Advanced Transition Metal Chemistry – Classification of Ligands by Donor Atoms
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Lecture – 34
Classification of Ligands – Nitrogen

Hello everyone. Once again, I welcome you all to MSB lecture series on transition metal chemistry. Ever since I started discussing on classification of ligands by donor atoms, I had no option other than writing lots of equations, probably it may be boring or you may think lot of memories needed. It is not true, that is the reason in my previous lecture I showed you how you can see, depending upon the lateral movements of electrons between the atoms, where electron density resides more, where electron density resides less.

And how the bond is polarized based on that one when you are using a substance, when you are using a reagent, how again that reagent polarizes before it attacks the coordinated atoms. So that in order to stress upon those things, I have no option other than writing some of these equations. Let me continue doing that one, of course it is inorganic chemistry, inorganic chemistry is incomplete without chemical equations, especially balanced chemical equations.

And then once we know how to write balanced chemical equations, we should also see the mechanistic path and all those things. For that one, understanding the sequence of reactions is very important.

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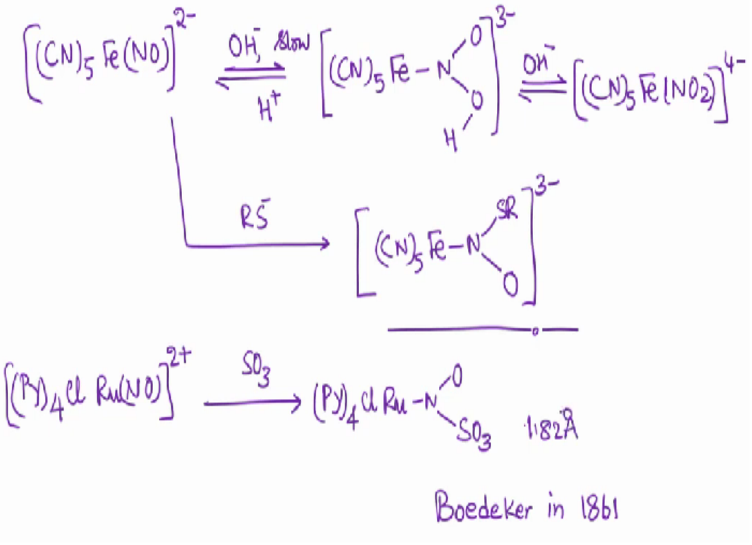

Now, let us look into some more reactions of coordinated NO. Let us take a simple NO coordinated complex pentacyanonitrosyl complex with 2– charge, use a base here, just slow step and of course if you add H will come back, it is a reversible reaction, the chare is 3– now, and again add one more OH^-; charge is 4–. So, let us consider the same starting metal complex and add RS^- so that we can make better comparison between these two reactions.

When you treat nitrosyl compounds with thiols it turns red colour and that is used for the detection of RS^- species or RS^- anions, from that point of view this is a very important reaction. Let us consider one more reaction here. Treat this one with SO_3. So, reaction of nitroprusside with sulfite to form nitrosylsulfito is the first example of a coordinated NO reported by this gentleman Boedeker in 1861. And of course, this has a very long NS bond, the NS bond distance is around 1.82 Å.

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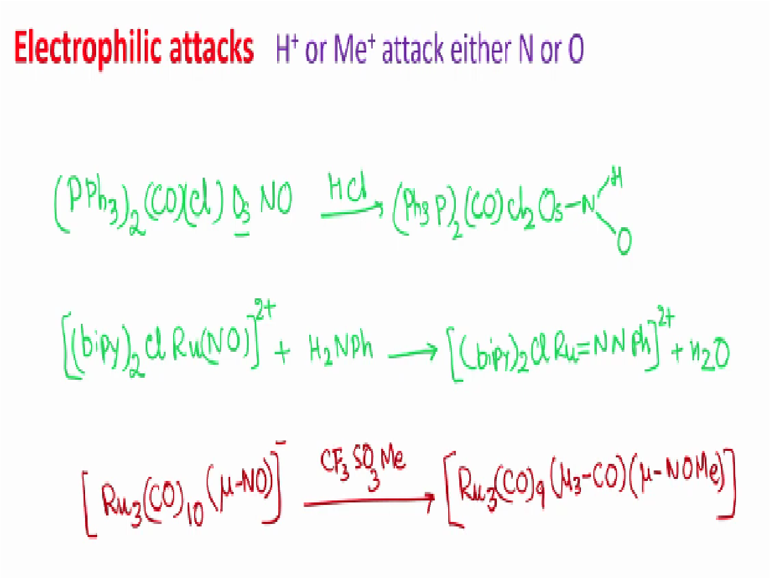

Electrophilic attacks H^+ or Me^+ attack either N or O

So, now let us look into the electrophilic attacks, example consider H^+ or Me. They can attack either N or O on a coordinated nitrosyl ligand. Let us look into both the cases. This is Osmium. On treatment of this one with HCl, it forms a component of this type. Now you know H^+ has attacked N. Now, let us look into another example, a bipyridyl complex 2,2'-bipyridyl complex of ruthenium.

While noting down these reactions, you shall also practice electron count, probably all reactants and products you should do electron count so that you will be familiar with this electron counting method. We can also have bridging nitrosyl complexes where N bridges two metal centres. What would happen if electrophilic attack occurs on a bridging NO? Let us consider one example here.

So, this is derived from $Ru_3(CO)_{12}$ a neutral carbonyl cluster. So, now, when you are replacing two carbon monoxide with one NO, NO is a 3 electron donor, so it is in short of one more electron, as a result it carries a negative charge here. So, when you treat this one with CF_3SO_3Me, it forms a complex of this type. I think this much information will do about nitrosyl ligand and the preparation of nitrosyl complexes and their further reactions with various reagents such as electrophiles and nucleophiles.

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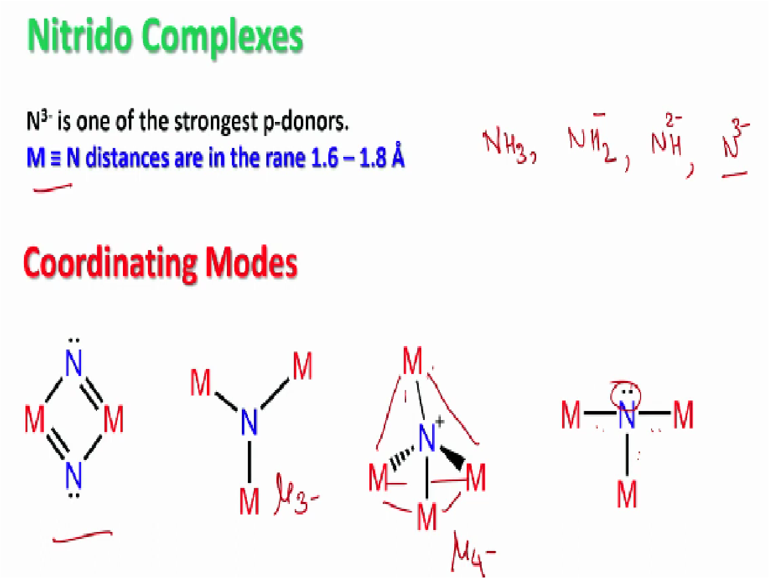

Nitrido Complexes

N^{3-} is one of the strongest p-donors.

$M \equiv N$ distances are in the rane 1.6 – 1.8 Å

NH_3, $\bar{N}H_2$, $\overset{2-}{NH}$, N^{3-}

Coordinating Modes

Now, let us move on to nitrido complexes. Consider the NH_3, from NH_3, if you remove one hydrogen, then it becomes NH_2^- amide and then if you remove one more then it becomes imide (NH^{2-}) and then if you remove the last hydrogen, then it will carry a negative charge N^{3-} then this is called nitride, nitrido complexes are also known. In fact, nitride is a 6 electron donor, is one of the strongest π-donors known.

And if you just look into $M\equiv N$ distance are in the range of 1.6 to 1.8 Å. The coordination modes I have shown here. It can bridge two metal centres in this fashion or it can also bridge three metals μ^3, it can also bridge four metal centres and there are examples where the four metals are arranged in a tetrahedral arrangement something like this. So, we will come across this kind of μ^4 bridging.

And of course, it can also bridge three metal centres in this fashion keeping the lone pair intact, so it can go to another one. So, if you see here, it is typically like ammonia here. It can be nicely compared to ammonia. We have covalent bonds, two electron covalent bonds are there and then still this lone pair is intact. Now, this can act as a metallo ligand. So, these are some of the very important coordinating modes of nitride ligand.

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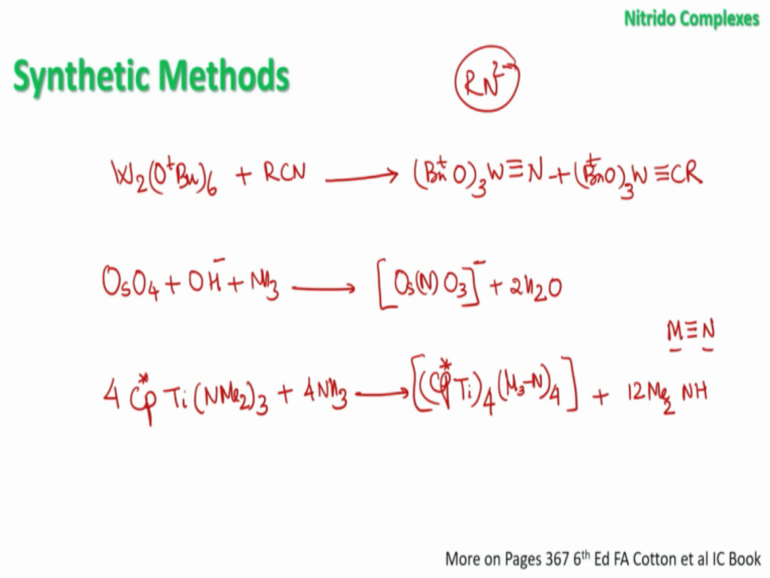

Nitrido Complexes

Synthetic Methods

RN^{2-}

$W_2(O^tBu)_6 + RCN \longrightarrow (Bu^tO)_3W\equiv N + (Bu^tO)_3W\equiv CR$

$OsO_4 + O\bar{H} + NH_3 \longrightarrow [Os(N)O_3]^- + 2H_2O$

$M\equiv N$

$4\,Cp^*Ti(NMe_2)_3 + 4NH_3 \longrightarrow [(Cp^*Ti)_4(\mu_3\text{-}N)_4] + 12Me_2NH$

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Now, let us look into the synthetic methods. So, for we are using metals in their high oxidation states. So, when this teritiarybutoxy, an alkoxy derivative is treated with isocyanide, it forms two complexes. One is nitride complex, other one is alkylidyne complex. If you take osmium tetroxide and treat with base, it can also form a nitride complex, so is giving 3 electrons, as I said one negative charge is there on this one.

And of course, whenever we write like this you should understand that we have something like this, a triple bond between metal and nitrogen. Similarly, we can also make nitrides having other ligands such as cyclopentadienyl ligand. So, here we have chosen a Cp*, Cp* means pentamethyl cyclopentadienyl. This is also called aminolysis reaction. These are some of the important methods of preparation of nitride.

And as I mentioned here if we can also make dianionic compounds of N, for example RN_2^- is there. So, this is also very important ligand in some metal complexes that can be used in metathesis and also in some organic reactions.

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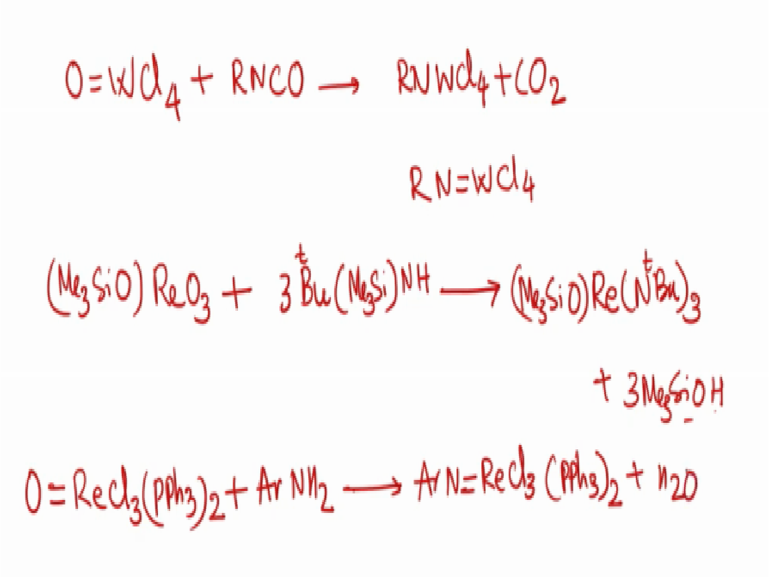

$O{=}WCl_4 + RNCO \longrightarrow RNWCl_4 + CO_2$

$RN{=}WCl_4$

$(Me_3SiO)ReO_3 + 3\,{}^{t}Bu(Me_3Si)NH \longrightarrow (Me_3SiO)Re(N^{t}Bu)_3$
$+ 3Me_3SiOH$

$O{=}ReCl_3(PPh_3)_2 + ArNH_2 \longrightarrow ArN{=}ReCl_3(PPh_3)_2 + H_2O$

So, let me give the preparatory methods of imido complexes. If you take tungsten oxytetrachloride and treat with RNCO, it forms, here we have double bond between tungsten and nitrogen. Treat this one with amide, secondary amine, we have on N, one trimethylsilyl group and a tertiary butyl group. So here, of course you keep it for a prolonged time it loses one molecule of water and it forms hexamethyldisiloxane. So, here also we have rhenium to nitrogen double bond. Take this compound and treat this one with a typical amine, aryl amine, usually here aryl groups considered are very bulky ones.

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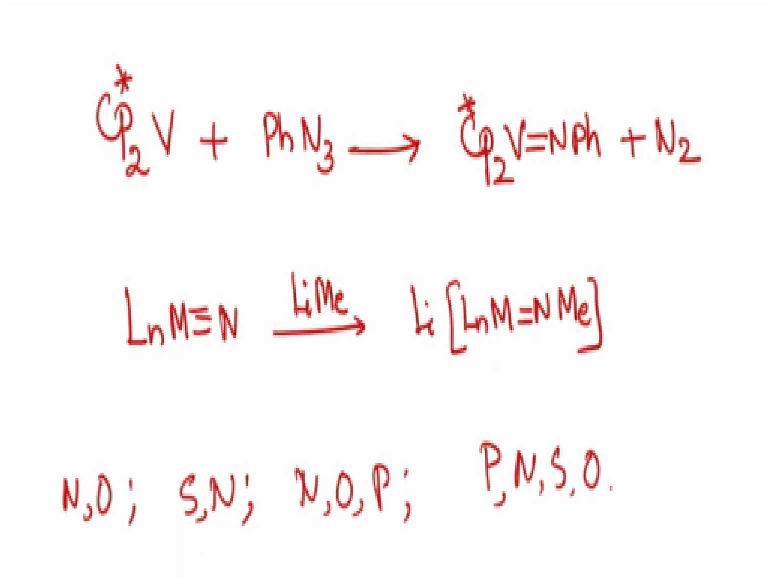

$Cp^{*}_{2}V + PhN_3 \longrightarrow Cp^{*}_{2}V{=}NPh + N_2$

$L_nM{\equiv}N \xrightarrow{LiMe} Li[L_nM{=}NMe]$

N,O; S,N; N,O,P; P,N,S,O.

Let me give you one more example here. One can also make imido complexes starting from inorganic azide such as phenyl azide. Let us consider vanadocene, here we have Cp* is pentamethylcyclopentadienyl, we have chosen or in general one can also start with a nitride complex like this. Treatment of this one with reagent such as methyl lithium can give a salt having imido bond.

So, these are some important reactions one can use to generate imide complexes and also I showed you earlier, nitride complexes. So, what are the other ligands that we have not touched when it comes to nitrogen donor ligands, we have plenty of macrocycles and also having hetero donor atoms. For example, we have N, O ligands and we have S and N donor ligands. And of course, N, O, P ligands are also there.

And there are macrocycles, where we have donor atoms such as P, N, S as well as O. So, it goes with our imagination and also the availability of appropriate reagents to make a variety of macrocyclic ligands having versatility in its coordination behaviour having several different donor atoms. And why people work with macrocycles is macrocycles have a marked kinetic stability compared to corresponding monodentate ligands.

And also they can stabilize metals in very unusual oxidation states because of chelate effect or encapsulation. And also they are very thermodynamically stable. From this point of view and also they can be very robust. When we make macrocycles, we will be having a suitable cavity and the size of cavity is also very important. When we choose the right metal of suitable size that fits into the cavity, again stability increases.

So, from that point of view, when we want to make a macrocycle or a cage like structures for a particular metal encapsulation, we have to keep all these things in mind to make sure that optimum size is left for metal to occupy that coordination site. And among amines, we have diamine, ethylenediamine is there, triethylenediamine is there; like that plenty of amines are there. Let me show you a couple of examples here.

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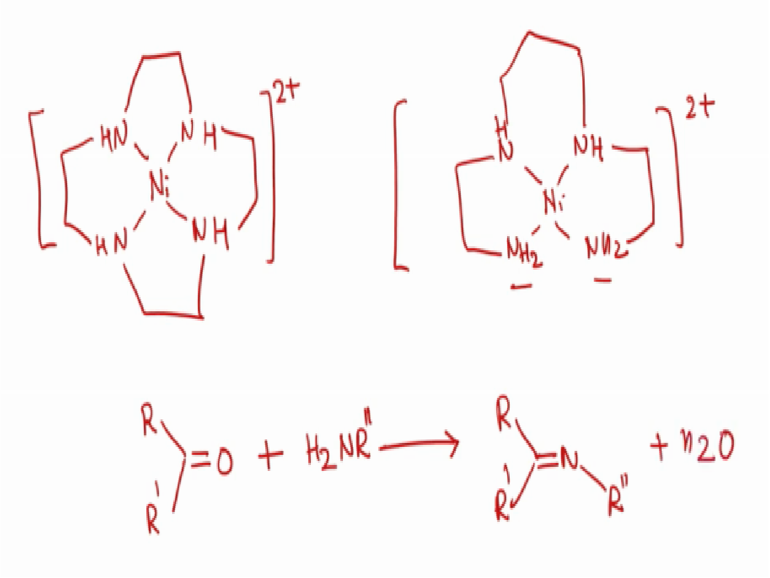

So, a typical nickel complex with neutral donor nitrogens. So, this is a cationic +2 charge. There are other types of compounds as well where one side of the chain is open having NH$_2$ moiety. Of course, in this case, completing the structure should not be any problem. So now this is another tetradentate ligand. The advantage of these things are, we can do further reactions on bound amine groups and of course we are familiar with, Schiff base ligands are very important in coordination chemistry.

Schiff base can have either nitrogen completely or nitrogen and also oxygen donors or sometimes they can be anionic so provided we have some protons that can be readily dissociated like OH group is there, SH group is there they can act as anionic ligands also. The typical preparation of Schiff bases involve the condensation of a ketone with amine, primary amine. So, this is a typical reaction that is used in making a variety of Schiff bases.

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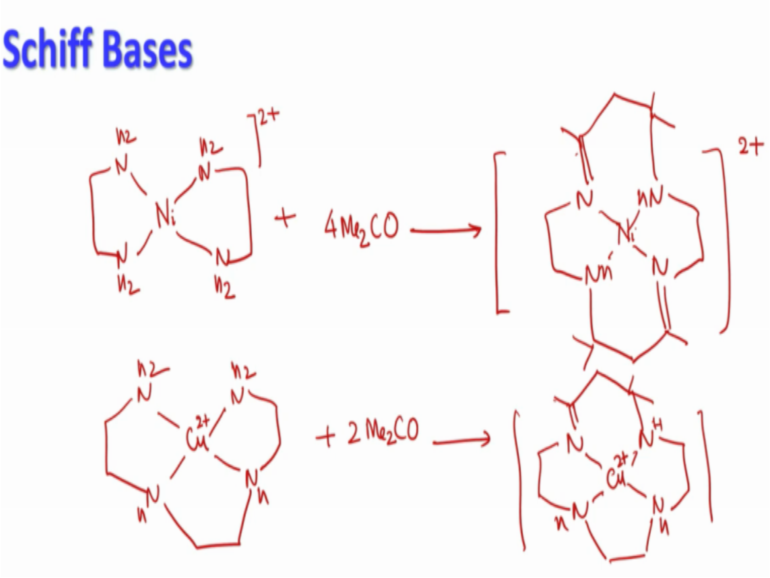

Schiff Bases

Let us look into how one can also generate a Schiff base with amine ligands bound to the metal centre. So, let us consider this cationic complex and treat this one with four equivalents of ketone. You can see here the formation of a Schiff base with bound ethylenediamine ligands. What would happen if here both sides are open, one can also perform reaction only one side is open. Let us consider another example here with copper 2+ ion.

So, this one, let us treat with the 2 equivalents of ketone here, this results in the condensation. Of course, the rest of this part does not participate in any reaction, whereas here, so this happens here. So like this, on bound amine ligands, one can also perform Schiff base reaction to generate the corresponding Schiff bases.

Let me continue talking a little bit more about nitrogen donor ligands especially giving some emphasis for macrocytic ligands in my next lecture before I conclude on nitrogen donor ligands and move on to oxygen donor ligands. Until then, have an excellent time reading coordination chemistry and try to understand the classification of ligands by donor atoms.