Introduction to Organometallic Chemistry
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Lecture - 9
Non-Carbon Ancillary ligands continued

In this lecture, we will look at some ligands which are alternatives to carbon monoxide. They have slightly different properties, but nevertheless they might be good substitutes. In order to modify the reaction properties or the property of the molecule in terms of its absorption or emission or some other property, which needs to be modified with respect to the carbon monoxide ligand.

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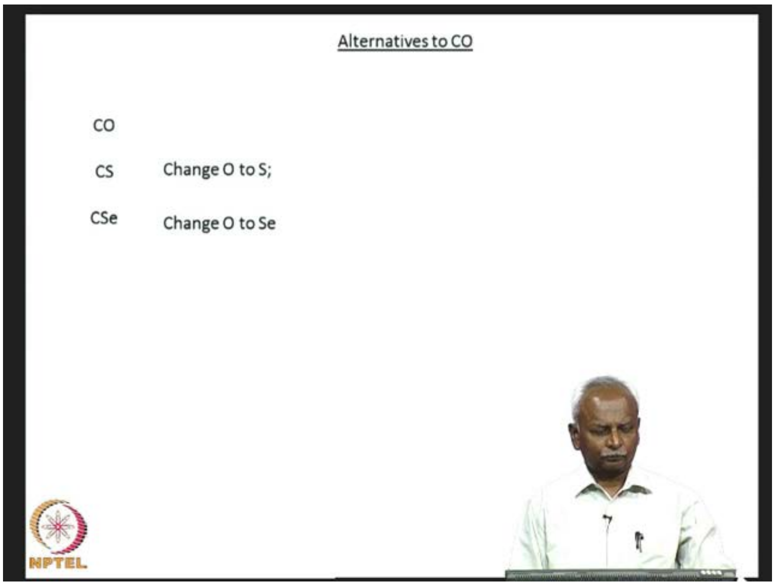

Alternatives to CO

CO

CS Change O to S;

CSe Change O to Se

So, in doing this, while we change from carbon monoxide to other ligands, we notice that we can very simply replace the oxygen by an element from the same group, that is sulphur or selenium. And if you do that, we do get some very good ligands, these ligands arewritten here carbon monosulphide and carbon monoselenide. These are excellent ligands, but the generation of these ligands, the preparation of molecules containing these ligands turns out to be quite difficult. And because of this and also because of the toxicity of carbon mono sulphide and carbon mono selenide, people have tried to move away from these ligands and look for alternatives.

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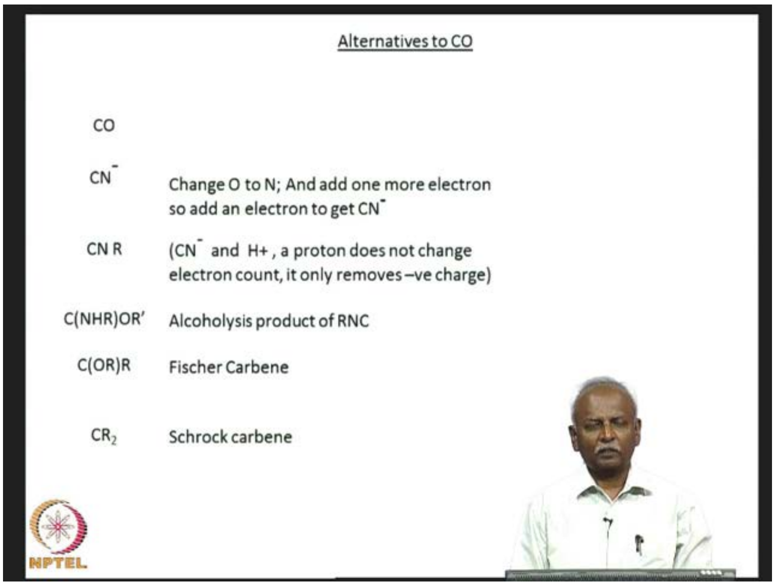

Alternatives to CO

CO	
CN^-	Change O to N; And add one more electron so add an electron to get CN^-
CN R	(CN^- and H+ , a proton does not change electron count, it only removes –ve charge)
C(NHR)OR'	Alcoholysis product of RNC
C(OR)R	Fischer Carbene
CR_2	Schrock carbene

So we also looked at, in the, in some of the lectures, we have looked at what would happen if we replace the oxygen by a nitrogen and because nitrogen has got one electron less, we would have to add one electron to CN. And that makes it CN minus and we havewritten it down here, CN minus. This is also a very good ligand, cyanide is an excellent ligand, but unfortunately because of this negative charge, you do have destabilization orsome kind of a negative feedback to the metal system. If it has, an zero oxidation state or a negative oxidation state.

So, we would like to look for a neutral ligand and hence, we cap the CN minus with a proton or an alkyl group and that brought us to alkyl isocyanides. And these arevery good ligands, superior ligands to CN minus, in terms of organometallic chemistry, but once again we realize that in the presence of some solvents like an alcohol they tend to get alcoholised, or they tend to react with alcohol and form these products, which are given here.

These can also be ligands, we have found that you have a carbon flanked by two hetero atoms and if you can do that, in a ring system. And we, if you have two nitrogens around the carbon which is bonded to the metal then you have N hetero cyclic carbenes if it is in a cyclic system, it turns out to be an excellent ligand. This also lead us to, the discussion of carbenes because once you have this carbon which is bonded to the metal and it is flanked by a hetero atom. Then it is called a Fischer carbene, if it has just got two alkyl groups, it is called a schrock carbene. So we realize that, replacement of oxygen by various substituents or other elements is a profitable exercise it leads us to some very good chemistry.

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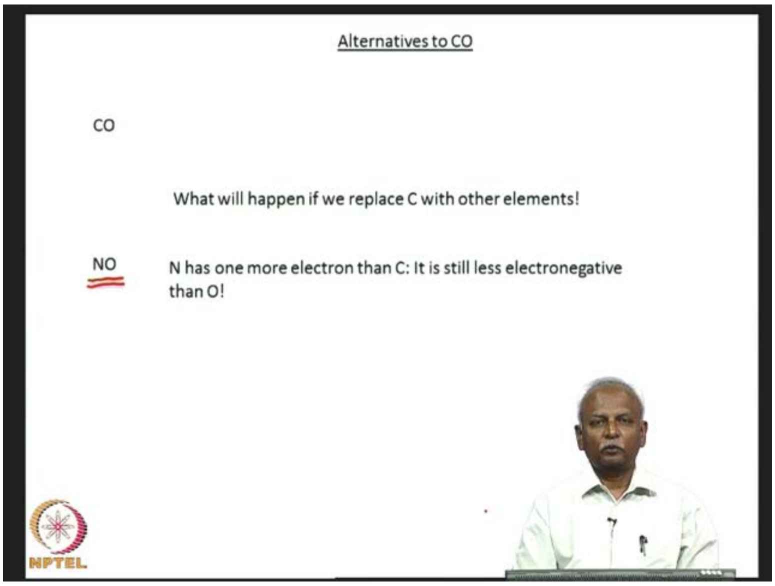

Alternatives to CO

CO

What will happen if we replace C with other elements!

NO

N has one more electron than C: It is still less electronegative than O!

Now, if we continue to do this, we will realize that there is a limitation to this exercise and it might be useful to look at replacing carbon itself with another atom. And hence we moved on to, in this lecture we move on to nitrogen and we end with nitric oxide. Nitric oxide, is a very interesting molecule it is in fact biologically relevant and it has been studied extensively in the recent past.

Nitric oxide has got, one extra electron compared to carbon monoxide, which is the most useful ligand in organometallic chemistry. So, because we realize that the atom that is bonded to the metal, in the case of carbon monoxide it is carbon, in the case of nitric oxide it is most probably going to be the nitrogen. And that is exactly what happens.

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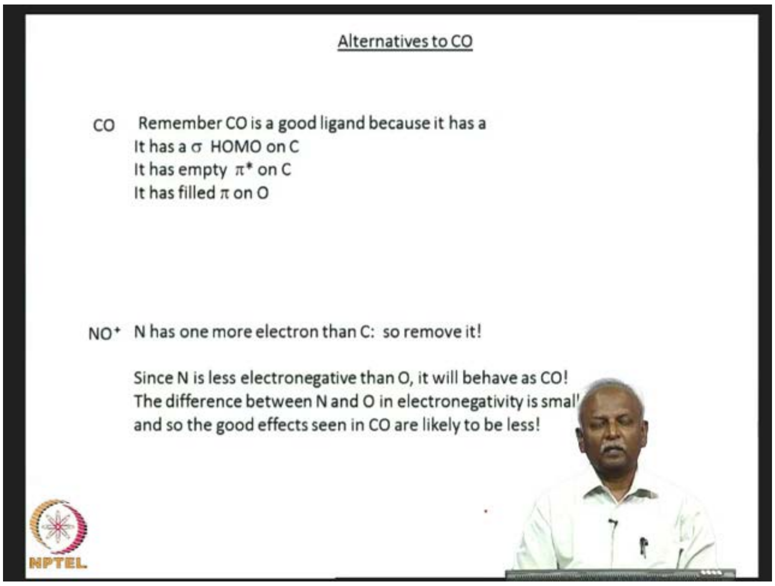

Alternatives to CO

CO Remember CO is a good ligand because it has a
It has a σ HOMO on C
It has empty π^* on C
It has filled π on O

NO^+ N has one more electron than C: so remove it!

Since N is less electronegative than O, it will behave as CO!
The difference between N and O in electronegativity is smal
and so the good effects seen in CO are likely to be less!

Let us just recap, some of the beautiful aspects of carbon monoxide, some things that make carbon monoxide an excellent ligand. First of all, we recollect that the homo on carbon monoxide is concentrated on carbon. This is a very important factor because then the donation of electron density from this molecule, to the metal turns out to be quiet significant.

And we also realize that, it has got a pi star orbital or an acceptor orbital on carbon so both of these acceptor and donor properties are localized primarily on carbon of carbon monoxide. And that makes it, a very good ligand and the filled pi which would lead to, four electron repulsion that turns out to localized on oxygen. And so that, repulsive interaction is minimized and the attractive interactions are maximized that makes carbon monoxide an excellent ligand.

So if we have, NO plus which would be isoelectronic to carbon monoxide then it turns out to be an excellent ligand as well. And let us look at, the disadvantages and the advantages. Since, nitrogen is less electronegative than oxygen, it will behave like carbon monoxide. Just like carbon was a donor atom, nitrogen will also be the donor atom, but then the difference between nitrogen and oxygen in terms of electro negativity, the difference between nitrogen and oxygen in terms of electro negativity is smaller.

Remember, that all these good propertiesof carbon monoxide arose from the fact that, carbon is much less electronegative compared to oxygen because of this, reduced electro negativity we had some excellent properties. Now, if you reduce the electro negativity between nitrogen and oxygen as we have done here, if this electro negativity difference is smaller then we are going to have poorerligating capacity. But nevertheless, the good effects of carbon monoxide still seem to persist. Although, they are likely to be less, they still seem to persist and NO plus is in fact an excellent ligand. So, most of this lecture will deal with nitric, the NO plus ion.

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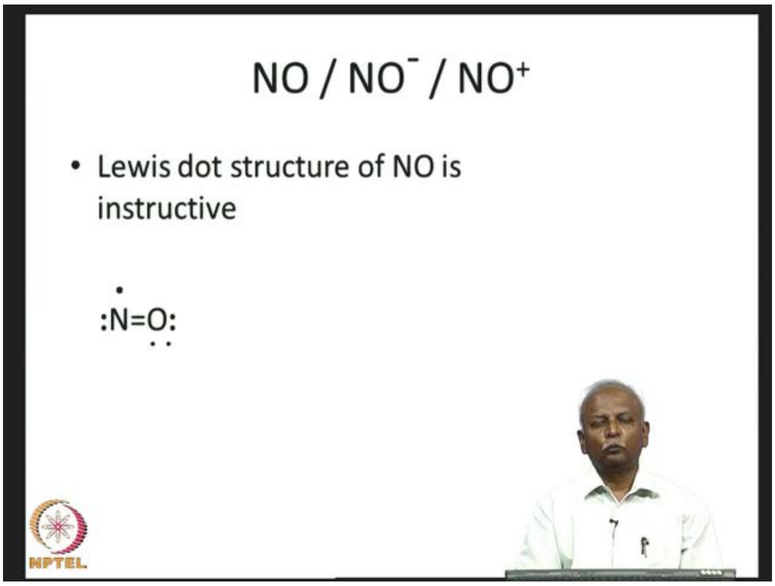

NO / NO^- / NO^+

- Lewis dot structure of NO is instructive

$$:\dot{N}{=}\underset{\cdot\cdot}{O}:$$

First of all, it is instructive to look at the Lewis dot structure of NO. If we look at, the Lewis dot structure we find that, there are two lone pairs on oxygen. Two lone pairs on oxygen and two, and a pair of electrons on the nitrogen, and a single electron on the nitrogen as well. This is the best Lewis structure, the closest that we can get to the octet on both atoms. You will notice that, nitrogen has got less than an octet it has got 7 electrons and oxygen has in this particular Lewis dot structure, it has got an octet.

So, nevertheless this is the best representation that we can get, resonance form that we can get. And we notice that, the single electron that is there on NO is localized on nitrogen. You will now understand that, the description that is given by the Lewis dot structure that we have written here and the MO picture are very similar. Let us look at the MO picture.

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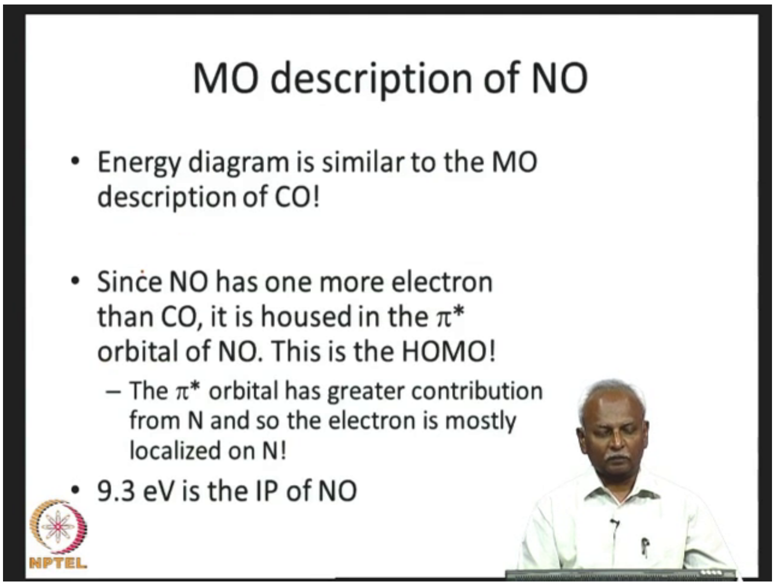

MO description of NO

- Energy diagram is similar to the MO description of CO!
- Since NO has one more electron than CO, it is housed in the π^* orbital of NO. This is the HOMO!
  - The π^* orbital has greater contribution from N and so the electron is mostly localized on N!
- 9.3 eV is the IP of NO

First of all we note that, the energy level diagram that we drew for carbon monoxide would be very similar to the energy level diagram that, we have for NO. So, these two diagrams, energy level diagrams would be approximately the same. In other words, we would have a set of core, set of core orbitals and there will be two orbitals, which are core orbitals. And they would be filled and then we would have one sigma and then we would have a pi, one pi and then we would have a sigma. And in fact, we should write two sigmas below the pi and so we have 1 sigma here, 2 sigma here and then a pi and then a 3 sigma, which would also be filled.

And then a pi, that is the two pi and the single electron that we talked about earlier, the single electron that we talked about would be, in fact located in this pi orbital. So, the energy level diagram turns out to be extremely similar. You have all these orbitals, which are filled with two electrons, 1 sigma, 2 sigma and 3 sigma are filled. And the 1 pi, which is set of degenerate orbitals has got 4 electrons and we have one extra electron sitting in the 2 pi. This turns out to be having anti bonding character and we normally indicate it, with a star.

So, the pi star orbital has got 1 electron on the nitric oxide. Since, the pi star orbital has got greater contribution from the nitrogen, the electron is mostly localized on the nitrogen side of NO. And this is something that, we can find out from EPR spectroscopy of nitric oxide. It tells us that, the nitrogen has most of the unpaired electron density and we can also tell from other aspects like, the after ionization the type of spectrum that we get, for ionization. It tells us that, the electron is localized on the pi star orbital and that electron is actually sitting mostly on the nitrogen.

So this electron, which is on the pi star orbital can be readily removed and in fact the ionization potential is about 9.3 electron volts. So, the ionization potential of NO is 9.3 electron volts and is readily removed. And then it gives you NO plus so that gives you, the ionization gives you results in the formation of NO plus, which is the molecule of interest because now, NO plus is iso-electronic to carbon monoxide.

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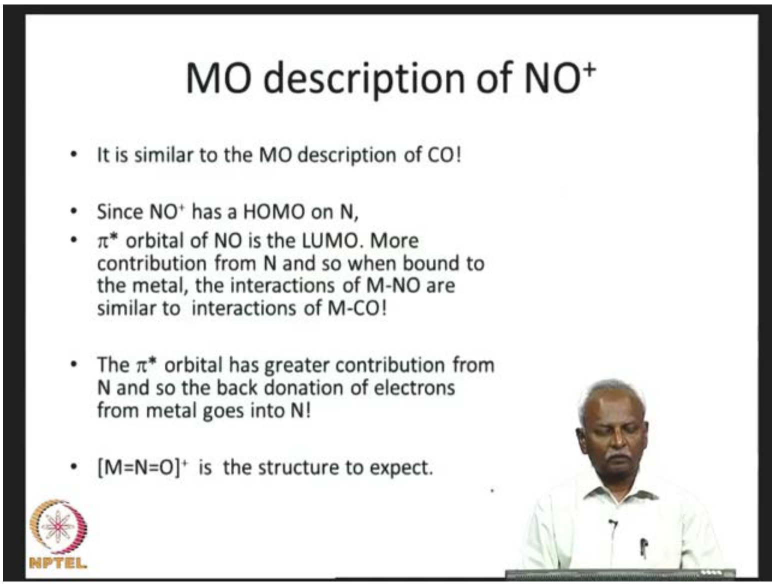

MO description of NO$^+$

- It is similar to the MO description of CO!
- Since NO$^+$ has a HOMO on N,
- π^* orbital of NO is the LUMO. More contribution from N and so when bound to the metal, the interactions of M-NO are similar to interactions of M-CO!
- The π^* orbital has greater contribution from N and so the back donation of electrons from metal goes into N!
- $[M{=}N{=}O]^+$ is the structure to expect.

The, after ionization the NO plus has a homo, which is completely on nitrogen and it is a sigma orbital. This homo, is actually a sigma orbital and it is localized on the nitrogen side. So, in fact if you draw a pictorial representation of this orbitals, we will have something like this. A pair of electrons, which is mostly on the nitrogen and a smaller amount on the oxygen and so and so this pair of electrons which is present on the nitrogen would be donated to the metal.

So, this is very similar to what we had for carbon monoxide. Carbon monoxide had a pair of electrons on carbon and that end was donated to the metal. Now, since the pi star orbital, on the nitrogen is mostly on the nitrogen, the donation of the electron density from the metal into the pi star orbitals of NO is also possible. So, if you have NO plus and if you have a pi star orbital on the nitrogen, this also results in the same type of stabilization, that we talked about in the case of carbon monoxide. The metal d orbitals specially, the d if this is the z axis then the d x z axis, d x z orbital will donate electron density into the nitric oxide.

So, because this has got greater contribution, the nitrogen has got greater contribution. As you can see from, the larger size of the orbital that we have drawn here on the nitrogen. Then this overlap turns out to be significantly more, in the case of the metal to nitrogen attraction compared to, the pi repulsion that you will have from the pi filled pi orbital on the nitric oxide. So this is very similar to, what we would expect for carbon monoxide and we can expect this type of resonance structure for MNO plus also. This is something, which is very familiar if you have gone through your interaction studies on the carbon monoxide metal system. Then you will be able to understand and picture this representation very easily.

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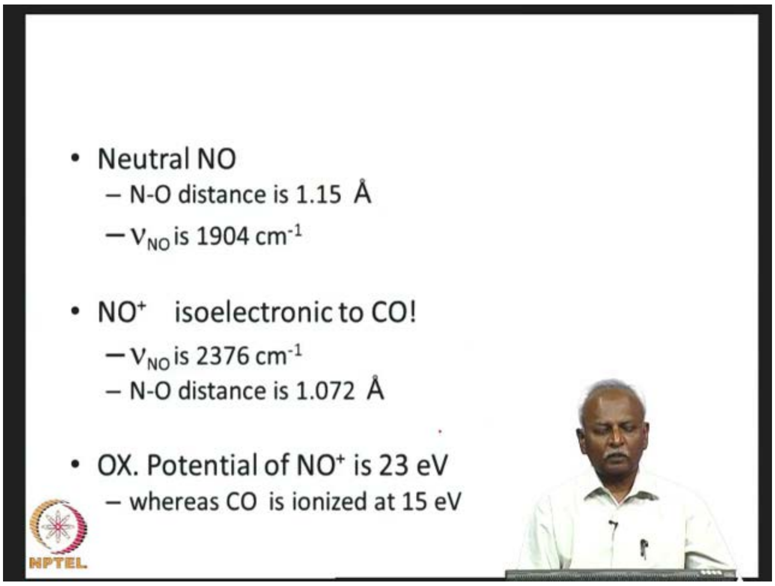

- Neutral NO
  - N-O distance is 1.15 Å
  - ν_{NO} is 1904 cm^{-1}
- NO^+ isoelectronic to CO!
  - ν_{NO} is 2376 cm^{-1}
  - N-O distance is 1.072 Å
- OX. Potential of NO^+ is 23 eV
  - whereas CO is ionized at 15 eV

Let us now look at, some of the features of nitric oxide and whether what we have been talking about in terms of the MO diagram, can be justified from the molecular properties. The neutral nitric oxide itself has, a bond distance, the nitrogen oxygen bond distance of 1.15 Angstroms. So, this distance is, slightly longer than what you would expect for a N triple bond O. And that is understandable because you have 1 electron on the pi star orbital which is anti-bonding. So that elongates, the nitrogen oxygen distance to 1.15

angstroms and the stretching frequency of the nitrogen oxygen bond is around, 1904 centimetre minus 1.

So, this stretching frequency changes significantly when you oxidize the NO, to give you NO plus. So NO plus, which is pictured here NO plus turns out to be isoelectronic to carbon monoxide. It has a new NO or nitrogen oxygen stretching frequency, corresponding or nitrogen oxygen stretching frequency is 2376 centimetre minus 1. And the nitrogen oxygen distance, reduces from 1.15, it reduces to 1.072 Angstroms. So you can see that, the bond order between nitrogen oxygen has increased as you go from NO, to NO plus. And this is understandable because we have removed anti bonding electron.

Now, let us look at the oxidation potential of NO plus itself, because this will give us an idea of how good a donor ligand, NO plus is going to be. You will see that, while carbon monoxide is ionized with 15 electron volts, if you supply 15 electron volts, carbon monoxide can be oxidized or ionized. NO plus can be oxidized only, if you supply 23 electron volts so that is a significantly larger number.

And that tells us that, it is going to be very difficult to remove an electron completely from NO plus. We are not going to that, remove it completely, but nevertheless this is an indication that, NO plus is going to be a poorer donor, compared to carbon monoxide. Carbon monoxide itself, is not a great donor ligand, but NO plus is going to be a weaker donor because of these two factors that we have just discussed.

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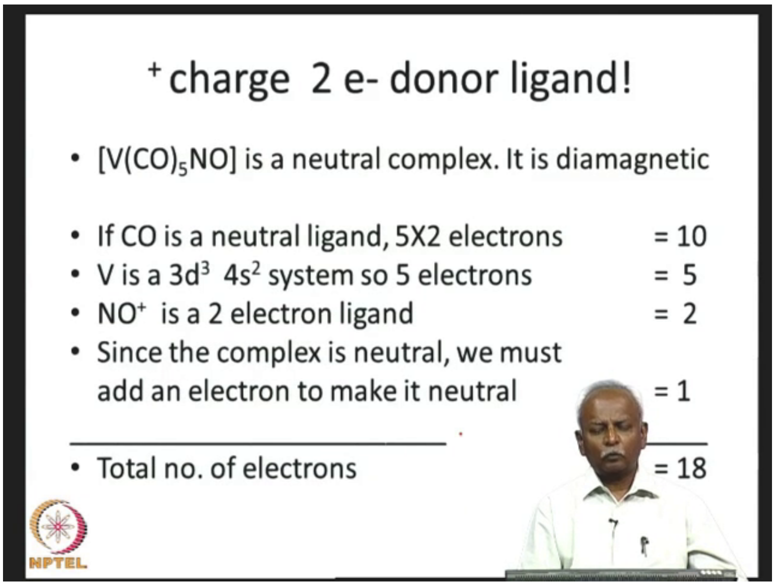

$^+$charge 2 e- donor ligand!

- $[V(CO)_5NO]$ is a neutral complex. It is diamagnetic
- If CO is a neutral ligand, 5X2 electrons = 10
- V is a $3d^3$ $4s^2$ system so 5 electrons = 5
- NO^+ is a 2 electron ligand = 2
- Since the complex is neutral, we must add an electron to make it neutral = 1
- Total no. of electrons = 18

So, let us look at a few complexes of NO plus and this will help us, to understand what is going to happen in these cases, when we have NO plus bonded to the metal atom. A very interesting complex is formed by, VCO5 complex to NO. This is a neutral complex and it turns out to be a diamagnetic system as well. This is very interesting, if you remember VCO6 was a paramagnetic system and NO plus is, NO is a paramagnetic system.

But if you react, these two species you get a diamagnetic species, not very surprising when you combine two paramagnetic species you could get a diamagnetic species and that is what we end up with. But let us look at, the electron count, let us see if we can understand the counting of electrons, the valence electrons in this molecule.

Carbon monoxide is a neutral ligand, it gives 2 electrons, each carbon monoxide gives two electrons. So, because we have 5 carbon monoxides on this metal complex. We end up adding, 10 valence electrons to the system. So, we have added 10 and then we note that vanadium is a, 3 d 3 4 s 2 system. So we have a total of 5 electrons on the vanadium, if NO is behaving as NO plus in this molecule. Then NO plus is a two electron ligand so we add 2 electrons, but we notice that there is a charge on the NO ligand. So, this is NO plus and because it is NO plus and the whole complex is neutral, you will notice that this complex is neutral then there must be an extra electron added to this molecule.

So, because we have a neutral complex and we have an NO plus ligand everything else is neutral, we add this one electron in the end. And that gives us a total of 18 electrons around the metal and this happens to be a18 electron molecule. And that is why, we can see that it is diamagnetic. We could have done this electron count in a slightly different way.

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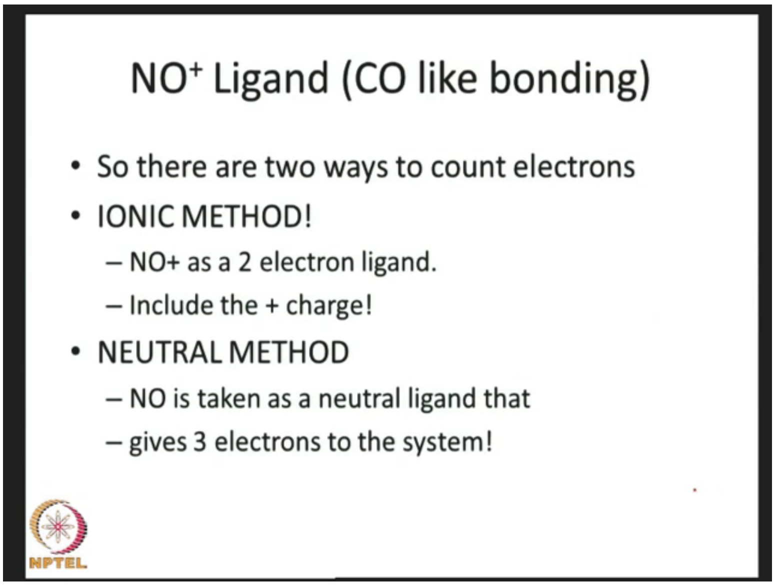

NO$^+$ Ligand (CO like bonding)

- So there are two ways to count electrons
- IONIC METHOD!
  - NO+ as a 2 electron ligand.
  - Include the + charge!
- NEUTRAL METHOD
  - NO is taken as a neutral ligand that
  - gives 3 electrons to the system!

And that brings me to this point that, we have two different ways of counting electrons. So, there is an ionic method what is popular in, popularly called as ionic method and there is another method, which is called the neutral method. So, there are two ways to count electrons around, this NO plus if you use it as a two electron ligand, we should include the fact that it has a positive charge. So, if it is in some way accounted for the charge, is accounted for an extra electron has to be added.

In the neutral method, which in some ways is easier you take NO, if it is bonded to the metal like carbon monoxide. Then we add three electrons to the valence shell from the nitric oxide. So if you have, NO bonding to the metal, just like carbon monoxide that means it is a linear molecule. In this case, V N O would have been close to 180 degrees then all the other carbon monoxides are also bonded in a linear fashion. And then you have, nitric oxide behaving like carbon monoxide and so in the neutral method we said that it gives 2, 3 electrons to the system as a whole.

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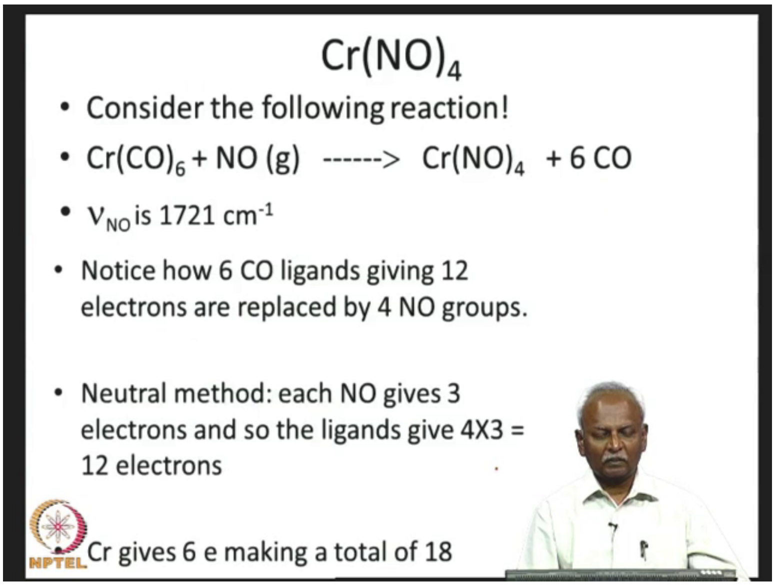

$Cr(NO)_4$

- Consider the following reaction!
- $Cr(CO)_6 + NO (g)$ ------> $Cr(NO)_4 + 6 CO$
- ν_{NO} is 1721 cm^{-1}
- Notice how 6 CO ligands giving 12 electrons are replaced by 4 NO groups.
- Neutral method: each NO gives 3 electrons and so the ligands give 4X3 = 12 electrons
- Cr gives 6 e making a total of 18

Let us take a look at, some other homolyptic molecules. Homolyptic molecules, let me remind you have got only one type of ligand around the metal. So, here we have the tetra nitrosyl complex of chromium. Consider the following reaction, which we do, which we can simply do by adding nitric oxide to chromium hexa carbonyl. We end up with this tetra carbonyl, tetra nitrosyl complex of chromium, which is also diamagnetic. And it has got a structure, which is very similar, a structure which is very similar to the structure of nickel tetra carbonyl. That is exactly what we have, chromium tetra nitrosyl complex.

Notice how we have replace 6 carbonyl ligands, 6 of them with 4 nitric oxide groups. So, if 6 nitric oxide, 6 carbon monoxide ligands are giving 12 electrons, 4 nitric oxide ligands must also be giving 12 electrons. So, that is exactly what we do in the neutral method, we say that each nitric oxide gives 3 electrons. So, we have 12 electrons that are being donated by the ligand.

12 electrons are being given by the ligand and chromium itself gives, chromium itself gives you 6 electrons. So, that makes a total of 18 so here once again we have an 18 electron system that is formed, which is pictured here. This is the 18 electron complex, but this time because nitric oxide gives more number of electrons compared to carbon monoxide. We tend to have, less number of nitric oxides and so we have this tetra nitrosyl complex.

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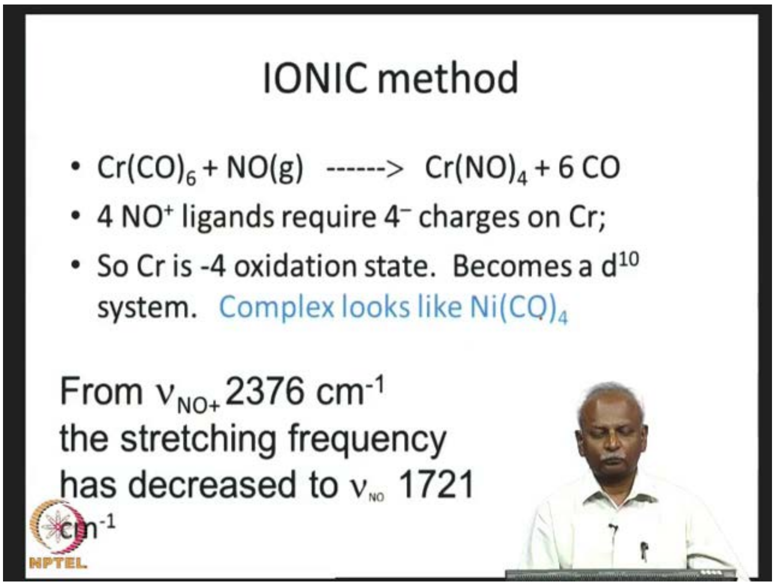

IONIC method

- $Cr(CO)_6 + NO(g)$ ------> $Cr(NO)_4 + 6\ CO$
- 4 NO^+ ligands require 4^- charges on Cr;
- So Cr is -4 oxidation state. Becomes a d^{10} system. Complex looks like $Ni(CO)_4$

From ν_{NO+} 2376 cm^{-1} the stretching frequency has decreased to ν_{NO} 1721 cm^{-1}

The same, the same electron counting can be done, using the ionic method. If you take chromium hexa carbonyl and treat it with nitric oxide and we form this complex. We will, let us assume that it is in the form of NO plus, since NO plus is isoelectronic with carbon monoxide. Let us make it NO plus so if there are 4 NO plus ligands around the chromium, we need 4 negative charges from the chromium. So, chromium must be in the minus4 oxidation state. So, if chromium is minus, in the minus 4 oxidation state, it has already got 6 electrons.

So, we add these 4 electrons to the 6 electrons on the chromium and we end with a d 10 system. You will notice that, the tetra negative, the 4 negative charges on the chromium seems, quite unlikely and that is why the ionic method is aclumsy in this particular instance. But because you have a complex which looks like Ni CO4, the assumption of a d 10 electronic configuration on the metal, is not unreasonable. And you will also notice that, the stretching frequency of NO plus which was, 2376 centimetre minus 1, has reduced to 1721 centimetre minus 1.

So, this drastic reduction in the stretching frequency can only happen if you have, a large population of the anti-bonding orbitals of NO plus. The NO plus if it is populated by a lot of electron density, from the metal. So the metal gives, a lot of electron density into the NO plus and this anti bonding electron density reduces the bond order between nitrogen and oxygen. And you almost get a double bond between, nitrogen and oxygen and that is why the stretching frequency has gone down to 1721 centimetre minus 1. If you remember, adding negative charges to carbon monoxide complexes, also reduces stretching frequency significantly. So, this is the ionic method.

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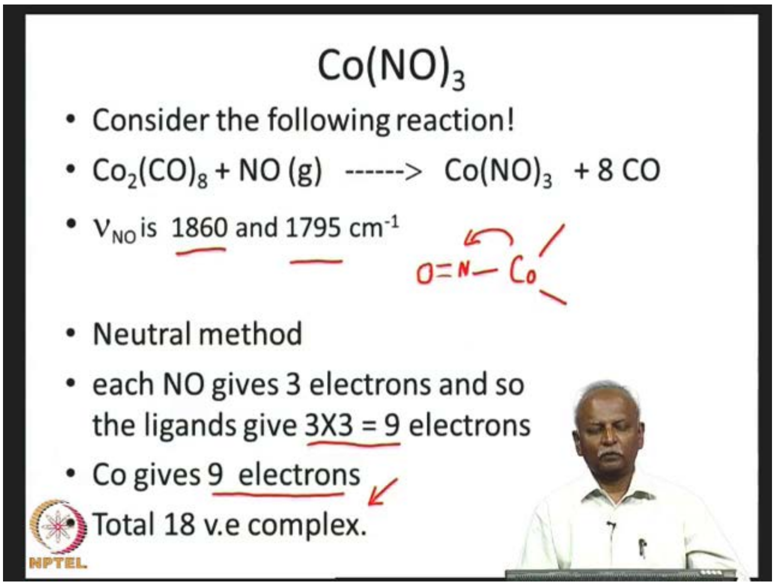

$Co(NO)_3$

- Consider the following reaction!
- $Co_2(CO)_8 + NO\ (g)$ ------> $Co(NO)_3 + 8\ CO$
- ν_{NO} is 1860 and 1795 cm^{-1}

$O=N-Co$

- Neutral method
- each NO gives 3 electrons and so the ligands give 3X3 = 9 electrons
- Co gives 9 electrons
- Total 18 v.e complex.

And now, let us look at the neutral method for another molecule Co NO 3. Co NO 3 is a molecule, which is trigonal in shape so this is the shape of the molecule. We have cobalt surrounded by 3 nitric oxide molecules. And we have, two stretching frequencies once again at 1860 and 1795 centimetre minus 1, significantly less than what you observe for NO plus. But nevertheless, these two stretching frequencies are indicative of the back bonding that you have, form cobalt onto the nitric oxide. So, from cobalt the electron density has flown into the nitric oxide pi star orbitals and so you have reduction in the stretching frequency.

Now, in the neutral method, if we assume that each NO gives 3 electrons. You will see that, a total of 9 valence electrons can be there added to the metal from the ligand system. And cobalt itself has got 9 electrons, cobalt has got 9 electrons, in its 3d manifold and so we have a total of 18 valence electrons for this complex also. It is interesting that, NO now forms very similar complexes to carbon monoxide in the sense that, they are all homolyptic. And you also notice that, there is large amount of electron density flowing into the pi star orbitals and that is again reminiscent of carbon monoxide chemistry. And that is the reason for, the reduction in the stretching frequency of the nitric oxide.

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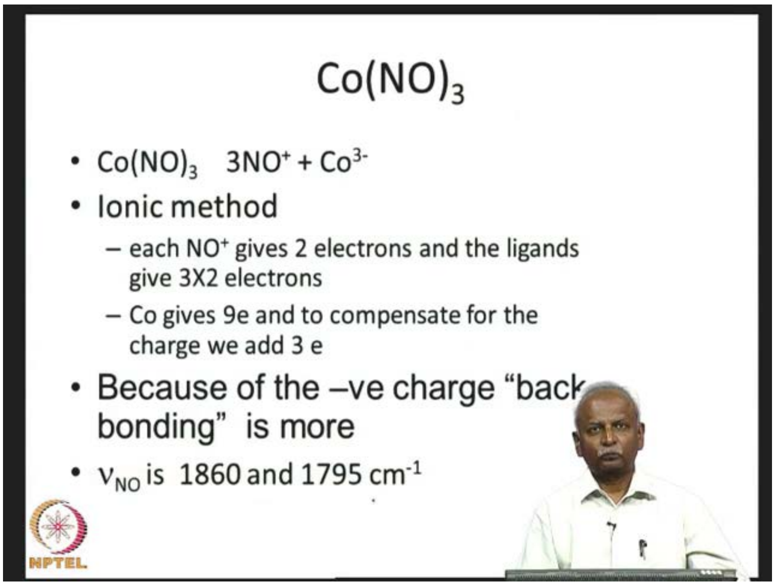

$Co(NO)_3$

- $Co(NO)_3$ $3NO^+ + Co^{3-}$
- Ionic method
  - each NO^+ gives 2 electrons and the ligands give 3X2 electrons
  - Co gives 9e and to compensate for the charge we add 3 e
- Because of the –ve charge "back bonding" is more
- ν_{NO} is 1860 and 1795 cm^{-1}

The same thing, if you use the ionic method of electron counting we notice that, if you use NO plus then cobalt, will have to be converted into cobalt 3 minus. That means we have, a total of 12 electrons on the cobalt and 6 electrons are coming from the nitric oxide. NO plus, can give only 2 electrons each and so we have 6 electrons from the ligand system and we have, we have 12 electrons on the cobalt. So, total of 18 electrons are there so this, excess negative charges is usually the reason, that is given for excessive back bonding between the metal and the nitric oxide. And this back bonding, results in reduction of the stretching frequency.

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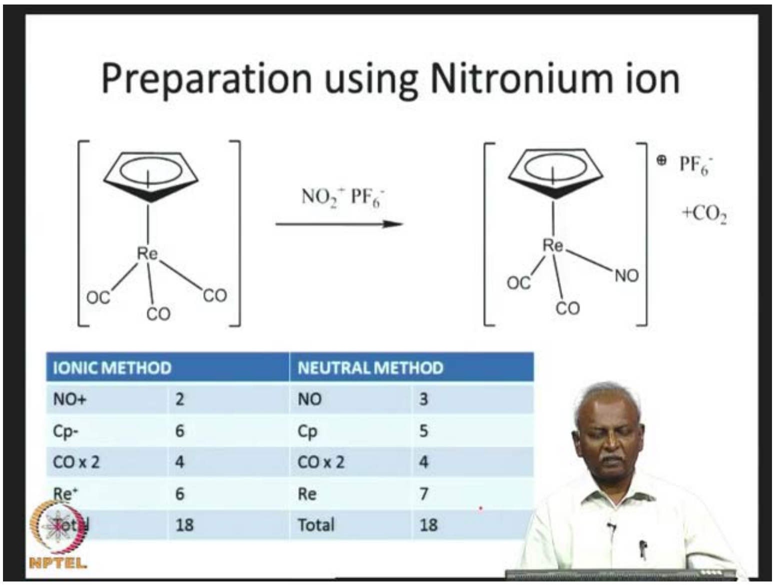

Preparation using Nitronium ion

IONIC METHOD		NEUTRAL METHOD	
NO+	2	NO	3
Cp-	6	Cp	5
CO x 2	4	CO x 2	4
Re^+	6	Re	7
Total	18	Total	18

Now, not all complexes are homolyptic, there are several instances where NO is just another ligand in the metal complex system. Now, we have not looked at cyclopentadienyl complexes, the here is an example where you have a cyclopentadienyl ligand, but nevertheless because it is instructive to do electron counting in a more complex system. We have chosen this particular example and it is also interesting because you are treating an organometallic complex with a nitronium or NO2 plus system. And that results in the formation of, an NO complex, a nitrosylligand is formed.

Now, let us do the electron counting in these cases, because this is something which really confuses students when you have both ionic, both the ionic method and the neutral method. Compared it will be easier for one, to follow what exactly is going on. Let us take the ionic method first, if you take the ionic method, you have two electrons from the NO plus and that is given here. And the cyclopentadienyl ligand, which is this ligand which is given here, you have 6 electrons, cyclopentadienyl anion you must remember is an aromatic system, which has given 6 electrons to the metal complex.

And each carbon monoxide, you have 2 carbon monoxides on the final ligand. So, here are the 2 carbon monoxides and these 2 carbon monoxides give, 4 electrons. And if you add up all the charges, you will notice that, you have a net positive charge. So, rhenium must be in a plus 1 oxidation state, rhenium must be in the plus 1 oxidation state. Since, it is a metal with 7 valence electrons, we end up with 6, adding 6. And this gives us, a total of 18 in this particular method. Using the ionic method, we have arrived at the an electron count of 18.

Now, the neutral method cannot give us a different electron count, but the way it arrives at this electron count, turns out to be different. Let us just take a look at, how itgets the same electron count of 18. NO gives 3 electrons so there is one nitric oxide and that gives us 3 electrons. Cp is a cyclopentadienyl ligand, now we consider it as C5H5 dot that is a cyclopentadienyl radical.

Carbon monoxide gives us, 4 electrons the electron counting does not change in that case, rhenium again gives us 7 electrons, because that is the number of valence electrons around rhenium. That gives us, again a total of 18, so you can see that the two methods of electron counting. Although, they appear to be very different, they arrive at the same number.

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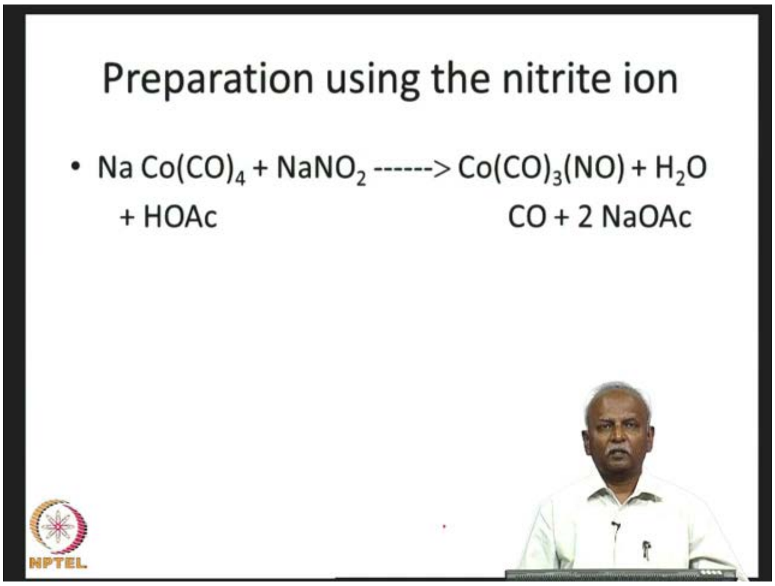

Preparation using the nitrite ion

- Na $Co(CO)_4$ + $NaNO_2$ ------> $Co(CO)_3(NO)$ + H_2O
  + HOAc   CO + 2 NaOAc

So, let us now look at, a little more chemistry of the NO ligand. Here is another example, where we have a cobalt complex, where we have replaced a ion. Where, we have replaced one of the carbon monoxide ligands in the sodium ion with nitric oxide. This time we do it, with the help of a nitrite ion, the nitrite ion helps us to generate NO in the coordination sphere of cobalt. And we have a cobalt, a tri carbonyl nitrosyl cobalt complex.

Now, once again you will, you can do this electron counting as an exercise. This time, we have already counted in 4 complexes, so you should be able to do the counting for this particular system. And find out that, in fact it is an 18 electron system. So, what is interesting in this molecule is a fact that, you are adding acetic acid and you are generating water. And these organometallic molecules, are quite stable under thisunder these conditions. So, organometallic molecules are not always incomparable with water.

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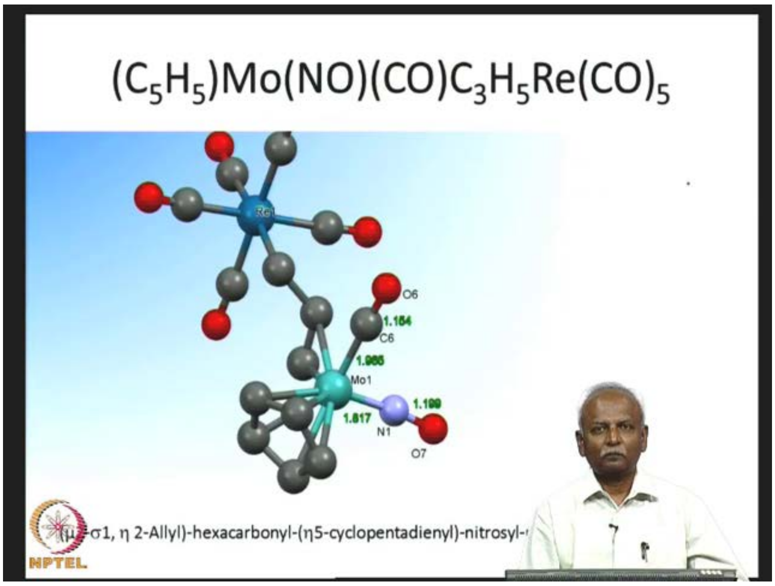
$(C_5H_5)Mo(NO)(CO)C_3H_5Re(CO)_5$

(μ-σ1, η 2-Allyl)-hexacarbonyl-(η5-cyclopentadienyl)-nitrosyl-

Now, I want to look at some of the structural features that weencounter, when we go to organometallic complexes containing nitric oxide. I have chosen a fairly complex system, butwe will confine ourselves to the, to the part of the molecule, that has got the nitrosyl moiety. So here, I have acomplex in which both carbon monoxide and nitric oxide are present, in the coordination sphere of molybdenum.

In the case of this, molybdenum centre which you can see here. This is a molybdenum centre, which is pictured in a light green blue colour and the nitrogen is, blue in colour. And you will see that the electron, you will see that the bond distance is around 1.817 angstroms and this is significantly less than, what you would expect for a metal nitrogen single bond. Similarly, the molybdenum carbon bond distance which is 1.965 angstroms and that is pictured here. This is the molybdenum carbon bond distance, it is less than 2 angstroms, which is what you would expect for single bond distance.

And this issignificantly smaller and the molybdenum nitrogen bond distance was also smaller than, what you would expect for a single bond distance. So, you can see that these bond orders must be greater than 1. In other words, the representation that we have for the nitric oxide complex and the representation that, we have for the carbon monoxide complex can be similar, to what I have shown here. These are good valence bond representations of the interaction, of carbon monoxide with the molybdenum or the nitric oxide with molybdenum.

You will also notice that, the bond angle, the bond angle that you have here, is close to 180 degrees. The bond angle between molybdenum nitrogen oxygen, is close to 180 degrees. So, all these factors, are very clearly indicative of the fact that, you have pi bonding interactions between nitric oxide and the molybdenum centre. Just like you have, pi bonding interactions between molybdenum and the carbon monoxide centre in this molecule.

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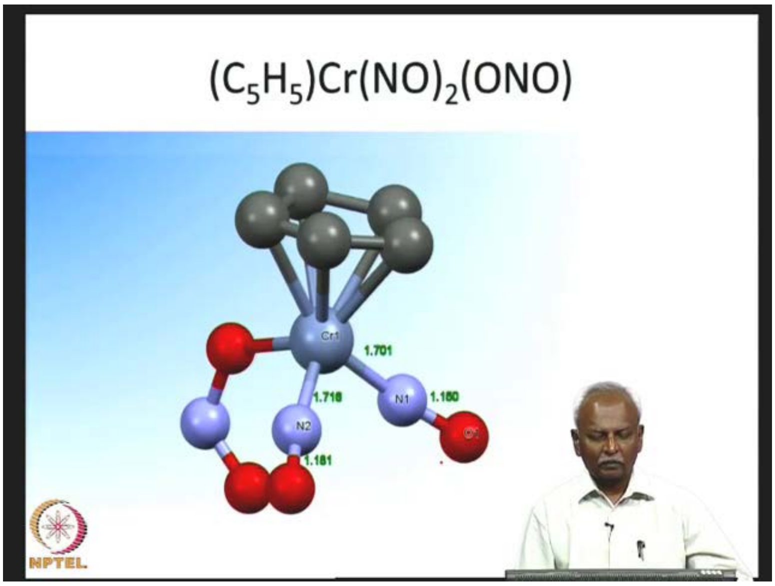
$(C_5H_5)Cr(NO)_2(ONO)$

So, here is another example of a complex which has got both nitrite and nitric oxide. Once again these bond distances, are quite small compared to what you would expect for single bond distances. In this case, because it is a chromium complex the bond distance is significantly less compared to the molybdenum nitrogen bond distance we encountered.

But here we have 2 nitric oxide molecules, which are bonded to the chromium andhere it is an interesting example because you have a nitrite ion, which is still bonded to the chromium, which is pictured here, this is a nitrite ion which is bonded to the, through the oxygen to the chromium molecule. The hydrogens on the cyclopentadienyl moiety are not shown, buteach one of these carbons has got a hydrogen. And if you had added hydrogens, the complex would have looked lot more complicated and so I have avoided adding the hydrogen atoms.

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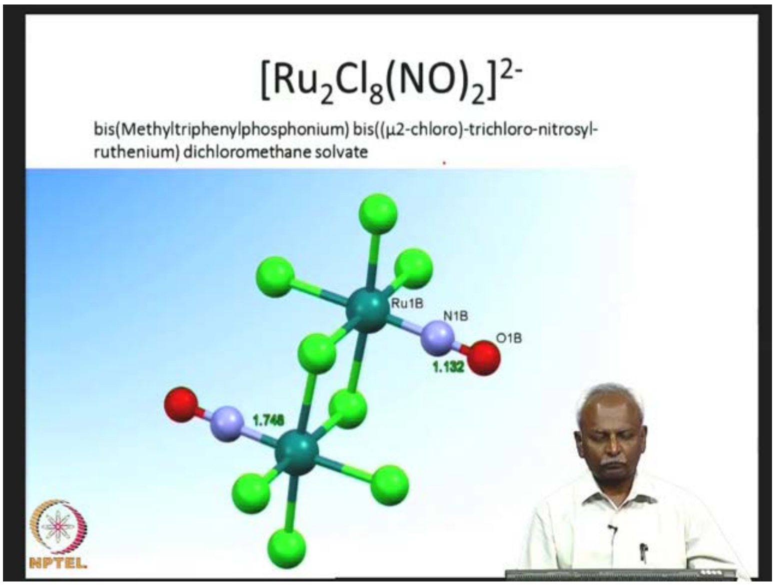

$[Ru_2Cl_8(NO)_2]^{2-}$

bis(Methyltriphenylphosphonium) bis((μ2-chloro)-trichloro-nitrosyl-ruthenium) dichloromethane solvate

Now, having said this much, I should also add that nitric oxide is a ligand, which is encountered in coordination chemistry also extensively. Here is a simple coordination compound of ruthenium, which has got chlorine atoms, these are all chlorine atoms. And these molecules have got,the nitric oxide coordinated to the ruthenium centre and here also the behaviour of the ruthenium nitric oxide bond, is very similar. You do have, pi type of interactions between the ruthenium and the nitric oxide.

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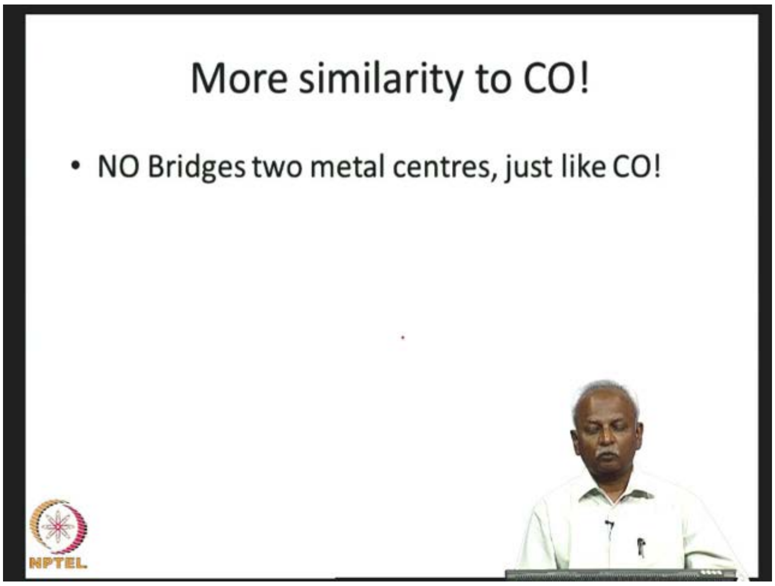

More similarity to CO!

- NO Bridges two metal centres, just like CO!

Let us proceed further. The similarity to carbon monoxide, does not end with the bond distances,it is also very similar in chemistry. So, nitric oxide bridges two metal centres just like, carbon monoxide. Now, we notice that carbon monoxide has got a great tendency to bridge two metal centres and nitric oxide.

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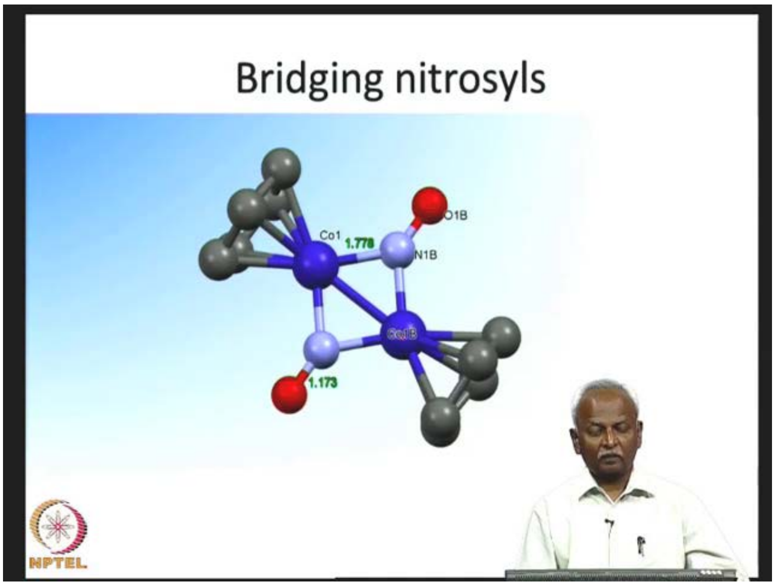

Bridging nitrosyls

Although, the number of bond distance, number of examples where nitricoxide is bridging two metal centres is less. Nevertheless, you do have quite a number of examples where, nitric oxide behaves just like carbon monoxide. Here is an example, between two cobalt centres this is a cobalt complex, which has which has got two cyclopentadienyl groups. And two nitric oxide units are bridging, the two cobalt nitric oxide is bridging two cobalt atoms.

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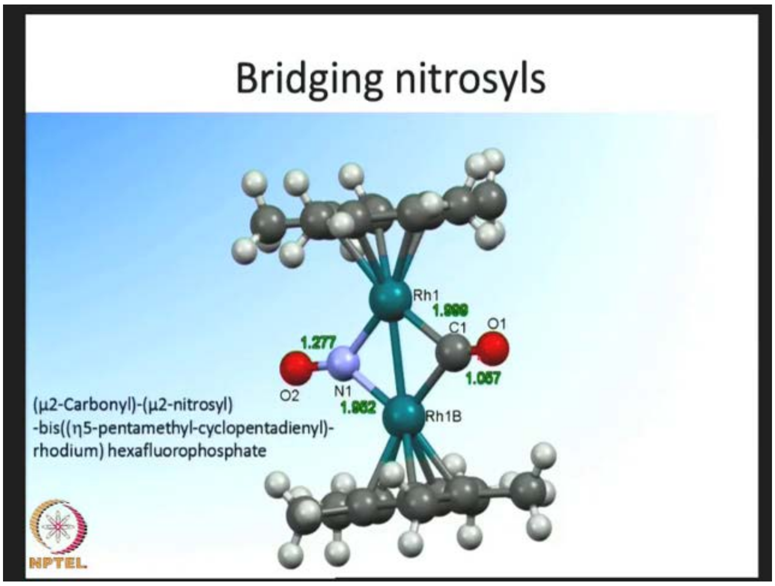

Bridging nitrosyls

(μ2-Carbonyl)-(μ2-nitrosyl)
-bis((η5-pentamethyl-cyclopentadienyl)-
rhodium) hexafluorophosphate

Proceeding further, here is an example where you have a carbon monoxide and a nitric oxide bridging the 2 rhodium atoms in this molecule. And you willnotice from the bond distances that, the nitrogen oxygen bond distance has elongated significantly from the bond distance, that you observed for free nitric oxide. That is free NO plus, had a bond distance of 1.1.5 Angstroms and you have a significant amount of bond lengthening in this case. And all of these factors are, reminiscent of carbon monoxide chemistry. You have the bond distances, which are close to what you would observefor a double bond, double bonded atoms. So, N double bond O is what you character, is what you would expect and that is what you observer here.

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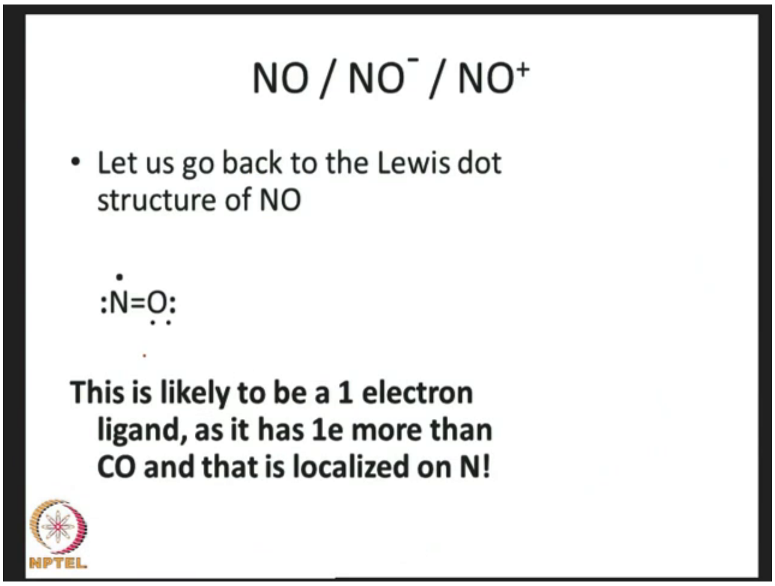

NO / NO⁻ / NO⁺

- Let us go back to the Lewis dot structure of NO

:N=O:

This is likely to be a 1 electron ligand, as it has 1e more than CO and that is localized on N!

So, in these cases it is very obvious that nitric oxide NO plus, is behaving very similar to carbon monoxide. If you go back to the Lewis dot structure, that we looked at earlier, we remember that it has got 1 electron on the nitrogen. And this 1 electron if you, if you recollect Cl dot, it is very similar to the system which has got 1 electron on the chlorine. So you, this is likely to be a 1 electron ligand just like chlorine. So, this 1 electron chemistry leads to, the chemistry of NO minus. So, just like Cl can give that one electron which is present on the chlorine, to the metal atom and behave as a one electron ligand.

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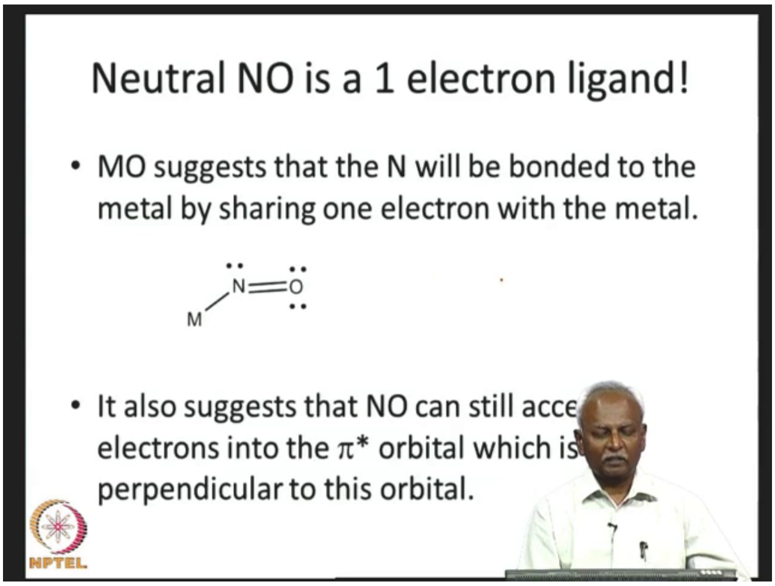

Neutral NO is a 1 electron ligand!

- MO suggests that the N will be bonded to the metal by sharing one electron with the metal.

- It also suggests that NO can still acce
electrons into the π* orbital which is
perpendicular to this orbital.

NO can also behave as a, one electron ligand and this will be like NO minus chemistry. The molecular orbital theory picture, is something that is more difficult to arrive at in the case of the bent NO system because you would have to calculate the energies of the bent and the linear system. And show that, the bent NO, if it is not ionized, the bent NO is the right structure for this molecule. And you will notice that, the nitric oxide has still got a pi star orbital, which is empty.

Even though this extra electron density will have to be, this pair of electrons, which is there as extra electrons on the nitrogen. But then there is one pi bond between the nitrogen and oxygen. And that pi star orbital is still empty and can accept electron density from the metal. So, back bonding is still possible when you have a bent NO, which is behaving like NO minus and some properties of this NO minus will be similar to what we have encountered for CO.

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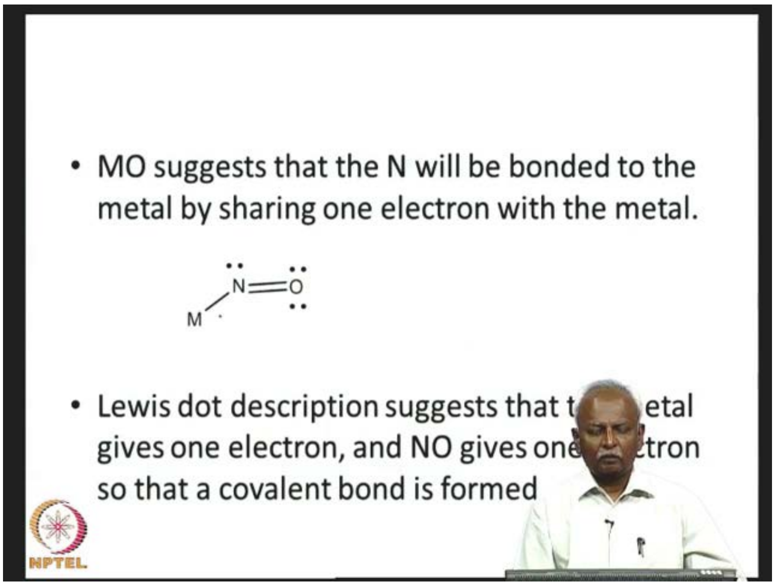

- MO suggests that the N will be bonded to the metal by sharing one electron with the metal.

- Lewis dot description suggests that t etal gives one electron, and NO gives one tron so that a covalent bond is formed

MO suggest that, nitrogen will be bonded to the metal because that is where the electron was generally found. And the Lewis dot structure also corresponds to them same or points to the same fact.

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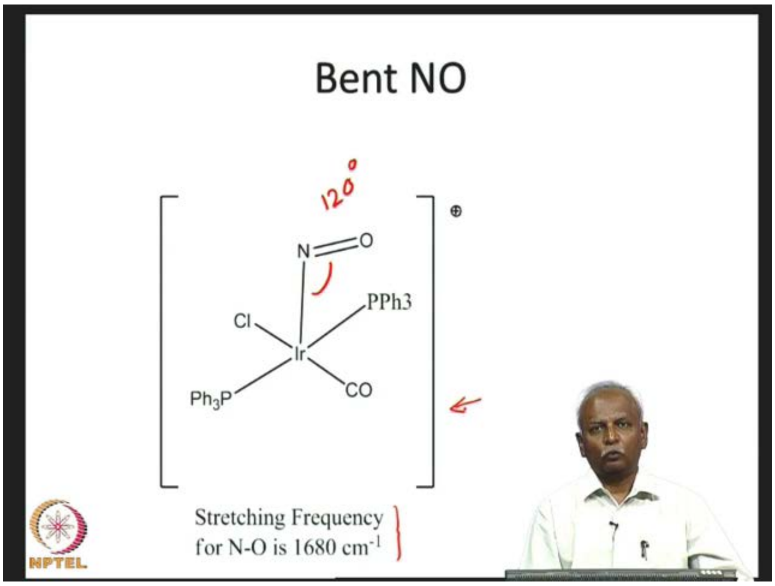

Bent NO

Stretching Frequency for N-O is 1680 cm^{-1}

So we have a covalent bond, which is formed between nitrogen and the metal just like, you have a covalent bond formed between chlorine and the metal. And here is an example where, we have a bent NO in a iridium 1 structure and this angle is close to 120 degrees. This angle is close to 120 degrees and the stretching frequency of these molecules are around 1680 centimetre minus 1,1700 centimetre minus 1. In many of the complexes, where the bonding is the bonding is bent or the MNO bond is bent. Then you end up with, the stretching frequency which is much lower than the frequency that, you observe for a terminal nitric oxide or a linear nitric oxide.

So, those are instances where the NO stretching frequency has been reduced from N triple bond O to, N double bond O. Here the stretching frequency is in fact, even further reduced and it goes close to 1680 centimetre minus 1. So, you can do the electron count for this particular molecule and it is an instructive exercise to do this, but you would count NO as a one electron donor.

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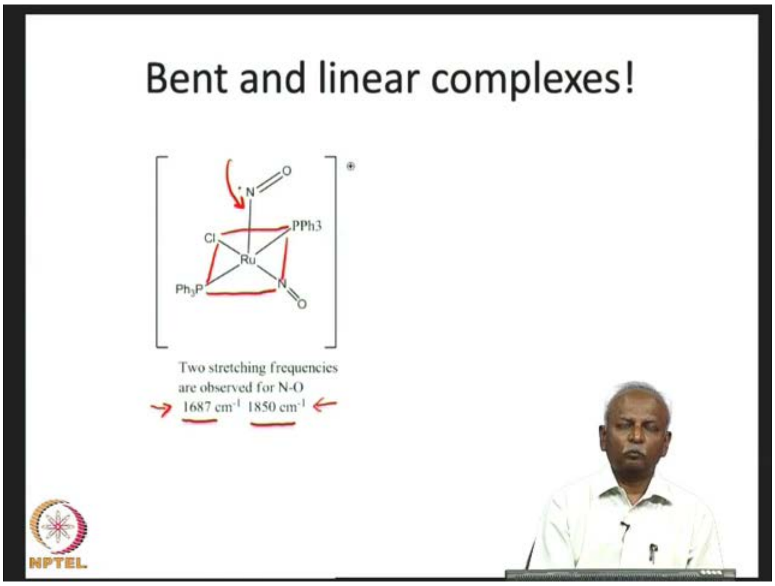
Bent and linear complexes!

Two stretching frequencies are observed for N-O

1687 cm^{-1} 1850 cm^{-1}

Now, a very, very interesting system is a ruthenium complex that, we have in front of us right here. This ruthenium complex, this ruthenium complex pictured here has got 1 bent NO and 1 linear NO. And we arrive at this information that, it has got 2 different types of nitric oxide, on the basis of the 2 stretching frequencies that, we have observed. The two stretching frequencies that we observe, are one is close to what you would expect for a bent NO that is a 1687 centimetre minus 1, and one stretching frequency is close to 1850 centimetre minus 1.

And that is what, you would expect for a linear nitric oxide and the structure of this molecule, this intriguing structure can be imagined as a square pyramid. In other words these 4 ligands, these 4 ligands the nitrogen chlorine and the 2 phosphorus atoms, are there in a plane and the nitric oxide, bent nitric oxide is there in the apex of this square pyramid.

Interestingly, most bent nitrosyl molecules have been found in the apical position of square pyramid molecules. Sometimes in octahedral molecules also, but we find that this bond distance is longer, this bond distance is longer and the nitrogen oxygen distance. In these cases are also corresponding to a double bond distance or lower than a double bond distance.

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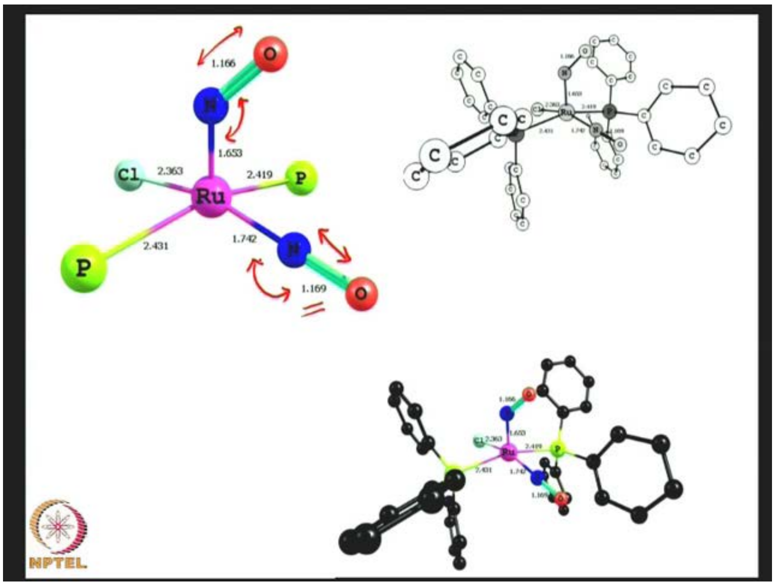

So, here is the metrical parameters given for you and you can see that, this distance between the metal nitrogen bond distance, is around 1.65 Angstroms. And you have a bent geometry, for this nitric oxide and you have a longer bond distance between this nitric oxide. And this NO in fact the bond distances, that you observe here between the nitrogen and oxygen, between the nitrogen and oxygen are very similar in the bent NO and the linear NO.

So, you cannot distinguish the bent NO and the linear NO on the basis of the bond distance between nitrogen and oxygen, but distinctly the MNO angle is very clear. One of them is 180 degrees, this one is 180 degrees and the other one is 120 degrees and the stretching frequency difference is also unmistakable. So, these are some interesting examples in NO chemistry and there are very few instances or no instances, where you would have this kind of a difference between the two ligands in the same molecule.

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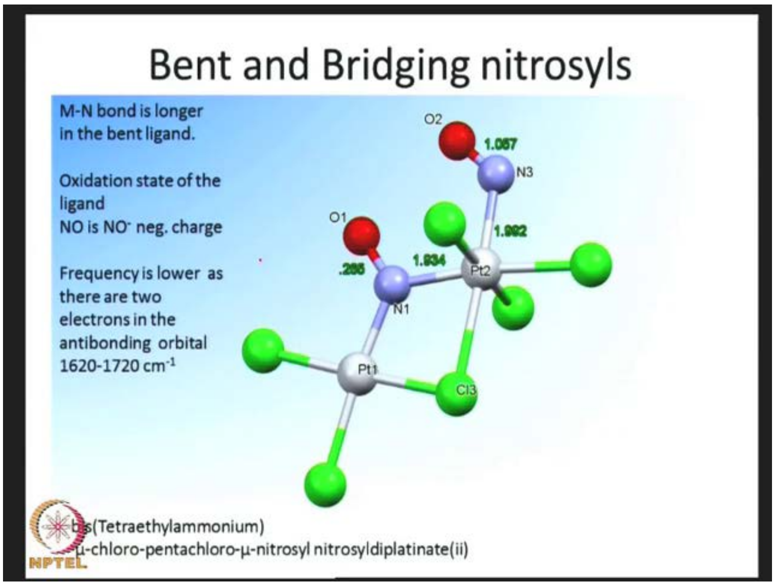

Bent and Bridging nitrosyls

M-N bond is longer in the bent ligand.

Oxidation state of the ligand
NO is NO$^-$ neg. charge

Frequency is lower as there are two electrons in the antibonding orbital
1620-1720 cm^{-1}

bis(Tetraethylammonium)
μ-chloro-pentachloro-μ-nitrosyl nitrosyldiplatinate(ii)

Now, we talked about bent nitric oxide and we also have bridging nitric oxide, in some molecules, both can be found together. Here is an example where you have a platinum, where you have a platinum atom which is bonded to both bent nitrosyl and also has a bridging nitrosyl molecule. And you can see that, this is a unique example, not many examples of these type of bridging and bent nitrosyls are known, but this is one unique example.

And the type of frequencies that, you observe for this bridging nitrosyls are significantly lower. It is around 1620 to 1720 centimetre minus 1 and that is because the bond order is in fact lower than a double bond order. And NO is in fact, you will have to use, NO minus for the electron count and you do not have the possibility of having an NO plus in this particular molecule.

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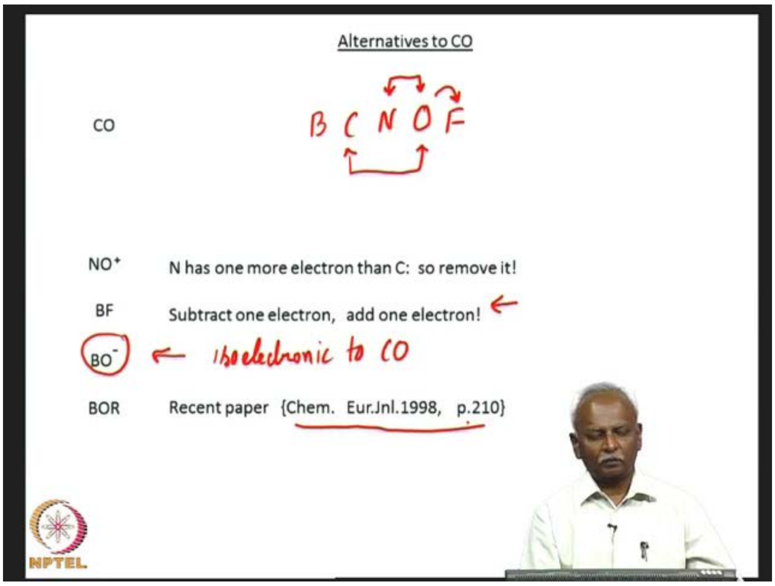

Alternatives to CO

CO B C N O F

NO^+ N has one more electron than C: so remove it!

BF Subtract one electron, add one electron!

BO^- ← isoelectronic to CO

BOR Recent paper {Chem. Eur.Jnl.1998, p.210}

So, we have looked at several examples now, for nitric oxide several examples of nitric oxide, bonded to the metal atom. One can ask the question, why not change the atom from carbon to boron, instead of carbon to nitrogen. So, if you look at the periodic table, we have boron carbon nitrogen and oxygen and we noted that, it would be good to have a good electro negativity difference between the two atoms which are bonded together. So we looked and carbon monoxide is a good example and if you, move to nitric oxide this electron electro negativity difference becomes smaller.

Now, instead of moving to nitrogen from carbon, why not move from carbon to boron. So, if you have an example where, you have BO, suppose you have BO and because we have 1 electron less on the molecular system, let us add an electron. So that will make it Bo minus, so this would should be is oelectronic to carbon monoxide. So this is isoelectronic, this is isoelectronic to CO now it is also possible to add an electron in terms of changing from oxygen to fluorine.

So, if I move from oxygen to fluorine, Iautomatically add one more electron. So, if you have BF then that should be isoelectronic to CO as well. So, we should expect some very good interesting chemistry with BF or BO minus and as we have done in other cases. We can cap the O minus, with an R group and a recent paper in thechemistry European journal in fact probes this aspect.

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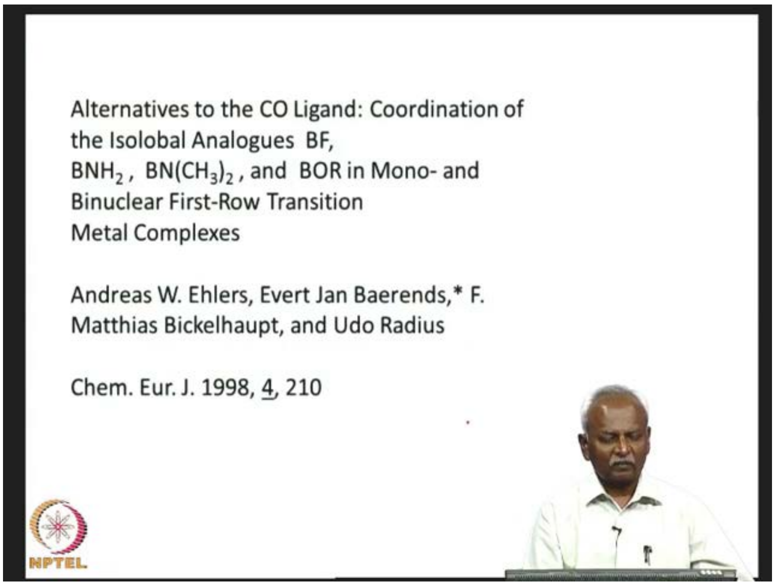

Alternatives to the CO Ligand: Coordination of the Isolobal Analogues BF, BNH_2, $BN(CH_3)_2$, and BOR in Mono- and Binuclear First-Row Transition Metal Complexes

Andreas W. Ehlers, Evert Jan Baerends,* F. Matthias Bickelhaupt, and Udo Radius

Chem. Eur. J. 1998, 4, 210

And they have looked at alternatives, to the carbon monoxide ligand and coordination of Isolobal analogues of BF, BNH2, BNCH32 and BOR in the first row transition elements.

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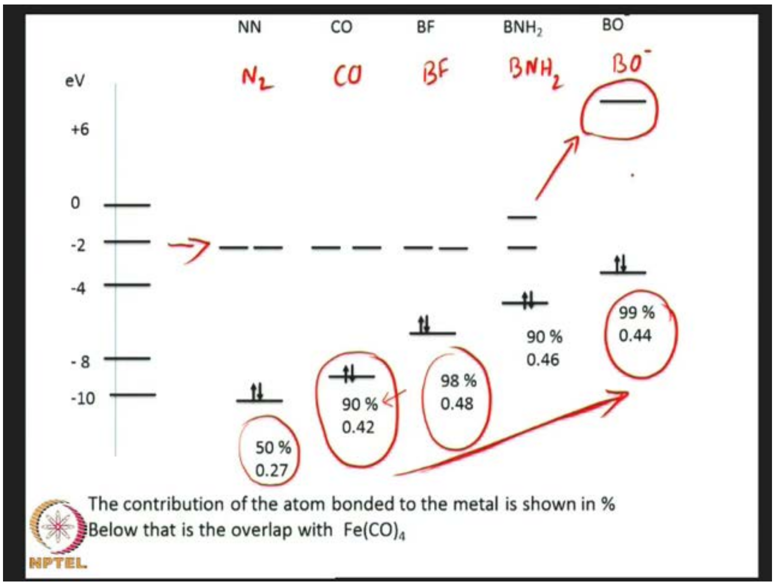

The contribution of the atom bonded to the metal is shown in %
Below that is the overlap with $Fe(CO)_4$

And the this is, this is just a conceptual paper where, they have looked at the Isolobal analogy, which we will look at later on. I have given you the salient features of this paper, what they have mentioned is the following. The highest occupied molecular orbital in carbon monoxide and that is the 3 sigma orbital, had a significant donor capacity. And that came from a donor orbital, which is a sigma orbital concentrated mostly on carbon. So, this 90 percent indicates the fact that, the donor orbital and carbon monoxide was localized mostly in carbon. Now, if you move to BF on the other hand because the electronegativity difference is even more, between boron and fluorine. The electron density on the lone pair, is localized mostly on boron and that is close to 98 percent, 98 percent of the electron density of the home is localized on the boron.

Similarly, if you go to nitrogen di nitrogen the electron density on one of the nitrogens will only be 50 percent because both atoms are equivalent, they are both isoelectronic. So, di nitrogen will end up with this N2, this is carbon monoxide and this is your BF molecule. So, in BF you have a very significant proportion of the electron density, the donor orbital on the boron. So if the, if you go in in a similar fashion to BNH2 and BO minus you find that the electron density will be mostly on the atom, which is less electronegative. And so the donor ability increases in this direction.

However, we will notice that the pi star, the acceptor orbital on BO minus has shot up an energy. So, BO minus is unlikely to be a good ligand, because the lower the energy of these acceptor orbitals, the lower the energy of these vacant or acceptor orbitals. These have to be, lower in order to accept electron density and these orbitals have to be higher in energy, in order to donate electron density. So, indeed the donor orbital electron density is increased and it is a better electron donor, but nevertheless the acceptor property of BO minus is unlikely to be of much use.

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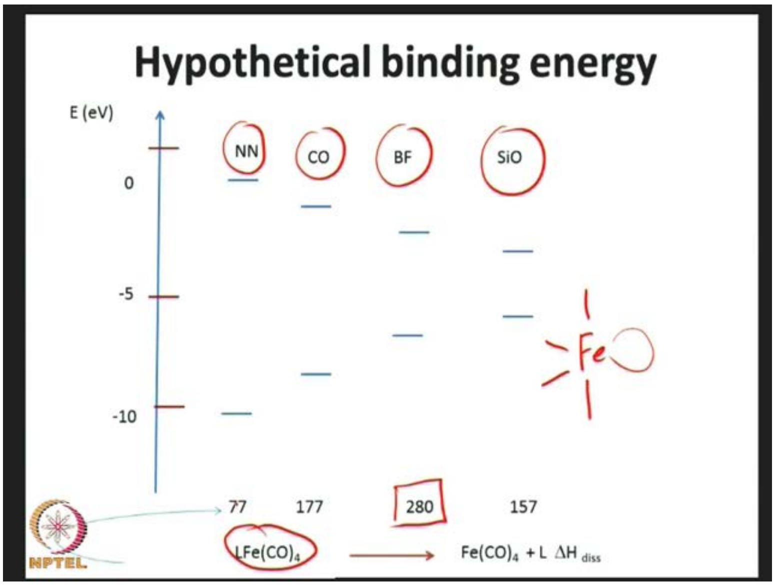

Hypothetical binding energy

$LFe(CO)_4 \longrightarrow Fe(CO)_4 + L\ \Delta H_{diss}$

Let us take a look at what has happened between 1998 and now and it has indeed been possible to make some complexes. However, before I proceed to give you an example, I have to show you that, they also calculated the hypothetical binding energy between a fragment FeCO4. FeCO4 is a fragment that you can hypothetically generate so that is just this system you have 4 carbon monoxides. And it has a vacant side where, a carbon monoxide would have been for FeCo5. And in this side, you can plug in di nitrogen carbon monoxide BF and SiO and if you do that, you find that the bond energy between BF. And this hypothetical fragment is a maximum 280kilo calories per mole, compared to 77 for di nitrogen and 177 for carbon monoxide.

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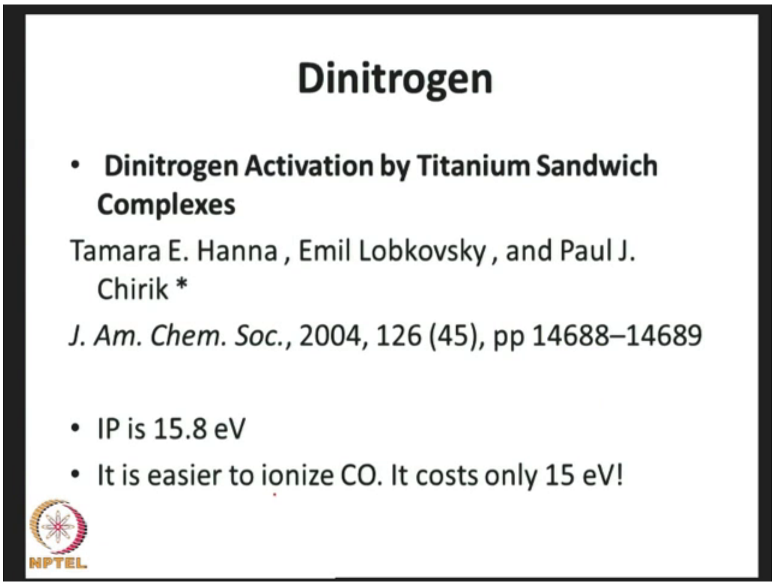

Dinitrogen

- **Dinitrogen Activation by Titanium Sandwich Complexes**

Tamara E. Hanna , Emil Lobkovsky , and Paul J. Chirik *

J. Am. Chem. Soc., 2004, 126 (45), pp 14688–14689

- IP is 15.8 eV
- It is easier to ionize CO. It costs only 15 eV!

So recently, it has been possible to make some complexes with BF and I will come to that in a moment, but I should also tell you that, di nitrogen as we have just seen, di nitrogen is also a ligand, which can be used and that chemistry has also progressed significantly. So here you have, some di nitrogen chemistry with titanium complexes primarily, promoted by or carried out by this person Paul Chirik.

And this paper has been, this initial paper is the, reference to this initial paper is given here. And one should note that, the ionization potential of nitrogen, di nitrogen is 15.8 electron volt and it is only slightly higher than, carbon monoxide which is 15 electron volts. So, and di nitrogen is likely to be a reasonably good donor, although it may not be a good pi acceptor.

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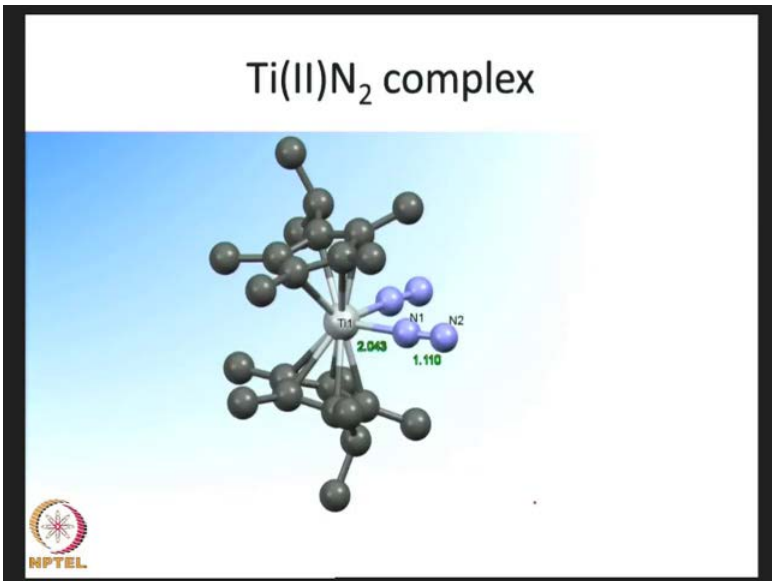

Ti(II)N_2 complex

So, in the case of high valent molecules or metals in the early transition group, which means titanium, vanadium and so on. So, you will have a tendency to, form electropositive systems and back bonding necessity might be less. And so here you have, a titanium two complex between two cyclopentadienyl rings and titanium. So, this is a system which bonds to, two nitrogen molecules. So, instead of the familiar carbon monoxide, we have 2 di nitrogen molecules. And you will notice that, the bond distance between titanium and nitrogen is not very short, but it is equivalent to what you would have for a sigma bond. You do not have extensive pi bonding and double bond character between the nitrogen and the titanium.

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- **Group 4 Transition Metal Sandwich Complexes: Still Fresh after Almost 60 Years**

Paul J. Chirik

Organometallics **2010** *29* (7), 1500-1517

And recently, the same person has published a review article, which gives you a review of the 60 years of di nitrogen chemistry in organometallic complexes.

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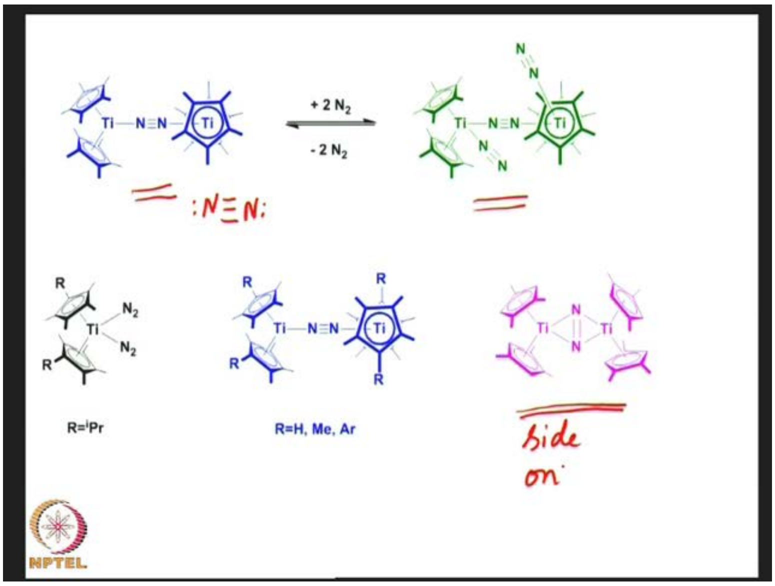

And here are some of the complexes that, they have studied and described. In fact, this is very interesting that, just by increasing the pressure of di nitrogen, one can go from a bridged di nitrogen complex, which is shown here. Bridged di nitrogen complex to, a system where you have 2 extra di nitrogens in a terminal position as well. You will notice that, the bridging of di nitrogen is slightly different from the bridging of carbon monoxide. Bridging of di nitrogen is achieved, by donating the pair of electrons on both ends of the di nitrogen molecule. So, there are two donor atoms on di nitrogen and both of these are equally efficient in donating a pair of electrons.

So, this is slightly different from the carbon monoxide bridging, but nevertheless you can see that you have a variety of binding modes, between di nitrogen and organometallic species. And here is another system, which is very, very different and the where, the what is called as a side on bridging. This is called a side on bridging mode of di nitrogens, present between the organometallic molecule and the di nitrogen.

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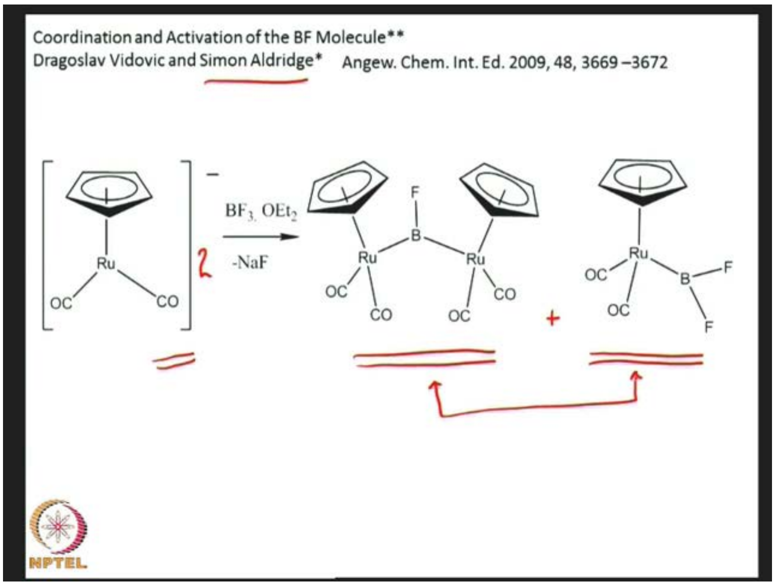

Coordination and Activation of the BF Molecule**

Dragoslav Vidovic and Simon Aldridge* Angew. Chem. Int. Ed. 2009, 48, 3669–3672

So, coming back to the BF molecule very recently it has been possible to, it has been possible for Simon Aldridge to synthesize a BF molecule, which is again a bridging molecule, which has been synthesized, by treating this carbonalate anion, with ruthenium carbonalate anion with BF three iterate, very simple chemistry. The negative charged species displaces, the two of these negatively charged species, notice that two ruthenium carbonalate species must be present.

So, two of them are present and they displace 2 fluorine atoms and form, it forms a nice bridging chemistry between the BF, is bridged between two ruthenium atoms. And this is very similar to, what you would have if a carbon monoxide is bridging except that now, we have BF which we are looking for based on our theoretical hypothesis that, BF would behave just like carbon monoxide.

So, here is a molecule which has been synthesized and characterized and in the same reaction system, you do have the formation of a mono BF two complex. But this is, this is formed in minor amounts and this is formed in major amounts. And depending on the solvent systems, one can in fact adjust the ratio of these two molecules that are present. So, this brings me to the end of today’s discussion on alternatives to carbon monoxide. Carbon monoxide can be in fact replaced by various other molecules, hetero nuclear di atomics. Some of them like, nitric oxide NO plus are extremely similar to carbon monoxide and they can be found in both bridging linear terminal and in bent forms. And this gives us some very interesting chemistry indeed.