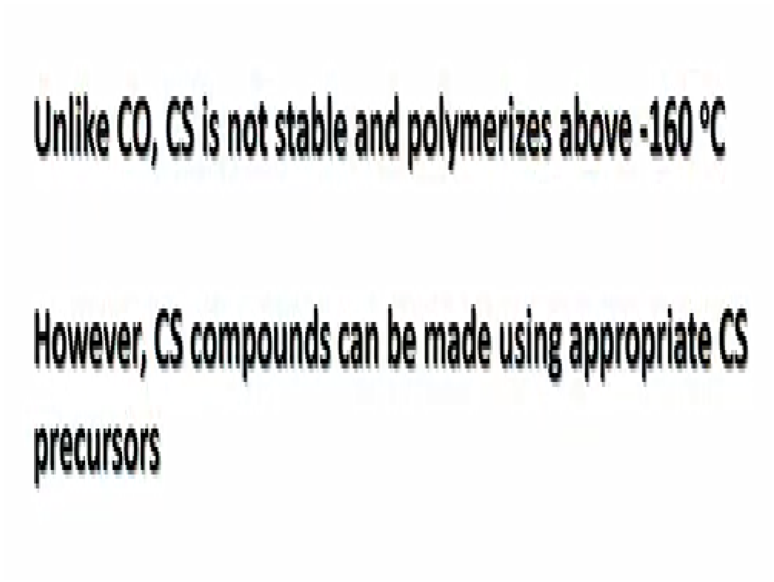
Advanced Transition Metal Chemistry – Classification of Ligands by Donor Atoms

Prof M. S. Balakrishna
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture – 31
Classification of Ligands – Carbon, Nitrogen

Hello everyone, welcome you all to MSB lecture series on transition metal chemistry. I have been discussing in the last couple of lectures about the classification of ligands by donor atoms and I completed discussion on hydrogen and we are midway with respect to carbon as donor atom, let me continue from where I had stopped. In my previous lecture, I had initiated discussion about CO analogue CS. Let me start about the chemistry of carbon thiomonoxide complexes.

(Refer Slide Time: 00:53)

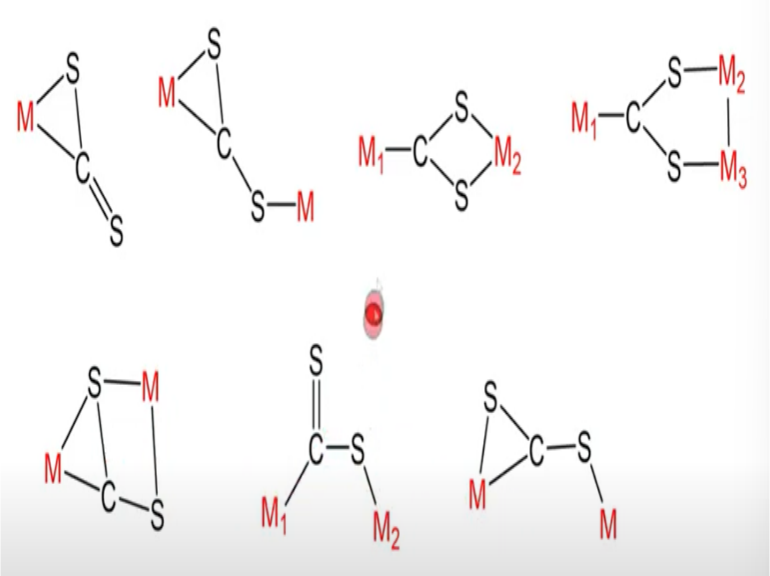


Unlike CO, CS is not stable and polymerizes above -160 ºC

However, CS compounds can be made using appropriate CS precursors

As I mentioned, unlike carbon monoxide, carbon thiomonoxide is not stable and polymerizes above –160 ºC. So, that means free CS does not exist in a stable form and however, CS compounds can be made using appropriate CS precursors and then very similar to carbon monoxide CS can be incorporated. There are examples of homoleptic CS complexes also. Let me show you preparation of a few carbon thiomonoxide complexes.

(Refer Slide Time: 01:35)



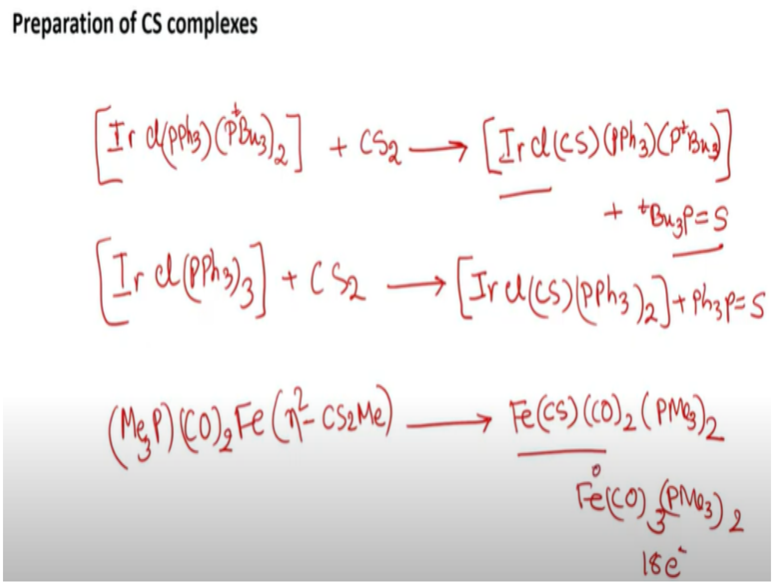
Before I start writing about the carbonthiomonoxide preparation, let me show you the coordination modes. Coordination modes are pretty similar to what we come across among carbon monoxide complexes, it can comfortably act as a terminal ligand very similar to carbon monoxide and since S soft here, it can readily bind to another soft metal in bridging fashion like this. On the other hand, this carbon can also donate its lone pair to two metal centres with or without metal-metal bond.

And it can also bridge three metal centres and also one can anticipate this kind of coordination also, in a trimetallic system, where sulfur lone pair goes to one metal and carbon takes another metal, whereas this double bond can bind to another metal. And of course, you can have carbon functioning as a bridged bidentate and then sulfur can go to another one or in one of these fashions.

There are examples in each case, let me show you a few examples or representative examples. Yeah, further when you look into carbon disulfide, very similar to carbon dioxide, it also shows following coordination modes. This is how it is going to bind breaking one of the CS double bonds and then it can also bridge two metal centres in this fashion η^2 and μ.

And it can also show this kind of coordination, where you can also come across trimetallic system in this way or one can also have something like this or this or this one. So, these are some standard and well-known coordination modes or binding modes of carbon disulfide.

(Refer Slide Time: 03:20)



Preparation of CS complexes

$$[IrCl(PPh_3)(P^tBu_3)_2] + CS_2 \rightarrow [IrCl(CS)(PPh_3)(P^tBu_3)] + {}^tBu_3P{=}S$$

$$[IrCl(PPh_3)_3] + CS_2 \rightarrow [IrCl(CS)(PPh_3)_2] + Ph_3P{=}S$$

$$(Me_3P)(CO)_2Fe(\eta^2\text{-}CS_2Me) \longrightarrow Fe(CS)(CO)_2(PMe_3)_2$$

$$\overset{0}{Fe}(CO)_3(PMe_3)_2$$

$18e^-$

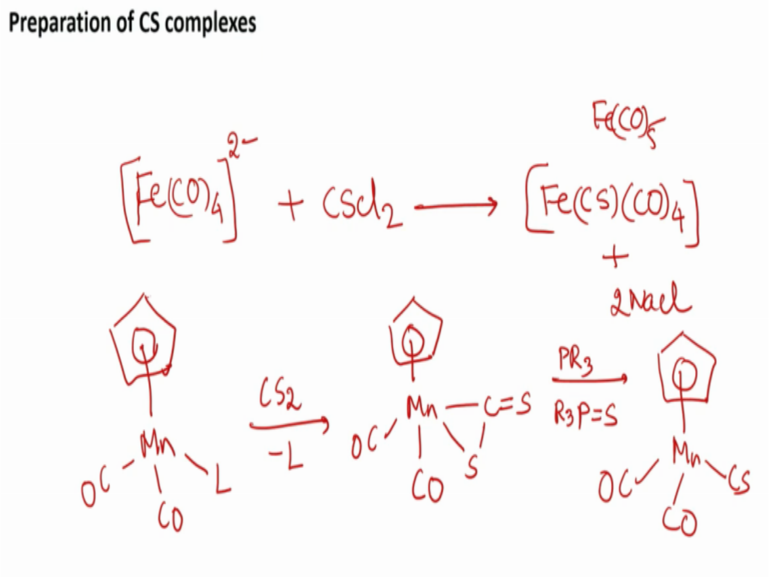
Let us look into the preparation of CS complexes. There are at least two to three very useful precursors, that can be conveniently used to prepare CS complexes, the simplest one is using carbon disulfide. I deliberately taken two different types of tertiary phosphines here. When you take this iridium tritertiaryphosphine chloride compound iridium in +1 state, and treat this one with carbon disulfide. So, now if you see here now it is giving you a compound very similar to Vaska's compound.

This is a trans compound and here why the sulfur is not obstructed by triphenylphosphine rather triteritiary butylphosphine because here the one that is more basic, so that would leave to form the sulphide, you should remember. If you have two different types of tertiary phosphines, the one that is better sigma donor will readily get oxidized as a result, N-butyl phosphine sulfide is formed by abstracting sulfur from CS_2, and of course if we consider another reaction, for example something like this, similar reaction.

Now, it does not have any option other than eliminating one of the triphenylphosphine as triphenylphosphine sulfide, but when choice is there the most basic one leaves. This is one method of making the CS complexes.

Another important method is, so this is thioacetate. So, this one also can give, so, this can also form a compound like this. So, this is very much similar to $Fe(CO)_3(PMe_3)_2$, an 18 electron complex, it is in zero valent state.

(Refer Slide Time: 07:12)


Preparation of CS complexes

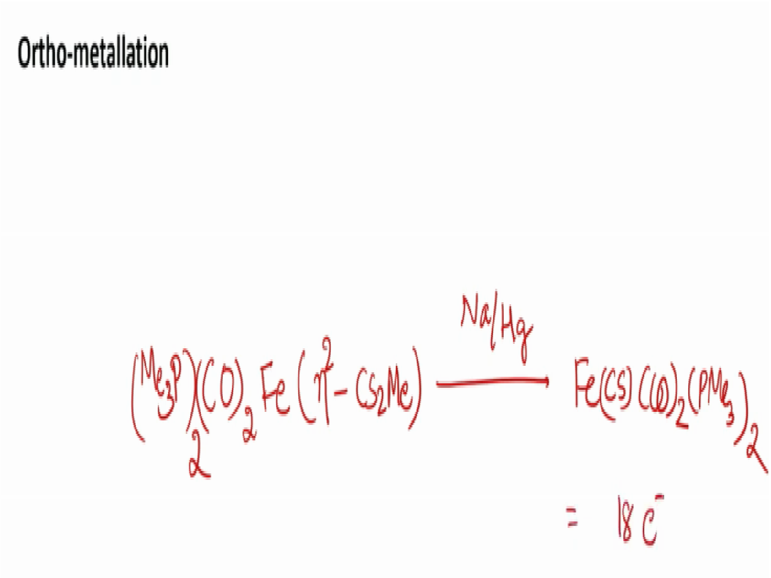
So, let us look into another example here. So, dianionic complex, so here the cation can be sodium. So, if that is the case, I can also see here $Na_2[Fe(CO)_4]$ for example. You take this one and treat this one with, this is thiophosgene. Phosgene we know it is $COCl_2$. So, we are using thiophosgene $CSCl_2$. This one can also give a compound very similar to $Fe(CO)_5$.

So, this comes along with, so if two sodium are there, 2NaCl will come out. This is a neat reaction, only thing is one has to be extremely careful while handling phosgene or thiophosgene, they are very poisonous gases. So, this is the third method in fact. We used thioacetate, we used carbon disulfide and also we used thiophosgene. In another method carbon disulfide can also be used, for example let us consider for variety, a half sandwich compound of manganese.

Suppose, we do not have a phosphine here, so we start with the reaction in which we do not have a phosphine to abstract sulfur from carbon disulfide, in that case, later one can also add a suitable tertiary phosphine to abstract S from CS_2 to form CS complexes. So, initially if we add CS_2 for this one, one of the ligands would come out and it forms an intermediate compound of this type.

This gives you some idea how CS_2 initially bind to the metal centre and eventually it cleaves one of the CS bonds, if phosphine is there it will abstract that sulfur to form phosphine sulphide and hence you get the corresponding CS compound. So, initially it forms a compound like this, now we will add a tertiary phosphine. It abstracts the sulfur to form, so this is how one can conveniently use one of the available methods to make these compounds.

(Refer Slide Time: 10:08)



Ortho-metallation

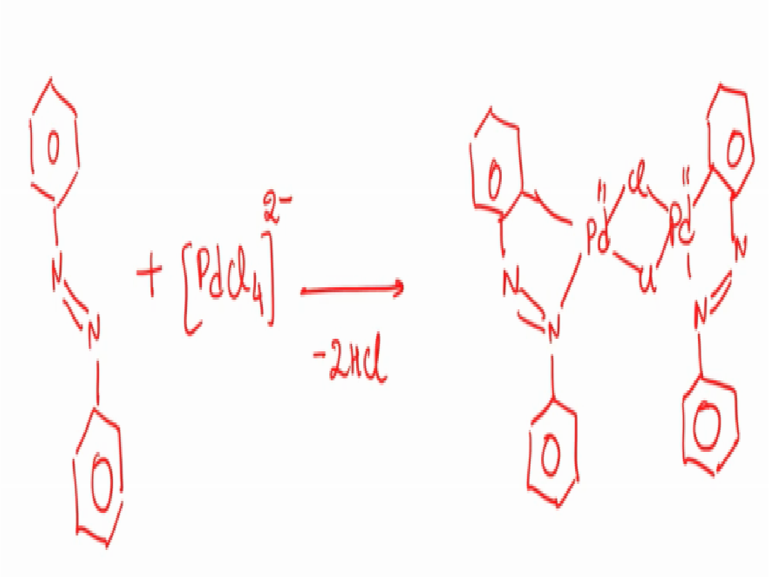
$$(Me_3P)_2(CO)_2Fe(\eta^2-CS_2Me) \xrightarrow{Na/Hg} Fe(CS)(CO)_2(PMe_3)_2$$

$$= 18e^-$$

Let me write one more method of preparation using sodium amalgam. An acetate complex, if you treat this complex with sodium amalgam, this is again an 18 electron species. So, these are the few methods that one can conveniently use to make carbon thiomonoxide complexes. And as I mentioned again thiomonoxide is a relatively good sigma donor and a better pi acceptor compared to carbon monoxide.

I did mention about ortho metalation. This is another important reaction we come across in case of carbon donor ligands especially when we have phenyl groups on a donor atom that is in close proximity to the metal, you can see CH activation and then there can be some elimination or it can be added oxidatively to form ortho metalated compound.

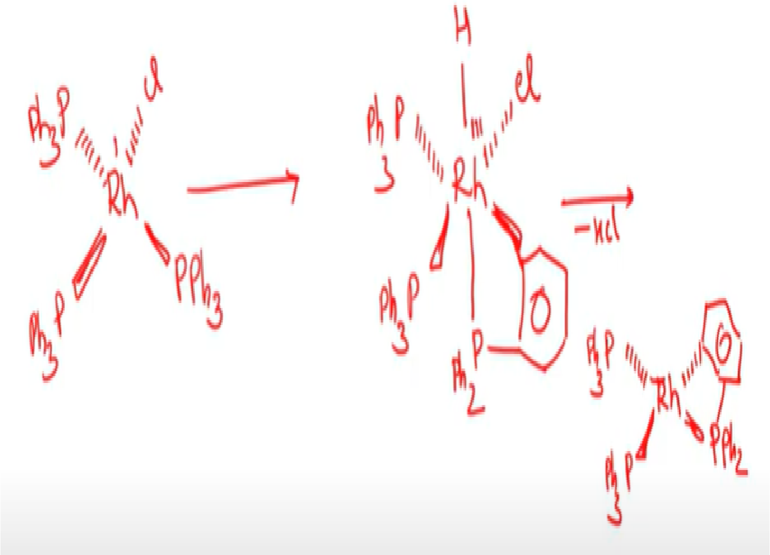
(Refer Slide Time: 11:49)



The first ortho metalated compound was made in 1960 from this reaction, let me write, show you the first example of ortho metalated compound that was with palladium with this diazobenzene. So, when this organic compound was refluxed in ethanol with potassium tetrachloropalladate, resulted in the elimination of two equivalents of HCl to form a compound like this. You can see palladium is in +2 state here in both.

This is the first compound which shows ortho metalation and later several ortho metalated compounds were made and also in fact people planned ortho metalation reactions and one disadvantage with this ortho metalation is there some time when you are using some tertiary phosphines especially having aromatic groups with not having any substitutes at ortho position, they can lead to ortho metalation and also they can deactivate the catalyst. One such example is seen with Wilkinson catalyst.

(Refer Slide Time: 13:47)



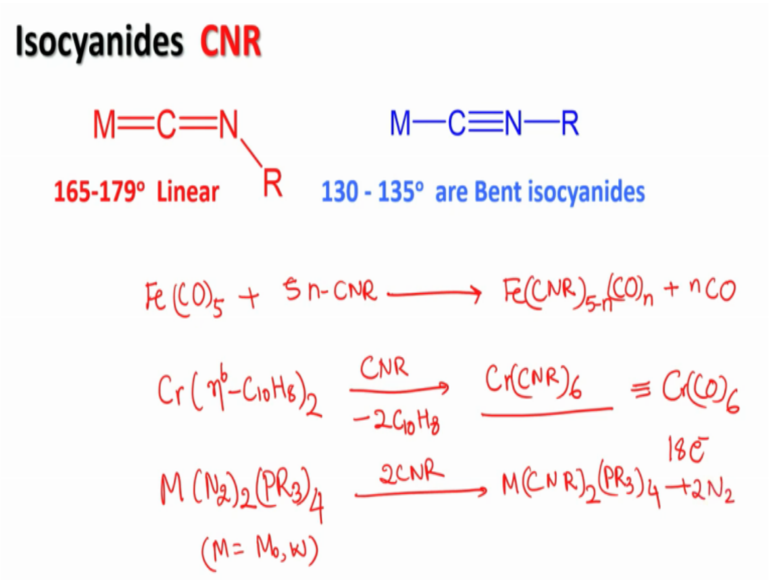
For example, if you take Wilkinson catalyst here with rhodium tristriphenylphosphine complex, so this can readily form oxidatively added compounds through ortho metalation and rhodium is getting oxidized from rhodium(I) to rhodium(III). Just I have shown one of the phenyl groups expanded so that ortho metalation can be seen here. Other two triphenyl phosphines remain, so something like this.

So, now you can see CH is added to rhodium, we have rhodium in +3 state, however there can be reductive elimination of HCl very similar to concerted elimination. So, this is a typical automatization reaction one can see it especially with triphenylphosphine or any bisphosphine having phenyl substituents.

And due to the steric problem if the phenyl groups come very close to the metal centre and there can be CH activation that can lead to either oxidative addition and that compound can also be stable or can be stabilized or eventually if you leave it or if you heat it little bit, the H elimination can be seen or even the elimination can be speeded up by adding a base such as triethylamine.

So triethylamine can abstract HCl as triethylaminehydrochloride and this reaction can proceed and to give eventually ortho metalated product. So, one has to be extremely careful for these kinds of reactions, and especially when we were using triphenylphosphine with platinum metals for catalytic purpose, these reactions are quite common and thus can deactivate the catalyst so that your rate of the reaction decreases dramatically.

(Refer Slide Time: 16:59)



Isocyanides CNR

$Fe(CO)_5 + 5n\text{-}CNR \longrightarrow Fe(CNR)_{5-n}(CO)_n + nCO$

$Cr(\eta^6\text{-}C_{10}H_8)_2 \xrightarrow[-2C_{10}H_8]{CNR} \underline{Cr(CNR)_6} \equiv Cr(CO)_6$

$18e^-$

$M(N_2)_2(PR_3)_4 \xrightarrow{2CNR} M(CNR)_2(PR_3)_4 + 2N_2$

$(M = Mo, W)$

Now, let us look into another interesting ligand system isocyanides. I have shown the binding mode. So, you can have either linear fashion it can bind or it can also show this bent mode here and the difference can be seen from the bond angle here, if it is 165 to 179 we can consider as linear and if it is in the range of 130 to 135 it will be bent. So, then there see how this isocyanide compounds are prepared.

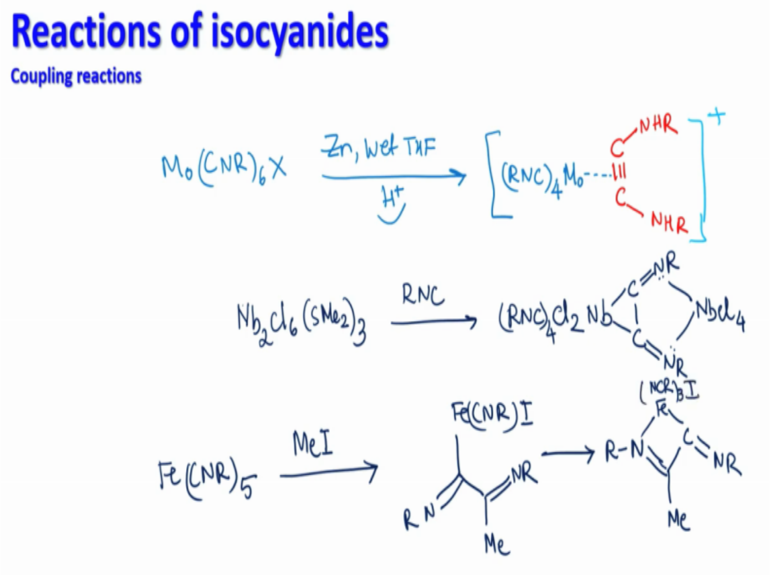
Isocyanide are again neutral ligands very similar to carbon monoxide or tertiary phosphines. So, some simple substitution reaction can be performed, this is the general reaction I am going to write. That means by choosing appropriate reaction conditions one can substitute all carbon monoxide on a metal centre to form homoleptic isocyanide complexes. You take this again zero valent complex, treat it with CNR, one can make homoleptic complex.

This is very similar to $Cr(CO)_6$, an 18 electron species. So, one can also make this compound. One can also start with a dinitrogen compound, of course you may be curious to know how dinitrogen compounds. Once I complete the carbon ligands, I shall move on to nitrogen, there I would be elaborating more about nitrogen, preparation of dinitrogen compounds and their reactivity and all those things.

If you take this dinitrogen complex of molybdenum or tungsten, plus here $2N_2$ come out. These are some of the important methods of preparation of isocyanide complexes and let us look into the reactions of isocyanide that means the reactions of bound isocyanides.

What are the reactions one can perform when an isocyanide ligand is coordinated to a metal centre? So, three reactions one can think of. One is coupling reaction, one is nucleophilic reaction and another one is electrophilic reaction.

(Refer Slide Time: 20:35)



Reactions of isocyanides

Coupling reactions

So, let us look into first, coupling reaction. Let us take a molybdenum complex, treat this one with zinc and wet THF. I am just writing four isocyanides on one side to show the coupling reaction. This is a dimeric complex of niobium. When it is treated with the isocyanide, of course excess of isocyanide, now you should remember they have lone pairs intact, these lone pairs will be donated to the other niobium that has 4 chlorides on it.

So, these are the examples for coupling reactions one can perform on bound isocyanides. Just take this one and treat this one with methyl iodide. This is another interesting example for this coupling reaction here, it gives metalated compound of this type. These are the few examples to understand the coupling reactions of isocyanides with various transition metals. One I showed you with molybdenum.

And another one I showed you with niobium and one I showed with the homolyptic iron complex penta isocyanide iron. So, let us look into more reactivity of bound isocyanides in my next lecture. Thank you.