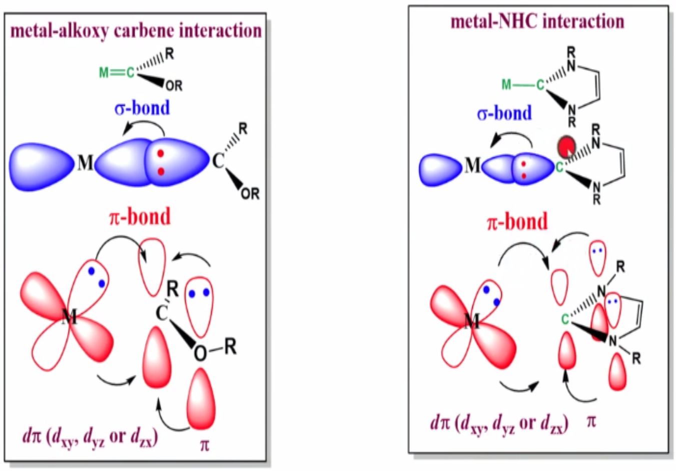
Advanced Transition Metal Chemistry – Classification of Ligands
Prof M. S. Balakrishna
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture – 30
Classification of Ligands - Carbon

Hello everyone. I once again welcome you all to MSB lecture series on transition metal chemistry. This lecture is 30th in the series. In my previous lecture, I started discussion on ligands having carbon as donor atoms, let me continue from where I had stopped. So, I showed you about the difference between Fisher carbene and Schrock carbene.

(Refer Slide Time: 00:42)

Bonding interactions between metal and various σ/π ligands



C→ M σ-donation + M→C π- backbonding + heteroatom→ C π- donation

And we have one more carbene called N-heterocyclic carbon and if we just look into N-heterocyclic carbene this is how a typical N-heterocyclic carbene looks like and this carbon has a lone pair very similar to carbon monoxide and that can be given to metal through sigma bond and then it has pi star, two pi star. It can take electron density from metal through back bonding. So, it also comes under nonclassical ligands along with carbon monoxide, phosphines and other olefins. I have also shown how the sigma bonding happens here.

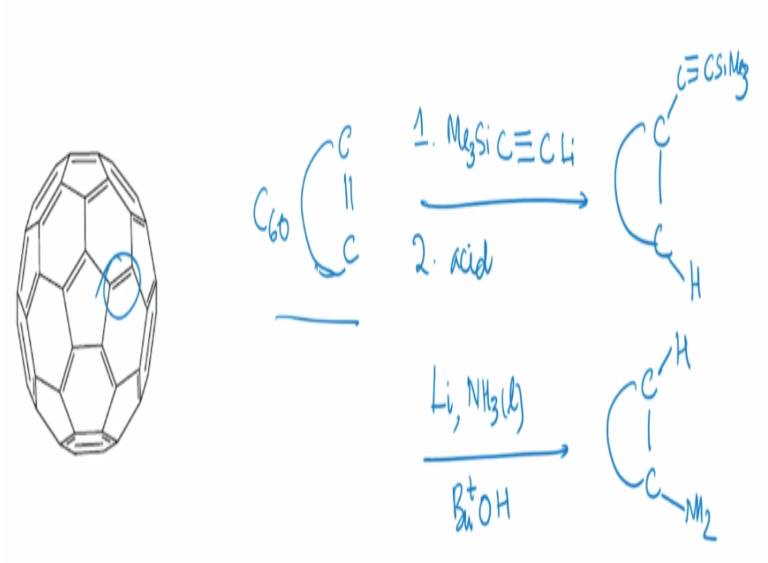
Sigma bond you can see here and then the back bonding again, pi star is there. And if you can see, when we have this pi star on carbon, there is a competition for electron donation from both metal as well as nitrogen, which has a lone pair. As a result, what happens it is always very easy it to take electron density within the molecule, rather than you know, taking from metal. As a result, what happens it has less inclination to take electrons from metal through back bonding.

As a result, what happens it is a good sigma donor, but relatively weak pi acceptor, compared to carbon monoxide or tertiary phosphines, for the same reason. Of course, this kind of lone pair of nitrogen coming to carbon pi star is also called "negative hyper conjugation" and that is more pronounced in case of phosphorus nitrogen bonds. And also, one way the back bonding from metal to phosphorus sigma star orbitals which is also called as negative hyperconjugation.

That means this N-heterocyclic carbenes as carbon donors can mimic similar type of chemistry, we come across with carbon monoxide and olefine chemistry and also phosphines and also they are as good as phosphines in some organic transformations as catalysts. And then of course in metal-alkoxy carbon interaction very similar this carbon lone pair goes to the metal through sigma bonding and once again here also metal gives electrons to pi star of carbon through back donation.

And once again here, oxygen lone pair also competes for this one. As a result, these alkoxy carbines and N-heterocyclic carbenes are relatively poor pi-acceptors compared to carbon monoxide and phosphines. I hope it is clear now, through orbitals, also I have shown how they interact while doing back bonding or in sigma bonding.

(Refer Slide Time: 03:15)

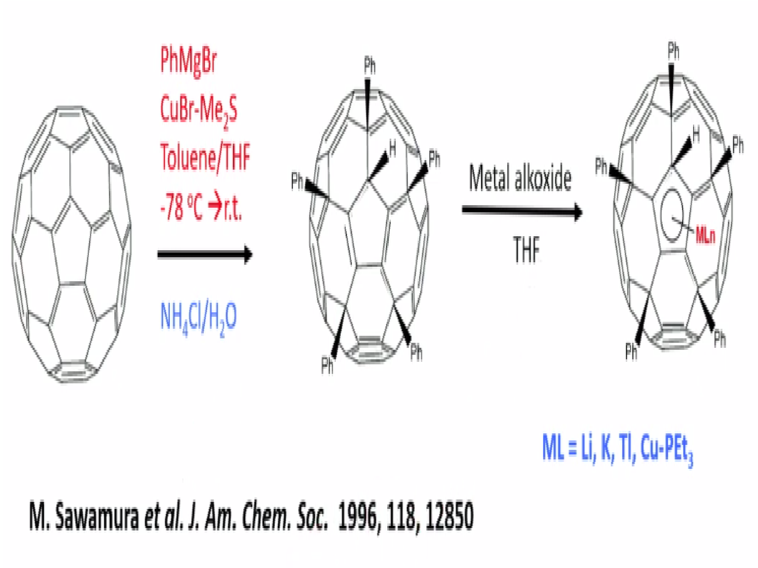


So, this is called fullerene and fullerene if you consider one side or one double bond. These double bonds can behave as isolated double bonds we come across in olefin. That means whatever the reactions we perform on olefins such as ethylene, similar reactions can be performed here. Let me show you a couple of reactions here. So, let us consider when isolated double bond something like this and this whole moiety I should call it as C_{60}.

So, if I am considering one of these double bonds, there is no harm in writing something like this, in this way you can represent and then let me treat this one with lithiated alkyne such as Me_3Si and then followed by adding acid. So, it can be a compound like this. In a similar way, in another reaction, if I take lithium in liquid ammonia giving and later add tertiary butanol it can form NH_2, so amination reaction can also be performed.

So, that means fullerene can also be considered as a simple organic molecule and one can perform reactions as shown here. There are several other similar reactions.

(Refer Slide Time: 05:09)

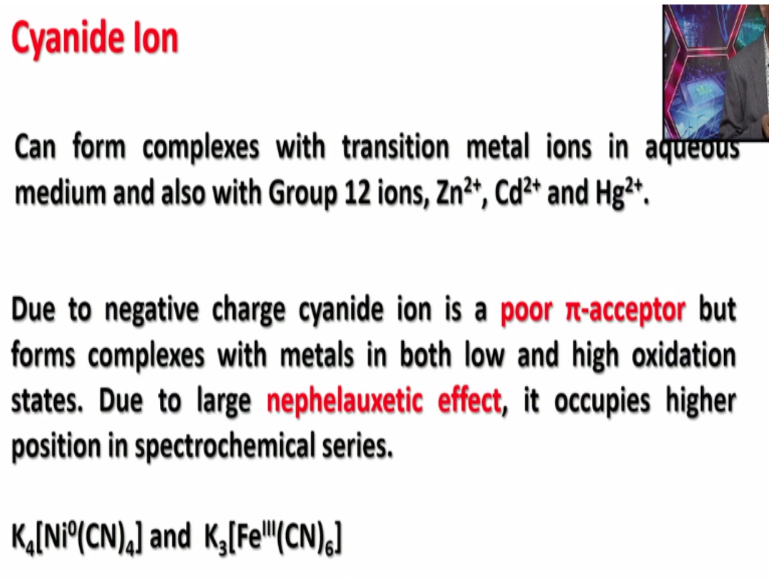


M. Sawamura *et al. J. Am. Chem. Soc.* 1996, 118, 12850

Another reaction I have shown here. You take this fullerene C_{60} and treat with Grignard reagents such as phenyl magnesium bromide in the presence of this cuprous bromide complex having dimethyl sulphide and you take this one in toluene and THF mixture at –78 ºC and addition has to be done at –78 ºC and then it should be warmed to room temperature and then excess of this one can be quenched using aqueous ammonium chloride that leads to the formation of this.

Yeah, can you recall, now it resembles C_5H_6, cyclopentadiene and when you add metal alkoxide to it, I have given metal alkoxides as one of these things here in THF and you can make it η^5 and you can see how sandwich compounds coming something like this. So, that means, one of the five membered rings can also be utilized as an η^5 ligand from C_{60}. This was reported in 1996. If you want more information, you can refer to this journal here.

(Refer Slide Time: 06:20)



Cyanide Ion

Can form complexes with transition metal ions in aqueous medium and also with Group 12 ions, Zn^{2+}, Cd^{2+} and Hg^{2+}.

Due to negative charge cyanide ion is a poor π-acceptor but forms complexes with metals in both low and high oxidation states. Due to large nephelauxetic effect, it occupies higher position in spectrochemical series.

$K_4[Ni^{0}(CN)_4]$ and $K_3[Fe^{III}(CN)_6]$

Now look into another important ligand among carbon donor ligands, that is cyanide ion. It can form complexes with transition metal ions in aqueous medium and also with group 12 ions, group 12 means zinc, cadmium, mercury. They have completely filled electronic configuration that means n $d^{10}(n+1)s^2$. Nevertheless, it can also form complexes with these metal ions also. Due to negative charge, cyanide ion is a poor pi acceptor.

That means due to that negative charge, cyanide ion is a poor pi acceptor, but forms complexes with metals in both low and high oxidation states. Due to large nephelauxetic effect, it occupies higher position in spectrochemical series. So, otherwise it should have been much lower, we come across something called as nephelauxetic effect and because of this one it occupies higher position in spectrochemical series.

I have given two very important complexes here. You can see here nickel in 0 valent state, tetracyanonickelate and counter cations have shown as potassium. This is one example of cyanide stabilizing metal in low valence state and of course we have another one here stabilizing iron in +3 hexacyanoferrate. I shall elaborate more about nephelauxetic effect and also how this is related to Racah parameters when I talk about electronic spectroscopy.

Nevertheless, I should tell you a little bit about nephelauxetic effect before I proceed. So, when an atom has more than one electron, there will be some electrostatic repulsion between those electrons you should remember that. The amount of repulsion varies from atom to atom depending upon the number and spin of the electrons and the orbitals they occupy. So Racah parameters were generated as a means to describe the effect of electron-electron repulsion within the metal complexes arising due to the formation of metal to ligand bond.

The Racah parameters are A, B and C. In the case of Tanabe-Sugano diagrams, each electron configuration split has an energy that can be related by the B value and also one can also use Orgel diagram to predict and calculate Racah parameters for various electronic configurations. The decrease in the Racah parameter B, as I mentioned A, B, C are there and the decrease in the Racah parameter B indicates that in a complex there is less repulsion between the two electrons in a given doubly occupied metal d orbital.

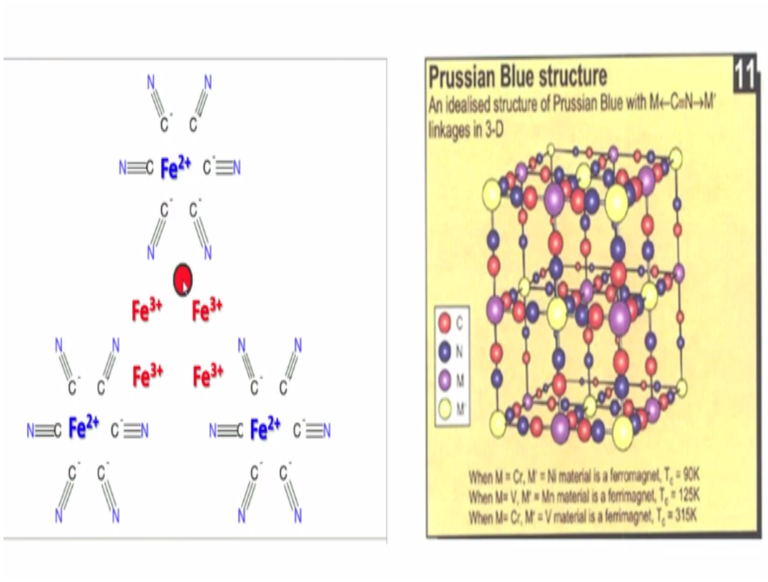
That means in e_g in their respective M^{n+} gaseous metal ion before it enters into ligand field. So, which in turn implies that the size of the orbital is larger in the complex. So, this electron cloud expansion effect may occur for one or both of two reasons. That means this expansion of electron count can be attributed to two important reasons. One of the two reasons is that the effort to positive charge in the metal has decreased because more and more electron density is coming from ligands through sigma donation.

Since the positive charge of the metal is reduced by any negative charge on the ligand, the d orbital can expand slightly. You should remember, I tell you again, since the positive charge of the metal is reduced by any negative charge on the ligand, especially anionic ligands approaching the metal, the orbitals can expand slightly so the overlapping with the ligand orbitals and forming covalent bonds increases orbital size, because the resulting molecular orbital is formed from two atomic orbitals.

So, the reduction of B from its free ion value is normally reported in terms of nephelauxetic parameter that we see in case of cyanide ligands that is the parameter beta (β) is nothing but the ratio of the B value of complex to the B value of free ion. Experimentally, it is observed that the size of the nephelauxetic parameter always follows a certain trend with respect to the nature of the ligand present.

So, I think you should remember to this extent about nephelauxetic effect and how Racah parameters are related to this one. When I discuss about electronic spectroscopy, I shall show you how to calculate by taking one or two examples.

(Refer Slide Time: 11:03)



Prussian Blue structure

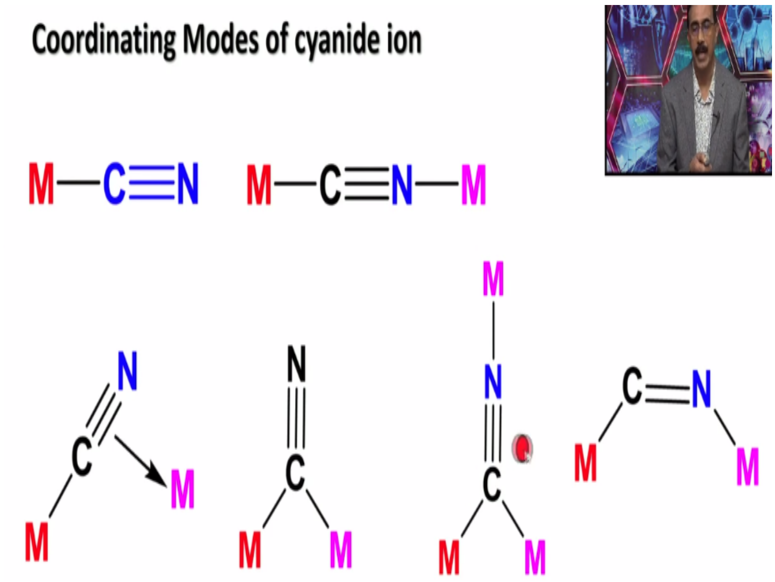
An idealised structure of Prussian Blue with M←C≡N→M' linkages in 3-D

When M = Cr, M' = Ni material is a ferromagnet, T_c = 90K
When M= V, M' = Mn material is a ferrimagnet, T_c = 125K
When M= Cr, M' = V material is a ferrimagnet, T_c = 315K

So, this one is Prussian blue, actually when you see textbook, they show simple $K_4[Fe(CN)_6]$ or something like that, actually this has $3Fe^{2+}$ ions and $4Fe^{3+}$ ions and Fe^{2+} ions are surrounded by 6 cyanides in this fashion and then these are surrounded by N binding in this fashion. So, this has a complex structure. If you are curious, this is how the structure looks like.

You can see here iron, the middle iron in +3 state are coordinated from six directions having octahedral geometry, in this fashion, and this continues in three dimensional form. So, this is how it looks like, for clarity, you can see the labelled carbon atoms with the different colour that should tell you how the arrangement is made for this Fe_{3+} and Fe^{2+} in the lattice. So, cyanide is one of the very important ligand in coordination chemistry.

(Refer Slide Time: 12:09)



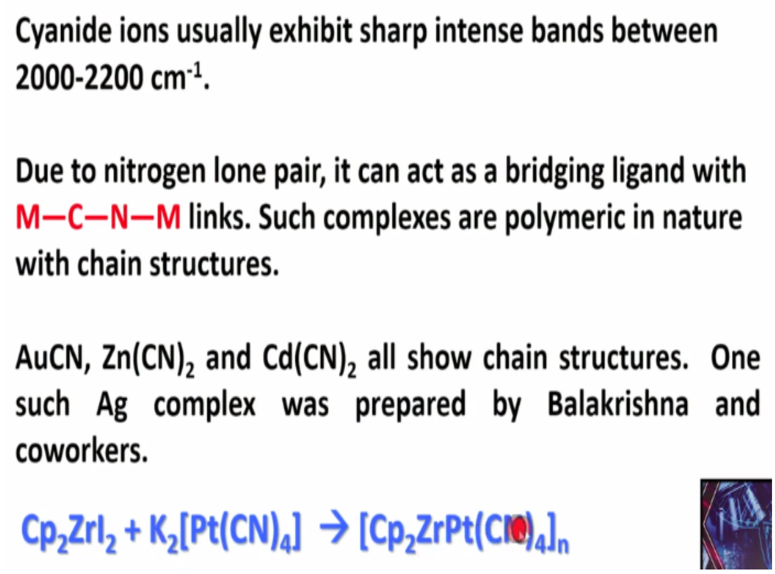
Coordinating Modes of cyanide ion

$M-C\equiv N$ $\quad$ $M-C\equiv N-M$

Let us look into the coordinating modes of cyanide ion. The simplest one is the terminal in this fashion and you should remember we have a lone pair on nitrogen, so it can also form bridging or dimetallic complexes through both carbon and nitrogen bond something like this. And also this triple bond can also coordinate to metal in this fashion or this carbon itself can bind to two metal centres very similar to carbon monoxide, bridging can be this type.

And you should remember there still, we are left with a pair of electrons here. So, third metal can come and coordinate to N in this fashion or if its bond is reduced, it can have a bent structure something like this, where both carbon and nitrogen are making bond with two same or different metals, it can be homo or hetero bimetallic complex. So, these are some of the important coordinating modes of cyanide ion.

(Refer Slide Time: 13:10)



Cyanide ions usually exhibit sharp intense bands between 2000-2200 cm^{-1}.

Due to nitrogen lone pair, it can act as a bridging ligand with $M-C-N-M$ links. Such complexes are polymeric in nature with chain structures.

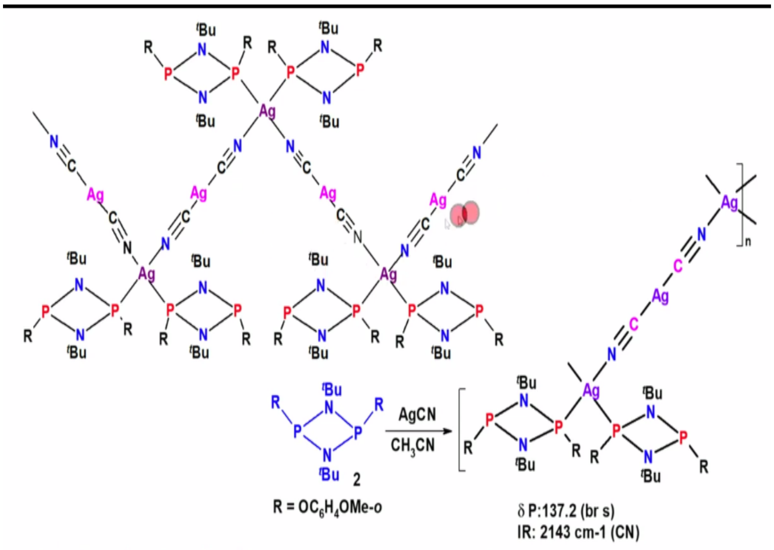
AuCN, $Zn(CN)_2$ and $Cd(CN)_2$ all show chain structures. One such Ag complex was prepared by Balakrishna and coworkers.

$Cp_2ZrI_2 + K_2[Pt(CN)_4] \rightarrow [Cp_2ZrPt(CN)_4]_n$

Then how to characterize cyano complexes to confirm that we have cyanide and it has a particular type of coordination mode, that comes from analytical and spectroscopic data. The important one is IR. So, IR shows a sharp intense band between 2000 to 2200 cm^{-1}. Due to the nitrogen lone pair, it can act as a bridging ligand with M-C-N links that is what I mentioned. So, such complexes are polymeric in nature with chain structures.

One such example I showed you that one is Prussian in blue and gold cyanide, zinc cyanide and cadmium cyanide all show chain structures. One such silver complex was also prepared in my group and that I will show you in the next slide. And for example, here you can see when zirconocene diiodide, this is called zirconocene diiodide, it is treated with hexacyanoplatinate to form a heterobimetallic complex of this type, it has a polymeric structure.

(Refer Slide Time: 14:15)



R = OC_6H_4OMe-o

δP:137.2 (br s)
IR: 2143 cm-1 (CN)

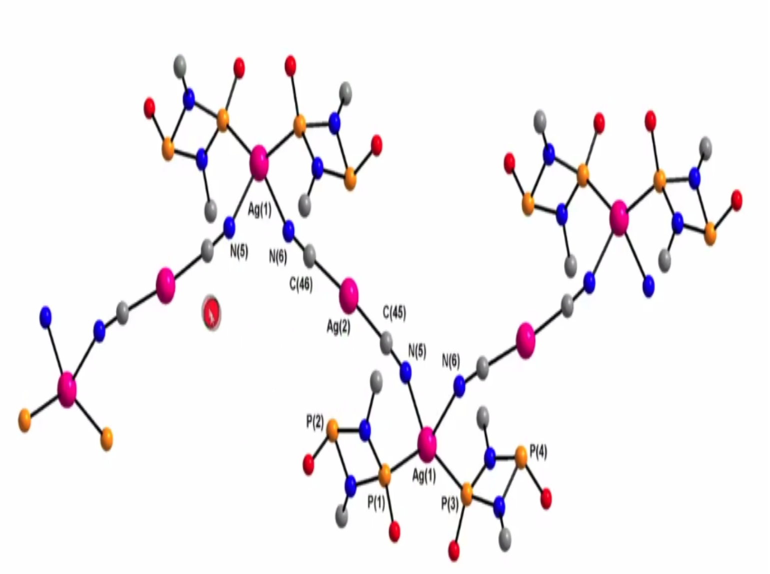
Chandrasekaran, P.; Mague, J. T.; Balakrishna, M. S. Dalton Trans. 2007, 2957.

You can see here, this is called cyclodiphosphazane. It is an inorganic heterocyclic ring having alternate phosphorus and nitrogen atoms and it is planar and phosphorus has a pair of electrons. Now, this one has a cis confirmation and this acts as a wonderful ligand system and we have explored its rich coordination chemistry and organometallic chemistry and also its utility in various applications.

So, one such ligand I have shown here. So, when this ligand, bridging bidentate ligand is treated with silver cyanide in acetonitrile, it forms one dimensional chain of this fashion. You can see here, silver is tetracoordinated having a tetrahedral geometry and two phosphorus from two different N_2P_2 rings are binding here and one nitrogen of cyanide is binding here and this one is cationic.

And this fragment is anionic because two cyanides are there, so that means charge balance is there. This is an anion, this is a cation and here one is four coordinated, one is two coordinated and it grows to have something like this, zigzag one-dimensional polymeric structure.

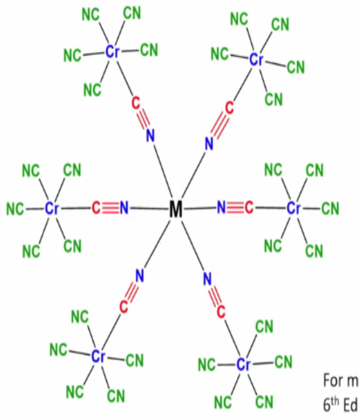
(Refer Slide Time: 15:33)



So, this is how the x-ray texture depicts for this molecule.

(Refer Slide Time: 15:36)

In K[FeCr(CN)$_6$], the green isomer has Fe^{II}—CN—Cr^{III} bridges, whereas the red isomer has Cr^{II}—CN—Fe^{III} linkages.



M = Si^{IV}, Ge^{IV}, Sn^{IV}

and

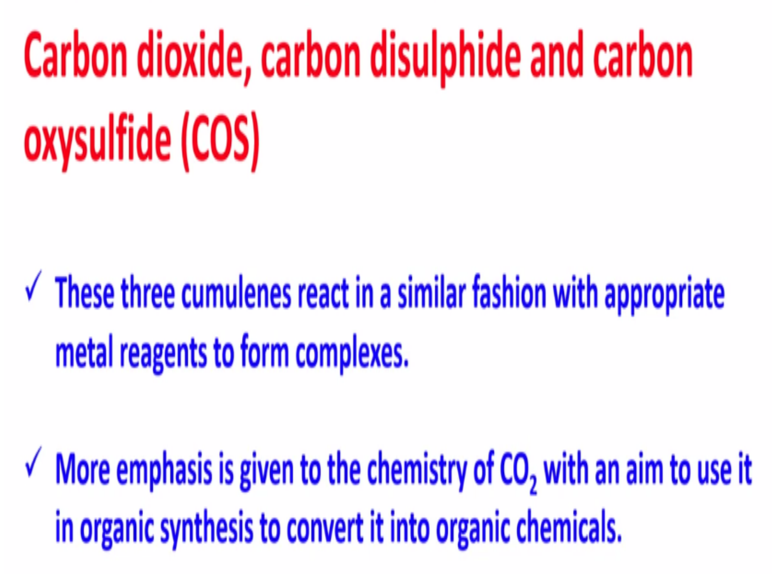
M = Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{I}, Zn^{II}, Co^{0}, Mo^{0} and W^{0}

For more examples please see **Advanced Inorganic Chemistry**
6th Edition FA Cotton, G Wilkinson, CA Murillo, M Bochmann
Pages 244-246

Another interesting compound is there. You can see here, where cyanide acting as terminal as well as the bridging ligand. For example, you see here KFeCr$(CN)_6$, the green isomer, that means it exists in two isomeric forms. Green isomer has iron 2 and cyanide 2 and chromium 3 binding to N, whereas in case of red isomer, opposite is true: chromium 2 binds to carbon and then iron 3 binds to nitrogen linkages, one such isomer, I have shown here. Of course, you should be able to tell which isomer it is.

Whether it is green isomer or red isomer from this data, from this information you should be able to tell. And here M can be a main group element as well, for example silicon, germanium or tin can also be used here and other metals such as chromium 3, manganese 2, or iron 2; so all these. That means you can make a series of complexes of this type here. And if you again want more information, very useful information is there if you read Advanced Inorganic Chemistry 6th edition and this information is there.

(Refer Slide Time: 16:44)



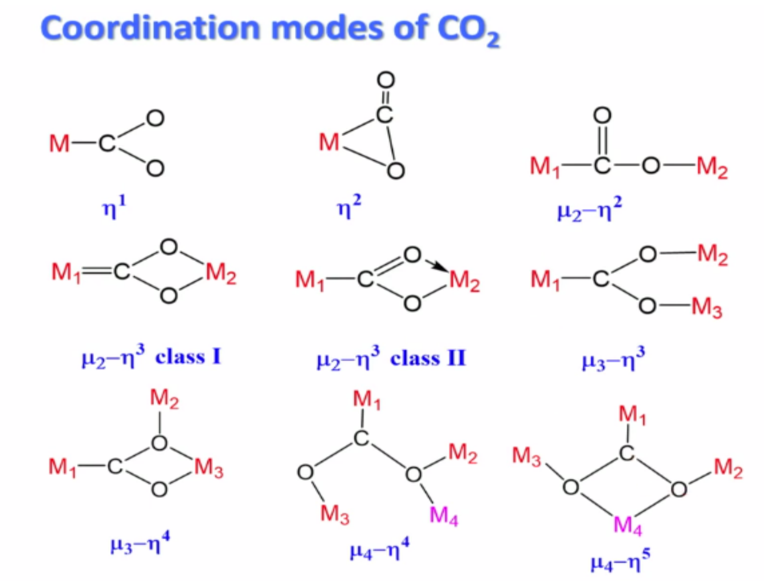
Carbon dioxide, carbon disulphide and carbon oxysulfide (COS)

- ✓ These three cumulenes react in a similar fashion with appropriate metal reagents to form complexes.
- ✓ More emphasis is given to the chemistry of CO_2 with an aim to use it in organic synthesis to convert it into organic chemicals.

So, now let us look into other carbon donor ligands. The important ones are carbon dioxide. From the point of reduction of carbon dioxide, a lot of groups show enormous interest and make lots of complexes eventually to reduce carbon dioxide, it is not very easy. Nevertheless, people have succeeded partially in converting that into useful organic molecules. And then let us also look into carbon disulphide and also carbon oxysulfide as ligands.

So, these three belongs to cumulenes category and these three cumulenes react in a similar fashion with appropriate metal reagents to form complexes, that is the reason I have put all these three together. And more emphasis is given to the chemistry of carbon dioxide with an aim to use it in organic synthesis to convert into useful organic chemicals.

(Refer Slide Time: 17:37)

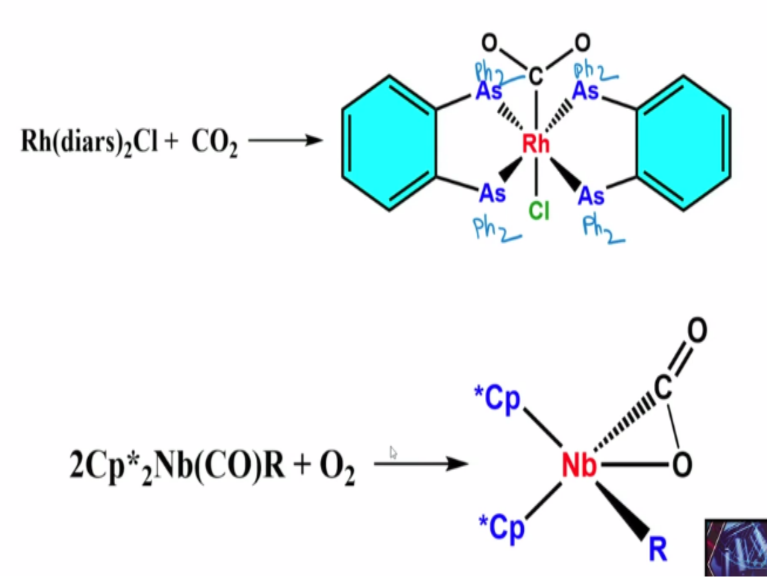

Coordination modes of CO_2

Now, let us look into all possible coordination modes of CO_2 and this is very important you should remember. So, when you want to activate carbon dioxide or when you want to reduce carbon dioxide and when it approaches a metal and how it interacts, one can see here. And it can also bind in η^1 fashion simply in this way or it can also bind in η^2 fashion. Initially breakage of one of the double bonds is very essential.

And bond has to be polarized and then it can be added in a concerted fashion like this or it can also bridge two metal centres in η^2 fashion in this way after breaking one of the double bonds, one of the CO bonds or it can also be η^2, μ^2 and η^3 because this one is η^3 because the hapticity is 3 here, but here it is bridging as well as chelating. One can also see +2 type where oxygen lone pair is coming in this fashion.

And also one can also see another type of μ^3 η^3, but all going to different metals or one can also have μ^3 η^4 or one can have μ^4 η^4 that means bridging 4 metal ions, μ^3 is bridging 3 metal ions, μ^2 is bridging 2 metal ions. And here also it is bridging or linking 4 metal ions here, but it shows η^5 coordination because here η^2, η^1, η^1, η^1, η^1 , SO η^5. Interestingly the examples are there for each case. We may have plenty of examples in some cases, but we have few examples in some other cases.

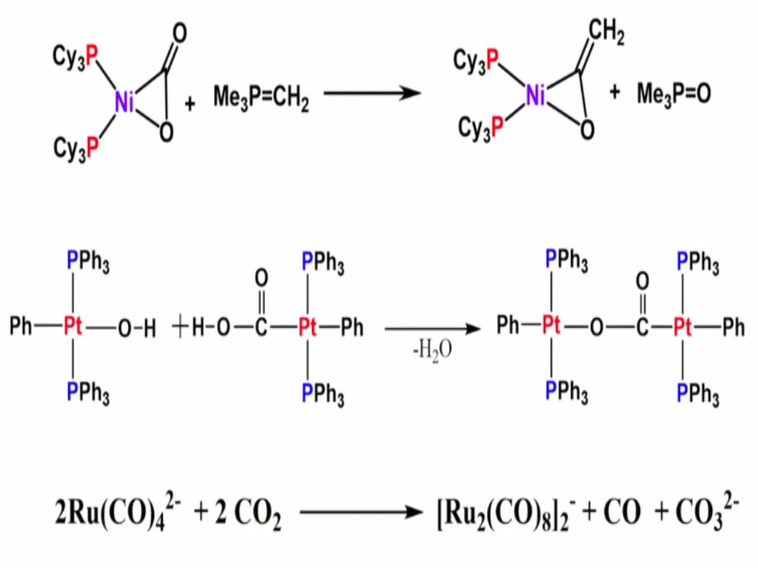
(Refer Slide Time: 19:21)



Let me show a couple of examples here: how one can initiate the binding of carbon monoxide to appropriate metal complexes. Here this is a rhodium diarsine chloro complex, rhodium(I) complex and again this arsine, diarsine is a neutral ligand very similar to diphosphine and for simplicity I have omitted As substituents, they should be Ph_2 here, initially it had something like this kind of structure here, square pyramidal structure.

And then CO_2 comes on the 6th position and then it forms a complex like this. And also, you can see here how concerted addition happens when you take this carbon monoxide and add oxygen, it appears like insertion of oxygen takes place here and it appears as if we have inserted carbon monoxide in an oxidative addition fashion. So, this is some sort of generating CO_2 by some other means, not directly taking carbon dioxide, but taking CO.

(Refer Slide Time: 20:41)

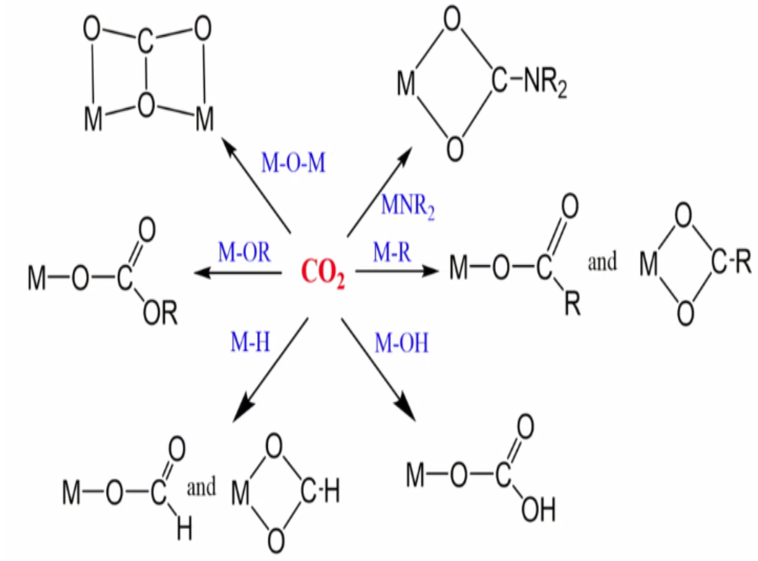


Other examples are there, you can see here. This one is a carbon dioxide bound complex, for example you take this one and treat with Wittig reagent and that means whatever the Wittig reagent does for a ketone, same thing can also be done on to a carbon monoxide on a metal centre. So, that means you can see something like this happening. Of course, once this goes off, this oxygen is abstracted to come here as trimethyl phosphine oxide.

And one can also generate a CO_2 using two appropriately substituted metal reagents, for example here in one hydroxyl group we have, in another one we have carboxylic group here. So, if you take these two, elimination of water takes place. So, here elimination of water condensation takes place to have a bridging CO_2. That means we came across few examples of coordination modes, I showed you here.

And you can get an example for all types of coordination modes if you look into textbook, especially 6th edition of Advanced Inorganic Chemistry by Cotton and others. You take this anionic homolyptic tetracarbon ruthenium complex and treat with carbon dioxide, you can generate something like this and then CO and $[CO_3]^{2-}$ comes out. That means here it acts as a source of carbon monoxide here.

(Refer Slide Time: 22:16)



Few examples, I have shown here very similar to what I showed in case of M-H, but it is slightly different to what are the different bonds CO_2 can be added I have shown here. For example, you take M-H bond and you can add CO_2 or you can insert CO_2 either in this fashion or in this fashion. So, that means I am giving you more avenues to use CO_2 or activate CO_2 molecule in your own metal complexes. So, for example if you have M-H bond still that can be used for reducing carbon dioxide.

And if you have M-OH bond still you can use it. Of course, we have to choose the right kind of ligands here for performing this reaction with better yield and better conversions. And then you can also insert carbon dioxide between metal to carbon bond in this fashion or it can also form something like this or if you take a metal to amide bond you can insert this one in this fashion or if you take simply an oxo bridge here metal complex you can insert CO_2 in this fashion.

So, these are all wide variety of reactions. That means there is plenty of scope to activate CO_2 depending upon what kind of other ligands we have on metal and what is its oxidation state and how this can facilitate the activation of CO_2 one should look into it thoroughly, then perform some reactions would be very easy. We stop here and continue discussing more about carbon donor ligands in my next lecture. Until then, try to look into more details about carbon dioxide and its complexes in standard textbooks.