Advanced Transition Metal Chemistry – Classification of Ligands
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Lecture – 29
Classification of Ligands – Hydrogen, Carbon

Hello, once again I welcome you all to MSB lecture series on transition metal chemistry. In my previous lecture, I was discussing about the classification of ligands. Under that, I was discussing about the ligands with hydrogen as donor atom, let me continue from where I had stopped. I gave different methods of preparation of metal to hydrogen bonds and also to make metal to H_2 bond, where H_2 acts as a neutral ligand.

And also, I showed you how a neutral ligand such as H_2 initially binds through sigma and then eventually with excess of electrons, when they move from metal to sigma star of hydrogen and H-H breaks and then that leads to the formation of two M-H bonds. So, let me continue giving preparation of some more compounds with different transition metals.

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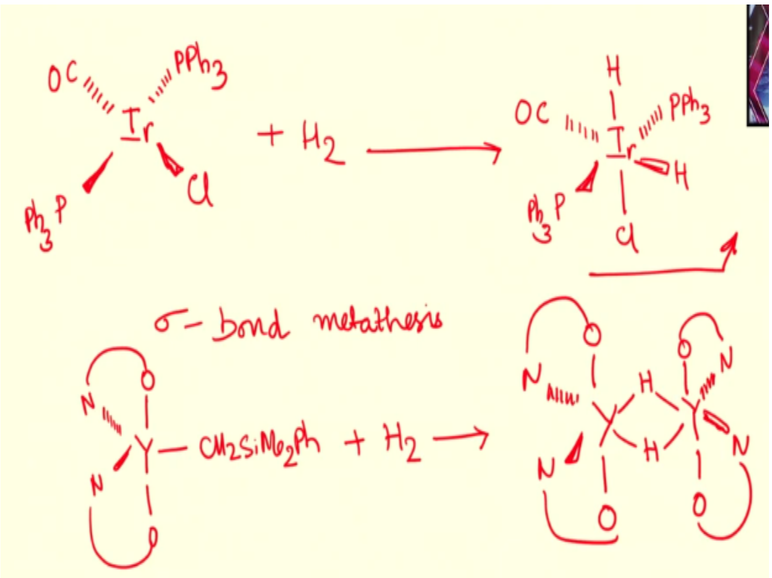

Now, let us look into oxidative addition method used in the formation of metal to hydrogen bonds. So, it is the square planar iridium(I) complex. This also called as Vaska's compound. So, when you add H_2 here, there will concerted addition, oxidative addition that leads to the formation of an octahedral complex, 18 electron complex having coordination number 6 with two M-H bonds, i.e. two iridium to hydrogen bonds.

As I mentioned I will be elaborating this reaction later keeping both thermodynamic and kinetic aspects to see how this reaction is reversible, I will give you more information about this reaction. Now, let us see; what are the other methods we have to make metal to hydrogen bond. Another important method is sigma bond metathesis; let me take one example here, NO bidentate ligand and having this group here, so dimethylphenyl methylsilane.

When you add H_2 to this, it forms a dimeric compound having two bridging hydrogen bonds, a symmetric molecule of this type is formed. So, that means there are some similarities between the formation of metal to hydrogen bonds from H_2 and also the formation of metal to carbon bond from olefins.

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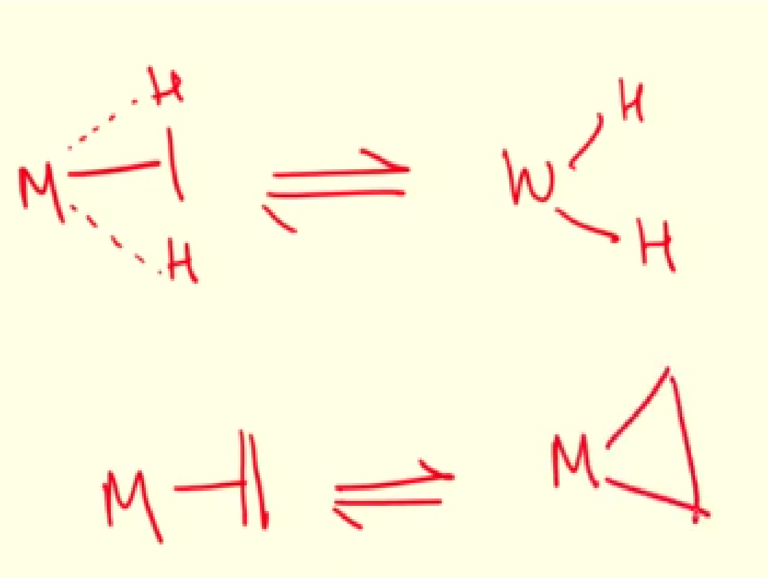

For example, it forms something like this initially, and one can also show something like this. This represents three bond concerted oxidative addition. This will be in equilibrium and then can split into two M-H bonds. And then if you, say for example tungsten complex of olefin or we can make it very general here, now this can also be in equilibrium something like this.

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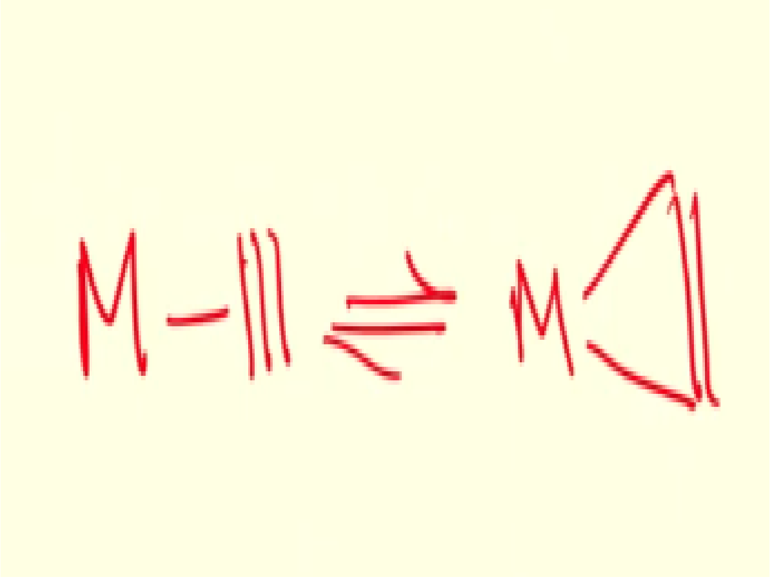

Or if we take acetylene, something like this. These are the two comparison I have made with olefins binding and its properties and of course here also how a triple bond being a pi can also change through back bonding to pi star of these olefins, it is more or less very similar to what happens in case of the interaction between H_2 and M. So, there the back bonding happens to sigma star in case of hydrogen, whereas in this case it is pi star.

So, now, let us look into more examples besides utilizing metal to hydrogen bond for hydrogenation reaction, is there any possibility of exploring other organic reactions? There are plenty of them. It is not just M-H bond formation good for hydrogenation of unsaturated molecules, but it can go beyond and it plays a significant role in many organic reactions. Let me start writing a few such reactions to make you familiar with the importance of M-H bond.

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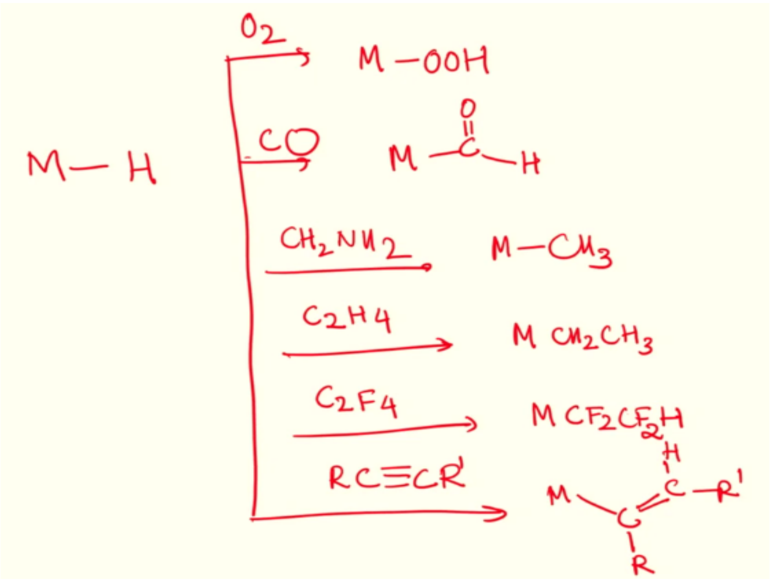

Let us consider one M-H bond, let us not worry about what other ligands we have. So, we will start with what would happen, I will keep on writing several reactions here. So, what would happen if I add oxygen to it. If I add oxygen, oxygen can be inserted between H and M bond to form something like this, or if I take CO, CO can also be get inserted something like this, and of course later with appropriate reagents one can take away this CHO group into the right kind of substrate if you use.

Then what would happen if I take CH_2N_2? So, in this case one can get M-CH_3 bond. If you take an olefins such as ethylene, then the insertion takes place here to form this type of compound, this is addition reaction happens here. Then if you take say for example fluorinated ethylene is the same thing, so here also one can get.

So, this entire fragment is inserted between M-H bond. These are all insertion reactions; if you take acetylene, can do these things. Apart from this, there are several other reactions, let me write few more reactions

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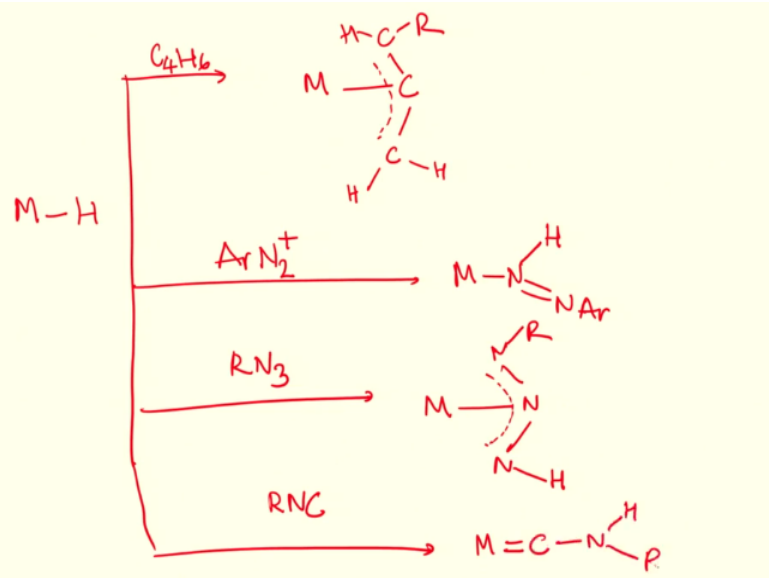

If you take C_4H_6 here it forms an interesting compound of this type. You take this cation, then again this whole fragment is inserted between M-H bond to give a species of this type or if you take an azide, organic azide. If you take isocyanide.

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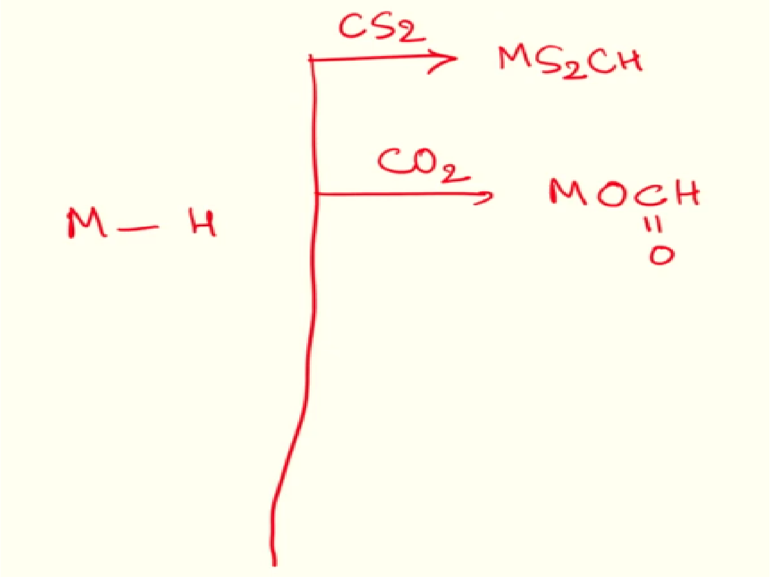

Some more examples I am going to show you. Let us take carbon disulfide, this is very important, it can form. If I take CO_2, lot of groups are working on reduction of carbon dioxide. If you take this one it forms. These are some of the important reactions and by knowing these reactions, probably if you want to look how these reactions happens, you should be able to use in several other organic transformation from this point of view.

Especially this carbon dioxide insertion is very important from the point of looking into easily available carbon source and how effectively or efficiently we can convert using cheaper metals, carbon dioxide into useful organic molecules. From that point of view, some of these reactions I showed is very important and there is enormous potential in using M-H bond for various organic transformations.

With this, so let me stop discussion on hydrogen donor ligands. Now, I shall move on to ligands having carbon as donor atom. Of course, you know that when we talk about carbon as donor atom, we have an entire new domain is there in front of us that is organometallic chemistry. This organometallic chemistry deals entirely with formation and reactivity and their structure and bonding and all aspects related to metal to carbon bond.

Nevertheless, since I am doing classification of ligands, I shall talk a little bit about what are the carbon donor ligands we have, how one can make these complexes and also how we can use these compounds in some applications such as homogeneous catalysis. So, now let us come to; this should have been lecture 30, however let me continue in this lecture and then probably in lecture number 30 also I will be continuing further talking about carbon donor ligand.

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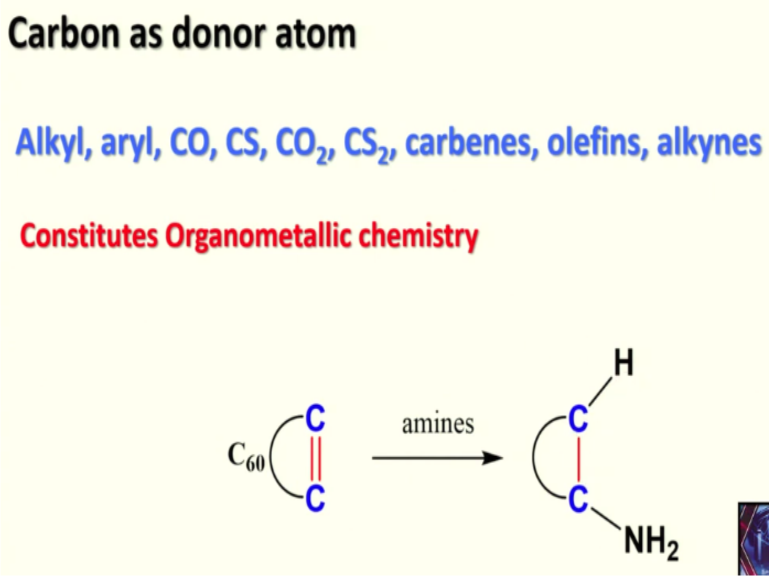

Carbon as donor atom

Alkyl, aryl, CO, CS, CO_2, CS_2, carbenes, olefins, alkynes

Constitutes Organometallic chemistry

When you talk about carbon donor ligands, some of these molecules or fragments will come into the picture. So, all alkyl whether you take CH_3, C_2H_5 or anything for that matter, all aryl, carbon donor ligands, besides that we have neutral ligands such as carbon monoxide and carbon thiomonoxide, but as I mentioned earlier, this is not freely available and we cannot isolate this one in pure form.

Nevertheless, we can convert some sources of CS and use it; in situ generate CS to metal bond, and then carbon dioxide very important, carbon disulfide and N-heterocyclic carbene, Fisher carbenes and a range of olefins and alkynes. All these are essentially carbon donor ligands and as I mentioned, a systematic study of all these ligands and more constitute what we call it as organometallic chemistry.

But, nevertheless here also let us look into the reactivity and some chemistry related to carbon donor atoms briefly. And this is called fullerene, C_{60} molecule you know that. This one can treat with amines to do addition reaction, very similar to what we do with isolated olefins, for example you treat with ammonia, you can get amines, you can make this way.

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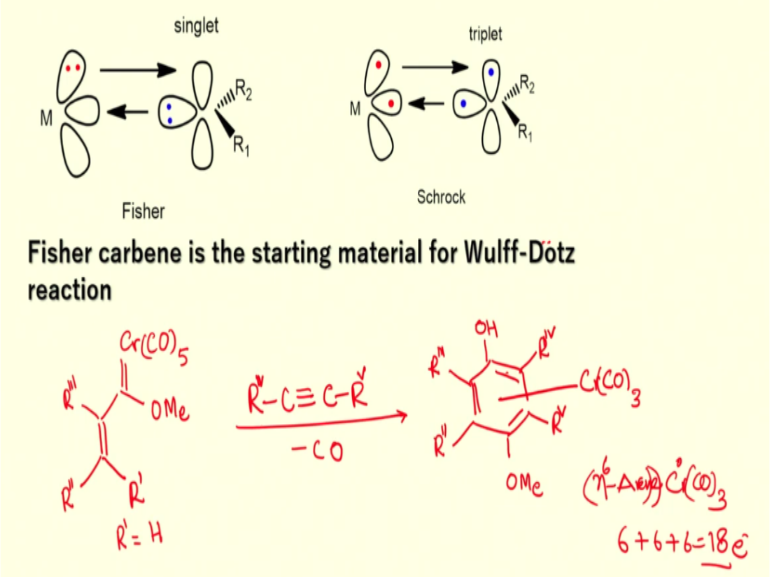

Fisher carbene is the starting material for Wulff-Dötz reaction

And here when we talk about carbon, we come across two type of carbenes here and this is a Fisher carbene; carbon is in singlet state that means lone pairs are there and it acts as a neutral ligand and it can even stabilize metal in zero valent state, and then metal always has some nonbonding electrons, these electrons can be taken to empty pi star orbital. That means, these Fisher carbenes can also act as good sigma donors and good pi acceptors. And in this one, Schrock is a triplet carbene, we are talking about.

So, that means it essentially forms bonds with metals and sharing electrons like this and of course when these two electrons go, you will be having C^{2-} that means 4 electrons are there occupying two orbitals and they make here metal to carbon double bond and mostly metals are in high valent state. And again, this compound is widely used in many reactions, metathesis and other things. So, now Fisher carbene is the starting material for Wulff-Dotz reaction. What is the Wulff-Dotz reaction; let me write here.

Two dots should be there. For example, you take Fisher complex of chromium pentacarbonyl, so R’ can be hydrogen, in this case it is hydrogen. When you treat this one with an alkyne, substituted alkyne. So, here we are using 3 carbon fragments, so this is 4 and then this is R 5 so that we know the relative position of that one in the product. So, here in this case when you treat this one with alkyne, one of the carbon monoxide comes out from chromium and then we get cyclisation product.

And then now this entire aromatic group binds to, and now you can see this is forming an η^6 arene I would say. This is an 18 electron complex, because chromium is in 0 valent state and

6 electrons are coming, 6 electrons we have and another 6 electrons, so it forms an 18 electron species here. So, this reaction is known as Wulff-Dotz reaction here. That means Fisher carbene starting material for these kinds of reactions.

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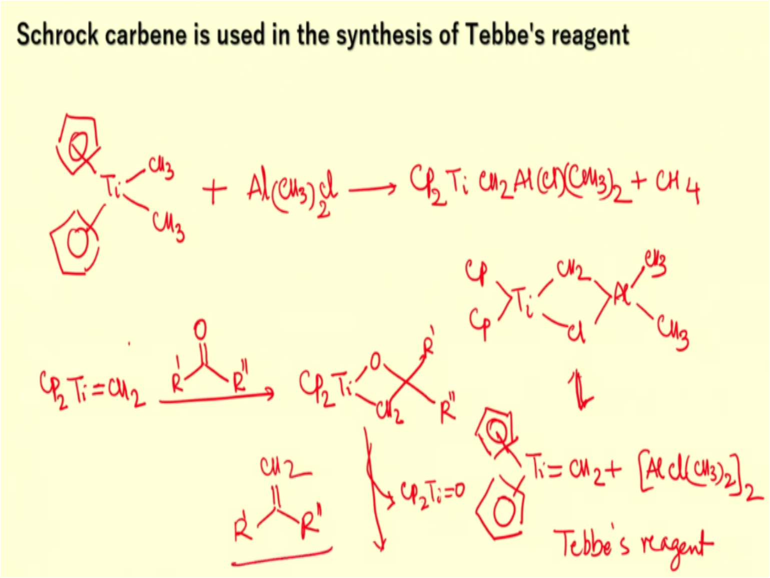

Schrock carbene is used in the synthesis of Tebbe's reagent

So, Schrock carbene is used in the synthesis of very important Tebbe's reagent. So, what is Tebbe's reagent and how it is formed? Let me write that to make you familiar with the Tebbe's reaction and also Tebbe's reagent. We are considering here Cp$_2$. So, this one later; I am going to write in this fashion, it is understood that is η^5 here. So, I will be writing this entire moiety, for simplicity I will be writing it as Cp$_2$Ti.

So, when you treat this one with dimethyl aluminum chloride, one can also write in a dimeric state, then you have to take half equivalent of this one plus one molecule of, comes out and of course you may be curious to know the structure of this one. Structure will be something like this. We have one methylene bridge is there and also one chloride bridge is there. So, this one readily detaches aluminum fragment to give plus here, what you get is half-equivalent of AlCl$_3$ dimer. So, this is called Tebbe's reagent.

So for what purpose this Tebbe's reagent is used? Let us take this reagent. If you treat this one with a ketone initially it forms an intermediate of this type and then here what happens Cp$_2$Ti this comes out and that leads to the formation of, so this function is very similar to Wittig reagent. So, this is where Schrock carbene used in the synthesis of Tebbe's reagent and Tebbe's reagent looks like an alternate to Wittig reagent. Let me stop at this juncture and continue in my next lecture discussing about ligands having carbon donor atoms.