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

**Professor. Sanjib K. Patra**
**Department of Chemistry**
**Indian Institute of Technology, Kharagpur**

## Lecture 18

## Unique Reactivities of bent Metallocenes (Contd.)

(Refer Slide Time: 00:34)

NPTEL ONLINE CERTIFICATION COURSES

Lecture 18: Unique Reactivities of Bent Metallocenes.....(*Continued*)

Students, learners, welcome once again for our course, Metallocene Based Catalyst for Polymerization. So, in the last class, remember we are continuing our discussion on the unique reactivities of the parallel and the bent metallocene. So, today we will continue about the unique reactivities of the bent metallocene mainly for the group four metals.

So, in the last class you saw that how the like tungsten, tantalum, bent metallocene are undergoes very interesting reactions and plays a important role in as a catalysts in various synthesis.

(Refer Slide Time: 01:28)

CONCEPTS COVERED

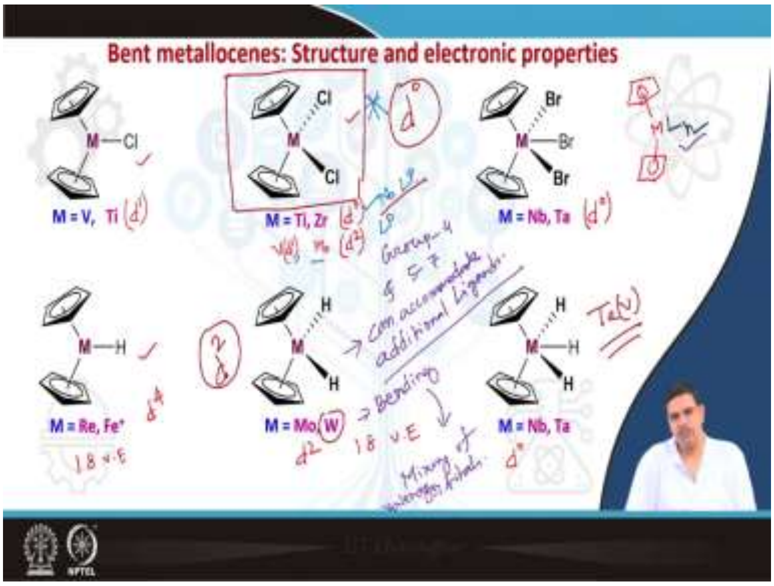
Properties and unique reactivities of common

- Bent metallocenes of Group-4 metals

So, today I will be continuing the discussion on the reactivities of the bent metallocene mainly for group-4 metals and you know that group-4 is titanium, zirconium and hafnium, I will mainly discuss about the titanium and zirconium that because the applications of the titanium and zirconium based bent metallocene are really remarkable in not only just in organics in synthesis in laboratory scale, but also in industries.

So, as example like you know that titanium and zirconium based metallocene are nowadays one of the best catalysts in alpha polymerization, and that is we will try to learn how it has been evolved? What are the unique properties are responsible for the development of the successful catalysts in alpha polymerization.

(Refer Slide Time: 02:35)

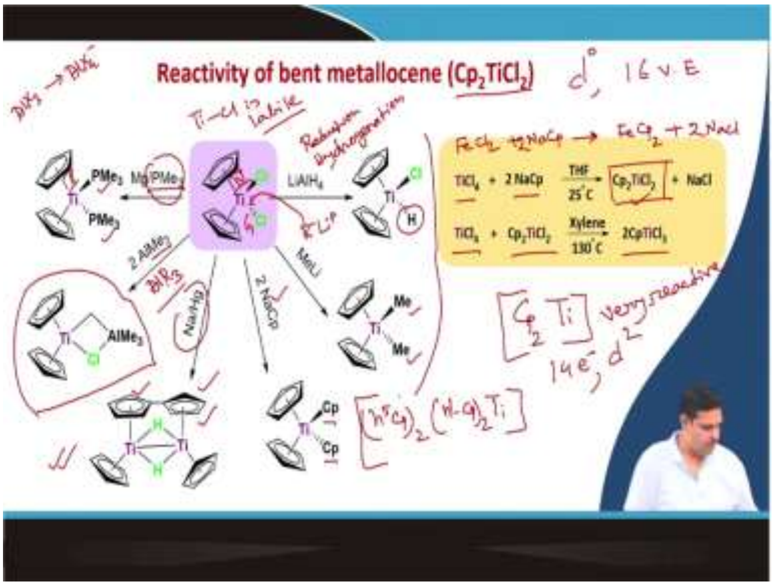


Bent metallocenes: Structure and electronic properties

So, let us continue our discussion on the bent, titanium and zirconium, this one we discussed in the last classes, but it is kind of a summary that how, what are the basic differences. So, in the last class, you will see that we have discussed about these tantalum compounds, that one tantalum of the oxidation state how interesting it is. We also discussed that how the tantalum three also like this one how the chemistry is interesting.

We also discussed the W, that is the tungsten, with the d2 electronic configuration, how it undergoes interesting reactivities. Today we will only, we will focus mainly on this system that is the titanium and zirconium and once again I will try to remind you that this is the d0 system where there is actually no lone pair, so, no lone pair and we will see how different in reactivities of this bent titanium zirconium d0 system from the others.

(Refer Slide Time: 04:02)



Reactivity of bent metallocene ($Cp_2TiCl_2$) $d^0$, 16 V.E

$FeCl_2 + 2NaCp \rightarrow FeCp_2 + 2NaCl$

$TiCl_4 + 2NaCp \xrightarrow[25^\circ C]{THF} \boxed{Cp_2TiCl_2} + NaCl$

$TiCl_4 + Cp_2TiCl_2 \xrightarrow[130^\circ C]{Xylene} 2CpTiCl_3$

$[Cp_2Ti]$ very reactive $14e, d^2$

$[(\eta^5\text{-}Cp)_2(\eta^1\text{-}Cp)_2Ti]$

So, let us see its interesting properties. So, first we will discuss the Cp2TiCl2 that is actually the d0 system as I told, d0 system and it is 16 electrons, 16 valence electrons. How to synthesise? Very easy as we have if you remember the synthesis of the ferrocene, if you take the ferrocene chloride and if you take the sodium CP, very easily you can get the Cp2 and you get the 2 sodium chloride.

So, similarly, you can synthesise from titanium chloride and two equivalent of sodium Cp, and you get the your Cp2TiCl2 bent metallocene, where two titanium chloride bonds are there and you can also synthesise the Cp2TiCl3 that is one Cp ring and three chloride bonds using the Cp2TiCl2 and one equivalent of titanium tetrachloride. So, synthesis is not really difficult quite easy and straightforward as you saw for the ferrocene synthesis.

Very unique properties ones of this one you see here that if you do the hydrogen shell reactions that is the reduction or let us better say hydrogenation, you can get the titanium hydride bonded a bent metallocene. Similarly, if you use the alkyl lithium R minus Li plus. So, it can easily replace, and you get the your dimethyl titanium metallocene and you if you use two equivalent you can replace the two chlorides very easily quite easily. Why I am showing? To show that yes this can undergo the easy substitution reactions because the titanium chloride bond is quite labile and easily you can substitute, and your the bent metallocene moieties is intact. So, that means you can functionalize your bent titanium metallocene as you wish.

Similarly, if you use the additional two CP minus, you can replace the two chlorides and forms the ETA 5 c1. So, this is very interesting structure ETA 5 Cp 2 and ETA 1 Cp 2 and here it is titanium. So, this is a kind of fractional it shows the fractional behaviour. So, always exchange with ETA 5 ETA 1 ETA 1 ETA 5 so, one ring is ETA 5 it can we convert it to ETA 1 like that.

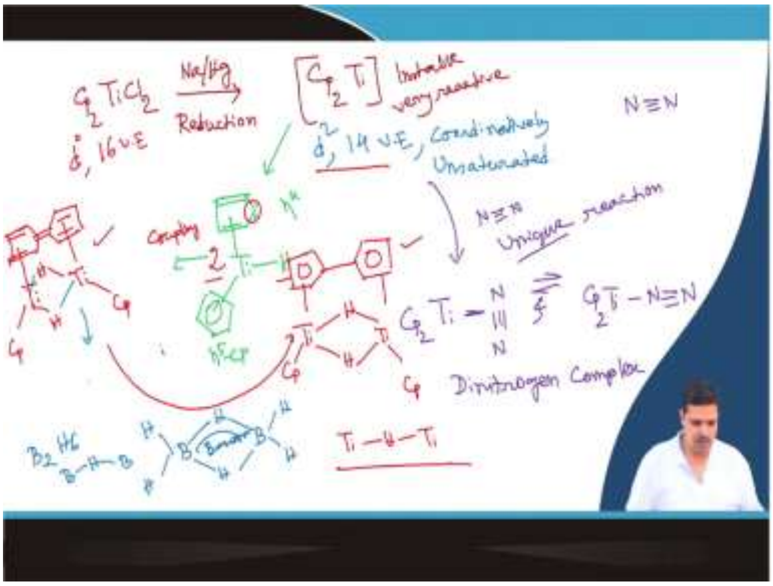
So, again it is if you react with any phosphines in presence of the metal then what happens? It takes the mgcl2, so, it acts as a chloride abstracting agent and in the vacant and the vacant position is coordinated by the phosphines and you get the titanium phosphine complexes. So, here you will see it is plus four oxidation state here plus four oxidation state, but here you see that it is plus two oxidation state.

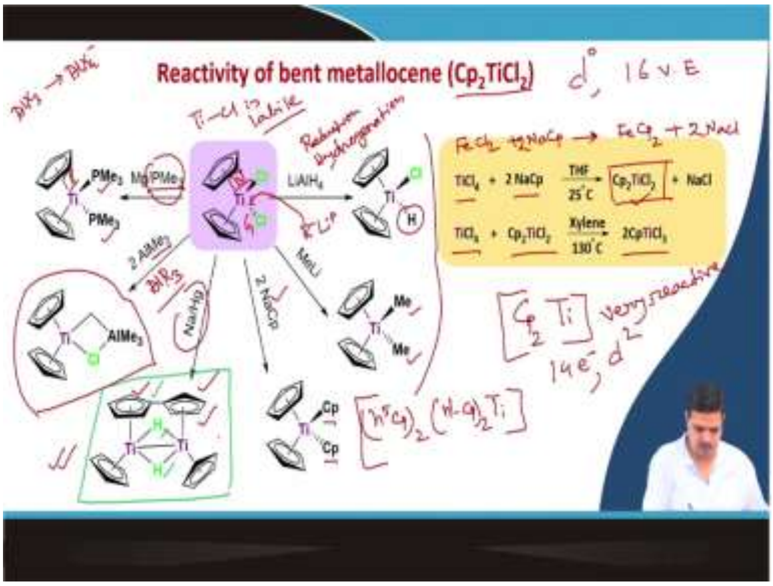
So, again so, d0 become d2 system. Here you see this is you are taking the AlR3 that is the aluminium alkyl, trialkylated aluminium, it undergoes very interesting reactions where you see that one chloride so, you know that AlR3 is positive oxidation state and it always try to take any chloride or extra R group to become the AlX4 minus. So, here you will see that AlX3 will be like AlX4 minus. So, this you see that here, this h2 group that is that the methyl group is inserted here and form that compound with the alkylated aluminium.

So, you can functionalize your bent titanium metallocene according to use you use and your applications and it is quite straightforward. Here you see that if you try to reduce do the reduction using the sodium amalgam it undergoes a very interesting reactions you will see here these two CP rings that this one and this one undergoes a coupling reaction and form a (())(10:15) machine complexes.

I will discuss in more detail about this one and also I will discuss the chemistry of the titanium Cp2Ti because this one is really very reactive, it is very reactive and this is actually prepared from the Cp2TiCl2 in presence of sodium amalgam, and this is you know, this 14 electron system and it has a d2 electron. So, you see that this substitution reactions these are all actually substitution reactions here these side so, it is quite straightforward. And if you do the reduction that is actually more interesting.

(Refer Slide Time: 11:18)




Reactivity of bent metallocene ($Cp_2TiCl_2$)

$TiCl_4 + 2 NaCp \xrightarrow[25^\circ C]{THF} Cp_2TiCl_2 + NaCl$

$TiCl_3 + Cp_2TiCl_2 \xrightarrow[130^\circ C]{Xylene} 2CpTiCl_3$

So, if you take the CP2 titanium, Cl2 and you do the reduction in presence of sodium amalgam what happened you get a very reactive instable compound. Let us try to find out that what are the difference in electronic elements. So, Cp2TiCl2, so, this is the d0 system and this is 16 valence electron and whether in the Cp2Ti you see that this is d2 system because the reduction is happening and it is 14 valence electron and it is you see co-ordinately unsaturated. So, this is 14 electrons and you know that the nitrogen dinitrogen it is very non-reactive very stable. The nitrogen nitrogen bond here is almost 946 kilojoules per mole.

So, it is very small and is a very stable molecule and it is a also nonpolar so very difficult to break the N 2 and it is a quite challenging process. But here it is so reactive it can react with the dinitrogen and form the dinitrogen complex. This is you will see that is very limited in literature. So, what happens this Cp2Ti forms dinitrogen complex in both ways like this one and like this way in both modes.

So, this is actually in equilibrium. So, here you will see that this is quite unique in reactivity, very unique reactions. Unique reactions it can react with dinitrogen and forms a dinitrogen complex. This is very interesting and very rare. More interestingly if you have seen the last slide this compound how this 2CP 2 titanium CP is coupled and form these 2 CP rings are basically bonded through a carbon-carbon bond and forms a dihydrogen like Banana Bond like compound.

So, how does it happen? So, this one undergoes after undergoes the reduction reactions. What happens here this titanium and one is like CP minus, so, this is a CP minus ETA 5 CP as it is and what happens one CP like that. So, this is so, you will see that it has become ETA 4 and that titanium hydrogen one bond. Now it is this one the two unit of this undergoes the coupling reactions, coupling reactions between this one, then what is happening.

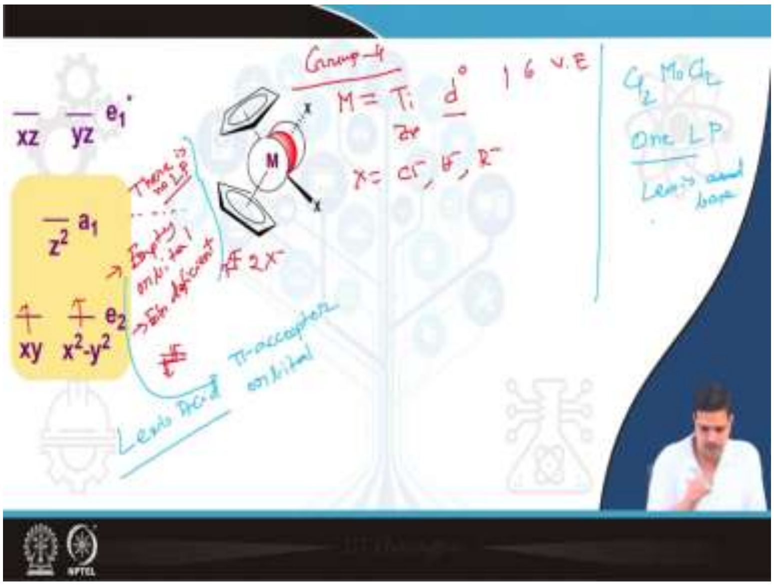
It is so, basically it is if you see two of these unit forming a coupling reaction, so like this one and you have a titanium this CP and you see it is a hydride. So, the here one hydride and one here hydride and interestingly it forms the titanium hydrogen bond just like a in B2H6, so it forms like this way we know that B2H6 we call BHB Banana bond, so, it is like that. So, we know that like that this is called the banana bond.

So, here similar it is forming like this one and then what happens it is undergoes the rearrangement and forms the like your final compound which is, so, titanium and here CP as it is here, you have two bridged hydrogen bond. So, your see this is the terminal, this terminal is now converted to the bridged two bridged hydrogen bond Ti H Ti. Now what happens here you have so, I think it would be better to write here not it will be always complicating.

So, I am writing the structure here, so that will more easily understandable so, here you will see that two bridged hydrogen bond here Cp here Cp that is ETA 5 obviously, and here we will draw the Cp ring so it is kind of a rearrangement between this one and this one and this one and you will see here you are getting. Basically, the if you see the previous this one you are getting.

So, this is very unique in reactivity. So, I removed this one so that it is easy to understand. So, in case these here you see that as it is being reduced to d0 to d2 system and becoming a 14 electron system. So, what happens here it is undergoing the dimeration reactions between these two units of the ETA 5 CP and ETA 4 CP and this is basically the carbene and it is undergoing the coupling reactions and then undergoes the rearrangement and what is the driving force is driving force is basically the aromaticity. So, it is becoming aromatic and forming the dimeration through the titanium hydrogen titanium bond. So, this is also very unique in reactions.

(Refer Slide Time: 21:37)



So, we know now the tantalum chemistry, tungsten chemistry, titanium chemistry. Now, let us go to the zirconium chemistry. How does it differ? Obviously the titanium and zirconium chemistry is very much similar because those are in the group four metal. Generally, if the titanium goes one reaction, the zirconium analogue will also undergo the same reactions in general.

So, let us discuss in more detail. So, here you see that if you remember that this one for titanium or zirconium here metal is either titanium or zirconium case and in these cases is d0 electron system if x is halide or let us say chloride or hydrides or any R the alkyls. So, what happens you initially how many electrons are there?

So, here is basically the this one electrons and these two electrons and then if it is like let us say the 2 halides like or 2 halides, then what will happen you will see that this one will have and this will have a nonbonding electron pairs. So, 1, 2, 3, 4, so, these four electrons will be filled up, filled it up and this one will have the like that and here you see there is no lone pair and the nonbonding this nonbonding orbital will have no electron, so is basically is empty orbital.

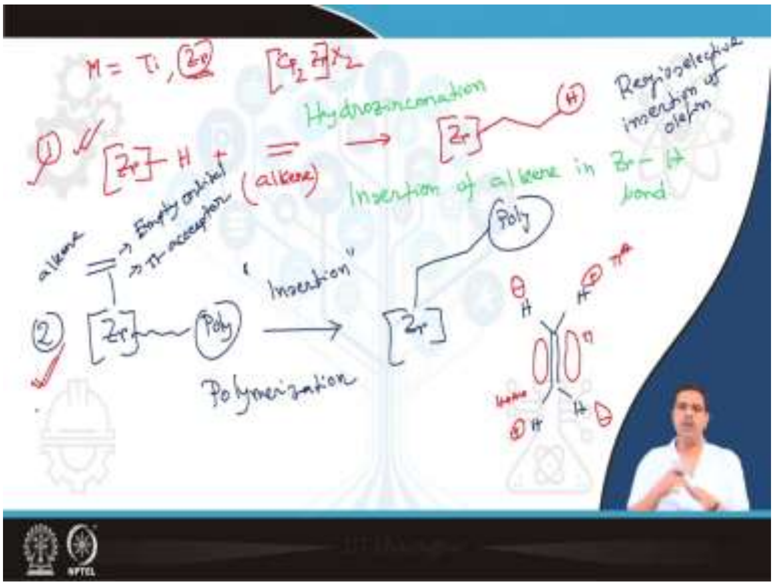
So, that is why it acts as an electron deficient compound, obviously these are 16 valence electron system, we now familiar with this one. So, this is 16 electron system d0 system, no electron on the nonbonding electrons, no lone pair. So, that is why it is electron deficient compounds.

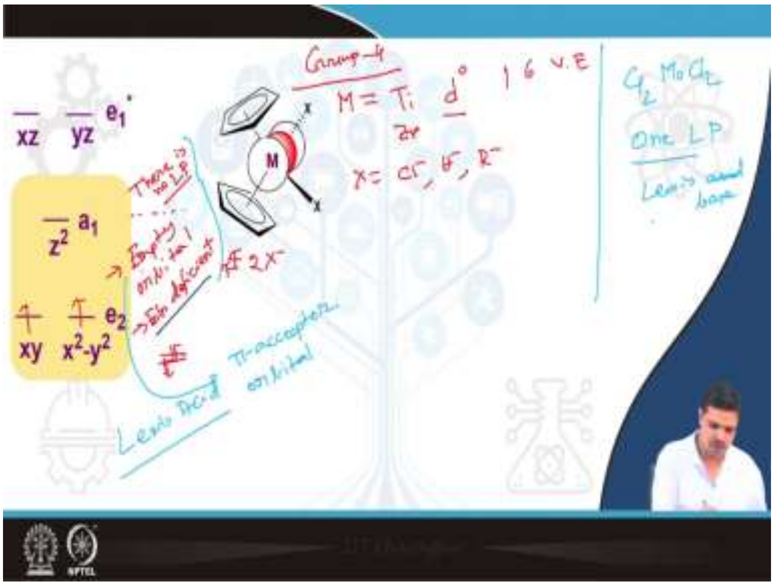
So, these are the group four the basic properties of the group four metals, metal bent metallocene chemistry, which is quite different properties and the reactivities due to these two reasons. So, we will try to see that how it differs from the other bent metallocene what we have discussed so far. So, obviously as there is no lone pair, so, this acts as a Lewis acid.

Now, we saw that like if it is like molybdenum CP2 Mo Cl2, Now, you will have it initially it was a d4 electrons now, you will have two lone pairs. So, one lone pairs two electrons in the non on the nonbonding and nonbonding orbitals and here will be become is a Lewis acid. So, extensively we have discussed sorry this will be Lewis base because you have a one lone pair.

So, we have discussed this electronic arrangement and the criteria in our previous discussion. So, now, let us see that what the reactions it can undergo considering the electronic factors of this CP2 ZR or CP2 titanium dichloride compounds. So, as I told this is electron deficient compounds and it has an empty orbital which can act as a pi acceptor orbitals. So, this one can act as a pi acceptor orbitals.

(Refer Slide Time: 26:58)





So, let us see what can give the extra feature for these metallocene compounds, where you have the metal is titanium or zirconium, mostly now, I will be more interesting interested to discuss the chemistry of the zirconium. So, two main applications based on this bent zirconium metallocene compounds with the structure of this the X maybe halides or hydrates or alkyls. One is the like this one, so, you have Zr.

So, you have a zirconium hydrate, I am writing it as this moiety is like this one or if you have any alkene this is alkene, then you will have this one and this hydrogen is basically that one. So, it is happening what is happening? So, it is basically insertion of alkyne in Zr, H bond. So, this is really very interesting other, compared to the other complexes, other bent complexes. So, another one is this is actually called the hydro zirconium reactions.

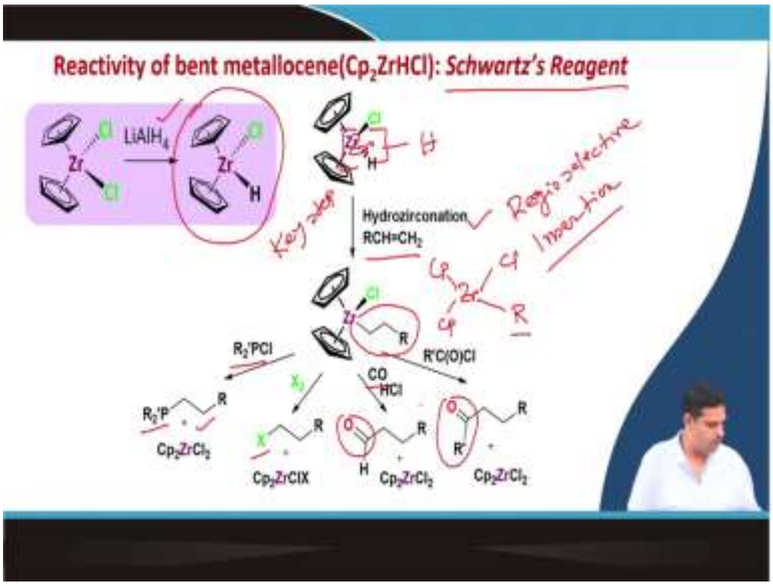
So, this is called the hydro zirconation process. Another interesting reactions it can undergo that is the olefin polymerizations suppose, I have this one and this I have the polymer end and this is the alkene coordination. So, this is the alkyne pi complex. So, it undergoes the like that and here it is my polymer end. So, what is happening here you see that again this is a insertion reactions.

So, this zirconium bent metallocene compounds are very unique in Regioselective insertion of olefin and here the polymerization and now you can correlate that what properties electronic arrangements are responsible for the these two reactions here you will see that as it has empty orbitals, these can coordinate with the alkene which has pi electrons empty orbitals and pi acceptor orbital which can act as a pi acceptor. So, that means, you know that alkene is like that, and it has a pi electrons like this one.

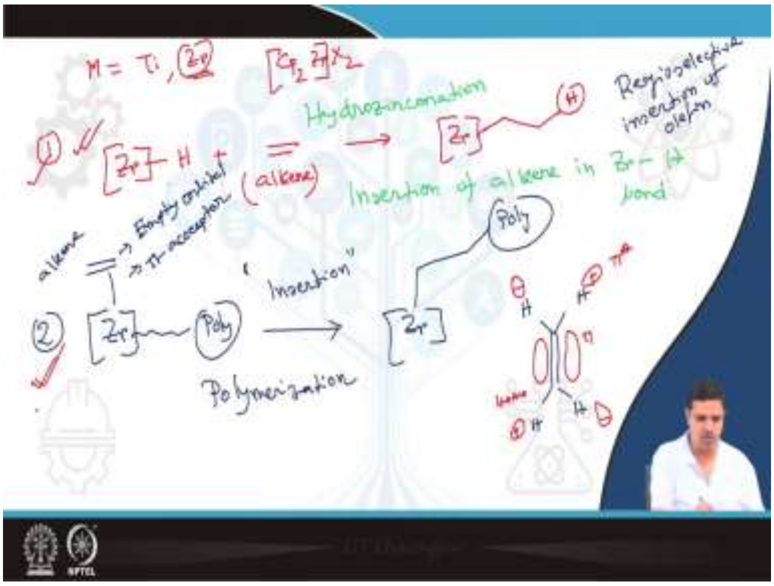
So, this is my is called you can call homo and it has a pi star like this one. So, pi star is like this one and this is the pi. So, this pi electrons is actually donated to the empty orbital of the zirconation bent metallocene and gives these kinds of interesting reactions and these reactions is basically made this bent metallocene of zirconium popular in industrial applications, because here you see this one is used as to functionalize the olefin which can undergoes selectively it undergoes the regioselective insertion of the olefin.

And second one this is actually the this course is all about this one is the polymerization of zirconium metallocene, how, why it is responsible and why this polymerization reaction undergoes, that is why we discussed about the unique reaction of properties of the bent metallocene. So, that we can understand the electronic factors which is actually responsible for undergoing this kind of reactions, which is alkene coordination and the insertion.

(Refer Slide Time: 33:48)



Reactivity of bent metallocene($Cp_2ZrHCl$): *Schwartz's Reagent*



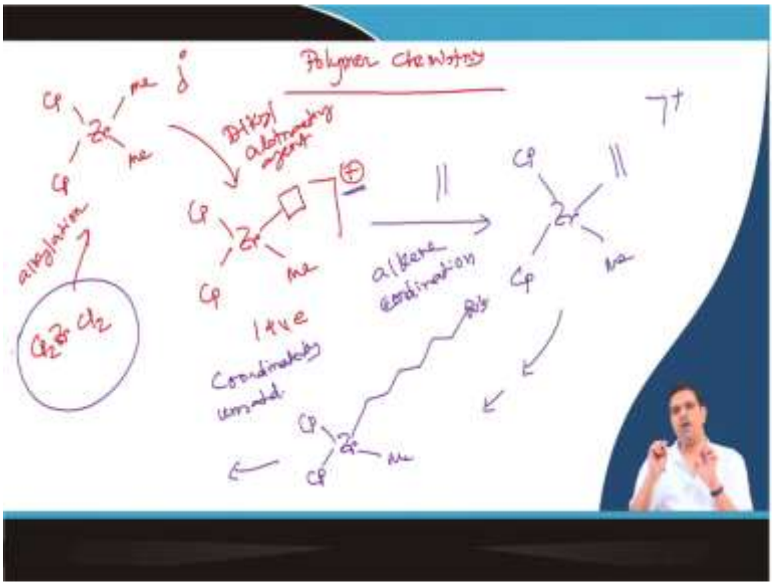
So, as I told that, this one is very popular catalyst that is the Schwartz's Reagent probably I am sure you have heard about that this is nothing but if you react with or reduce with hydrogenate with lithium aluminium hydride. So, you are getting basically the zirconium hydroid one example you see here that is the thing I wrote here. So, zirconium hydrate complex.

And it has a huge applications here you will see that you see that this is hydrogenation reactions. This is called the hydrozirconation reactions and it is Regioselective and you see that this one is inserted these zirconium this alkene is inserted into the zirconium hydrogen bond and it undergoes then a different substitution reactions and give is a functionalized alkanes.

So, this step is very key step that is the regioselective insertion reactions and this is very popularly called the Schwartz's reagent that is the this one, is used in organics and you will see that how this alkyne is converted to different functionalize alkanes like, if you now once it is you form the zirconium carbon alkylated that is you will see you are basically converting a zirconium and here the chloride and here the R group and here CP.

So, you are converting the hydride to the to the zirconium alkyl complex and then going and reacting with like your X2 . So, that is that any halides, you are basically functionalizing your alkyl here it is you see that is X if you react with the phosphine chloride you will get here the phosphine, if you react with carbon monoxide, you will get the formulation here and if you react with in keto you will get the acetyl here. So, this is very popularly used in organic synthesis for functionalizing the alkyne.

(Refer Slide Time: 36:49)



And another one as I told that zirconium complex that is which is used in polymerization in polymer chemistry although this one we will discuss in very detail in the next classes, how does it undergoes, I am just writing you showing first you have to do the methylation. So, that actually do from the zirconium from this one, CP2 Zr Cl2 and you do the alkylation you can do by (())(37:35) reactions or by using the trialkyl aluminium complexes.

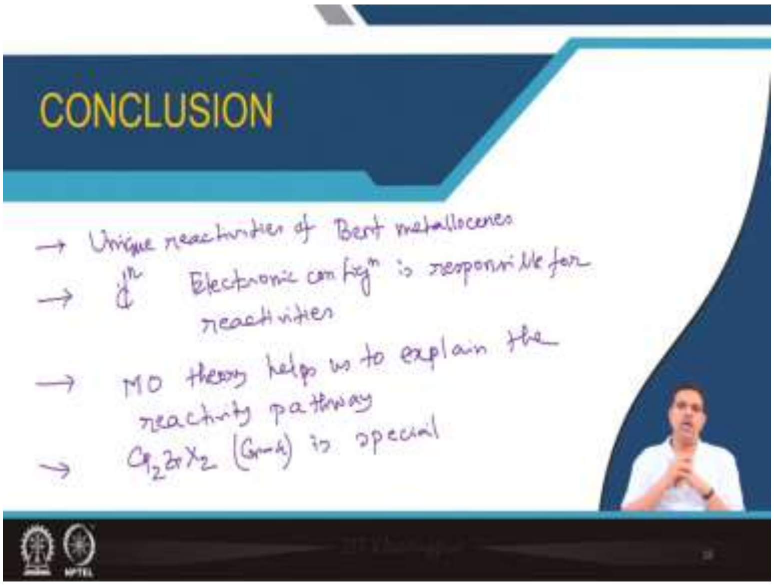
Then what do we do this one we use the alkyl abstracting agent again you can use the trialkyl aluminium and forms the methyl and this one. So, you will see there is a vacant position here. So, it is basically now again you see that this is the d0 system. Now, it is 14 electron system valence electron system here and this one is actually responsible for olefin polymerization.

So, this one actually undergoes the olefin polymerization how because you see that if you take the alkene it has a vacant space and vacant coordination site. So, it reacts like this one and undergoes insertion reactions. So, this is alkyne coordination, this methyl abstracting is the step is essential to create the unsaturation co-ordinately unsaturation because you know that if we do not offer a space for the incoming substrate, then it can cannot come to the close proximity of the metal centre.

So, this is important and another important So, is the dual role important point is that we are putting the cationic charge here. So, that means the alkene can coordinate more easily. So, feasibility of the alkene coordination will be more if we make the cationic complexes.

So, two roles why we are abstracting one methyl group to make a co-ordinately unsaturated compound and also for electronically it is more feasible for the coordination of alkynes. So, unsaturated compounds. So, now, it will go under several insertion reactions and alkyne coordination reactions and then you will get basically the growth of the polymers here like that. So, this is the simplified strategy, the mechanism for the polymerization, how this category of the bent methylation compounds favours the alkyne coordination and alkyne insertion which are the basic key steps for the Alpha olefin polymerization.

(Refer Slide Time: 41:10)



CONCLUSION

→ Unique reactivities of Bent metallocenes

→ $d^n$ Electronic config$^n$ is responsible for reactivities

→ MO theory helps us to explain the reactivity pathway

→ $Cp_2ZrX_2$ (Gr-4) is special

So, in these classes we discussed the unique reactivities of bent metallocenes and now, it is very clear that how different in reactivities from the parallel metallocenes compounds as example like ferrocene, nickelocene, chromocene like that and we discuss that how the electronic arrangement, electronic configuration is responsible for reactivities in different fashion.

And we saw we by using the simplified molecular orbital diagram we discussed helps us to explain the reactivity pathway and then, at the last we will discuss we saw that how the category of this CP2 Zr X2 that is the bent metallocene zirconium that is a group four transition metal compounds is special from the other bent metallocenes, although you saw that many of the bent metallocene of like tungsten, tantalum or titanium are heavily used in metal in catalysis and also in stoichiometric transformation of various organic compounds which are still used in laboratory scale and many of these are in industrial scale.

So, in the next class, we will be continuing about the discussion about our polymerization. Now we will enter to the coordination polymerization using the metal catalysts. And we will see that how this the metal catalysts have a special feature for making or controlling the tactility regioselectivity of the alpha olefin polymerizations. So now, students, I am very confident that you will be now able to correlate the electronic factors and the reactivities of the bent metallocene and now, we will have a very clear idea why bent metallocenes are interesting and why they are so different from the parallel metallocenes.

(Refer Slide Time: 44:54)

REFERENCES

- The Organometallic chemistry of the transition metals by Crabtree, Wiley, Sixth edition, 2014
- Organotransition metal chemistry from bonding to catalysis by John Hartwig, University science books, 2010
- Organometallic chemistry and catalysis by Astruc, Springer, 2007.

So, these are the references you can read and the last few classes I have taken the content or the discussion from these three books. So, thank you and we will see in the next class, where we will be entering to the polymerization of the metals catalysts, which are actually the coordination we call the coordination polymeration. Thank you and see you in the next class.