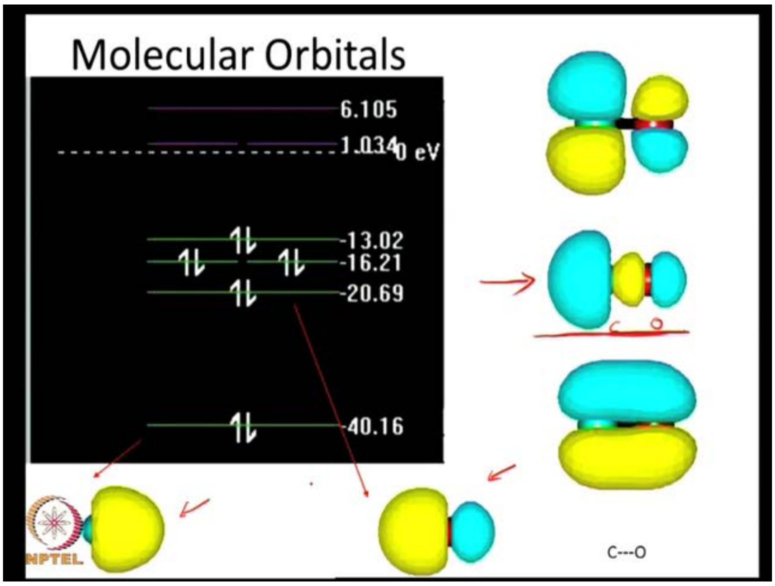
- Back donation is not important or significant!

- Nature of 5σ orbital. Is it anti bonding?
- Why CO frequency goes up in $[M(CO)]^+$

So, back donation is not important or significant when you have a metal, which is positively charged. When the metal is positively charged, back donation is not important. If back donation is not important, then the significant interaction is donation of electron density from the 5 sigma or the 3 sigma. In some books, it will be referred to as the 3 sigma because they ignore the core orbitals. In other books, it is referred to as the 5 sigma. This is the highest occupied molecular orbital on carbon monoxide. The carbon marks stretching frequency will go up if it is anti bonding in nature. That is one explanation that is given.

The other explanation is that because you have a positive charge, this positive charge makes the carbon delta plus. If carbon is delta plus, it attracts electron density towards itself. It is behaving more like nitrogen. The carbon oxygen bond strength is temporarily increased. The frequency is enhanced. That is why; the CO stretching frequency goes up in the case of metal carbonyls with a positive charge.

(Refer Slide Time: 52:16)

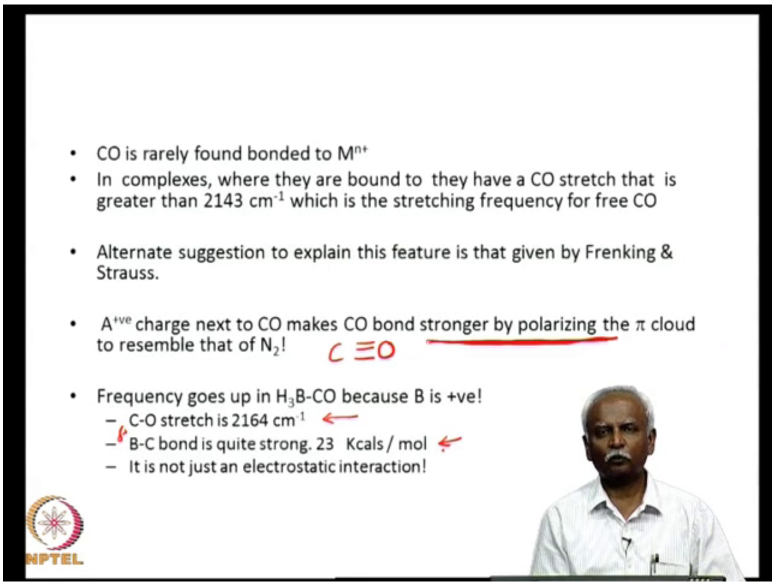


Molecular Orbitals

So, here I have just reviewed for you all the orbitals, which are of importance. This is the sigma orbital, which donates electron density. You will notice by looking at the 3 sigma orbitals. This is the first sigma orbital. This is the second sigma orbital. This is the third sigma orbital, which is the highest occupied molecular orbital. The number of nodes between the carbon and oxygen keeps increasing.

In this case, it is the maximum. Usually, the anti bonding character is indicated by a node between the 2 atoms. Here, although it is not extremely obvious, there was a hint that there is a note between oxygen, which is present here and carbon present here. That would lead to a slight weakly anti bonding nature for this orbital. However, it is now confirmed or it is assumed that the positive charge on the carbon is primarily responsible for the frequency shift. The anti-bonding nature of this highest occupied molecular orbital is minimal if not non-existent.

(Refer Slide Time: 53:31)



- CO is rarely found bonded to $M^{n+}$
- In complexes, where they are bound to they have a CO stretch that is greater than 2143 $cm^{-1}$ which is the stretching frequency for free CO
- Alternate suggestion to explain this feature is that given by Frenking & Strauss.
- $A^{+ve}$ charge next to CO makes CO bond stronger by polarizing the π cloud to resemble that of $N_2$! $C \equiv O$
- Frequency goes up in $H_3B$-CO because B is +ve!
  - C-O stretch is 2164 $cm^{-1}$ ←
  - B-C bond is quite strong. 23 Kcals / mol ←
  - It is not just an electrostatic interaction!

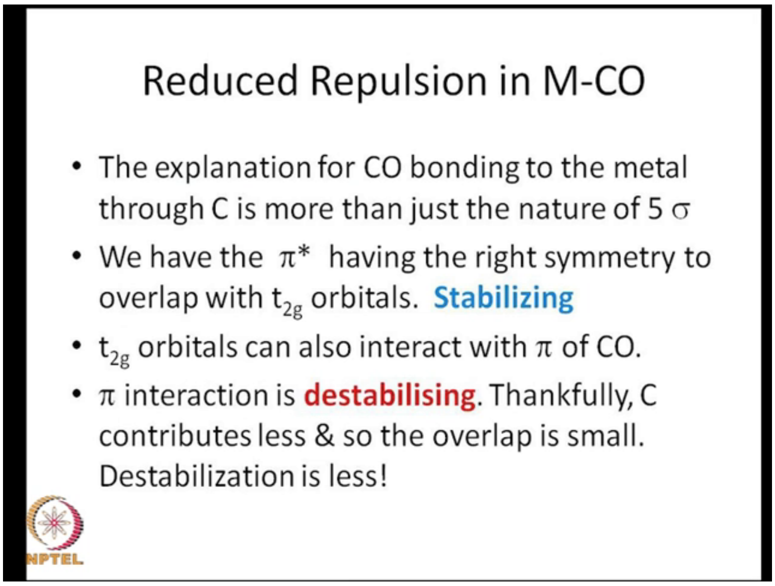
So, let me summarise by saying that CO is rarely found bond with 2 positively charge metal atoms in complexes where there bond to positively charge centres. Then, the frequency goes up beyond 2143 centimetre minus 1. There are 2 suggestions, which are given by 2 different groups of people. One group suggested that was the anti bonding nature of carbon monoxide highest occupied molecule orbital. The alternate suggestion that was given by franking and straws is now shown to be a better explanation. That suggests that the charges are in fact due to the polarisation of the pi cloud, stronger pi bond because of the polarisation of the pi cloud.

So, that carbon monoxide now resembles nitrogen because the carbon has been ripped off an electron. Some electron density is been removed from carbon and that positive charge makes carbon more electro negative. The polarisation makes the pi cloud, the pi bond between the 2 atoms stronger. You have stronger super bond between carbon and oxygen.

So, one other way to look at this phenomenon is to look at the stretching frequency in BH3CO. This is because BH3 does not have a filled orbital filled pi orbital. Now, to donate electron density, you have a stretching frequency going up beyond 2143. It is a mild increase observed about 20 centimetres minus 1 increase in the BH3CO complex. CO stretch goes up as indicative of the fact that you have a slight positive charge on the boron.

This positive charge on the boron is responsible for increasing the CO stretching frequency. You will notice that this is not electrostatic bond. It is quite strong. BH3CO interaction is almost 23 kilocalories per mole in strength. So, it is not just an electrostatic attraction. It is a covalent interaction between the BH3 and the carbon monoxide.

(Refer Slide Time: 55:42)



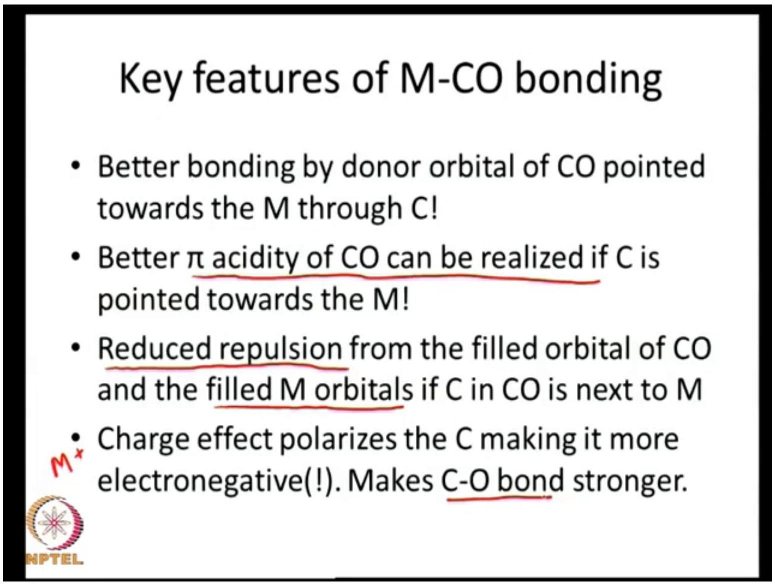
## Reduced Repulsion in M-CO

- The explanation for CO bonding to the metal through C is more than just the nature of 5 $\sigma$
- We have the $\pi^*$ having the right symmetry to overlap with $t_{2g}$ orbitals. **Stabilizing**
- $t_{2g}$ orbitals can also interact with $\pi$ of CO.
- $\pi$ interaction is **destabilising**. Thankfully, C contributes less & so the overlap is small. Destabilization is less!

There are several reasons why carbon is bound to the metal in carbon monoxide. One reason is that the donor orbital is mere localised on carbon. The second reason is that the acceptor orbital, which is pi star on carbon monoxide, has greater contribution from carbon leading to more stabilisation when the carbon is bound to the metal. There is yet another reason. There is a pi orbital on carbon monoxide, which has a similar p orbital on carbon. It is also suitable for interacting with the metal filled orbital.

If this filled orbital interacts with the pi orbital, there will be destabilisation. But, because carbon contributes less to the pi orbital on carbon monoxide, it is better for the carbon to be pointed towards the metal. This will lead to a greater stability of the metal complex. One has maximise the back bonding interaction re pointing the carbon towards the metal and reduced repulsion due to the filled pi orbital on carbon monoxide interacting the filled t 2 g orbitals.

(Refer Slide Time: 57:07)



## Key features of M-CO bonding

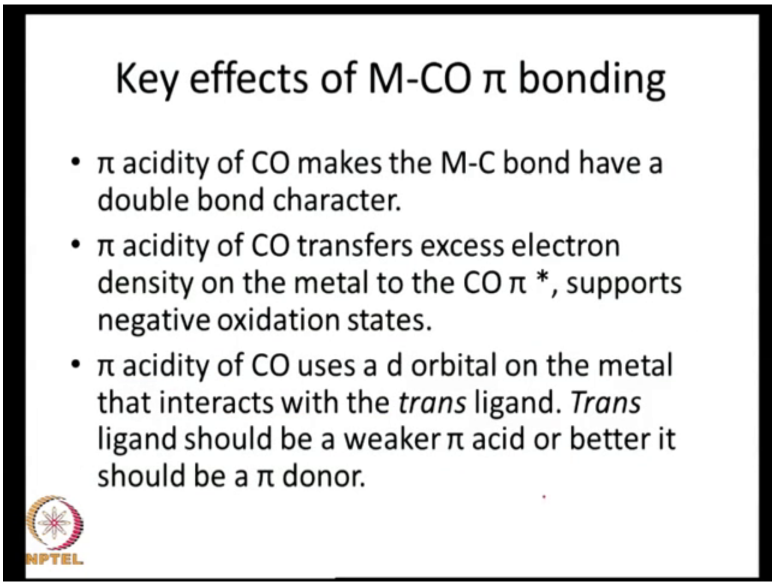
- Better bonding by donor orbital of CO pointed towards the M through C!
- Better π acidity of CO can be realized if C is pointed towards the M!
- Reduced repulsion from the filled orbital of CO and the filled M orbitals if C in CO is next to M
- Charge effect polarizes the C making it more electronegative(!). Makes C-O bond stronger.

$M^{x}$

So, there are several factors that we have seen key features of metal carbonyl bonding. We have better bonding by having the carbon and pointed towards the metal. Better pi acidity of the carbon monoxide can be realised only if you point the carbon end. This is because carbon monoxide has brought pi star orbitals and is more concentrated on carbon. It will also have reduced repulsion between the filled orbitals on carbon monoxide and the filled metal orbitals.

So, this leads to reduced repulsion, better pi bonding and better sigma bonding when you have carbon monoxide interacting through the carbon end of carbon monoxide. Lastly, there is a charge effect, which polarises the carbon making it more electro negative when there is a possible charge on the metal. So, if you have a positive charge on a metal, then the charge effect makes the CO bond stronger. So, that leads to strong or higher stretching frequencies.

(Refer Slide Time: 58:10)

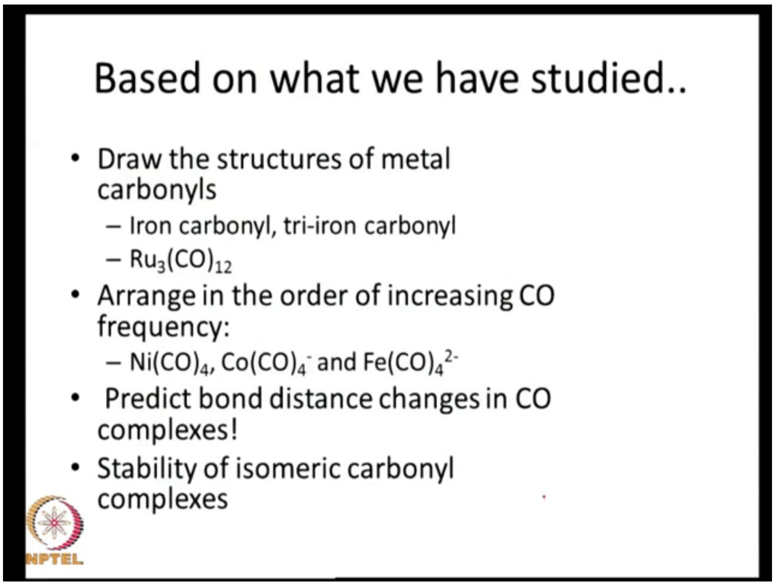


## Key effects of M-CO π bonding

- π acidity of CO makes the M-C bond have a double bond character.
- π acidity of CO transfers excess electron density on the metal to the CO π *, supports negative oxidation states.
- π acidity of CO uses a d orbital on the metal that interacts with the *trans* ligand. *Trans* ligand should be a weaker π acid or better it should be a π donor.

So, we have covered several aspects of pi acidity and these are listed here.

(Refer Slide Time: 58:16)



## Based on what we have studied..

- Draw the structures of metal carbonyls
  - Iron carbonyl, tri-iron carbonyl
  - $Ru_3(CO)_{12}$
- Arrange in the order of increasing CO frequency:
  - $Ni(CO)_4$, $Co(CO)_4^-$ and $Fe(CO)_4^{2-}$
- Predict bond distance changes in CO complexes!
- Stability of isomeric carbonyl complexes

Based on what we have studied, one should be able to draw the structures of complexes, predict the structural features and also predict stability of the metal complexes. This should lead to a better understanding of the spectral features.