Advanced Transition Metal Chemistry – Classification of Ligands by Donor Atoms

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Lecture – 33
Classification of Ligands – Nitrogen

Hello everyone. I welcome you all once again to MSB lecture series on transition metal chemistry. We have started discussion on classification of ligands by donor atoms. So, far I have completed discussion on hydrogen, carbon and nitrogen I just began in my previous lecture and I gave a little information about the donor properties of nitrogen and how the nitrogen behaves very similar to isocyanides and carbon monoxide.

So, that one can do some reactions if you know a little bit more about how we can perform on coordinated nitrogen some reactions that might be helpful for those who are working in the nitrogen reduction and carbon dioxide reduction systems and other such similar reactions. From that point of view, let me continue from where I had stopped.

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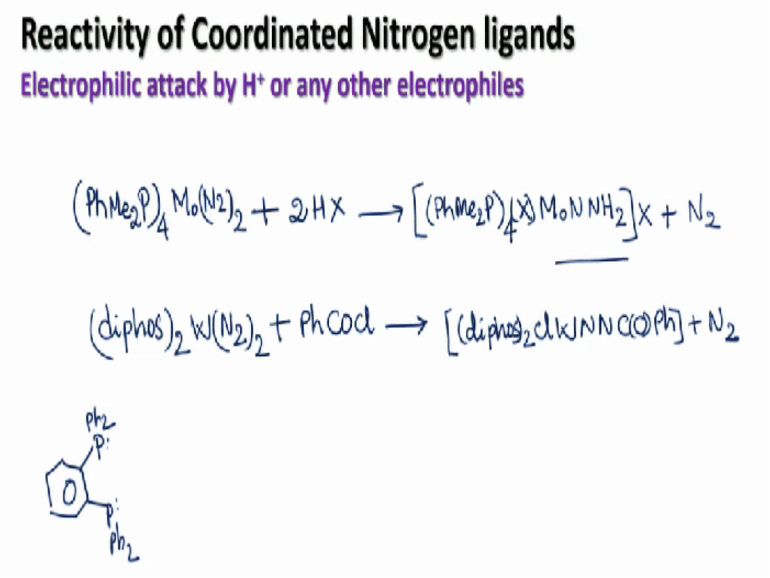

Reactivity of Coordinated Nitrogen ligands

Electrophilic attack by H⁺ or any other electrophiles

$$(PhMe_2P)_4Mo(N_2)_2 + 2HX \longrightarrow [(PhMe_2P)_4(X)Mo\underline{NNH_2}]X + N_2$$

$$(diphos)_2W(N_2)_2 + PhCOCl \longrightarrow [(diphos)_2ClWNNC(O)Ph] + N_2$$

Let us look into the reactivity of coordinated nitrogen ligands or nitrogen donor ligands. So, how this electrophilic attack by H or any other electrophiles results in new products that we can see in a couple of reactions by choosing very specific examples. Let us consider a simple phosphine and nitrogen complex. So, when we have phosphines and when we try to put dinitrogen, we should remember we should go for very strong sigma donor ligands.

Among phosphines if we have alkyl groups, they are good sigma donors, from that point of view you, can see in most of these reactions, we are using alkyl bound phosphines, not the aryl, and of course here to have some moderate sigma donor ability, one can also replace one of the alkyl groups with aryl groups such as phenyl. So, when this compound is treated with HX, so in this reaction one of the N_2 is liberated whereas other N_2 is reduced to form this kind of product.

Diphos is a bidentate ligand, I shall show you the structure. Diphos is nothing but this is one, 1,2-bis(diphenylphosphino)benzene. The mechanism of N_2 reduction in biological system is not really clear, however, the reactivity of coordinated N_2 is well studied. The reaction involves usually hydrazido, imido and nitride species. The possible reactions one can anticipate are electrophilic, nucleophilic or coupling reactions.

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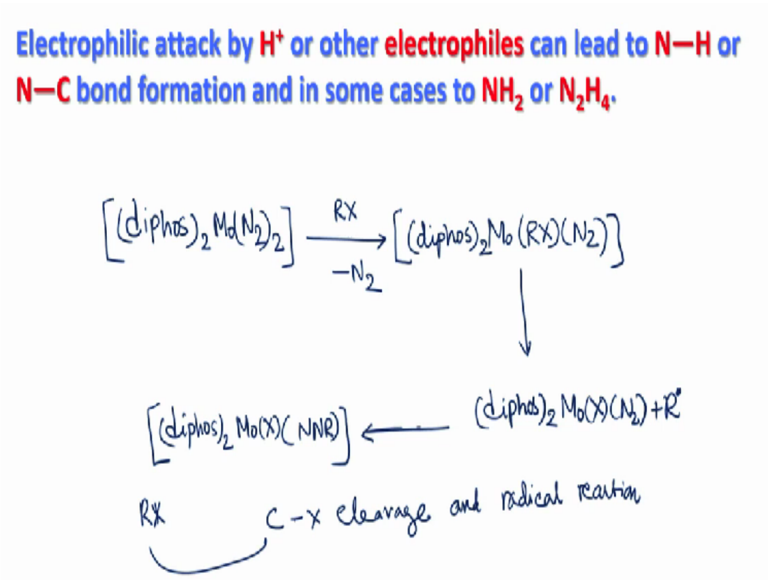

Electrophilic attack by H^+ or other electrophiles can lead to N—H or N—C bond formation and in some cases to NH_2 or N_2H_4.

So, now let us look into the electrophilic attack by H or other electrophiles. The same reaction I am considering again. The addition of RX here can lead to C—X bond cleavage and radical reaction.

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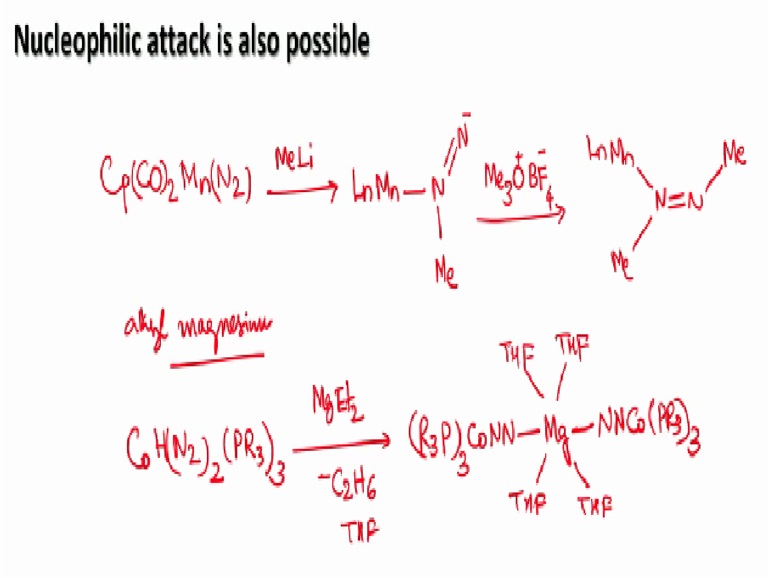

Nucleophilic attack is also possible

Now, let us look into nucleophilic reaction. What would happen if a nucleophile attacks the nitrogen centre. A manganese complex is chosen for this purpose having cyclopentadienyl ligand and two carbon monoxide. When this is treated with methyl lithium, initially it forms an intermediate of this type, of course here counter cation is lithium. On further treatment with $Me_3O:BF_4$ a good methylating agent.

And when we treat this with typical alkyl magnesium such as diethyl magnesium it gives an interesting magnesium complex having two cobalt moieties. So, this ethyl group abstracts hydrogen from cobalt to give C_2H_6 and of course here we have this reaction is carried out in THF. So this is another reaction that depicts the nucleophilic reaction of coordinated nitrogen.

So, with this let us move on to consider another interesting ligand called nitrosyl ligand, nitric oxide we call it as nitrosyl, NO is a bio regulatory agent produced endogenously. Disturbances in the production and regulation of NO are known to cause central nervous system disorder and asthma besides many other diseases. Iron nitrosyl complexes help to balance the beneficial effects of NO against its potentially fatal effects. Of course, one should remember the fact that the NO is also a very toxic gas.

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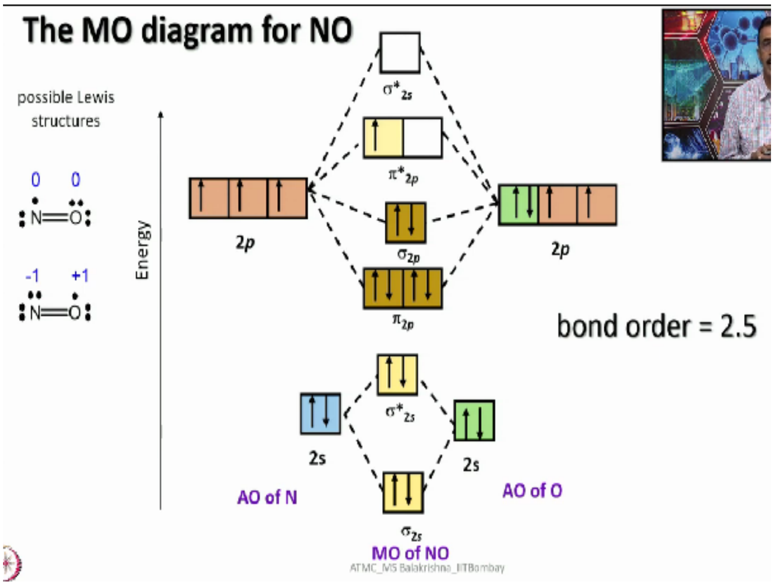

The MO diagram for NO

bond order = 2.5

Now let us look into the MO diagram of NO, before we proceed for preparatory methods and reactivity and other things. You can see here the MO diagram and of course if you count valence electrons in NO, 6 electrons are coming from oxygen and 5 electrons are coming from nitrogen. So, that means we have totally 11 electrons. So, 2s electrons can be left for all practical purpose, because they are not adding anything to NO bond. So, now you consider 3 electrons and of course here 2 electrons are there, they form antibonding and bonding.

What is interesting is about two p electrons here and two p electrons here. And if you see here we have 4 electrons and here 3 electrons. If you start filling in this fashion, we will be left with one electron in antibonding orbital that leads to the bond order of 2.5. So, that is the reason why NO has a tendency to lose one of the electrons readily is to have bond order 3. So, the moment you remove this electron to generate nitrosyl cation, we have the bond order 3 and that is stabilized so because of this reason, NO acts as a nitrosyl cation.

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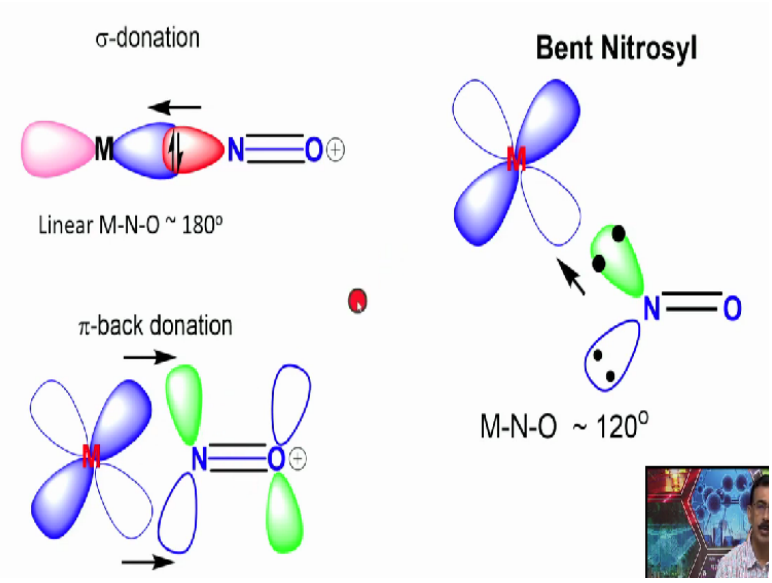

So, let us look into the binding properties. And of course, nitrogen has a lone pair here and that lone pair can be readily donated to the metal to form a sigma bond and this is sigma donation and then in the linear fashion when it binds, the angle should be around 180 or it will be close to 180°. Ad when it binds in bent fashion, what happens it can have an M-N-O angle of about 120 °.

And then because of the presence of π* orbital, you can anticipate back donation with NO as well very similar to carbon monoxide and this is how one can show the interaction of filled metal orbital with π* of nitrosyl ligand. This is back bonding. That means this also a sigma donor as well as a pi acceptor and the relative strength also I already showed you a couple of times earlier in a table.

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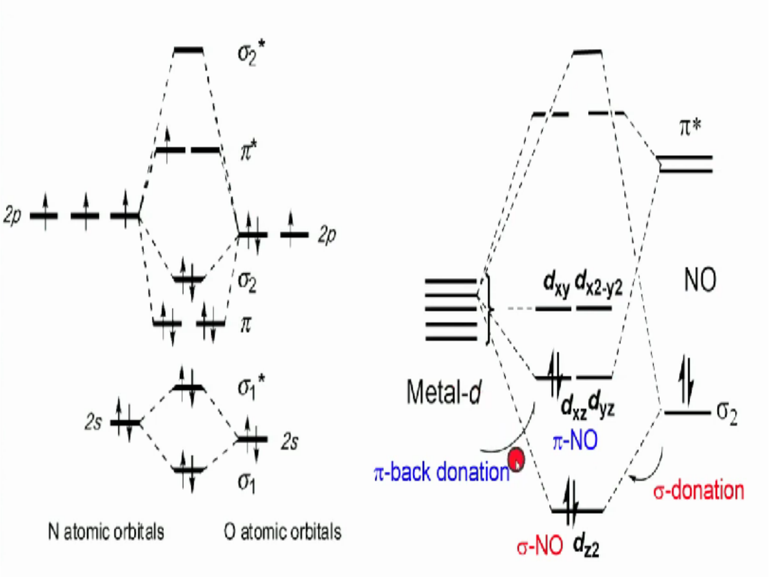

So, this one again I am bringing to show what would happen when a metal binds, so that means this MO diagram depicts the interaction of NO with metal, but now you can see the focus should be only on these electrons that can go as sigma to the metal. So, you can see here these two electrons are donated to appropriate metal orbital, so either $d_{x^2-y^2}$ or d_{z^2} to establish a sigma bond, and then metal has electrons in d_{xy}, d_{xz} or d_{yz}.

So, those things what happens they can be shared with pi star of this one. So, pi star and metal d orbital having pi symmetry would overlap again to generate pi bonding and pi antibonding orbitals, so in which these electrons are placed. So, this represents that donation from metal to NO and this represents NO to metal sigma bonding. This is a typical MO diagram for a metal nitrosyl complex.

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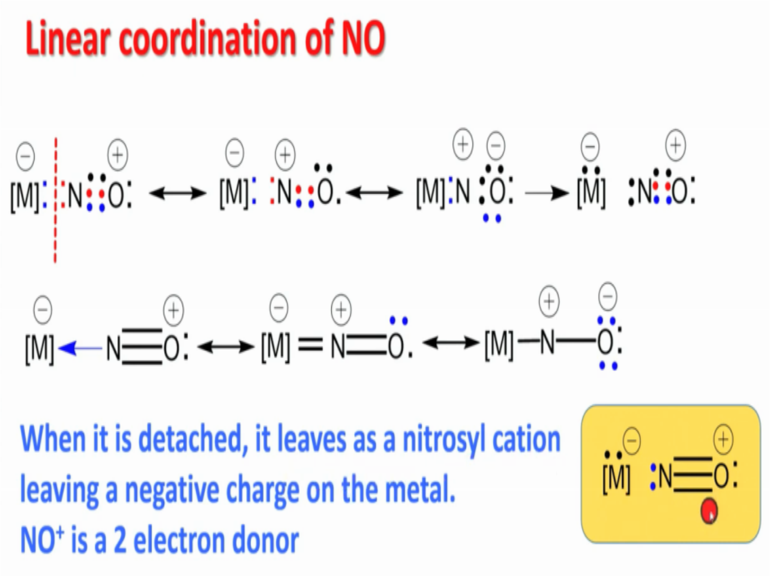

Linear coordination of NO

When it is detached, it leaves as a nitrosyl cation leaving a negative charge on the metal.

NO^+ is a 2 electron donor

Now, let us look into the properties of linearly coordinated NO and of course one can also see the similarities between the way I have written the movement of electrons from oxygen to metal through nitrogen here and this can be very similarly compared to what would happen with carbon monoxide with minimum back donation and maximum back donation with of course having sigma bond intact.

In the same way one can also write, when there is minimum sigma donation, this should happen, when slightly back donation is there this bond is weakened, this bond is strengthened. So, these three extremes one can think of in case of NO ligand as well. So, when it is detached, it leaves as a nitrosyl cation, so leaving a negative charge on the metal, so in that context NO^+ is a 2 electron donor.

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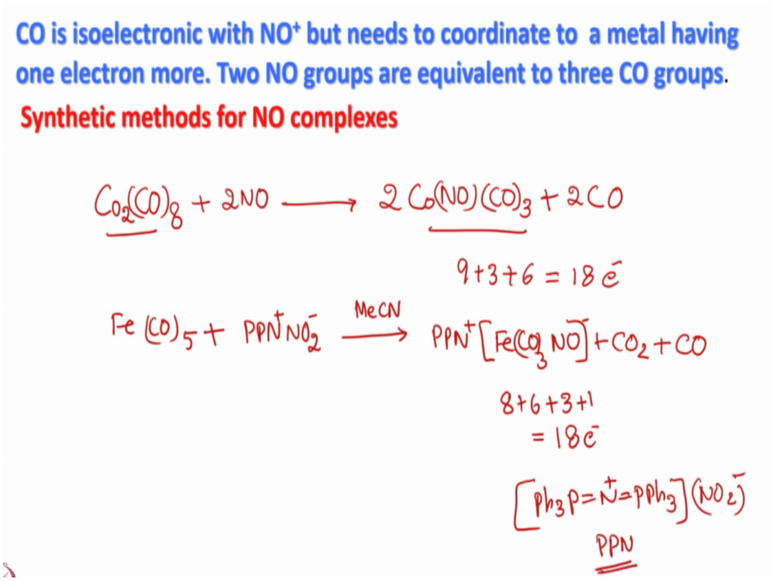

CO is isoelectronic with NO^+ but needs to coordinate to a metal having one electron more. Two NO groups are equivalent to three CO groups.

Synthetic methods for NO complexes

$$\underline{Co_2}(CO)_8 + 2NO \longrightarrow 2\,\underline{Co(NO)(CO)_3} + 2CO$$

$$9+3+6 = 18\bar{e}$$

$$Fe(CO)_5 + PPN^+NO_2^- \xrightarrow{MeCN} PPN^+[Fe(CO)_3NO] + CO_2 + CO$$

$$8+6+3+1 = 18\bar{e}$$

$$\underbrace{[Ph_3P=\overset{+}{N}=PPh_3]}_{PPN}(NO_2^-)$$

If you just count the electrons we have 10 electrons in NO^+ and similarly in case of carbon monoxide also 4 + 6 =10 electrons are there in the valence shell. So, it is obvious that both are isoelectronic, but NO^+ needs to coordinate to a metal having one electron more, so that means in order to generate nitrosyl cation it has to bind to a metal and it has to give that electron, then only it becomes NO^+ and then that would be isoelectronic with carbon monoxide.

So that means two NO groups are equivalent three CO groups. Let us look into the synthetic methods that are available for making NO complexes in the laboratory. Simplest method is treating directly NO gas. For example, let us consider $Co(CO)_8$ and treat this one with 2 equivalents of NO. So it is very interesting to analyse this one with the structure of this one, half a molecule up this one.

You know why $Co(CO)_4$ cobalt tetracarbonyl exists as a diamond because it is a 17 electron species. In order to satisfy 18 electron rule what happens it will establish a CO-CO bond and hence attains 18 electrons, as a result it stabilized as a dimeric species, whereas in this case when you replace one of the carbon monoxide with NO, now NO is a 3 electron donor, when it is linear. So, now it is 3 electrons, if it is giving Cobalt has 9 + 3 + 6 so 18 electrons are there.

So, that is the reason this can be stabilized simply as a monomeric species. You should know the difference why it is stabilized as monomer species, whereas $Co(CO)_4$ is a 17 electron species and this is an 18 electron species. Let us look into another reaction, where we are using a reagent of different type to generate metal to nitrosyl bond. Let us consider the $Fe(CO)_5$ and treat this one with PPN, I am not sure whether you are familiar with this cation, it is a very bulky cation, usually used to stabilize anions.

I shall write the structure of that one later after completing this equation. So you take this one and treat this with NO_2 salt in isonitrile, it is a counter cation, and what we get is $[Fe(CO)_3NO]^- + CO_2 + CO$. So, now let us count the electrons here. So, if we take Fe there is 8 + 6 + 3, so one negative charge is there. So, you will understand why a negative charge is there on this one because in order to satisfy, because we had taken out carbon monoxide and 4 electrons have been taken out and in its place we have only one NO that is a 3 electron donor.

So with this charge, it becomes 18 electron species. So, everything one should explain very satisfactorily provided we understand this method of electron counting. Now, you must have realized how important it is to know how to do electron counting. And PPN, what is PPN? PPN is nothing but this bulky cation. This is called PPN. Let us look into a couple of more methods of preparation of nitrosyl compounds.

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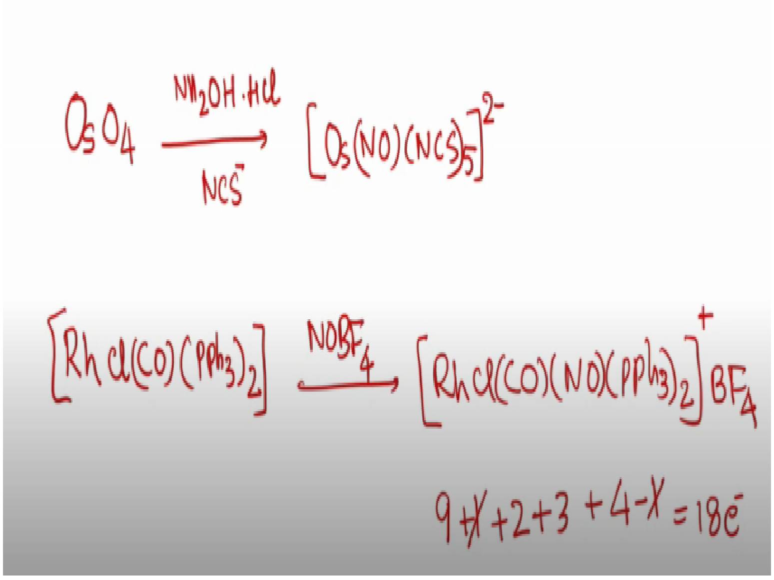

Let us consider now very different one. So far, we discussed with 2 metal complexes in zero valent state, now let us go to another metal in high valence state, osmium tetroxide. In osmium tetroxide osmium is in +8 state. So, when this is treated with $NH_2OH.HCl$ in presence of NCS, isocyanide ligand, thioisocyanide ligand, one can make. So, this is another way of making nitrosyls with metal in high valence state.

Let me write another interesting reaction here. Let us consider rhodium chlorocarbonyl bis triphenylphosphine complex. When this is treated with $NOBF_4$, so now let us count electrons here. So, this one, let us go with neutral method. So, this is now cationic, so this in +3 state, if you go with this one 9 + 1 + 2 + I will leave it here and + 4, so now it is 16 + now this is 3 and the charge is now positive, so we have a negative.

So, since positive charge is there, you subtract 1, so it goes. So, it is 18 electron species. So, you can always verify this way to know what kind of donor nitrosyl group is. Since I told you nitrosyl when bent 1 electron donor and also when it is linear 3 electron donor. So, this helps in understanding this one. I think these four methods are sufficient and if you are interested in looking into more methods, always you can go to right kind of textbooks.

Now, let us look into the reactions of coordinated NO. So, due to the difference in the electronic structure of linear and bent coordination modes, I already mentioned, reactivity of coordinated NO can be very different. So, linear MNO groups can be readily attacked by nucleophiles, whereas in bent structure lone pair on nitrogen are susceptible for electrophilic attack, but there can be some exceptions.

Reactions of linear MNO, that is linear metal nitrosyl bonds with nucleophile such as OH^-, OR^-, SR^- or NH_2^- usually occur at the nitrogen atom, you should remember when reaction happens with linear MNO, with nucleophiles, the reaction usually occurs at N atom and also can occur at oxygen as well. So, well known example is a nitroprusside with hydroxide ion to give a nitro complex. I think let me continue showing some of these reactions in my next lecture.