# Advanced Transition Metal Chemistry – Classification of Ligands by Donor Atoms

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## Lecture – 32
## Classification of Ligands – Carbon, Nitrogen

Hello everyone. Once again, I welcome you all to MSB lecture series on transition metal chemistry. This lecture is 32nd in the series. In the last few lectures, we are discussing about the classification of ligands by donor atoms and let us continue discussing on various ligands because ligands are integral part of coordination chemistry.

If you understand the nature of coordination modes, the nature of the donor atom and how they can bind and what are the binding modes, it comes very handy later when you want to use them in some applications, especially in material science or in homogeneous catalysis or even in drug discovery or in biological studies. So, from that point of view, understanding systematically the nature of the ligands and binding properties is very important.

With this let me continue from where I had stopped. In my previous lecture, I had initiated discussion on synthesis of isocyanide complexes and the reactivity of bound isocyanide complexes. With a few examples I showed you, one can make coupling products from isocyanide complexes, at least in order to see coupling reactions happening, we have to have minimum of two isocyanides on a metal centre.

And in case if we have more, probably apart from one or two, others will remain as terminal isocyanides and depending upon what stoichiometry we are using, two or more set of isocyanide ligands can participate in coupling reactions.

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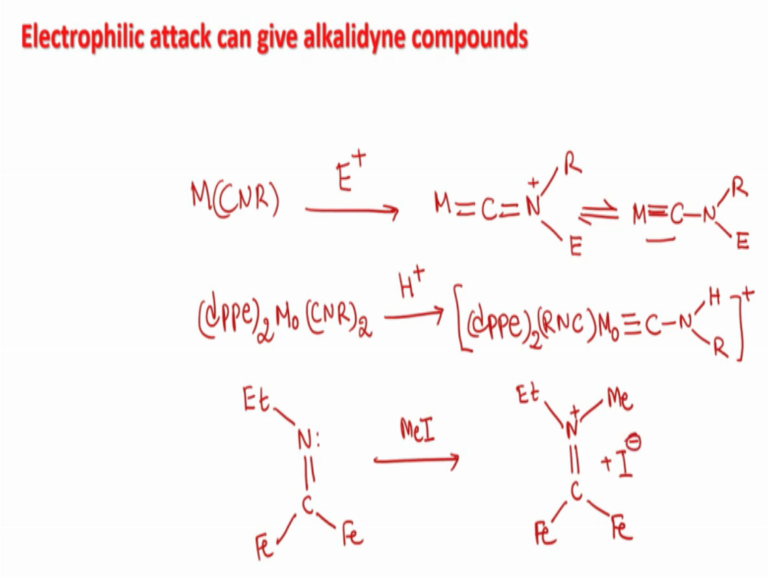

Electrophilic attack can give alkalidyne compounds

So, after completing the discussion on coupling reactions, let us look into electrophilic attack. So, usually electrophilic attack can give alkalidyne complexes. Let us start with one simple general example to make you familiar with these kinds of electrophilic reactions that happens with bonded isocyanate ligands. Just for understanding I have taken only one CNR, it does not mean that it is a monoligated metal complex or something.

Let us assume we have several other ligands on metal. And this intermediate species will be in equilibrium with, so this is the end product, you can see this is alkalidyne moity here. Let us take a specific example now to understand this reaction. Perhaps you know what is dppe; 1,2-bis(diphenylphosphino)ethane. So bridging isocyanides have very high nucleophilicity and are readily attacked.

For example, if you take a complex where isocyanide is acting as a bridging ligand, let us consider this example here, treat this one with methyl iodide, of course here. So, with these examples, let us move on to nucleophilic reactions. So nucleophile attacks either at carbon or nitrogen that can give alkalidene complexes unlike electrophilic reactions where we got alkalidyne complexes. Let us look into a few examples in this case.

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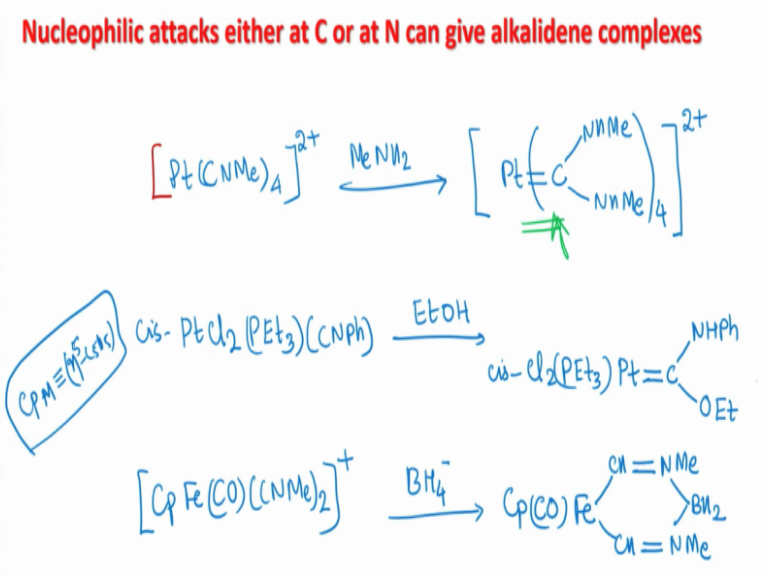

Nucleophilic attacks either at C or at N can give alkalidene complexes

So, this moiety is referred to as alkalidene. That means if you have metal to this is alkalidene and if you have metal to carbon triple bond this is called alkalidyne complex, it is like acetylene, alkyne type. Let us look into one more example here. When you treat this one with the ethanol, this is another interesting example for the formation of alkalidene complex. So, unless otherwise no specification is given when Cp is written assume it cyclopentadienyl ligand having hapticity of eta 5.

So, in general one should remember if nothing is mentioned about this one and if something is shown this indicates it is $\eta^5$-$C_5H_5$, so iron in +2 state. Then this is treated with sodium borohydride. I have given three different types of examples to show how nucleophilic reaction occurs either at carbon or at nitrogen that leads to the formation of alkalidene complexes. With this, I stop discussion on ligands having carbon as donor atom.

Of course, as I mentioned carbon monoxide is the most common ligand with respect to carbon donor atoms. And since you are all familiar with carbon monoxide, I did not discuss in an elaborated manner about those compounds, nevertheless we came across it while discussing lot of other reactions of CO compounds or metal complexes having one or more CO.

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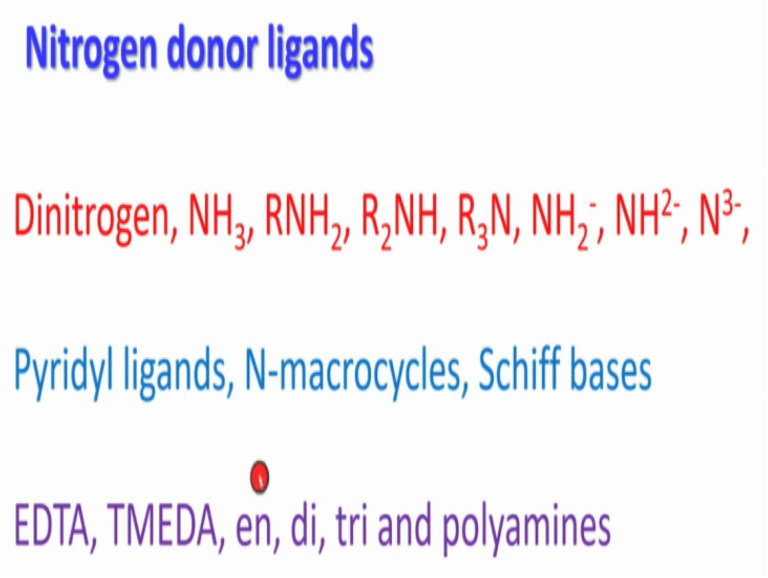

Nitrogen donor ligands

Dinitrogen, $NH_3$, $RNH_2$, $R_2NH$, $R_3N$, $NH_2^-$, $NH^{2-}$, $N^{3-}$,

Pyridyl ligands, N-macrocycles, Schiff bases

EDTA, TMEDA, en, di, tri and polyamines

Now, let me move on to nitrogen donor ligands. Nitrogen donor ligands are plenty. One can see the list here, it is never ending. The simplest but hard ligand with very weak sigma donor and very weak pi acceptor ability is dinitrogen, a neutral ligand. It can be a two electron donor or it can be four electron donor. And then ammonia the most common classical ligand we come across and then all primary amines, both alkyl and aryl and also secondary amines and tertiary amines.

And of course, from $NH_3$, if you eliminate one H it leads to the formation of $NH_2^-$ this can also act as a ligand or if you remove two hydrogens then we get amide and then if we remove all the hydrogen atoms then we get nitride. All these are very good ligands and numerous examples are known in each case. And when we come to cyclic heterocycles, where the pyridine ligands are very prominent. We have plenty of pyridine ligands and also N-macrocycles and also Schiff bases.

And apart from this we also have EDTA, ethylenediaminetetraacetic acid where we have 2 nitrogen atoms along with 4 carboxylate oxygens and TMEDA another very useful ligand, tetramethylethylenediamine (TMEDA) and ethylenediamine itself is an excellent bidentate ligand that forms very stable five membered rings. And also, apart from ethylenediamine we also have diamine, triamine, tetramine and also polyamines.

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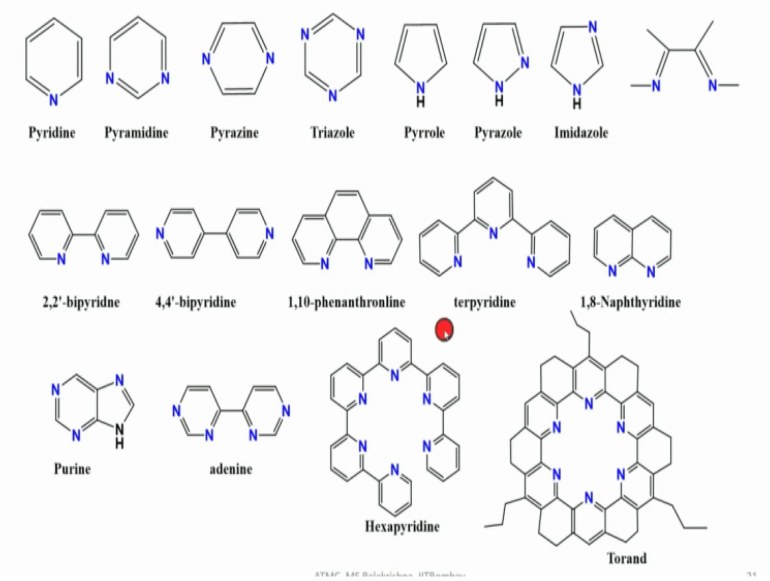

To make you familiar with nitrogen donor ligands, I have listed some important nitrogen heterocycles here, you can see lot of, this can be a bidentate ligand, this can also be a bidentate ligand. This triazole can be tridentate ligand and pyrrole can act as an anionic ligand. Besides acting as anionic ligand, it can also act as a neutral ligand, 4 electron donor when it is $N^-$ and imidazole we have and we have something like this, imino system.

And when it comes to bipyridines we have 2,2'-bipyridine, very useful for chelating to a metal centre. And this is very useful for bridging especially. This ligand is widely used in making metal organic frameworks. And then in photophysical studies 1,10-phenanthroline is very important and terpyridine and also 1,8-naphthyridine, purine, adenine and also we have hexapyridine, torand.

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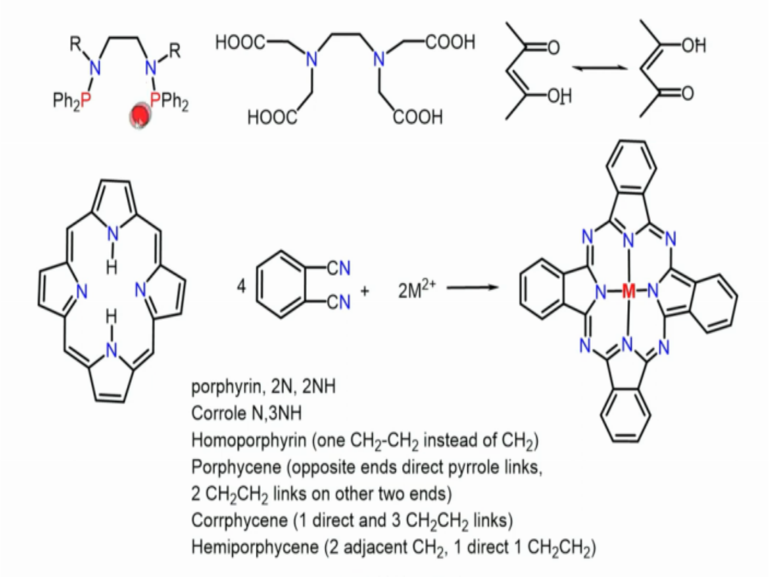

porphyrin, 2N, 2NH
Corrole N,3NH
Homoporphyrin (one $CH_2$-$CH_2$ instead of $CH_2$)
Porphycene (opposite ends direct pyrrole links, 2 $CH_2CH_2$ links on other two ends)
Corrphycene (1 direct and 3 $CH_2CH_2$ links)
Hemiporphycene (2 adjacent $CH_2$, 1 direct 1 $CH_2CH_2$)

Apart from those, we also have ethylene derived phosphine, here nitrogen can also act as a ligand. Many times, when nitrogen is very close to phosphorus because of the establishment of multiple bonds between phosphorus and nitrogen, on most of the occasion nitrogen lone pair is not available for bonding. In this case, although nitrogen is trivalent what happens phosphorus is taking electrons from nitrogen lone pair to its sigma star, so that we call it as negative hyperconjugation.

In case of metal complexes, we call it as back bonding. Because of these things, whenever a nitrogen is next to phosphorus, it loses its donor abilities because its lone pair participates in binding with phosphorus. In some books they say it is dπ-pπ interaction, it is not dπ-pπ interaction, it is dπ-σ* interaction that is called negative hyperconjugation. And of course, ethylenediaminetriacetic acid, I told you this will always exist in the stable form having here zwitterionic form.

And that is the reason if you look into the pK a, third and fourth pK a values are very high because it is on NH and not so easily it can be deprotonated. And acac is there and that is of course this is an oxygen donor ligand. An then we have porphyrins, the simplest porphyrin, I will show you at the end how to prepare this one. And another one is phthalocyanine. Phthalocyanine is prepared from this dicyanobenzene.

And one should remember that this can be prepared only in presence of a metal so that this grows surrounding the metal that means it is an encapsulating ligand. And then it usually does not exist independently without metal ion. And of course, about these things, I already mentioned in one of my previous lectures.

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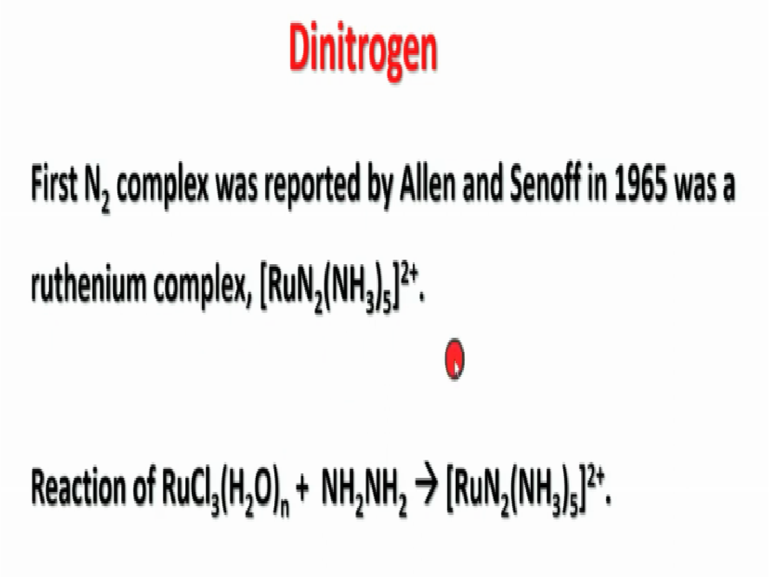

Dinitrogen

First $N_2$ complex was reported by Allen and Senoff in 1965 was a ruthenium complex, $[RuN_2(NH_3)_5]^{2+}$.

Reaction of $RuCl_3(H_2O)_n$ + $NH_2NH_2$ → $[RuN_2(NH_3)_5]^{2+}$.

So now let us look into few ligands one at a time. Let us first look into dinitrogen. And dinitrogen chemistry is very important because we have plenty of it in the atmosphere. One can make lot of useful nitrogen compounds, as simple as ammonia. People always look for very mild conditions to make ammonia unlike Haber's process that requires high temperature and high pressure.

For that one, the better option is looking for ideal metal complexes. So, the first dinitrogen complex was made by Allen and Senoff in 1965. They used this method of treating ruthenium trichloride trihydrate with hydrazine to get this pentaammine dinitrogen ruthenium dicationic complex. Of course, we have several methods, I shall tell you later.

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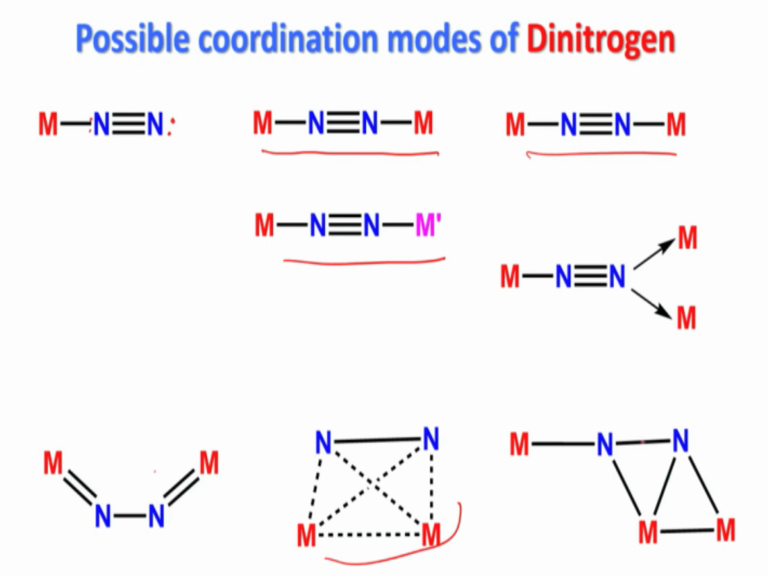

Possible coordination modes of Dinitrogen

First let us look into the possible coordination modes of dinitrogen. So, nitrogen if you see here, this has two lone pairs are there. So, these lone pairs can go to metal, so it can act as a terminal ligand or it can also act as a bridging ligand where both the lone pairs on nitrogen are utilized and of course this is same as that one and of course you can also have two different metals, homobimetallic system or heterobimetallic system.

You can have or this lone pair can go to two metals, so you can have a trimetallic system or we can cleave one of the bonds in this fashion you can also form some sort of imino type compound here where we have this bent structure or one can also see this kind of binding or one can also see this kind of binding also once if we break two bonds between nitrogen atom.

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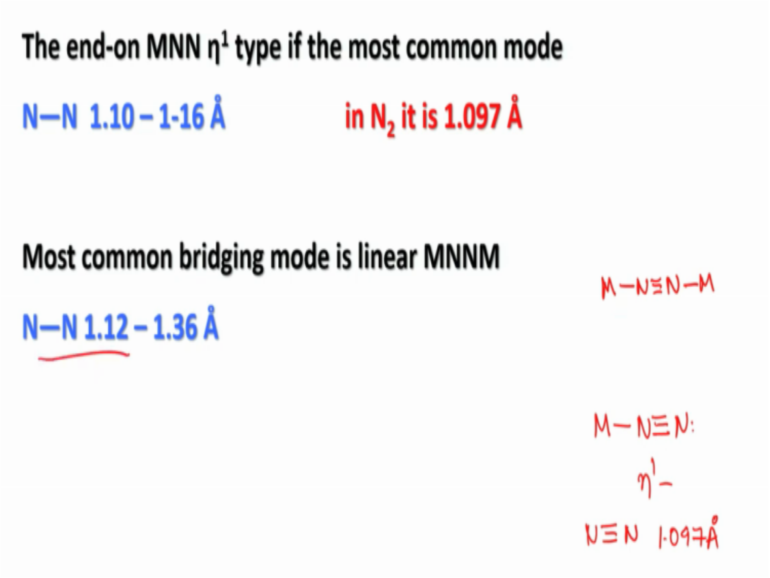

The end-on MNN $\eta^1$ type if the most common mode

N—N 1.10 – 1-16 Å    in $N_2$ it is 1.097 Å

Most common bridging mode is linear MNNM

N—N 1.12 – 1.36 Å

$M-N\equiv N-M$

$M-N\equiv N:$

$\eta^1-$

$N\equiv N$ 1.097Å

The end-on; the end-on is when we have 1, so $\eta^1$ type is the most common mode. In most of the metal complexes we see this one and, whereas other lone pair remains intact. This is the most common one, this is called end-on and this also called as $\eta^1$ mode. this is the most common one. And just if you look into free nitrogen, in free nitrogen the distance between N-N is 1.097 angstrom units.

Whereas in case of nitrogen compounds it increases and it can range anywhere between 1.10 to 1.16 Å. Most common bridging mode is linear, this is the one. So, that means you can assume that the triple bond is still intact that indicates that the bridging nitrogen is linear, it is almost close to 180 degrees, in that case what happens N-N distance will be around 1.1 to 1.36 Å. So, now let us look into the synthesis of nitrogen complex. if I want to make for a specific application, how to make dinitrogen complexes in the laboratory.

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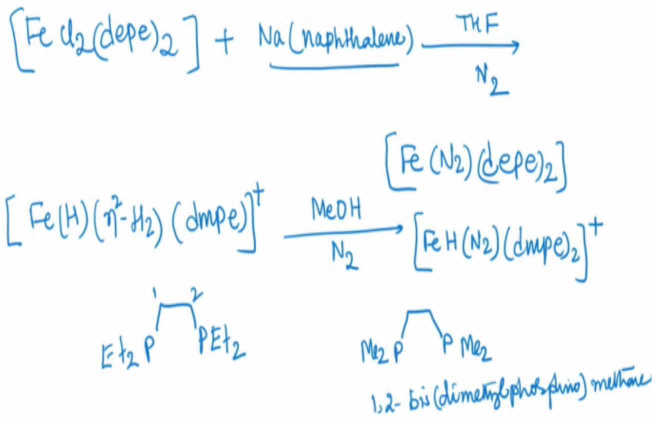
Synthesis of $N_2$ complexes



First one is the reduction method. Of course, reaction has to be carried out under positive pressure of nitrogen because we are inserting nitrogen. This is one of the methods, of course here depe is bisdiethylphosphinoethane, very similar to dppe, so 1,2-bis(diethylphosphino)-ethane and this is a chelating ligand, so chelating ligands are in this fashion and it is a square pyramidal molecule.

So, one is using a reducing agent, you can do substitution reaction that means replacing one neutral ligand with another one. Example if we take, treat this complex with $N_2$ in methanol, it can just simply substitute hydrogen molecule to form dinitrogen complex. As I mentioned, depe is nothing but as you can see 1,2-bis(diethylphosphino)ethane and similarly this is also 1,2-bis(dimethylphosphino)ethane. So, these two are widely used methods in the preparation of dinitrogen complexes.

Of course, if you want to look into more always you can go to Advanced Inorganic Chemistry by F A Cotton and others, you can see a lot of examples and also you can see some literature that one can use and also reviews are there about dinitrogen complexes, one can get more details. So, before I proceed to look into reactivity of coordinated nitrogen, let me show you some similarity between various other ligands.

For example, ligands such as isocyanide, carbon monoxide, dinitrogen or nitrosyl ligand we can perform at least two types of reactions, if not three. So, they are nucleophilic substitution reactions or nucleophilic or electrophilic reactions. That means how electrophilic reactions and nucleophilic reactions can be started in these, let us look into some similarities.

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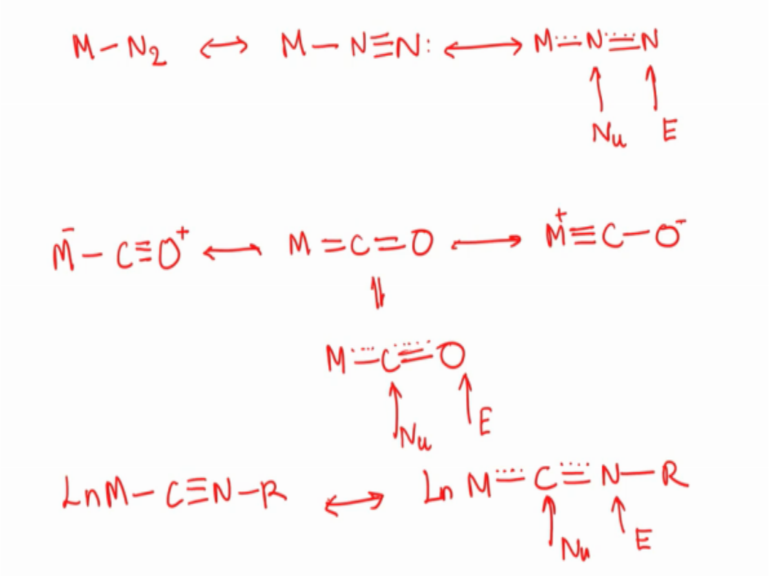

So, M-$N_2$ can be conveniently written in this fashion. So, that means this one we can show in a format like this, due to the movement of electrons, so something like this. So, now, the moment I write like this, delocalization of electrons you should be able to know where nucleophilic attack happens and where electrophilic attack happens, one should remember about this one.

So, later when you are using electrophilic attack or perform nucleophilic attack, you should be able to tell, where this nucleophile and electrophile are going to attack the bound ligands. This is very similar to what we come across in case of carbon monoxide. Carbon monoxide if I take like this to start with has a positive charge and it has a negative charge, that means electron rich because now carbon monoxide has donated a pair of electrons to sigma bonding.

As a result, what happens there will be net positive charge and then depending upon how much back bonding occurs, next stage is something like this, almost we have ketonic and bond strength is weakening as far as CO is concerned. And then in the extreme case what happens, one can see something like this, this one, so more and more electrons are donated from metal to π* and as a result, what happens, metal to carbon bond strength increases and CO becomes weaker.

And now if we consider this one something like this, we can see here something like this. So, now we can see how nucleophilic attack happens, where electrophilic attack happens and same strategy one can be used to understand the reactivity of bonded cyanide as well, isocyanide as well. Now, you can see the similarities between some of these ligands. So, since similarities we are seeing, that is the reason, we can see a variety of reactions that happens on bonded one.

So, in some cases, coupling can happen readily, but invariably you can come across nucleophilic as well as electrophilic reactions. Let us look into more such reactions with bonded nitrogen that is very important from synthetic point of view. Until then have an excellent time reading chemistry, especially coordination chemistry and especially getting more information from textbooks about the ligands and their behaviour when they are brought very close to the metal centre.