Metallocene and Metal-carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts

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Lecture 17

Unique Reactivities of bent Metallocenes

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Lecture 17: Unique Reactivities of bent Metallocenes

Welcome to our classes. So, we will continue today the discussion about the unique reactivities of bent metallocenes. In the last class if you remember, we have extensively discussed about the basic difference between the parallel and the bent metallocenes. And we discussed about the some basic and unique the activities of metallocenes, the ferrocenes which was the first metallocenes some of the common parallel metallocenes and then we started the discussion of the unique electronic properties and tried to correlate the reactivities of such bent metallocenes.

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CONCEPTS COVERED

Properties and unique reactivities of common
- Bent metallocenes

KEY POINTS

- Bent metallocenes
- Reactivities

If you remember in the last class, we discussed that how the electron pair, the lone pair present in the bent metallocenes governs the reactivities. So, today we will cover the unique reactivities of the bent metallocenes and we will try to then understand that how these properties are essential useful for many important organic transformation and also for in the catalysis for the value added compounds or in polymer industries. So, let us start our discussion.

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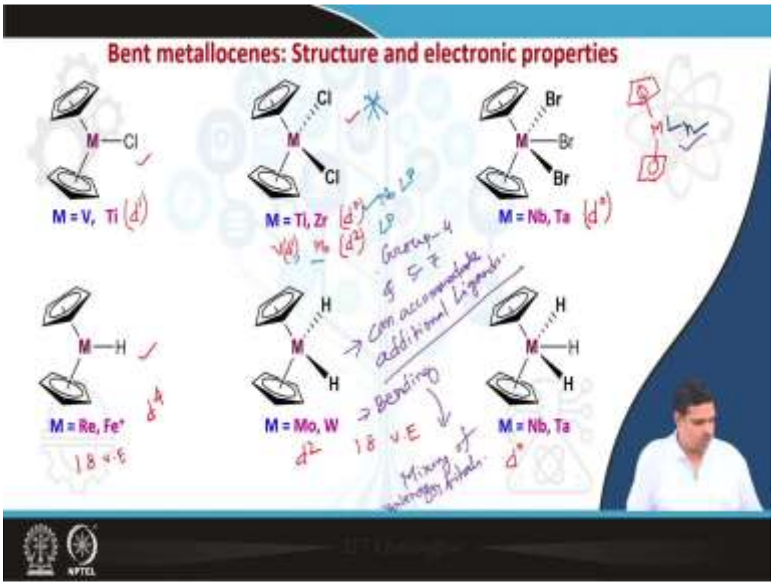
Bent metallocenes: Structure and electronic properties

So, this one actually, we discussed in the last class if you remember, I just want to highlight a few basic points which will be helpful in our classes today. So, if you recall the last class, so, this is actually in a category of what we will be discussing in the following classes in the catalysis of polymerization. So, this titanium zirconium in this bent metallocenes you see that these are basically d 0, you see that means there is no lone pair, no lone pair that means, there is no electrons in the non-bonding orbitals.

And unlikely in molybdenum, the similar analogue of the molybdenum you see that there is a lone pair and we saw in the last class that how this presences of the lone pairs differentiates the reactivities. As an example, if you have a lone pair it may act as a Lewis base if it is vacant it may acts as a Lewis acid like that. So, we discussed in a category wise that how this electronic factor and the number of metal apart from the metal Cp how many metal ligand bonds are possible, how the electronic factors governs the unique reactivities etc.

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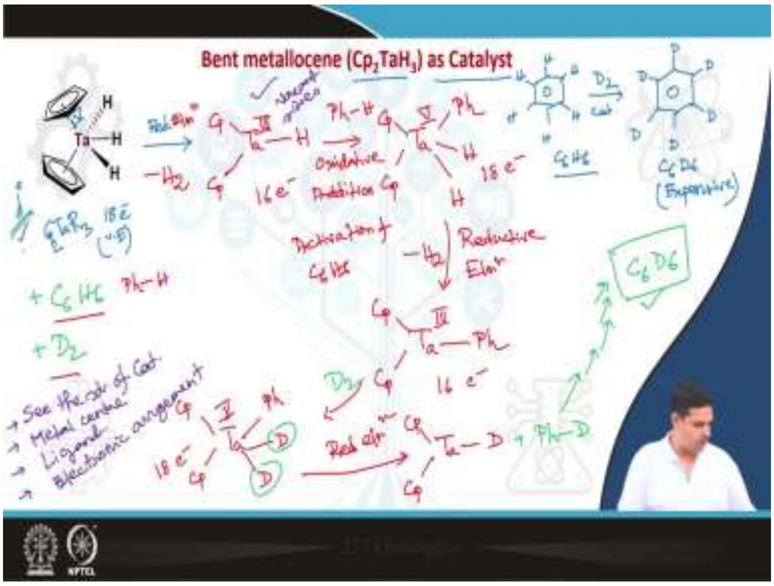

Bent metallocene (Cp_2TaH_3) as Catalyst

So, today what I will do, I will try to give some flavor that how this unique reactivities of some of the selected metallocenes compounds are possible and how interesting it is and how these are useful for in catalysis chemistry. And actually, many bent metallocenes compounds not only the bent metallocenes for as a polymerization catalyst, many bent metallocenes compounds are very much used for in other domains of organic synthesis or to make the value added compounds may be stoichiometric or maybe in as catalysts.

So, let us see this one this example. So, this is tantalum. So, this is basically a case of Cp 2 tantalum and is R 3 category that means, you see that tantalum is in plus 5 oxidation state so, this is plus 5 oxidation state. And it is 18 electron rule, 18 electron valence electrons. It has 18 electron valence electrons. Now this compound you see that as it is a tantalum is a plus 5 oxidation state that means it is d 0 that means there is no electrons in the nonbonding orbital.

As you see that the Cp 2 Ta H 3 as a catalyst, so which kind of catalyst is it is useful it is actually industrially used for these very useful reactions as example here this is the benzene the normal benzene, here all are just normal benzene and if you want to make its deuterated version so that means is it C 6 H 6 and this is C 6 D 6, you need this and catalyst, this catalyst. And you know that what are the applications of the deuterated solvents? These are used for recording NMR spectra, we do normally use CBCL 3, we also sometimes use the deuterated benzene, deuterated toluene, deuterated dichloromethane, deuterated (())(6:30) or the deuterated water according to its solubility.

So, how this is very expensive this one is very expensive and you can check the price in online. And this one you know is quite cheap, although benzene is in category of carcinogenic chemicals, harmful chemicals, but sometimes you have to use in lab with the all the precautions fine. So, this catalyst is used for transforming the normal benzene to the deuterated benzene. How does it work, so, let us see I will discuss the mechanism.

So, you know that this is a d 0 system so that means it is a d 0 system. So, what first step will be the reductive elimination because what you have to do, you have to add you see to get from the benzene to the (())(7:36) benzene. So, what I need to add? I need to add here the normal benzene and C 6 H 6 and the (())(7:54) d 2. Now, it is already d 0 system that in the tantalum 5, so there has to be reductive elimination reactions. So, in reductive if there is a reductive elimination then what will happen? It will I am not writing the ring, so just try writing the C 5 and you have to assume that these are inter 5 Cp, I am writing in short.

Now, if it is reductive elimination, then what will happen? Now, you have a instead of 3 hydrogen, 3 tantalum hydrogen, you have single tantalum hydrogen bond. So, now it will become now tantalum 3 oxidation state and it is 16 electron system, fine. Now, what you have to do you have a C 6 H 6 that is the benzene. Let us now Ph, H I am writing in this way to understand easily, so what will happen now, can you guess what will happen? Yes, there will be oxidative addition.

You remember in one class, we have discuss the four unique reactions in organometallic chemistry that is the oxidative addition, reductive elimination, then the insertion reaction and elimination reactions, elimination is mostly, beta elimination is very common, sometimes alpha and gamma. So, these 4 reactions if you see in the catalytic cycles, these 4 reactions basically operated in a repeated way, sometimes single sometimes multiple. So, you see that this oxidative addition of Ph H, so what will happen now? So, it will be like, so this is my Ph, this is H and this is H. So, you will see again the tantalum converts to tantalum 5.

Now, now this is a kind of activation of the phenyl benzene. So, as I told that during the previous discussion this oxidative addition is basically the activation of your substrate. So, you see here so, this is a kind of activation of your C 6 H 6. Now, I phenyl benzene is now inserted reacted with the catalyst, now you see leftover is the d 2, how does it react? So, now, obviously, there will be reductive elimination and reductive elimination of what? It is actually the hydrogen.

Now, what will happen again tantalum, now Cp cyclopentadienyl as I told is eta 5 and you see that again the phenyl is there. Now, what will be the next step, any guess? Yes, next step is now react with the ditorium so, this one. So, what will be the reaction then? Yes obviously, the oxidative addition. So, this is again my 3 oxidative state now, this is tantalum, now, Cp, CP now, you have a again phenyl, ditorium and ditorium to you will see this one, so this ditorium and this ditorium.

Now, next reaction what will happen? Next reaction will be obviously similar now it is 5 oxidation state. Now reductive elimination, any idea reductive elimination of what? So, this is you see that it is 18 electron this 16, 16 then 18 electron then 16 electron then 18 electron so this is basically kind of settling between 18 and 16. So, now, what we will see now, this is again reductive elimination and you what you are getting? You are getting the Ph-D. So, you see that one hydrogen has been replaced in phenyl in benzene ring is replaced by one ditorium atom.

Now, what happens, the same if it is repeated another 5 times eventually what you will get? You will get C 6 D 6, is very easy no, is just based on the simple 2 reactions oxidative addition and reductive elimination and you are getting your the desire (())(13:58) benzene. So, you see how interesting this bent metallocenes, lot of examples, lot of applications even not only in academic scale in laboratory, but also in industries.

So, you see that this is really very fascinating chemistry of the bent tantalum and you have to remember that see this is d 0, so that means this is d 0 that means it has to be, how will see this is how will you predict or the propose the mechanism we have to see it very carefully, the 3 steps you have to see it very carefully the catalyst, that you see the what are the electronic in the first what you see you will see the catalyst, see the structure of catalyst, metal centre, ligands, electronic arrangement.

Why electronic arrangement? To check what kind of reaction it can undergo, like if it is d 0 then it cannot undergo the oxidative addition at first, it has to undergo the reductive elimination and then only there will be 2 reason you will see here there is a reduction and then it is actually giving you vacant space. Here you see this the coordination number here 3, 3, 6, 7, 8, 9. Now here coordination number here to decreasing so, you are basically here coordinating the vacant it is creating the vacant sites here, in the 16 electron system, why? So that it can react with the substrate.

So, by electronic factor electronic arrangement by the ligand involvement and by the metal centre, you have to have some idea that what kind of reaction it can undergo and then you see the substrate that he has these substrate, whether it will undergo oxidative or reductive elimination then you judge it and then you proceed accordingly. So, I will also show some example where you can propose the mechanism not just by kind of remembering, but by a very logical way. So, you have to be that how many electrons whether it is 18 electron or 16 electrons, you know that 18 electrons have been stable so, it just it has to undergo the 16 electron system or 14 electron system to participate with the reaction with the substrate.

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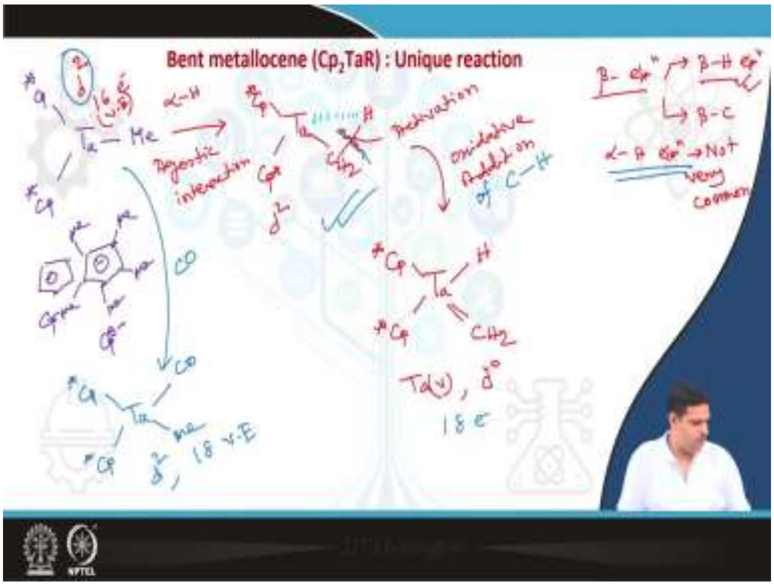

Bent metallocene (Cp_2TaR) : Unique reaction

Now, after that interesting example of tantalum 5, let us come to the some unique chemistry of the tantalum but here plus 3 oxidation state. So, one example is this one. Here it is methyl and here is Cp star, Cp star means actually the so you know that Cp is this one, so this is Cp minus. And what is Cp star? Cp star is basically the penta-methyl same but the this is called the Cp star iron. So, is basically penta methyl version of the cyclopentadienyl and iron. Now here you see that this tantalum 3, tantalum 5, the earlier one that is the tantalum 5 that means d 0.

Now, obviously, how many have electrons will be here? So, this is actually the d 2 system obviously, so this is the d 2 system and 16 electron complex 16 electron valence electron actually this is, rather it is better to say 16 valence electrons. Now, this one is very interesting, this tantalum undergoes a very unique reactions that is why I thought to show this example.

See we previously I mentioned that in organometallic chemistry the beta elimination is very common, beta hydride elimination is very much common, sometimes beta carbon elimination also possible, but this one is very common. But if you see the alpha H elimination this is possible, but not very common, this is one of the example where you see the alpha elimination, how does it happen?

So, you tantalum. So you have a now so this is CH 2 and this is H and it undergoes like this kind of interaction, can you tell what type of interaction it is? It is, yes, this is called the agostic interaction, we have seen the agostic interaction mostly for the beta hydride agostic interaction, but here we see that this is alpha hydrogen agostic interaction very interesting.

So, now, so, this is basically is now is activating activation, what does it happen in agostic interaction? Basically the sigma electron of the CH bond is donated to tantalum and on the return back bonding the electron pairs is now grind to the sigma orbital of the CH as a result the CH 1 is becomes weak and this is called the activation, and what happened it undergoes after that oxidative addition. So, this is d 2.

Now, you see what will happen? Now, this is Cp, Cp star and this will undergo the oxidative addition and here it will be like this one. So, you will see that the oxidative addition of the CH bond so, this is basically the brakes and form the tantalum 5 again and it becomes d 0 system again. So, here you will see that how interesting this chemistry is. So, here you will see that the d 2 system is undergoing the alpha H interaction.

So, this is basically as it is a this electro pairs so, this is donate to the sigma star orbital of the CH this bond is now weak the CH bond, this bond is now breaking, undergoes the oxidative addition of CH and forms the again the tantalum hydride complex which is again d 0 and it is 18 electron system that is the valence electron.

And also you will see that is a very common reactions you have a 16 electron system, so coordinately will be unsaturated, also electronically unsaturated so, it easily undergoes the reactions ligands like carbon monoxide or phosphines and satisfies the 18 electron configuration. So, this is CO, this is methyl, again you see this is obviously d 2 and 18 valence electron. So, this is really interesting and very unique alpha H agostic interaction as I and undergoing the alpha H elimination which is very rare not very common.

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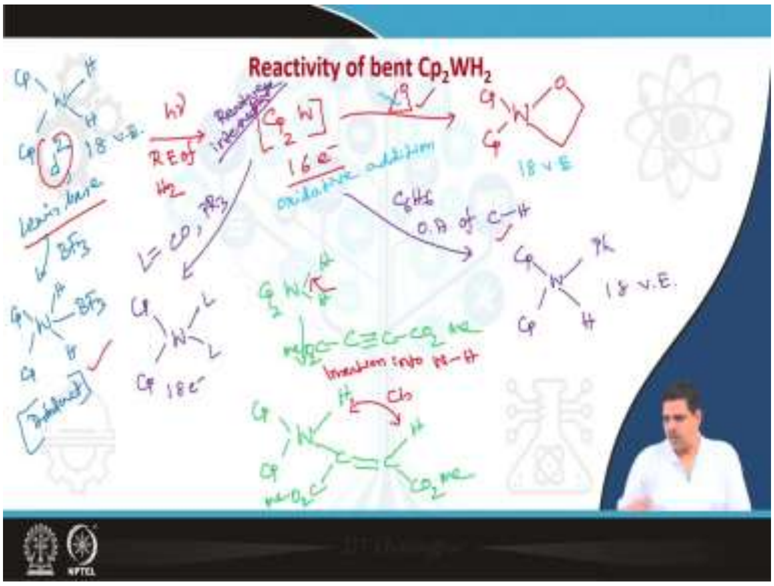

Reactivity of bent Cp_2WH_2

Now, I am I will be discussing some of the very unique reactions of the Cp 2 W H 2, that if you remember how what will be it is electronic how many electrons will be on the non-bonding electrons. So, let us Cp 2 W H 2. So, if you recall, so it will be in Cp, Cp this is H, H. So, this is again d 2 electron and it is 18 valence electron. So, it has a non-bonding electron pairs as a lone pairs, so that means it can act as a weak base Lewis base. And that is why it is like it Cp 2 W H 2 is act as a Lewis base and form adduct with B F 3. So, you know that B F 3 is a Lewis acid. So, it form adduct like W B W Cp, Cp, here hydrogen and B F 3. So, this is adduct, acid base adduct simple.

More interesting here you see that this one if you irradiate with light and what happened the reductive elimination of H 2 because you know it has d 2 system and 18 electron, so it can undergo easily the reductive elimination and forms the Cp 2 W. So, now here now, it is very interesting. So, it is 16 electron system, now, initially it was 18 electron system and this one can undergo a series of very unique and very interesting reactions.

As example, it reacts with cyclic ether and undergo the oxidative addition reactions like this way. So, if it is oxidative addition then what will happen? So, this one and like this one, so, oxidative addition here this reaction is the oxidative addition. So, again it will become the 16 electron system 18 electron system valence electron system. So, is basically you see that here again CO bond activation is happening.

Now, another interesting reactions is similarly, if it react with the C 6 H 6 that is the benzene, what you will get? Obviously you will get this one so, again it is oxidative addition reactions of C H bond. So, here also again it is 18 valence electron, very interesting no. This is very reactive intermediate that is after this is very highly reactive intermediate because it is called also transient species that means you are creating this reactive species by photosynthesis.

Now, as it is 16 electrons it can also undergoes the simple coordination reactions with other ligands like carbon monoxide or PR 3, maybe this one so, it forms the like this one so, it is very common. The most interesting is that this is used for one very interesting reactions, which is if you take the Cp 2 W this one and react with activated acetynyl acetylenic compound as example, CO 2 Me, CO 2 Me both side ester. And it undergoes insertion reaction so alkene and in WH bond and what will happen you will get like this is CO 2 Me and CO 2 Me.

So, you will see here how what does it what is happening here this one, so it undergoes the insertion reactions of the alkene into W H bond and it is Cis fashion, so it is regio selective Cis fashion. So, this you see that how these tungsten bent tungsten bent metallocenes compounds where metal is tungsten and it is d 2 system can undergo various interesting reactions which are not actually possible for the 3d parallel metallocenes. And all for all these unique reactions the responsible is the electronic arrangement.

Like here it is d 2 system and 18 valence electrons and this d 2 is you will see that is act as a Lewis base so, it is excess electron as a lone pair and forms the adduct not only that, after the reductive elimination, it can undergo the various oxidative addition reactions basically the bond activation reactions and you will see that it can activate the CH bond, it can activate the CO bond, it can undergo the insertion reactions of the acetylene into W H bond that is here. We if remember we discussed in the classes what are the insertion reactions. So, basically insertion is just opposite to the elimination reactions.

So, today what we have done, we have discussed some of the unique reactions of some selected bent metallocenes compounds. And in the next class, we will be continuing to discuss the unique reactivities of the bent metallocenes specially with the special focus on the group 4 metals, as example, the titanium and zirconium. And then we will try to understand what unique properties are actually responsible for using as a catalyst in all alpha olefin polymerization reactions. So, till then, bye and see you in the next class where we will be continuing the chemistry of interesting bent metallocenes compounds.