Introduction to Organometallic chemistry
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Lecture - 4
Ligand Substitution Reactions

We will now consider in this lecture a few aspects of metal carbonyl compounds the origin of 18 electron rule, and how some substitution reactions can be carried out with metal carbonyls.

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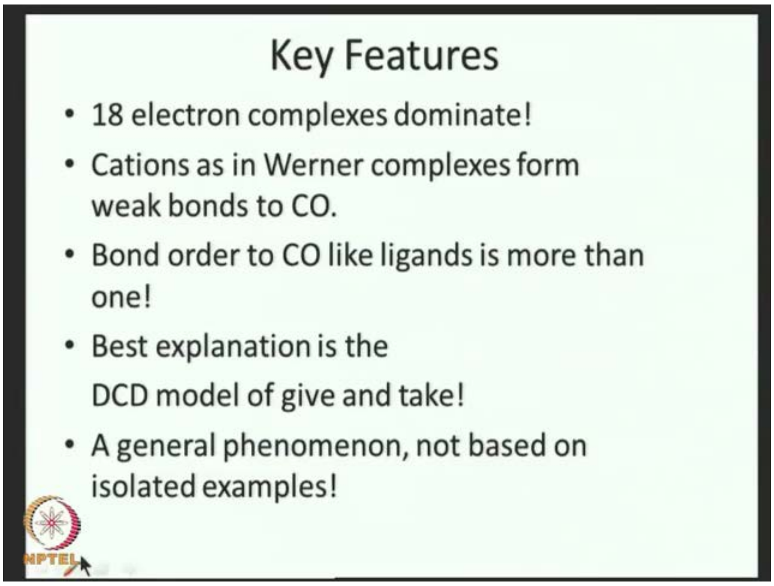

Key Features

- 18 electron complexes dominate!
- Cations as in Werner complexes form weak bonds to CO.
- Bond order to CO like ligands is more than one!
- Best explanation is the DCD model of give and take!
- A general phenomenon, not based on isolated examples!

As I had mentioned in the lecture on metal carbonyls, carbonyl compounds are like alkanes in organic chemistry. In many of the compounds where carbon monoxide is the only ligand, you will find that there are 18 electron complexes. These are the only complexes that can be synthesized and they are found in a stable situation. The only exception was the vanadium hexa carbonyl, which was black paramagnetic solid. And we noted that was really an exception and it could readily reduced to give you VCO 6 minus which was a diamagnetic species and a very stable compound.

Although you can generate anionic species, cations as in the case of although you can generate anionic species. We noted that cationic complexes as Werner complexes are not readily synthesized and they form very weak bonds to carbon monoxides. They do form compounds with carbon monoxide, but the bonds are generally weaker. The bond order to carbon monoxide or carbon monoxide like ligands are in general more than one. You do have a partial bond order of greater than 1 and a maximum of 2. We will go through this in today's lecture also.

So, we consider the fact that best explanation for explaining, all these factors that we have observed with metal carbonyls is to use, what is called the DCD model or Dewar Duncanson Chatt model or Dewar Chatt Duncanson model. These are the names of the three people Dewar, Chatt and Duncanson, who initially gave this give and take sharing of electrons. The ligand gives electrons to metal and then metal in turn gives electrons back to the ligand this give and take phenomenon is synergistic phenomenon, which we will consider today and this leads to a very stable situation in metal carbonyl chemistry.

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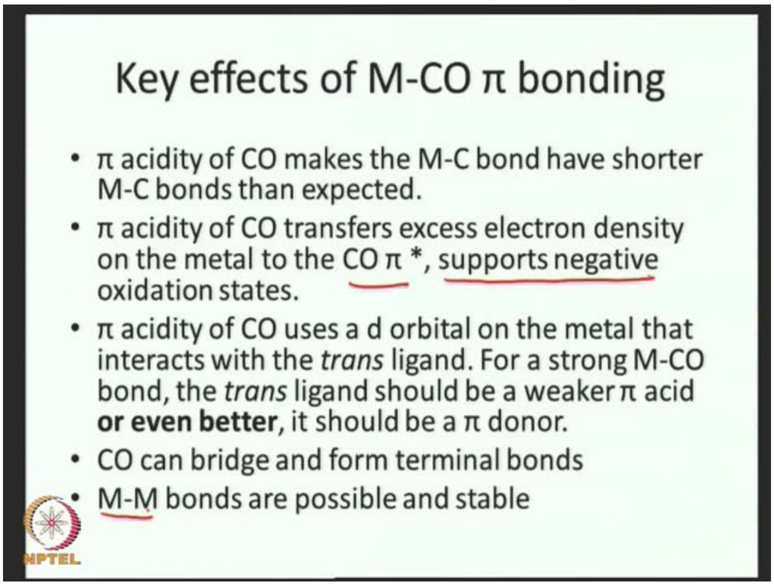

Key effects of M-CO π bonding

- π acidity of CO makes the M-C bond have shorter M-C bonds than expected.
- 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. For a strong M-CO bond, the *trans* ligand should be a weaker π acid **or even better**, it should be a π donor.
- CO can bridge and form terminal bonds
- M-M bonds are possible and stable

The key factors which stabilize the metal carbonyl bond was the pi acidity of the carbon monoxide and since we have covered this before we will just quickly go through this. The pi acidity or the accepting ability of carbon monoxide from the pi star orbital of carbon monoxide leads to stabilization of negative oxidation states. So, metals in negative oxidation states, can be supported because you can pump in electron density into the anti-bonding orbitals of the carbon monoxide.

This results in the strong bond between carbon monoxide and the metal and we also found that the carbon monoxide can form bridges between two metal atoms. And even without bridging metals can form metal metal bonds as in two instances which we looked at Mn 2 CO 10 and Mn 2 CO 8. They are very rarely formed metal metal bonds and they are quite stable.

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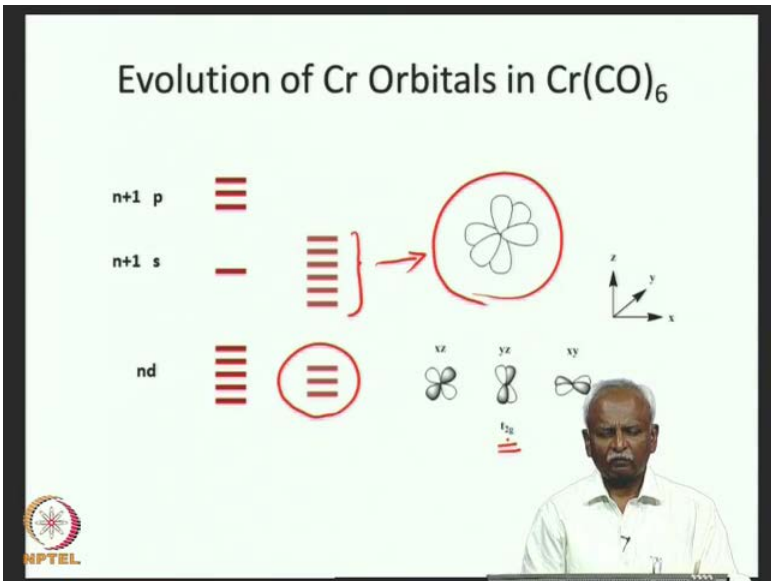

Evolution of Cr Orbitals in $Cr(CO)_6$

Let us for the sake of completion look at how, the orbitals in chromium are evolved in Cr CO 6 and we will look at what is called this, partial bond order and origin of the eighteen electron rule. So, talk about, first we will talk about the origin of eighteen electron rule and in order to look at the bonding in Cr CO 6, we first generate 6 orbitals which are suitable for interacting with carbon monoxide lone pairs. So, here are the 6 orbitals on chromium and the valence bond formalism is the most convenient one in order to understand this bonding picture.

So, octahedral set of ligands can be accommodated in the 6 orbitals which are formed by d 2 sp 3 hybridization. So d 2 sp 3 hybridization is what is needed in order to accommodate 6 ligands in an octahedral space. And that is exactly what we have done here, here are those 6 hybrid orbitals which have the shape, which is given here in this on my right side and on the left side I have given you an approximate or a crude level of diagram, which leaves out 3 d orbitals in a lower line set of orbitals, lower line orbitals which are the dxz dyz and dxy and these are all the t 2 g set of orbitals in an octahedral field.

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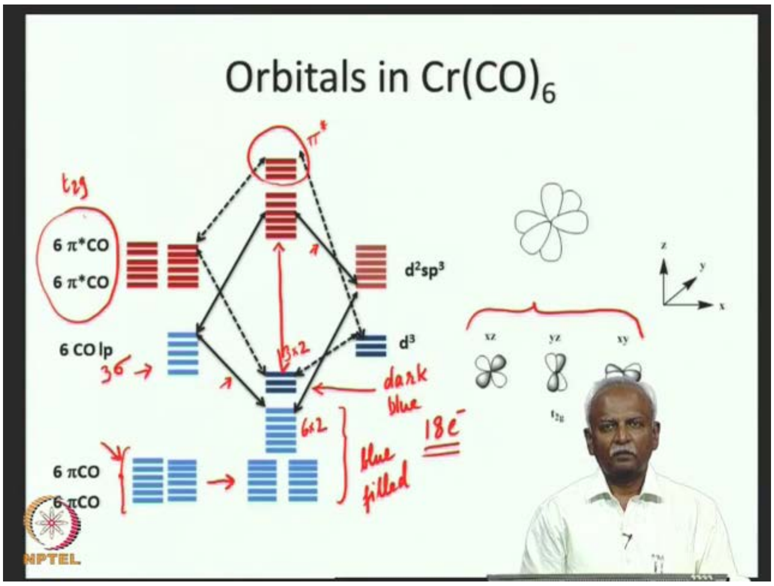
Orbitals in $Cr(CO)_6$

And when we do that, we can interact with 6 carbon monoxides in, carbon monoxides you, carbon monoxides you have 6 lone pairs which are pointed towards the metal. And that is what is called as the 3 sigma or in some books it might be given as 5 sigma, if the 2 core electrons are also counted, the core electron are carbon. And 2 core electron on oxygen, if they are counted then this becomes 5 sigma, but it is a sigma orbital on carbon monoxide. In addition to this sigma orbital, which is at a slightly higher energy level we have, this is sigma which is at a higher level.

We should remember that the carbon monoxide has got 2 sets of pi orbitals, these pi orbitals if you have 6 of them they will be 6 into 2, 12 pairs of electrons on carbon monoxide which are bonding orbitals. In general we do not consider the interaction of this pi bonding orbitals with a metal because they are low lying in energy. And secondly, their overlap is small because if you remember carbon monoxide has a smaller low the bonding orbital of carbon and a larger low on oxygen. So, these are the orbitals which are reasonably non interacting and so we will transfer them to the molecular orbitals in the same energy level.

And the 6 lone pairs are now stabilized by interacting with the 6 d 2 sp 3 hybrids which are, available on the metal. So, the empty orbitals are pushed up in energy, so the empty orbitals are pushed up in energy shown by this arrow here. And the filled orbitals are stabilized, which is shown by the arrow on my left side and so all the filled orbitals are shown in blue. So, the blue are filled orbitals they are filled with 2 electrons each and if you recollect the metals has caught 3 d orbitals which, are in fact stabilized by interaction with the empty orbitals on carbon monoxide.

If there are 12 bonding pi pairs on the carbon monoxide, say there must be 12 anti-bonding orbitals also. Fortunately, for us only 3 of those have the right symmetry to interact with the t 2 g set. So, this is the t 2 g set and only 3 of these orbitals, there are 3 on the metal and only 3 of this 12 pi star orbitals have the right symmetry. They have the t 2 g symmetry is also should have t 2 g symmetry and have the right symmetry to interact and show they are pushed up in energy. So these are the pi star on carbon monoxide, which are been pushed up and there are interacting with the filled orbitals on the metal. The filled orbitals on the metal are shown in dark blue.

So these are also dark blue and they are filled. So all the blue orbitals are filled and the red orbitals are empty. Now if you count the electrons around the metal, which are mostly on the metal. Now, so will realize there are 6 into 2 12 electrons which are coming from carbon monoxide and 3 into 2 which are coming from the metal. So you have a total of 18 electrons, you have total of 18 electrons in Cr CO 6. And you can see that this is a typical energy level diagram, that would stabilize the chromium hexa carbonyl system extremely well because the bonding orbitals are all stabilized and anti-bonding orbitals are reasonably higher in energy. And this gap is significantly large so this gap is significantly large and that leads to a very stable situation.

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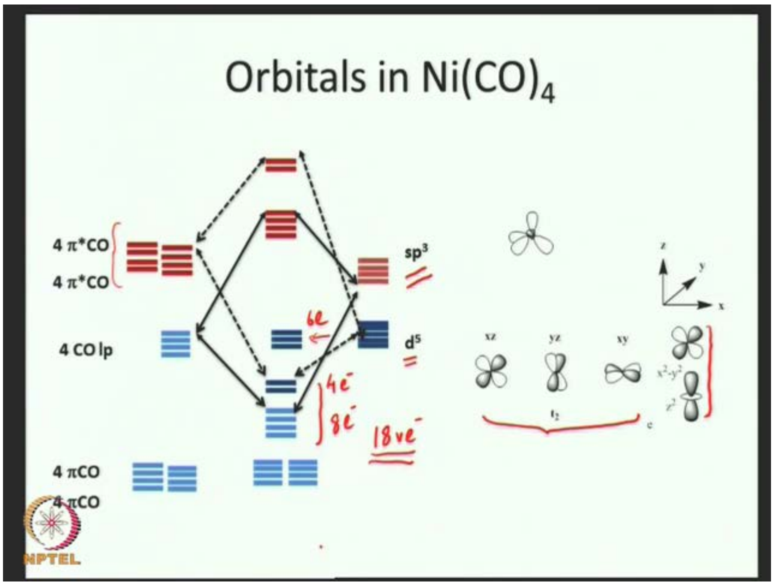

Orbitals in $Ni(CO)_4$

Now, let us take a look at what would happen in another molecule and that molecule is tetrahedral system, that is also nickel tetra carbon. Once again we found that, nickel tetra carbonyl has got compliment of 18 electrons around itself. And now let us look at why although the coordination geometry is different, although the tetrahedral geometry is adopted by this molecule, we still have a set of 18 electrons. You will remember that in order to generate vacant orbitals on a metal in a tetrahedral coordination sphere, you need to use the s and 3 p’s. And if you have sp 3 hybrid orbitals and 5 d’s are lower in energy, you will notice that the 2 d orbitals which we have labeled as having e symmetry.

These are orbitals which are having e symmetry and these 2 orbitals are slightly different from the t 2 set of orbitals. Now we do not have the g symbol because now we do not have center of symmetry in this particular molecule. So we have t 2 set and e set and the t 2 set remains, non interacting and it is the same level of d orbitals. Now, if you have 2 e orbitals and these e orbitals are capable of interacting with a carbon monoxide in a pi fashion. These 2 orbitals are stabilized. So, out of the 4 into 2, 8 pi star orbitals on carbon monoxide, only 2 of them can be stabilized by interaction with a d orbitals having e symmetry.

So, you will notice that if we fill up these orbitals, now we have 4 into 2 8 electrons, here you have4 electrons here. So, that makes a total of 12 electrons and 6 electrons here, because of the 3 orbitals here, we have total of 6 plus 4 plus 8 and that again makes up for 18 valence electrons in a metal. Now, we believe that because the carbon monoxide has pi orbitals, these pi orbitals are not interacting significantly, it is this 18 valence electrons that are around the metal. So that is how you get 18 valence electrons, both for nickel case and in the chromium case.

So, if you work it out for any other geometry also you will end up with a total of 18 valence electrons. Now, let us take a look at the pi bond order in these molecules. If you look at the previous case the chromium hexa carbonyl system, the pi bonds number of pi bonds formed where because of these 3 orbitals, which are having this t 2 g symmetry. This t 2 g symmetry has got 6 electrons and these 6 electrons are the ones, which are having pi interactions with the chromium hexa carbonyl. Although there are 6 ligands, there are only 3 pi bonds that is coming from these3 orbitals, which are located here this d 3 system.

So, you can see that the maximum bond, pi bond order that can be there for chromium hexa carbonyl is only 0.5, the maximum pi bond order in hexa carbonyl chromium is only 0.5 double bond order. So, the pi bond order is not fully 6, but it is 3. Similarly, if you look at Ni CO 4, you realize that although you have 4 carbon monoxides only 2 orbitals on the metal are stabilized and there are 4 electrons which are interacting in a pi fashion.

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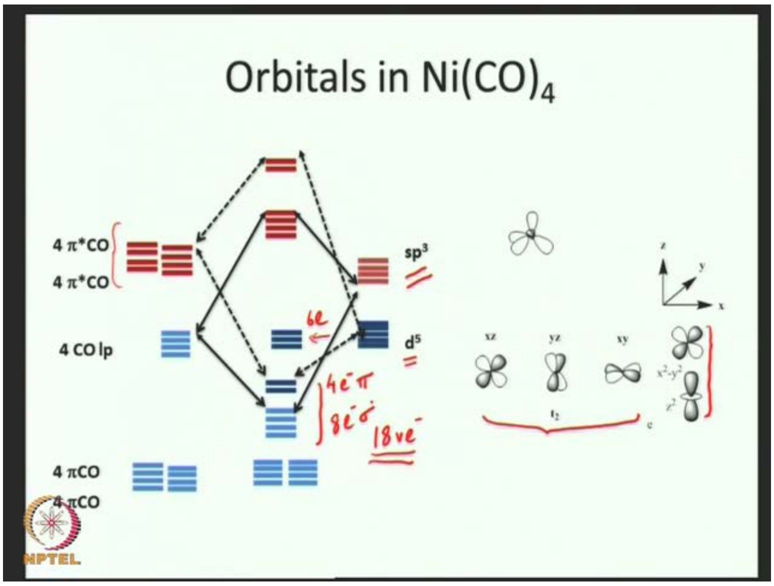

Orbitals in Ni(CO)$_4$

So, these 4 electrons are interacting in a pi fashion and these 8 electrons are working in a sigma fashion. So, the sigma bond order between carbon monoxide and the metal is 1 because 2 electrons are shared in the orbital. So, you can say that the bond order is 1. Whereas, in the pi bond order it is only 0.5 once again you notice that, the bond order that is present, the pi bond order that is present between the ligand and the metal is not 1, but 0.5. Now, we can lets analyze this a little bit and see why is it that it is only 0.5 and we will do that after briefly looking, at another complex which is Pt Cl 4 2 minus.

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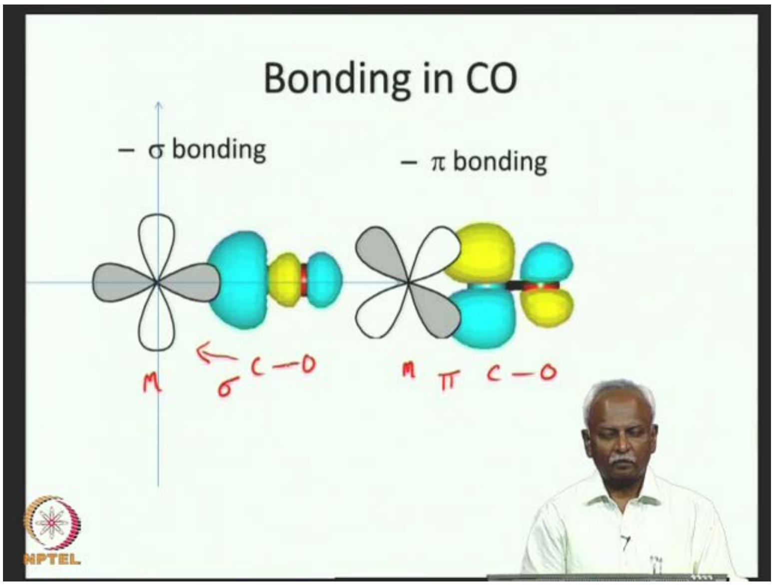

Bonding in CO

- σ bonding
- π bonding

We will come back to this, let us first look at that the partial bond order. If you look at the bonding in detail between a metal and a carbon monoxide, you notice that there are two interactions which are present. One is the carbon monoxide interacting in a sigma fashion, it gives a pair of electrons which is orbital, which is there on the metal. And two it is interacting in a pi fashion with a t 2 g set of orbitals and one of them is picturing here with a pi star orbital. So, this is a sigma interaction and this is a pi interaction so here is the metal and here is the carbon monoxide. So, we can write this sigma interaction and the pi interaction in this fashion, but notice that both the sigma and the pi interaction are being shared.

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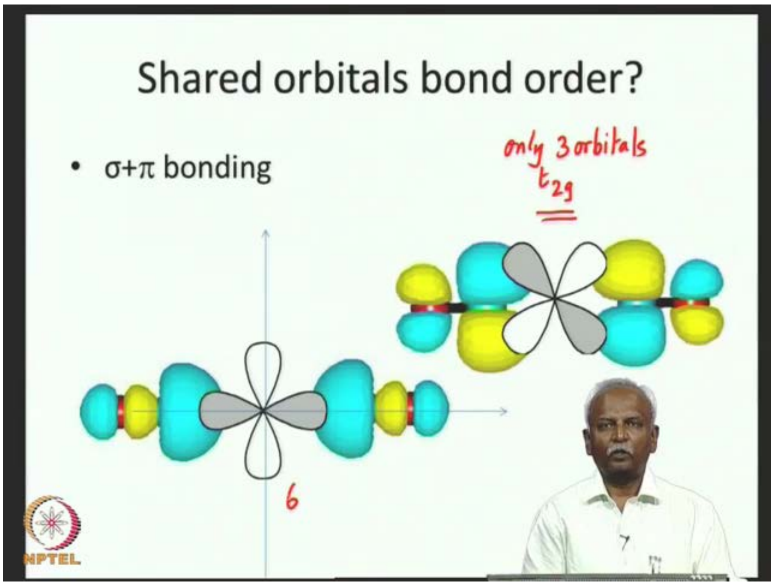

Shared orbitals bond order?

- σ+π bonding

So in the case of the sigma orbital, you notice that the same orbital has to be shared with the ligand in the transposition, but in the case of sigma orbitals we generated 6 equivalent orbitals, on the metal using d 2, 2 d orbitals and the s and the 3 p orbitals. So, there are sufficient number of empty orbitals on the metal.

On the other hand, the pi bond order has to be only shared with the d set of orbitals and we have only 3 orbitals which are labeled as t 2 g. So, this t 2 g has got only 3 orbitals, only 3 orbitals are available. So, only 3 orbitals are available on the metal for the pi bond order whereas, 6 orbitals are available for the sigma bond order. So because of this the pi bond order can only be 3.

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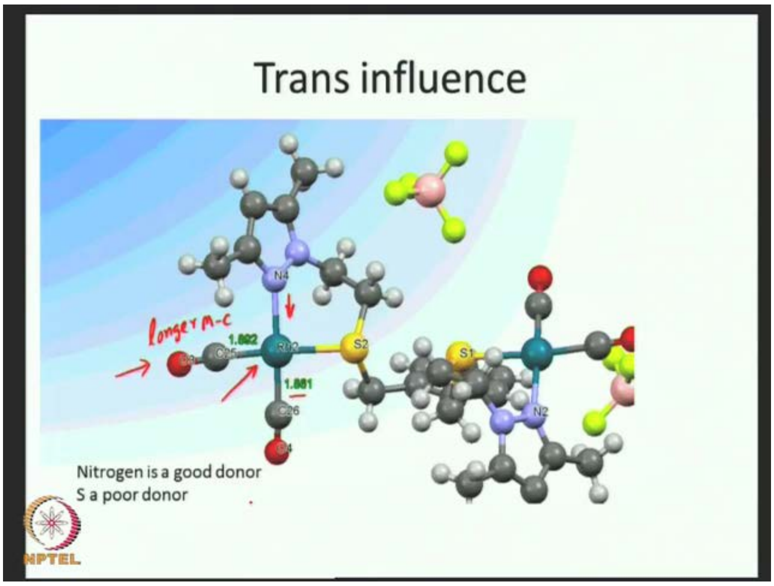

Trans influence

Nitrogen is a good donor
S a poor donor

So, this has got significant importance in the case complexes thus grounds its structure of the complexes. And here I have pictured for you two examples, two examples where we have carbon monoxide bonded to the metal atom in this particular instance, you have seen a rhodium atom. This is a rhodium atom which is bonded to 2 carbon monoxides, one carbon monoxide is Trans to a nitrogen and the nitrogen is a good donor ligand.

And it pumps in an electron density to the rhodium and because of that the rhodium carbonyl bond, which is present is quite strong because you have electron density flowing from that direction. It pumps in an electron density into the carbon monoxide pi star orbitals, because you have a pi system on the opposite side, which is pumping in electron density.

On the other hand this carbon monoxide has got the bond distance of 1.892 angstrom, this is longer, this has got a longer metal carbon bond. And this has got a shorter metal carbon bond, 1.861 and if you have a weak donor opposite carbon monoxide, if you have a weak donor this results in a longer bond. So, this pi interaction that is present in the opposite Trans geometry is very often essential for influencing or determining bond distance between metal and carbon monoxide.

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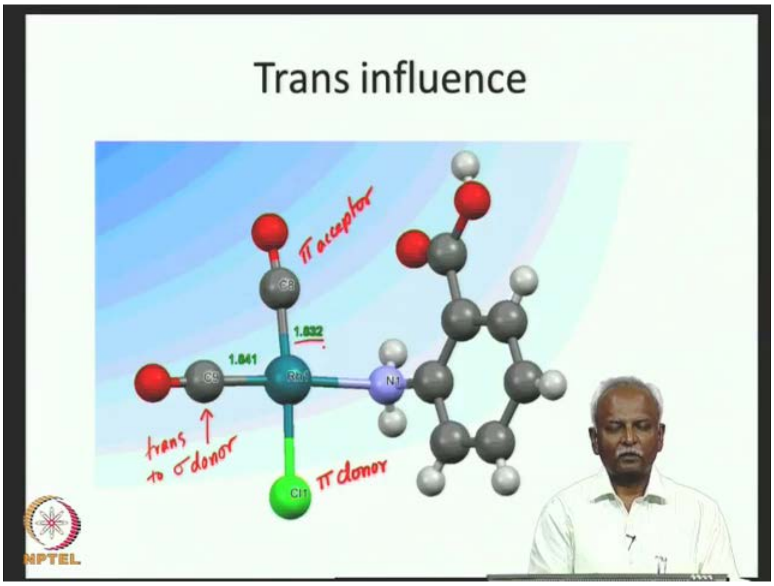

Trans influence

So, we have one other example here, once again you have in this case we are both one is pi donor this is the chlorine, which is a pi donor and this is a carbon monoxide which is a pi acceptor. So, we have a pi acceptor which is trans to a pi donor and the bond distance is significantly short, is it 1.832 angstroms whereas, on the other hand you have 1 carbon monoxide, which is this carbon monoxide which is trans to a sigma donor.

So because you only have sigma donor and not pi donor, this distance is longer it 1.84 angstrom. So this 1.84 angstrom is longer than 1.832, which is because of this pi interaction, which is present. So, let us go back now and see, the continue with our discussion on 18 electron rule. The eighteen electron rule as we discussed with nickel tetra carbonyl, comes about because we have a stable set of 18 electrons in the metal waste orbitals.

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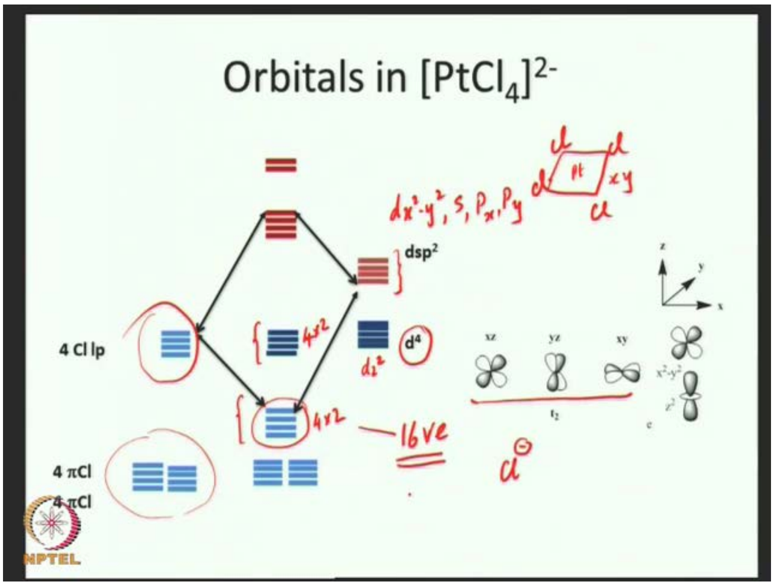

Orbitals in $[PtCl_4]^{2-}$

And in some instances we also know that, there are complexes which have less than 18 electrons and they are also stable. A classic example is this tetra ((Refer time: 21:17)) Pt Cl 4 2 minus and this is the system, which has got 8 electrons and these 8 electrons are in in a stable system. Let us try to understand, how this could have been come about. Suppose you have 5 d orbitals and 1 s and 3 p orbitals on the platinum, you can make 4 orbitals which are available for interaction with the ligand. And these 4 orbitals could be made from the d x square minus y square, the s and the p x and the p y orbitals, if you have 4 ligands along the in the x y plane.

So, if you assume that the 4 ligands on Pt Cl 4 2 minus is present in x y plane, if this is the x y plane, if you have 4 chlorines which are present in the four corners of the x y plane, that I have drawn for you here. So, the d x square minus y square s and the p x and the p y can combine together to form a dsp two hybrid. And this dsp two hybrid will now be stabilized with interaction of 4 lone pairs of the chlorine, which I pictured here and this 4 lone pairs will be stabilized by the interaction with these empty orbitals.

And that leaves out the dz squared orbital, dz square orbital and what we had earlier written and as the t 2 set. So dxz dyz and dxy and the dz square orbital will combine together and will form as a set of d 4, d orbital which are left ((Refer Time: 23:22)) at the level of the d orbitals in platinum. So this is approximately going to be present in the same energy level and we can fill in 4 into 2, 8 electrons here so that will be 8 electrons here and 4 into 2, 8 electrons which are stabilized onto chlorine. So a total 16 valence electrons are present, 16 valence electrons are present when it is square planar complex.

Now, one might wonder why is this different from the 18 electron rule, why is it that so many compounds are formed which have all 16 electrons and they, and especially they are square planar in nature. That comes about because of the difference in energy between the d orbitals and the s and the p orbitals. When the p orbital is significantly higher in energy then the tendency of the metal to use the p z and the d z square to form octahedral complexes is less. It prefers to involve only the 3 d 4 s 4 p x and the 4 p y orbitals. This results in a complex that has only 4 hybrids mainly d x square minus y square 4 s 4 p x and the 4 p y orbitals.

This is suitable for interacting with 4 ligands which are present in x y plane and it leads to a square planar complex. So, instead of forming complex in which we have 6 ligands, it prefers to have a square planar complex and we stabilized only the 16 valence electrons systems. So, once again the nomenclature of the notation that we have used, these are metal d orbitals and they are felt and they had 8 electrons, and they had 8 electrons from the chlorine, which is also felt.

You can also recollect that Cl minus has got several 4 pairs of electrons on itself, only 4 of them has been stabilized by interaction with the metal and the other 8 of them, the other set, the other set is not interacting with the metal atoms and they remain unperturbed in energy. Although they can interact with these d orbitals, we in general, we keep them unperturbed in an approximate energy level diagram.

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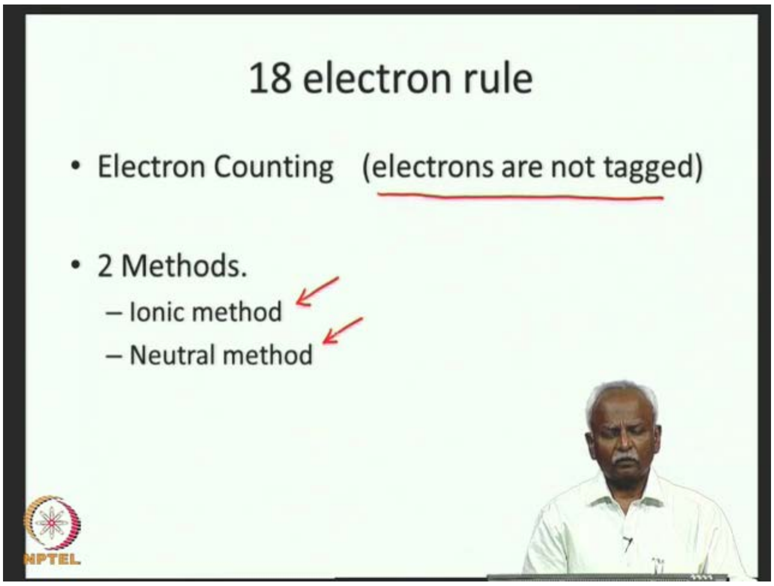

18 electron rule

- Electron Counting (electrons are not tagged)
- 2 Methods.
  - Ionic method
  - Neutral method

So, let us now go to the 18 electron rule and the electron counting. As we have just mentioned this 18 electron rule could turn into 16 electron rule especially, if there are square planar complexes. We should always remember that electrons are not tagged, what I mean by this is that, once the molecule is formed you cannot distinguish between the electrons coming from the metal or the electrons that are coming from the ligand. They are all equally orbiting the atoms in the molecule and they cannot be identified with the specific atom.

So there are two methods which are used in order to count the electrons. This is just book keeping, in other words I want to account for all the electrons in the molecule or want to see, how many are associated with the metal. And since we know that in octahedral complexes and in some systems, we do have stabilization after 18 electron species. We would like to do this electron counting, in order to get quick way of identifying stable molecules versus unstable molecules. There are two general ways by which one can do this electron counting, one is called the ionic method and the other is called the neutral method.

As the name suggests in the neutral method, all the ligands are considered as neutral species whereas, in the ionic method an arbitrary decision is made based on electro negativity of the atom, to associate the charge with the ligand or with the metal. So we will encounter this, we will try to understand this with some examples.

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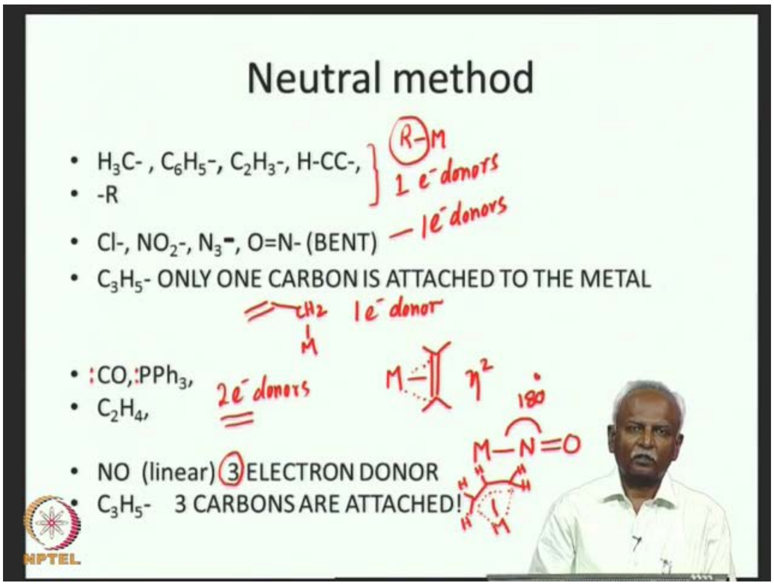

Neutral method

- H_3C- , C_6H_5-, C_2H_3-, H-CC-,
- -R
- Cl-, NO_2-, N_3-, O=N- (BENT)
- C_3H_5- ONLY ONE CARBON IS ATTACHED TO THE METAL
- :CO,:PPh_3,
- C_2H_4,
- NO (linear) 3 ELECTRON DONOR
- C_3H_5- 3 CARBONS ARE ATTACHED!

But first let us take a look at the, first let us take a look at the some of the ligands that are pictured here, which are one electron ligands. So, if you have any alkyl group so here I have pictured several alkyl groups, the simplest of them is the metal radical. And so the metal radical, if you have in the place where I have drawn the dash, if you have R dash M, I have only written the R this part of the group. And so if you have an R dash then let us assume that this will give one electron from alkyl group and one electron from the metal. And so in the neutral method, we consider these as one electron donors.

These are one electron donors. Similarly, if I have a Cl NO 2 or an N 3 or a bent ((Refer Time: 29:03)) radical, all of them are also one electron donors. So, here Cl dot is the actual donor NO 2 dot N 3 dot and NO dot, these are one electron donors again. Now this is purely a matter of electron book keeping so one should not confuse this with their charge on the atom.

Now if you have C 3 H 5, which is this group here it can be attached to a metal at the CH 2 position and only one carbon is attaches to the metal then we call this is also one electron donor. So, this is also one electron donor, on the other hand carbon monoxide which has a pair of electrons given, giving, is given to the metal and tri phenyl phosphine again 2 electrons are there on the phosphorous these 2 electrons are given to the metal.

So, these are 2 electron donors. Now, if you have a molecule like an ethylene complex where, the metal is bonded to 2 carbons, where the metal is bonded to 2 carbons in equidistant fashion, is this distance that is there between the metal and the 2 carbons is almost the same. Then we call it as a eta 2 ligand, this is a eta 2 ligand and it is a neutral species and in the neutral method, we assume that it gives 2 electrons because the pi orbital which has, which is there on the ethylene is donated to the metal, so in NO, this is again system where, we have or we could have some complications.

If you have a molecule in which this bond angle is 180 degrees, this bond angle is 180 degrees then this is a linear NO and in the neutral method it is considered as a 3 electron donor. So you will notice that, this is an unusual ligand which is a total of 3 electrons in the metal when, you have a linear geometry. Again if you have C3 H5, this is a system where we have C3 H5 and if all 3 carbon atoms are in interacting with the metal in an equidistant fashion then this also turns out to be.

So each one of these lines has got a hydrogen so this is also considered as a 3 electron donor. So you will notice that, if you use a neutral method you have to assume that the ligands completely neutral and look at the number of electrons that it will donate in that particular state, when it is in the neutral state. So metal radical will generate or will give 1 electron to the metal. Similarly, a chlorine radical will give 1 electron to the metal. So the neutral method assumes that the ligand is in without charge and then it counts the number of electron that can be given.

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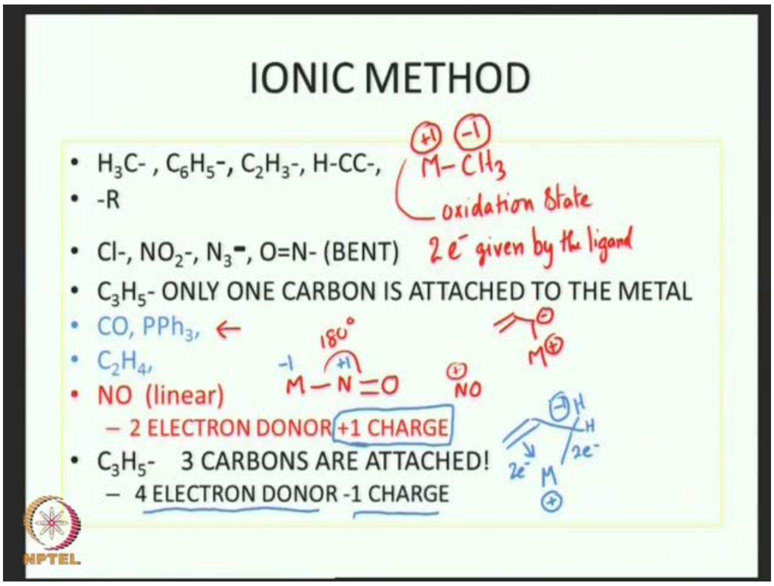

IONIC METHOD

- H_3C- , C_6H_5-, C_2H_3-, H-CC-,
- -R
- Cl-, NO_2-, N_3-, O=N- (BENT)
- C_3H_5- ONLY ONE CARBON IS ATTACHED TO THE METAL
- CO, PPh_3,
- C_2H_4,
- NO (linear)
  - 2 ELECTRON DONOR +1 CHARGE
- C_3H_5- 3 CARBONS ARE ATTACHED!
  - 4 ELECTRON DONOR -1 CHARGE

In the ionic method there is a slight difference, we use our knowledge of electronegativity of different atoms and assign a charge based on the electronegativity. In most instances the charge is based on the electronegativity and here I have metal radical the same species same set of species is talked about here. And we have for example, CH3 is a metal anion so it is CH3 minus in the instance.

The same molecule that we talked about earlier, MCH3 is now talked about as M plus 1 interacting with CH3 minus 1 or in other words CH3 minus is interacting with a plus. So this charge, that we write on the top of the metal is purely a matter of formality, it is not a real charge which is present on the metal. For the electronic book keeping, we assign such charges and this charge is what we call as a oxidation state.

So one should not mistake the oxidation state for an actual charge on the metal. Similarly, Cl minus NO2 minus N3 minus or all ligands, which will be negatively charged because they are more electronegative than the metal itself. And they all are 2 electron donors in all these instances, we have 2 electrons being given by the ligand, 2 electrons are given by the ligand and the metal is supposedly in positive oxidation state. Similarly, if you look at C3 H5 minus which is ((Refer Time: 35:10)) now in this instance we will have to write it like this, if it is only interacting with one carbon it is C3 H5 minus and there is a negative charge on the ((Refer Time: 35:23)) group and there is a positive charge on the metal.

Once again this is concerned as a minus charge ligand and a plus one charged metal atom. However when we look at the ionic method also, there are some species which do not give any, are not associated with any charge. Here is an example carbon monoxide and tri phenyl phosphine and we give a pair of electrons to the metal, but nevertheless there is no charge associated with this ligand. It is a neutral specie whichever method you consider the neutral method or the ionic method, they are neutral ligands. Similar is the situation with C2 H4, the same ethylene complex will have a 0 oxidation state metal and ethylene is also considered as the neutral specie.

NO, when it is present in a linear fashion in other words, M N O is present with the angle of 180 degrees then we end up assigning a plus 1 charge because MO plus is a ligand which is isoelectronic with carbon monoxide. And it gives a pair of electrons to the metal so the most convenient way of understanding a linear nitric oxide in the ionic method is, to associate a positive charge. Let us just indicate that a little more clearly so we have a positive charge associated with the ligand and so in this instance the metal is negatively charged and nitric oxide is positively charged.

So you have a negatively charged metal atom interacting with NO and that gives you the particular description that we are talking about. So C3 H5 minus, will now be an ((Refer Time: 37:28)) group, but if all 3 carbon are associated with the metal. We can consider it in this fashion, we can think of it as if the pi bond of the ((Refer Time: 37:44)) system is also donating 2 electrons and ((Refer Time: 37:49)) group the CH2 group is also giving 2 electrons. So total of 4 electrons are given by then ((Refer Time: 38:00)) group and a minus 1 charge is associated with the metal.

So, the metal has plus 1 charge and the ((Refer Time: 38:07)) group has got a minus 1 charge. So I think you should be able to figure out some of the other examples where, you have an odd electron carbon pi system interacting with the metal we usually, have a negative charge. And if you have an even number of pi electrons interacting with the metal then you have a neutral species and in case of ethylene, it would be 2 electrons. If you have butadiene there would be 4 electrons and so on.

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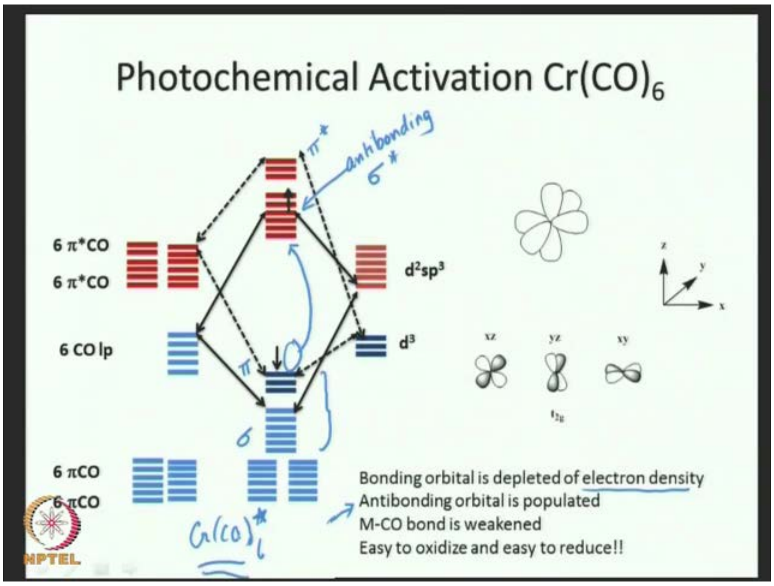

Photochemical Activation $Cr(CO)_6$

Bonding orbital is depleted of electron density
Antibonding orbital is populated
M-CO bond is weakened
Easy to oxidize and easy to reduce!!

So, if you go back to Cr CO 6 which I have pictured here one can understand how, you have a stable system if you have 18 electrons and you have either in the neutral method or in the ionic method. You have a total of 6 electrons being donated to a carbon monoxide resulting in Cr CO 6.

Now, I want to talk to you about, how one can substitute one of the ligands on this molecule with another ligand. Now, if you remember we have a stable system of 18 electrons and the dark blue colored and the blue colored orbitals are the filled orbitals, these are all the filled orbitals. And the filled orbitals are contributing to the bonding situation and there are no orbitals in the anti-bonding orbitals, which are destabilized and are pictured here. So these are anti-bonding orbitals, these anti-bonding orbitals and you can talk and you can think of it, as if they are sigma star and these are sigma bonding orbitals and these are pi bonding orbitals and these are pi star orbitals on the metal complex.

So, in Cr CO 6 all the blue ones are filled, blue orbitals are filled and if you promote through photo chemical activation. If you move one of the electrons from the ground state to the higher energy state, then what will happen is you will be removing one electron, you will only have 5 electrons in the bonding orbital and you will be populating the anti-bonding sigma star orbital. Now, this is easy to understand you are removing electrons from the bonding orbital. So, the depletion of electron density would lead to loss of pi bond order. The anti-bonding sigma orbital is populated and so that will lead to a weakening of the sigma bond.

So, it is easy to see that if I photo chemically excite Cr CO 6, I would be destabilizing the metal ligand bond. One of the bonds, it would be easier to break one of the bonds in Cr CO 6, because of this photo chemical excitation. Now, I would like to point out just one other factor, in the excited state you have a low lying orbital which is empty and so you can add an electron to this photo chemically excited species Cr CO 6.

You can photo chemically excite it and then it would be easier to reduce this excited state species, easier to reduce that excited state species and because you have added one electron in the higher energy orbital, it would be easy to oxidize this Cr CO 6 also. So, photo chemically excited molecules turn out to be easy to reduce and easy to oxidize.

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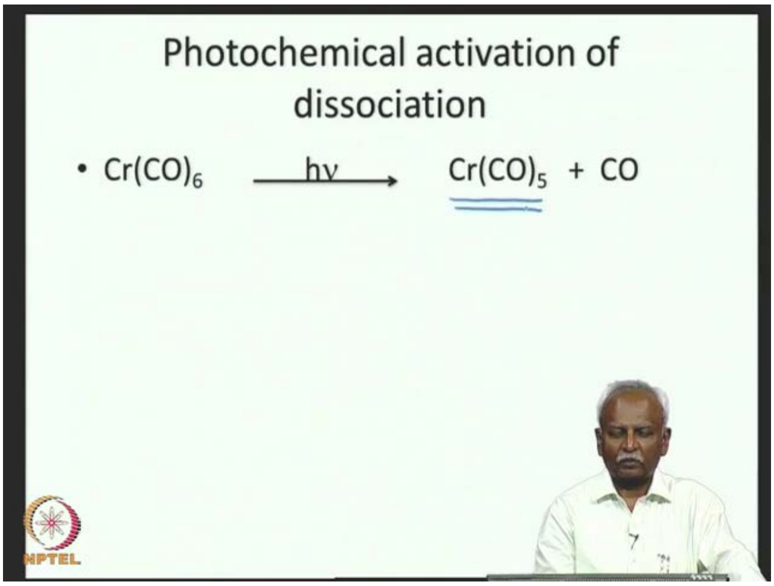

Photochemical activation of dissociation

- $Cr(CO)_6 \xrightarrow{h\nu} \underline{\underline{Cr(CO)_5}} + CO$

So here is the actual reaction, here you can ((Refer Time: 42:12)) Cr CO 6. When it is dissolved in acetonitrile it will lead to a coordinately unsaturated species Cr CO 5, which will have an weakened orbital with more electrons in it and free carbon monoxide.

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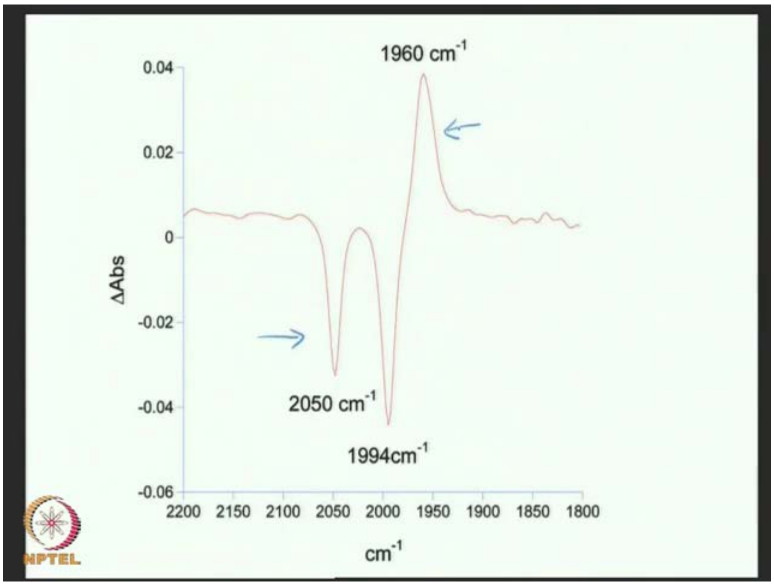

And this Cr CO 5 can be in fact studied in a matrix, in a very cold matrix. If you ((Refer Time: 42:37)) this Cr CO 6, it will be possible to look at the depletion of the infrared band which, corresponds to Cr CO 6. So, these are bands which are depleted and some new bands corresponding to the Cr CO 5 species would be formed in intermediate fashion.

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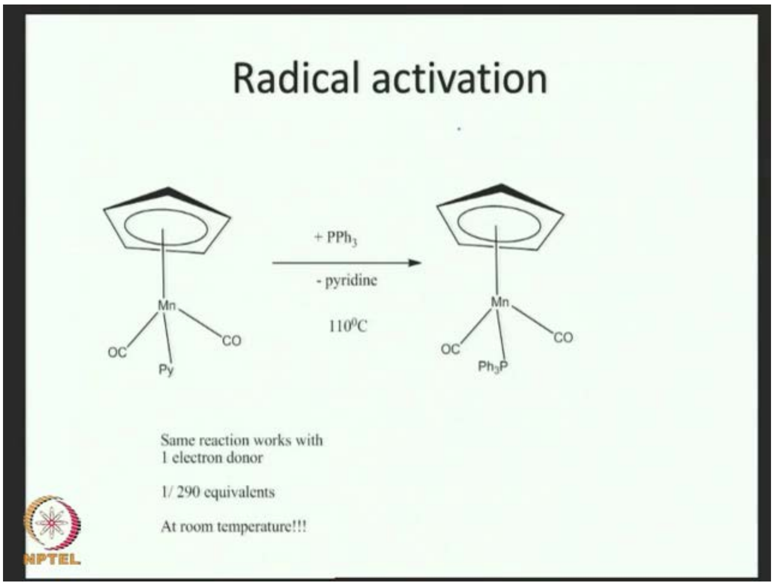

Radical activation

Same reaction works with
1 electron donor

1/ 290 equivalents

At room temperature!!!

So, one can in fact study there species, one can also trap the Cr CO 5 with a ligand.

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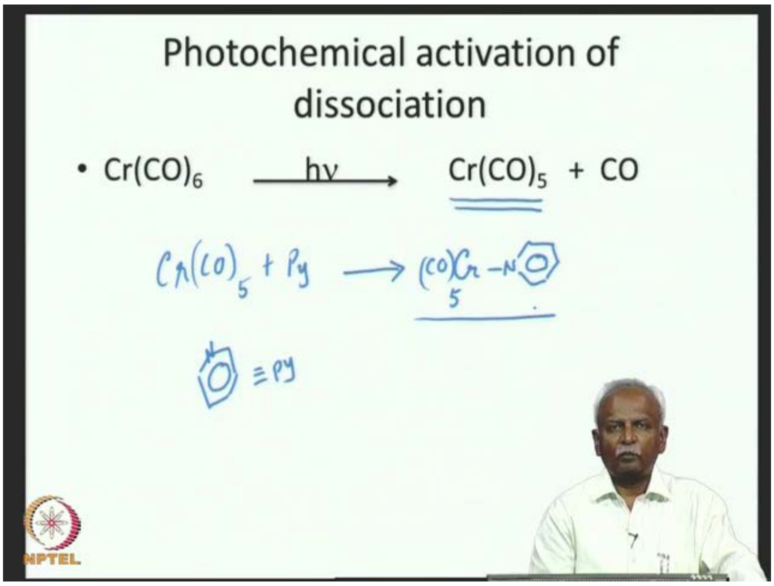


Photochemical activation of dissociation

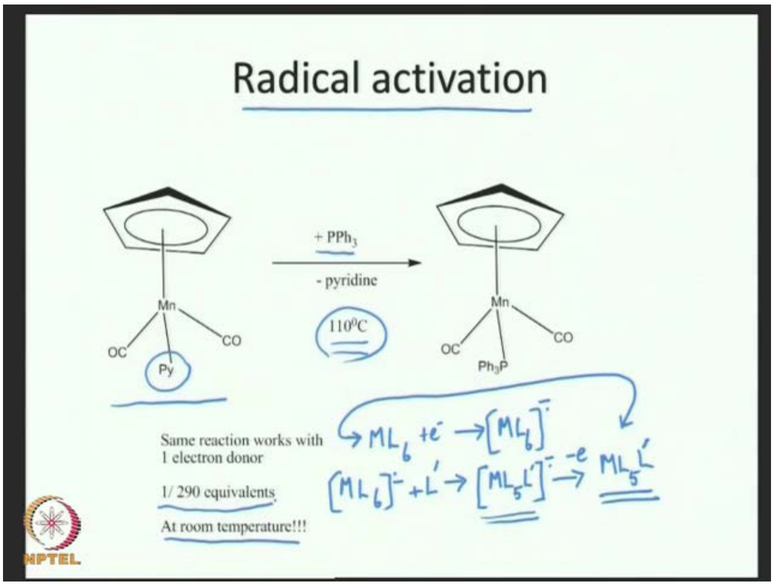
- $Cr(CO)_6 \xrightarrow{h\nu} \underline{\underline{Cr(CO)_5}} + CO$

$Cr(CO)_5 + Py \longrightarrow \underline{(CO)_5Cr-N}$

$= Py$

If you do not have a cold matrix, and if you carry out the reaction in solution, if you add pyridine which is a good donor ligand. One can in fact form a nice complex, in which the nitrogen is coordinated to the chromium. So, you can have substitution of 1 chromium with a pyridine ligand and this would be thermodynamically a more stable situation, because you do have removal of 1 carbon monoxide which is a pi acceptor. And replacement with a good sigma donor and so that leads to a stable situation for the Trans carbon monoxide, the carbon monoxide that is Trans to the pyridine.

(Refer Slide Time: 44:11)



Radical activation

$\xrightarrow[\text{- pyridine}]{\text{+ PPh}_3}$

110°C

Same reaction works with 1 electron donor

1/ 290 equivalents

At room temperature!!!

$$ML_6 + e^- \rightarrow [ML_6]^-$$

$$[ML_6]^- + L' \rightarrow [ML_5L']^- \xrightarrow{-e} ML_5L'$$

So, we can also carry out the same deactivation. We can also carry out the destabilization of one of the ligand using the radicals. Here I have pictured a reaction which is destabilization of this pyridine bond, manganese pyridine bond is destabilized by heating it in 100and at 110 degrees. So, thermally one can break one of these bonds in this particular instance, the weakest bond is the pyridine manganese bond.

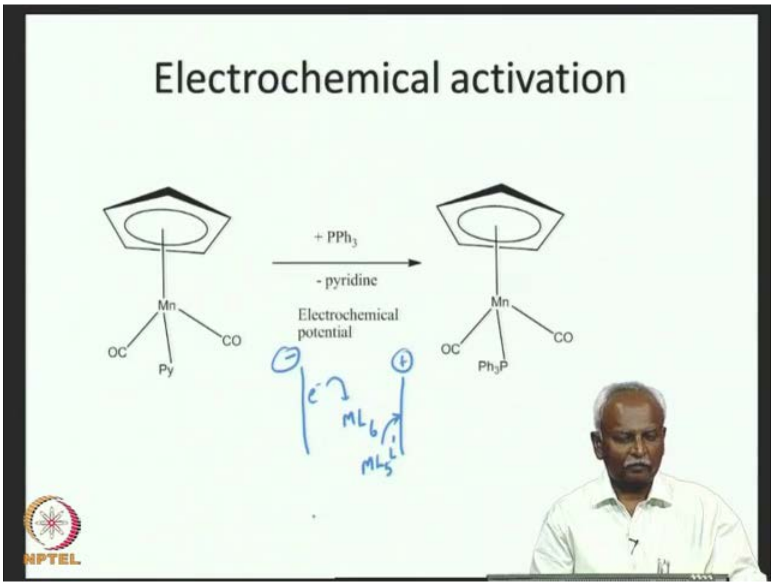
And the pyridine manganese bond is broken, when you heat it and if you have a good ligand like triphenyl phosphine, a good ligand like triphenyl phosphine then it attaches itself to the manganese in the vacant coordination site. So, this is one way in which we can activate by heating it to 110 degrees, but at the same time it is possible to do radical activation of this whole reaction.

How does one carry out radical activation, remember you have an 18 electron system, which has got a set of filled orbitals, which are the stabilizing bonding orbitals and a weakened anti bonding set of orbitals. If I add an electron, if I add 1 electron to this manganese system, here if I add 1 electron then it will become an unstable situation. And it will tend to lose an electron, loose a ligand and form have an weakened coordination fill up. So, in general it has been found that the negatively charged 18 electron species that we have pictured here, can be activated towards substitution by making them, by destabilizing them, by adding an electron.

So, this is equivalent to saying ML 6 plus E gives you ML 6. It is a negatively charged radical species and this ML 6 negatively charged species undergoes substitution reactions very readily. So it becomes ML 5 L dashed and then this species can get re oxidized back to ML 6 or rather it will become ML 5. Let us just work this out again, this ML 5 L dashed will lose an electron and form ML 5 L dashed. Essentially, we have converted an ML 6 to a substituted species ML 5 L dashed by adding an electron and subtracting an electron.

And so you need a very small amount, in fact 1 by 300 equivalence of an electron can be added to this species, and one normally carries this out by adding sodium in stabilized and naphthalene sodium ((Refer Time: 48:06)) anion and that is a good reducing agent. And if you have a very small amount of that, you can carry out the substitution reaction and now, the same reaction which was proceeding at 110 degrees is now going at, now proceeding at room temperature. Same substitution reaction can be carried out at room temperature by adding a very small amount of an electron donor.

(Refer Slide Time: 48:37)



Electrochemical activation

So, radical activation of this reaction can also be carried out, it is easy to see that addition of an electron can be done by electrochemical action, which means that at the surface of the electrode you pump an electron, you add an electron to the metal complex and then at the other electrode, at the other electrode you accept the electrons from the substituted species. So, this will now give the electron back here and so you can have a complete circuit and electrochemically activated species undergo substitution reactions fairly fast.

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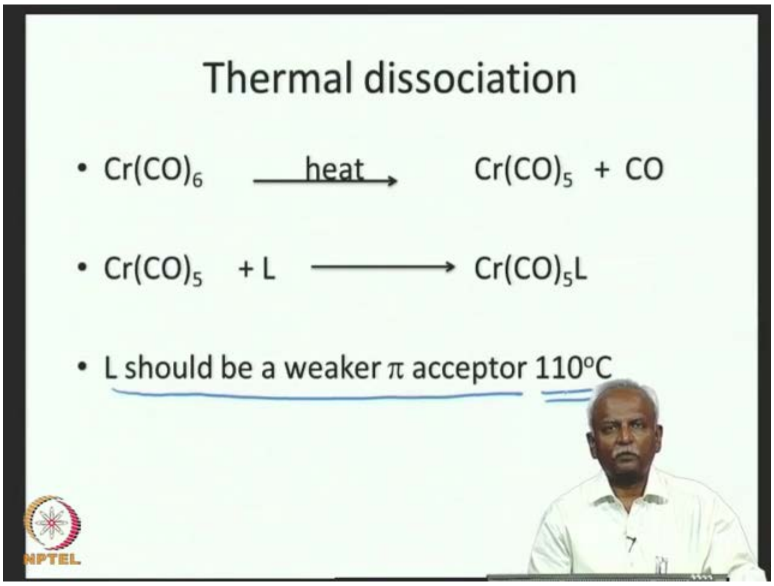
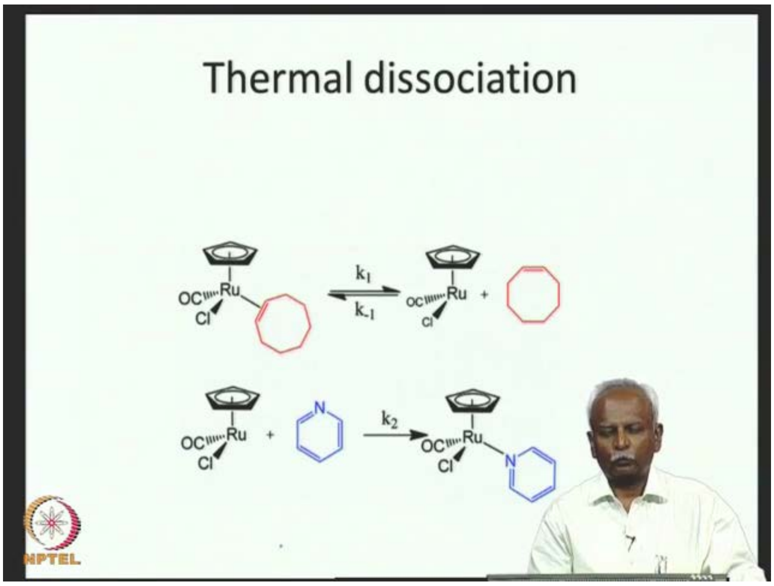


Thermal dissociation

- $Cr(CO)_6 \xrightarrow{heat} Cr(CO)_5 + CO$
- $Cr(CO)_5 + L \longrightarrow Cr(CO)_5L$
- L should be a weaker π acceptor 110°C

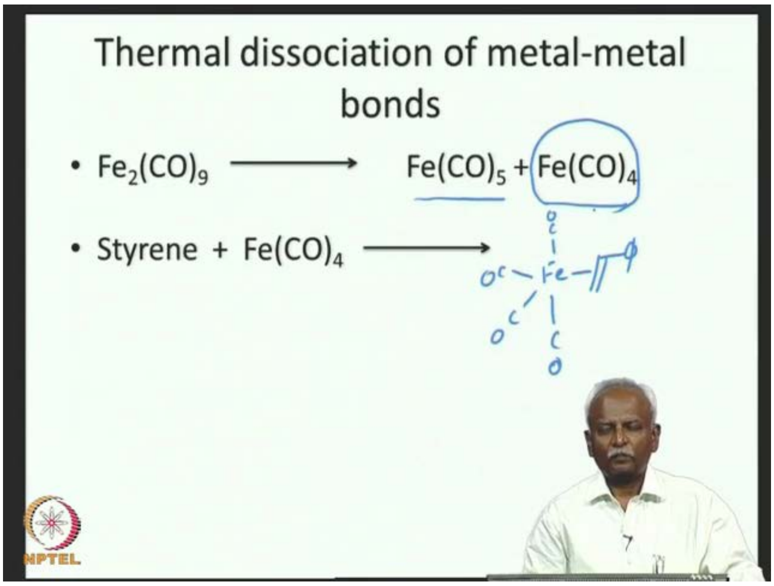
Now, we have seen how or why the electrochemically ((Refer Time: 49:28)) species undergoes faster reaction because it has got electron in the anti-bonding orbital. I have already told you that, one can always heat the metal complex sufficiently high in order to destabilize one of the ligands. And this is the usual most convenient way it is done in the laboratory, but the ((Refer Time: 49:50)) is that L should always be weaker pi acceptor and one needs a high temperature. Typically, boiling toluene reflexing and toluene is what is carried out and what is done and so temperature of 110 degrees is used in order to break one of this metal carbonyl bonds.

(Refer Slide Time: 50:12)


Thermal dissociation

So, thermal disassociation is always possible and in some instances in favorable instances, it is possible to isolate or characterize this intermediate ((Refer Time: 50:23)) and trap the intermediate with a more stable or with a more stronger ligand. So, here I pictured one example where, you can dissociate a weak ligand cyclooctene. Cyclooctene is a weak ligand and that is dissociated in the process, when you heat it in this ((Refer Time: 50:46)) complex.

(Refer Slide Time: 50:49)


Thermal dissociation of metal-metal bonds

- $Fe_2(CO)_9 \longrightarrow Fe(CO)_5 + Fe(CO)_4$
- Styrene + $Fe(CO)_4 \longrightarrow$

So thermal dissociation is the, thermal dissociation of metal ligand bond is commonly encountered, but when you have a metal metal bond, it is usually the weaker bond that his present in the system. So if you heat Fe2 CO9 it is likely that it will dissociate to give you Fe CO 5 and Fe CO 4 and the metal metal bond is broken. In this case and the Fe CO 4 is coordinately unsaturated.

So, it will react with styrene to form a styrene complex containing four other carbon monoxides. So, this is the complex that you get by heating Fe2 CO9 in the presence of styrene. You would end up with a complex formed between coordinately unsaturated species, which was generated which is Fe CO 4 and that is formed by breaking the metal metal bond .

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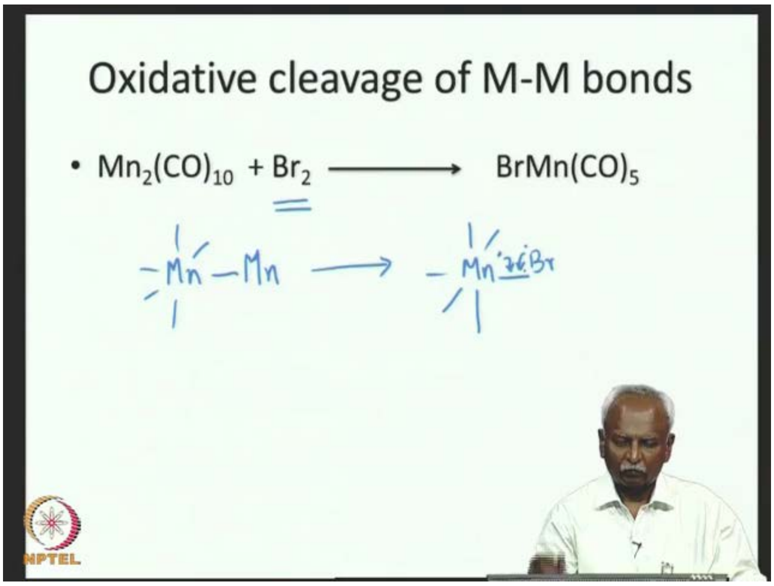
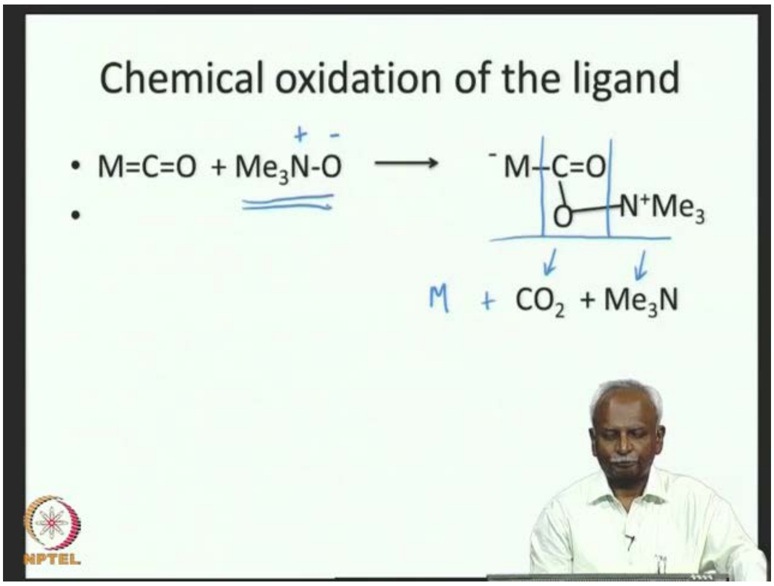


Oxidative cleavage of M-M bonds

- $Mn_2(CO)_{10} + Br_2 \longrightarrow BrMn(CO)_5$

One can also cleave oxidatively, cleave a metal metal bond and that can be done by addition of a compound, which will add on to the manganese in this case. So Mn2 CO 10 is having a manganese manganese bond. And if you heat it this manganese manganese bond will break and so you would end up with the manganese radical, you will end up with the manganese radical. And that will readily react with bromine and form a nice single bond by utilizing these two radicals, these two one electrons which are present, one electron which is present in manganese and one electron which is present in bromine will form a nice manganese bromine bond. And so you will end up with this bond here.

(Refer Slide Time: 53:07)



Chemical oxidation of the ligand

- $M{=}C{=}O + Me_3\overset{+}{N}\text{-}\overset{-}{O} \longrightarrow {}^{-}M\text{-}C{=}O$ / $O\text{—}N^{+}Me_3$
-

$M + CO_2 + Me_3N$

So, there is one last consideration that we should, there is one last example that I would like to take up. If you want to do a substitution reaction especially, with ligands like carbon monoxide one can treat the carbon monoxide containing compound with an oxidizing agent, mild oxidation agent like trimethylamine n-oxide, trimethylamine n-oxide might be pictured as having Me3 N plus and O minus.

So, this form of trimethylamine n-oxide can attack the carbon monoxide in such a way that, you can form this intermediate where you have an oxygen carbon bond between the metal carbonyl and the trimethylamine species. And this will now break very readily to dissociate, to give you carbon dioxide and trimethylamine.

So, this will give you trimethylamine carbon and carbon dioxide and then you will end up with a weakened coordinate site on the metal. Now, you will have metal with a ligand so oxidation, chemical oxidation of the ligand is one convenient way with which we can remove carbon monoxide from the metal complex. Not always is this possible, but in many instances trimethylamine n-oxide and pyridine n-oxides are weak oxidizing agents that will decompose a carbonyl complex.

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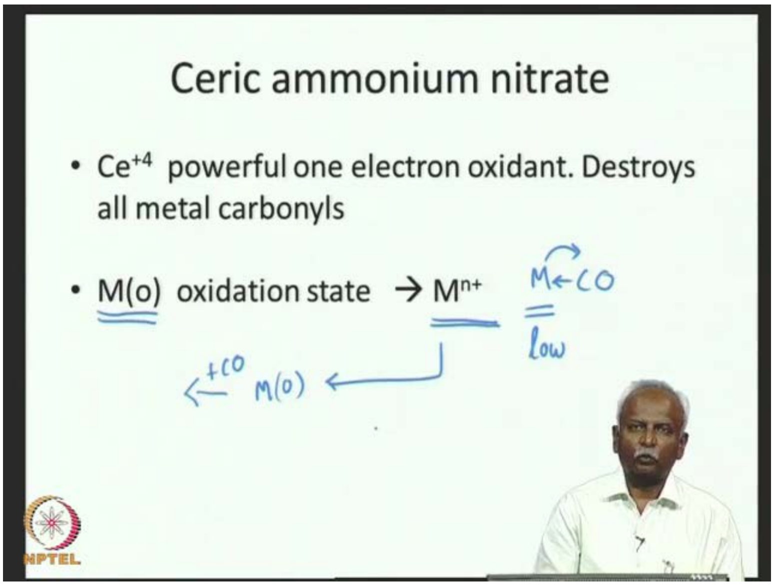

Ceric ammonium nitrate

- Ce^{+4} powerful one electron oxidant. Destroys all metal carbonyls
- M(o) oxidation state → M^{n+}

$M \leftarrow CO$

low

$\overset{+CO}{\longleftarrow} M(0) \longleftarrow$

If you use a very strong oxidizing agent like, ceric ammonium nitrate which is cerium plus 4 oxidation state. It is a very powerful 1 electron oxidant and so if you use small, even small amounts of ceric ammonium nitrate, they tend to oxidize the metal which is usually present in low oxidation states. It tends to oxidize it to the maximum oxidation state and once the metal is completely oxidized, it does not stabilize the metal carbonyl bond. We realize that this has to be in a low oxidation state, in order to stabilize the carbon monoxide, metal carbonyl interaction. So, if you oxidize to a high oxidation state it forms a very unstable complex and the carbon monoxide leaves the metals coordination sphere and you will destroy the organo metallic complex completely.

In general it is formed, it is known that ceric ammonium nitrate is a oxidant which can be used to decompose any organo metallic species, that you want to decompose. So if you look, if you remember we made metal carbonyls by reducing metals in high oxidation states to 0 oxidation state and then reacting them with carbon monoxide. So this was the reaction which we used. So, it is not surprising that if you take metal in the 0 oxidation state, you will be able to oxidize it completely to Mn plus and also remove the carbon monoxide from the coordination sphere.

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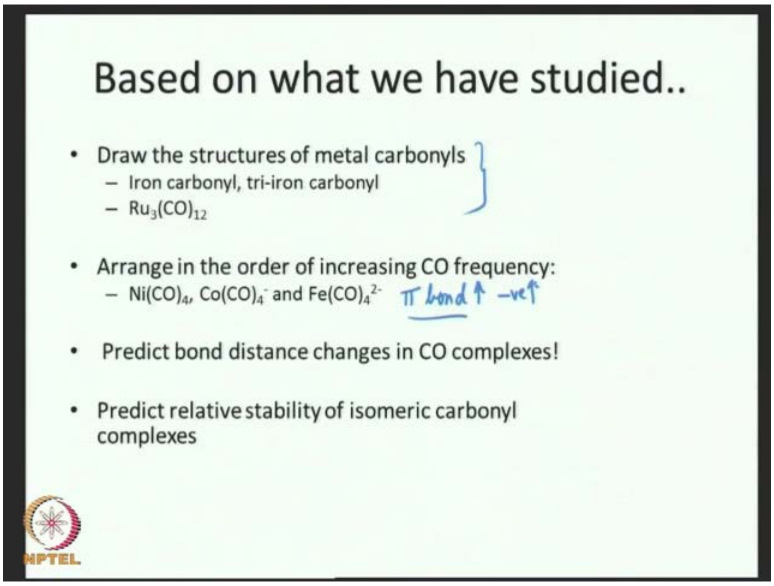

Based on what we have studied..

- 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 $Fe(CO)_4^{2-}$ π bond ↑ −ve↑
- Predict bond distance changes in CO complexes!
- Predict relative stability of isomeric carbonyl complexes

So, based on what we have looked at so far in metal carbonyl chemistry, one should be able to draw the structures of various metal carbonyls. And as we have noted earlier these can be poly nuclear species and the difficulty with poly nuclear species is the fact that, you can have bridging carbonyls and the terminal carbonyls. And that is only the difficulty that we have, but nevertheless the number of carbonyls that are arranged around the metal, is not a difficulty because you can use the 18 electron rule to figure out, how many carbon monoxides should be there on the metal.

One can also arrange the carbon monoxides in terms of the stretching frequencies, or in the terms of the strength of the metal carbon monoxide bond order because the more the negative charge on the metal. The more is the electron density that is pumped into the pi star orbitals and that increases the pi bond order. So the pi bond order is increased when you have negative charge, pi bond order goes up, negative charge goes up these two are positively correlated.

One can also in the same fashion predict the bond distance charges in carbon monoxides complexes. You can also predict the relative stability of carbon complexes because we noted that if you have a Trans ligand which is a good pi donor or a good sigma donor then you will have a stabilization of the metal carbonyl bond.

So, these are some of the things that, we have learnt from the metal carbonyl chemistry that, we have concerned so far. There are, as I said different ways by which you can distinguish between these metal carbonyls using spectroscopic. Finally, I will say that there are more complex factors that we not considered in these lectures. Specially, triply bridging carbon monoxide and large metal clusters.