# 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 15
## General Synthetic Strategies for Metallocenes (Parallel and Bent)

(Refer Slide Time: 0:30)

NPTEL ONLINE CERTIFICATION COURSES

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

SANJIB KUMAR PATRA
DEPARTMENT OF CHEMISTRY, IIT KHARAGPUR

Welcome to our course again. Today, we will discuss the general synthetic strategies for metallocenes mainly for bent, but we will just discuss very briefly about the parallel metallocenes compounds, because the strategies are very much similar. So, in the last classes, we have discussed extensively the bonding and the structure of the metallocenes compounds, and we saw that depending upon the metal centers, oxidation states, you will see that there is a variation in structures and of course, there is a variation in electronic nature HOMO and LUMO and the relative energies of the d-orbitals participating in the bonding.

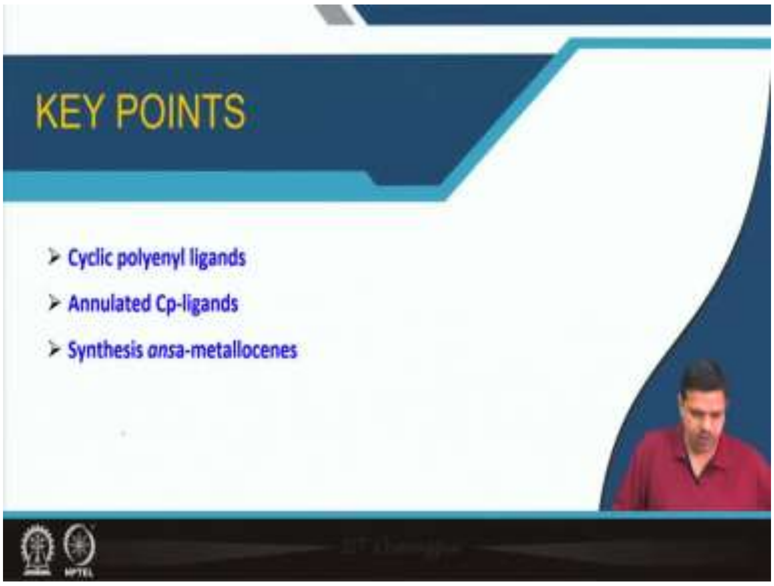
(Refer Slide Time: 01:46)

CONCEPTS COVERED

- Synthesis of cyclopentadienyl (Cp) and annulated-Cp ligands
- Design and Synthetic strategy for *ansa*-metallocene compounds

So, now today we will discuss some of the hormone general synthetic strategies, and then we will discuss the reactivity's with the help of the bonding what we have discussed in the last class. So, today, we will mainly covered the concept of synthesis of cyclopentadienyl and also annulated-Cp ligands, which are more interesting for our metallocenes based catalysts, chemistry. And of course, we will see how we can design and synthesis, our desired ansa-metallocenes compounds.

(Refer Slide Time: 02:14)

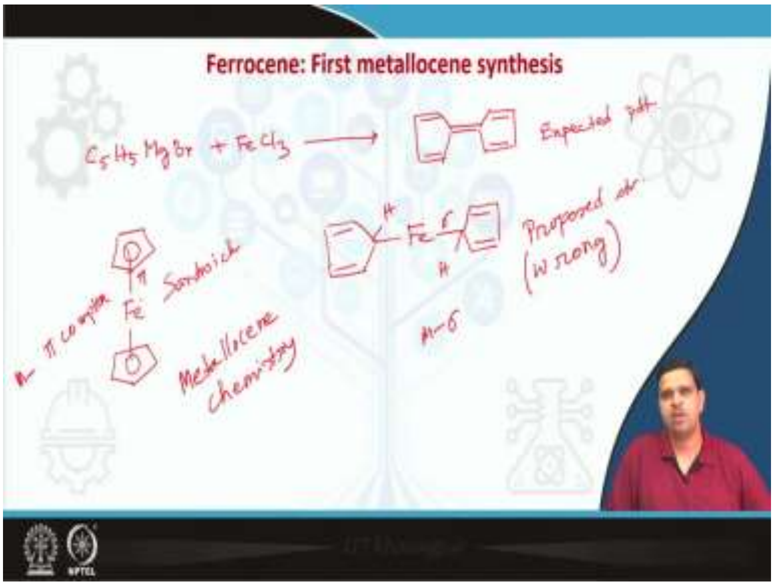


KEY POINTS

- ➢ Cyclic polyenyl ligands
- ➢ Annulated Cp-ligands
- ➢ Synthesis *ansa*-metallocenes

The key points, cyclic polyenyl ligands and annulated-CP ligands, synthesis of ansa-metallocenes we are now familiar about the ansa. So, most of the cyclopentadienyl based ansa-metallocenes compounds is required for our catalysis reactions, polyolefin catalysts reaction to restrict the rotation of the Cp ligands and to induce the chirality, to lower down the symmetry. And this is important, we will discuss in the next classes, how it influences the tacticity in the resultant polymers. So, before that, we have to know that how we can design our catalyst and how we can design our ligands.

(Refer Slide Time: 03:06)



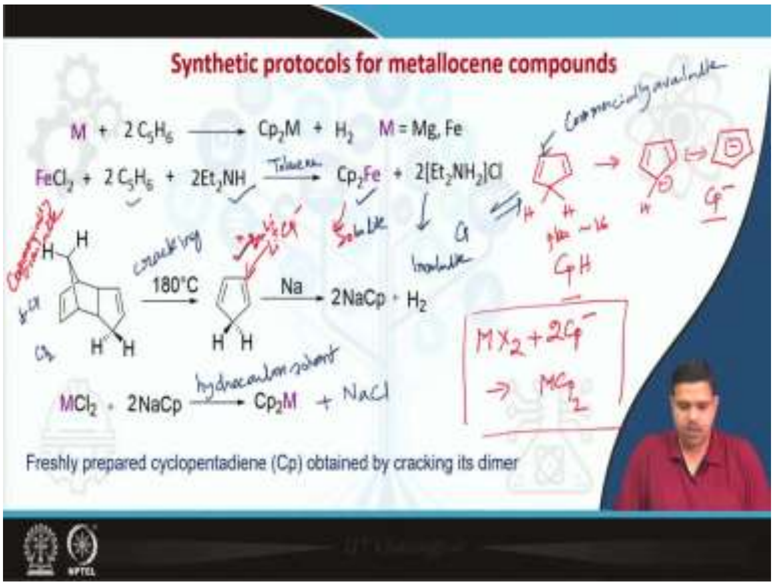
Ferrocene: First metallocene synthesis

So, as I told that, when we will come to the metallocenes, we cannot ignore the parallel metallocenes compounds and we really cannot ignore the ferrocene, because ferrocene was the first metallocenes which was synthesized and in the last classes we discussed that how this metallocenes was discovered, it was accidental. So, just to recap, (())(3:38) is actually was trying to make the make the (())(3:52) by these reactions, so what he was using the Grignard cyclopentadienyl Grignard and in the presence of ferric chloride and he was thinking for the strategy of oxidative coupling.

So, Cp minus then Cp dot and then the thought that there will be coupling and this desired product was like this one because, this was expected product but, the characterization confirm a different product formed and that time it was proposed as this one although it was the wrong structure that we discussed in the beginning of our classes. So, this here hydrogen here hydrogen, so, it was it was that time it was proposed structure however, it was wrong and later that (())(5:10) established the real structure of the ferrocene which was like sandwich type of structure like this one. So, and for that in 1973 it (())(5:20) were awarded the Nobel Prize.

So, it was from there it a different chemistry was started that is the metallocenes chemistry and as you know the fundamentally the bonding is very interesting. So, here you see the metal pi complex, the proposed one is actually the metal sigma complex, metal you see this is a sigma complex, this is the pi complex. So, after that there was a lot of interest to develop this chemistry and later it was found that this is not only the academic this interest for academic perspective, it has lots of applications in materials and organic synthesis and of course, in polymer chemistry.

(Refer Slide Time: 06:37)



Synthetic protocols for metallocene compounds

$M + 2C_5H_6 \longrightarrow Cp_2M + H_2$  M = Mg, Fe

$FeCl_2 + 2C_5H_6 + 2Et_2NH \xrightarrow{\text{Toluene}} Cp_2Fe + 2[Et_2NH_2]Cl$

$\xrightarrow{180°C}$ $\xrightarrow{Na} 2NaCp + H_2$

$MCl_2 + 2NaCp \xrightarrow{\text{hydrocarbon solvent}} Cp_2M + NaCl$

Freshly prepared cyclopentadiene (Cp) obtained by cracking its dimer

$MX_2 + 2Cp^- \rightarrow MCp_2$

What I do I will not discuss individual synthetic strategy I will discuss as a common synthetic protocols so that it is easy to understand and also easy to remember. So, here so, if let us say this one, this is C5 H6 and this proton is the PK is 16 around. So, if we can use a suitable base this can be protonated, deprotonated and you will get like this and you see that it is aromatic in nature so, this is my Cp minus and this is called Cp H do not be confused with these 2 hydrogen and why it is written Cp these are convention here it is Cp H and this we will write as Cp minus.

So, if we de-protonate the Cp H then if we react with any MN C2 M X 2 with 2 Cp minus you should get the M Cp 2. And if suppose it is a sodium salt so, it will that X will be removed as in X. So, this is the general protocols synthetic protocols however there is one another point you have to remember that this Cp H it is not commercially available. And do you know the reason this one is not commercially available, any reason for that? Yes, it actually undergoes the disorder reactions and it is actually the undergoes the dimerization like this one. So, this you can consider as Cp 2.

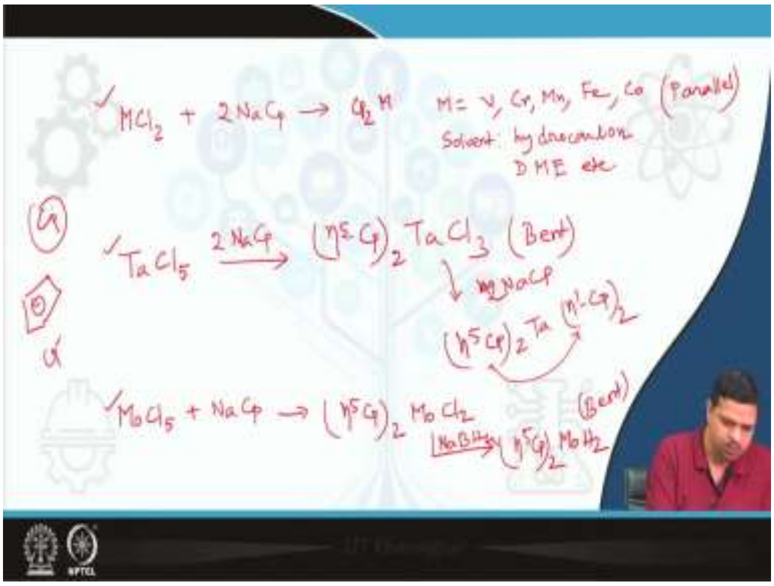
So, you have to do the reactor disorder reactions, if we heat it 180 degree centigrade it forms the cyclopentadiene. So, cyclopentadiene this is the di-cyclopentadiene, so Cp 2 we call also di-Cp and you can easily crack this is called cracking of the di-Cp. So, if you crack it you will get the Cp H and then use any strong base you will get the Cp minus and then you can react with the metal halides although here the MX bond should be labile otherwise the reaction will be not easy and then you can get your desired M Cp 2.

We use for this kind of reaction, so use general use the hydrocarbon solvent, hydrocarbon solvent, do you know the reason why? Yes, this is to make the process easy purification easy because in hydrocarbon solvent your metallocenes will be soluble, but the sodium X here were what will form here? Sodium chloride, that will be in soluble so, you can easily filter it and you can get your desired metallocenes.

So, as example here you see that iron chloride and you use the cyclopentadiene and use a amine base and you are getting the Cp 2 Fe and if you use like Toluene here so, this will be soluble and this is insoluble. So, you can easily separate and you can get your ferrocene compounds or this study can be applied for other metallocenes compounds.

So, main thing you as I told that this is you have to remember you cannot start from the direct Cp H because it wants you by the this one with time it slowly undergoes the dimerization, so, this is the commercially available this one. So, this is dimerization is a reversible process if you heat it then it will again go to the monomer form. So, this is the general synthetic protocol even this one if you use the butyl lithium you will form the Cp minus Li plus and this Cp minus you can react with your the metal chloride to get your desired metallocenes compounds.

(Refer Slide Time: 12:14)



✓ $MCl_2 + 2NaCp \rightarrow Cp_2M$

M = V, Cr, Mn, Fe, Co (Parallel)

Solvent: hydrocarbon, DME etc

✓ $TaCl_5 \xrightarrow{2NaCp} (\eta^5\text{-}Cp)_2TaCl_3$ (Bent)

$\downarrow$ NaCp

$(\eta^5\text{-}Cp)_2Ta(\eta^1\text{-}Cp)_2$

✓ $MoCl_5 + NaCp \rightarrow (\eta^5\text{-}Cp)_2MoCl_2 \xrightarrow{NaBH_4} (\eta^5\text{-}Cp)_2MoH_2$ (Bent)

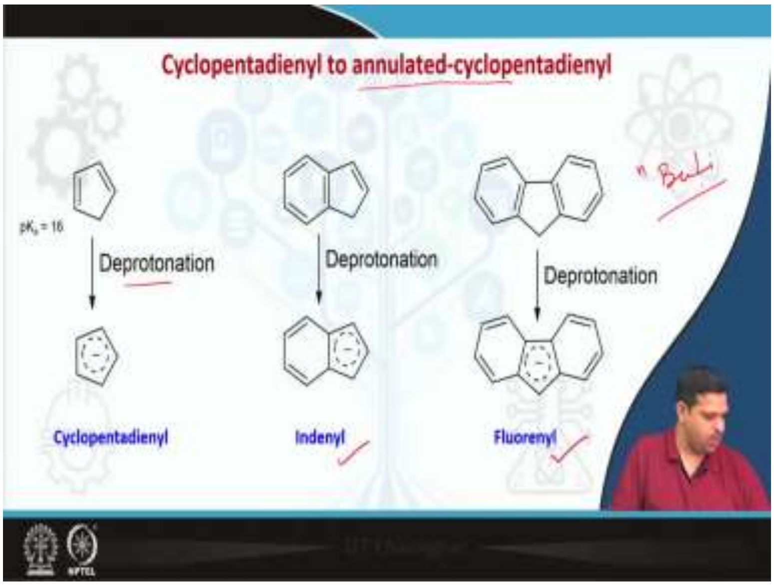
So, in a similar strategy you can make lots of metallocenes compounds whatever you desire to make. So, as I told that this one and you if you take this one and you will get your Cp 2 M, I just point out what metallocenes you can prepare following this strategy. Here this M may be vanadium, chromium, manganese, iron like that, cobalt, solvent as I told you can use Toluene, hydrocarbon solvent is favoured and sometime hydrocarbon, sometimes you have to use also DME di-methoxyethane like that, fine.

Similarly, you can not only the 3d transition metal metallocenes you can also make the group 4 to group 6 metallocenes compounds by following the same strategy like if you take the penta-chloro tantalum, if you take the sodium Cp, 2 sodium Cp you can get the eta 5 Cp 2 tantalum CL 3 we discussed the bonding of this kind of compounds in the last class it is this is a bent of course, and these are actually the parallel. So, similar you can you can make it. And if you add one more sodium Cp you can make the eta 5 Cp 2 tantalum eta 1 Cp 2.

So, here you will see that this is very interesting because you can have a fluxional behaviour. So, there is a exchange between eta 5 and eta 1 mode. So, you will get the fluxional behaviour for this kinds of compounds. Then similarly, if you take the MO penta-chloro-molybdenum compounds and the sodium Cp you will get the MO eta 5 Cp 2 MO Cl 2 and if you do the you can make this kind of compound. So we discussed in the last classes about the bonding, so this is also another example of the bent metallocenes.

So, there are a lot of synthetic protocols you can apply to make any of the metallocenes compounds. So, as example you can see molybdenum, tantalum here the general protocols mainly for 3d transition metallocenes, although these are not restricted to the 3d same protocol can be applied for other metallocenes compounds. So, you see that the synthesis is quite easy and straightforward and this so, so far what we have discussed the synthesis only the Cp ligands that is the simple cyclopentadienyl ligands which is called the Cp minus.

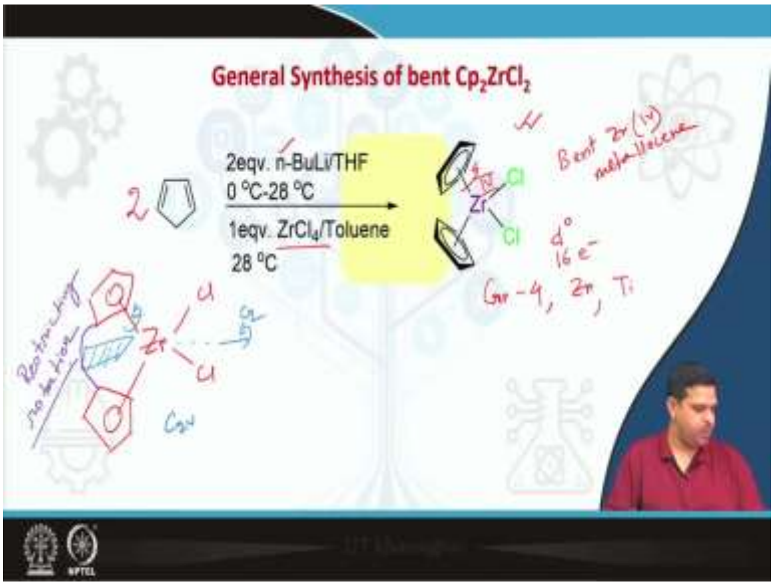
(Refer Slide Time: 17:09)



Cyclopentadienyl to annulated-cyclopentadienyl

So, similar strategy can be followed for the annulated cyclopentadienyl or sometimes called the fused cyclopentadienyl. So, here the same strategy, so, you have to do the deprotonation as we have done for the Cp minus, here it is called indenyl so, this is the indenyl, if we do the deprotonation you have got indenyl there is a flooring you if you do the deprotonation you get the fluorenyl with the proper base mainly the we use butyl lithium, n butyl lithium mainly for the deprotonation. So, we will discuss about the some of the representative synthesis of the for the annulated cyclopentadienyl metallocenes compounds.

(Refer Slide Time: 18:01)



General Synthesis of bent $Cp_2ZrCl_2$

2eqv. n-BuLi/THF

0 °C-28 °C

1eqv. $ZrCl_4$/Toluene

28 °C

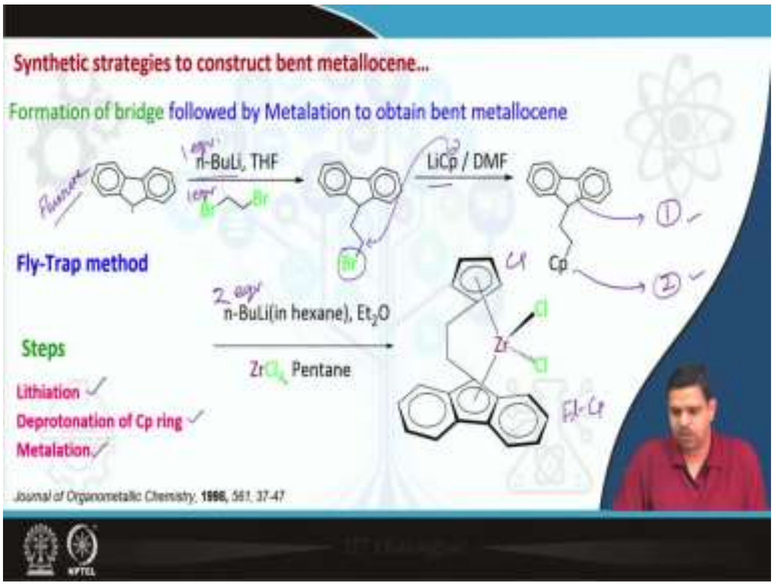
So, again as I told that this is one example for the group 4 metals, that is the zirconium, same thing can be applied for zirconium and titanium. So, here it is you see for oxidation state that means, if you remember the last test class, so, this is a d 0 system, 16 electron system, we extensionally discussed the unique nature or bonding nature of this kind of complexes, which are the actually the basic skeleton these are the basic skeleton for the polyolefin catalyst we will discuss in the future classes.

So, you will see that synthesis is straightforward, you use 2 equivalent of n-BuLi, where because you need the 2 equivalent of the Cp ligands and then you add the zirconium chloride, tetrachloride and you will get your the bent zirconium metallocenes what is oxidation state is 4. So, this is the general synthesis protocol for most of the metallocenes compounds whether it is parallel or bent.

So, what I will discuss now, I will discuss the some of the representative synthetic protocols. You will see that that this one as I told that this can undergoes the rotation because if it is so if I draw like this one zirconium and chloride, and here like that, you see that this is a C 2 V point group because you have here C 2 and this is the plane sigma V plane, so this is C 2 V. And also you see there is a rotation. So, now if I thread it, how we will thread it? Because this rotation is at room temperature is sufficient, so it will not be restricted to like this one, so it will be rotation. So, we cannot really impose a permanent symmetry.

So, for that one if you can thread it like this one with engineering your metallocenes like this one if I like thread it, then what will happen? I am restricting rotation so, I will get a permanent symmetry. So, for that we have to design our metallocenes compounds and before that we have to design our ligands in such a way that I can get a particular metallocenes with a particular symmetry.

(Refer Slide Time: 21:29)



**Synthetic strategies to construct bent metallocene...**

Formation of bridge followed by Metalation to obtain bent metallocene

**Fly-Trap method**

**Steps**

- Lithiation ✓
- Deprotonation of Cp ring ✓
- Metalation ✓

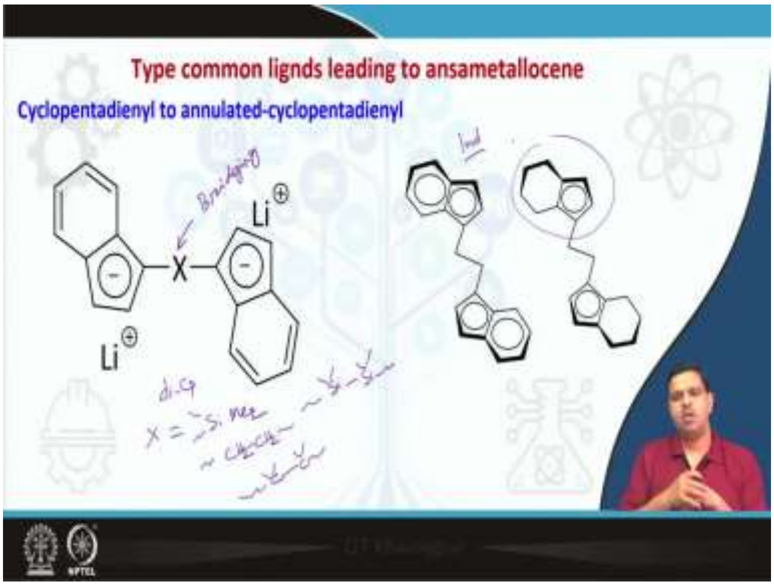
Journal of Organometallic Chemistry, 1998, 561, 37-47

And now, I will discuss some of the representative metallocenes synthesis so that you can understand that how you will progress and start from a commercially available Cp or annulated Cp moieties. So, here you see this is the fluorine you can commercially buy and you are using n-butyl lithium here. So, to deprotonate this position and you will then it will react with the monobromo, so you have to take this one in a good stoichiometry, 1 is to 1 so, this is one equivalent you have to take and this one equivalent you have to take very carefully and then what you will get? You will be getting the bromo-ethane functionalized fluorenyl compound.

Now, you will see here I am reacting with Li Cp this one so, Cp minus again will react with react here. So, this is and bromo is good living group. So, here how what you are getting? So, this one is 1 Cp that is the 1 Cp moiety and this is there another Cp moiety. Now, if you do the deprotonation again, so here you need a 2 equivalent n-butyl lithium and then if so, it will be basically the Cp minus here and Cp minus here and then you react with the tetra chlori-arconium you will get the metallocenes desired metallocenes.

So, again this is you see that this is the Cp and this is the fluorenyl CP. So, you will get very simple strategy and how you are getting a different metallocenes by the bridging of this C 2 and the by bridging of these 2 Cp by engineering your ligand and this can be applied further for different metallocenes compounds. So, here are the steps in summary. So, you do the lithiation then to functionalize your Cp to induce the, to install the another Cp moiety in your ligand to make the di-Cp. So, here not only the Li-Cp minus you can also put another fluorenyl Cp here. And finally, the deprotonation of the Cp rings for the metallocenes and then the metallocenes this is very simple strategy.

(Refer Slide Time: 24:41)

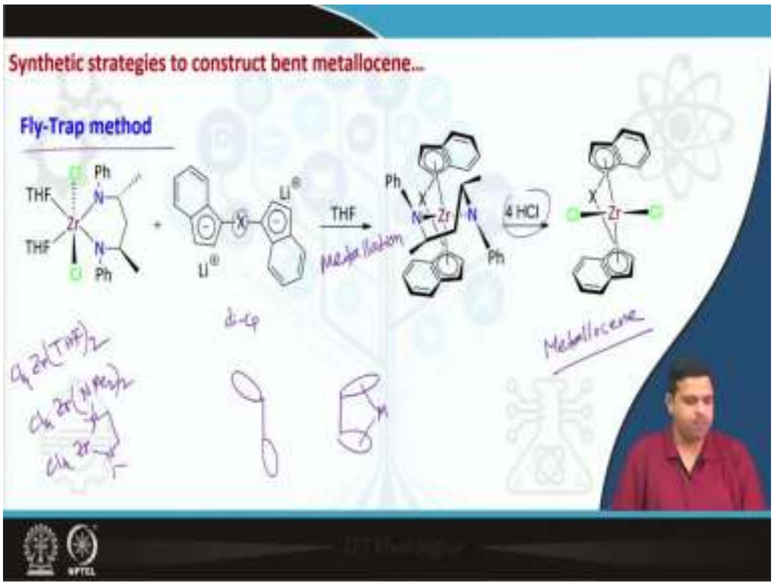


Type common lignds leading to ansametallocene

Cyclopentadienyl to annulated-cyclopentadienyl

So, in general, so here you see that what we are doing? We are making a di-Cp and this is my, this is called the bridging, this x maybe like Si Me 2 moiety. So, maybe CH 2 CH 2 different maybe alkyl even di-silicone moiety like that one even the amine based bridging. So, this is basically to thread the 2 Cp ligands to induce a particular symmetry and to restrict the rotation. So, as example, you see here the 2 ligands here, this is the ethane bridge and you can this is the your indenyl and this is the indenyl based and this here you will see that this is the cyclohexion annulated CP. So, you can make or engineer our ligands what according to the our target, fine.

(Refer Slide Time: 26:14)



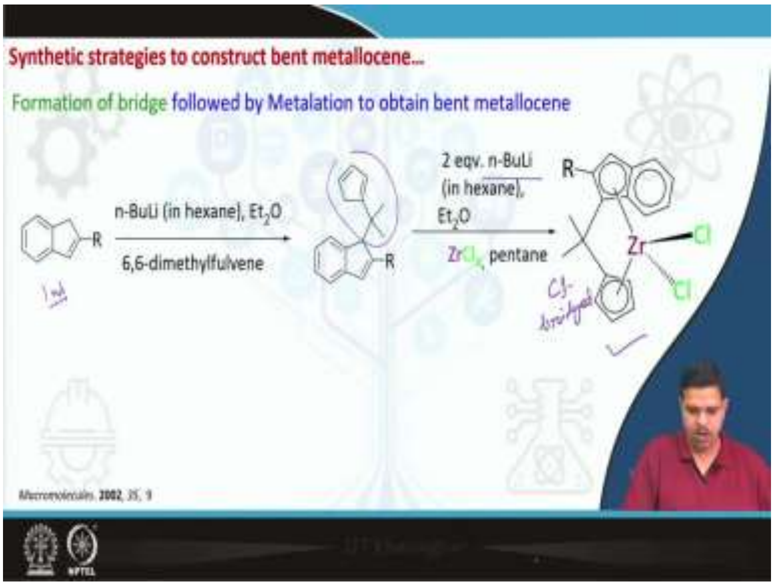
Synthetic strategies to construct bent metallocene...

Fly-Trap method

So, similarly, you will see here what would be the general synthetic protocols with this, this is my di-Cp. So, as I told X maybe anything according to your wish and these are the common precursors, so we as you see in the last scheme we use the zirconium tetra chloride and these are different precursor we use this is to make the reaction better to make better solubility in solvents. So, and also like this one in Me 2 like this one or also use the different chelating ligands like your like this one.

Here you see that the same reaction so, if you do the delithiation you will get the di-CP. And then you do the metallation here and you are getting your desired metallocene compounds and this amine can be removed by treating with HCl H plus acid so that amine will be removed and you will get your metallocenes. So, here you will see that how you can, so this is basically you it is called the fly trap method, fly trap method means you see that you have initially this is the a wing, you can just compare the wing of a bird. Now, what we are doing after putting the metal then what you are basically trapping this fly like this one. So, this method is called the fly trap method.

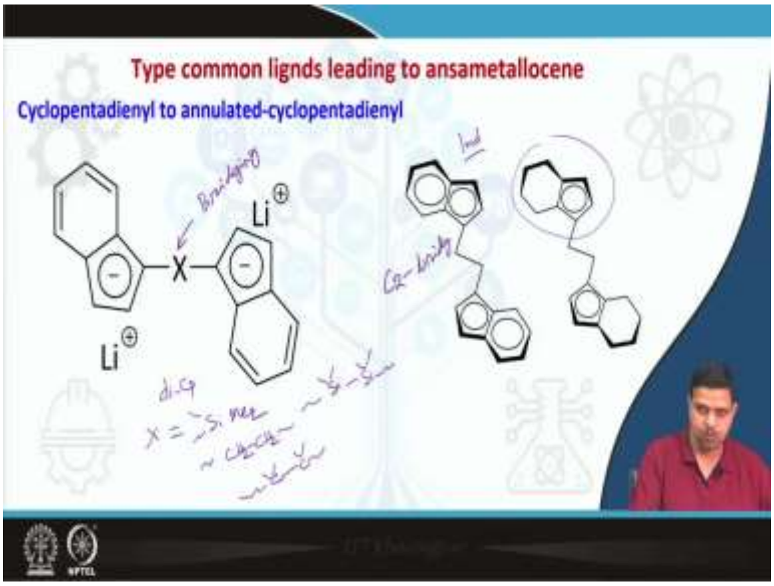
(Refer Slide Time: 28:33)



Synthetic strategies to construct bent metallocene...

Formation of bridge followed by Metalation to obtain bent metallocene

Macromolecules. 2002, 35, 9

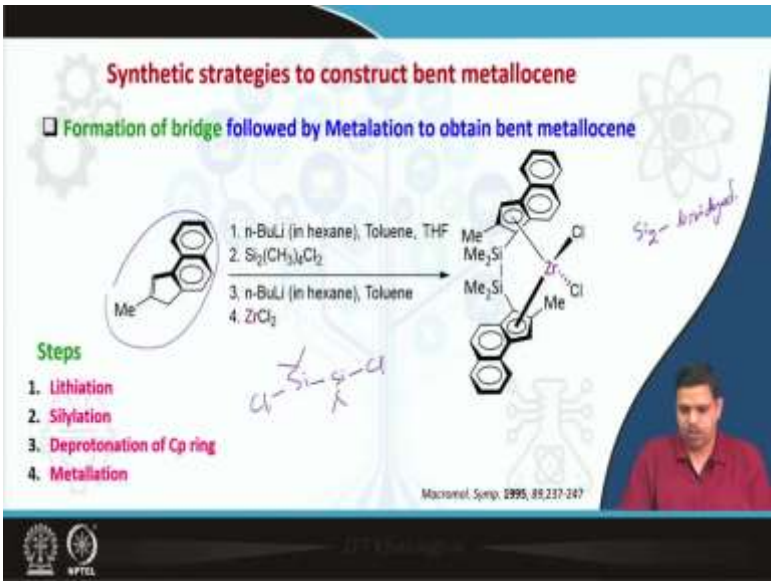


Type common lignds leading to ansametallocene

Cyclopentadienyl to annulated-cyclopentadienyl

So similarly, you can make a varieties of metallocenes compounds you see here again. So, you are functionalizing your this is again is indenyl, you are functionalizing your indenyl here with this group by deprotonation and then 6, 6 dimethylfulvene but you can do in what you can follow this method according to your base. Now, last step is to make the Cp minus here you have to do the n butyl lithium you have to use the n butyl lithium to make the deprotonated, anion to make the anionic ligand and then as usual you will react with zirconium tetrachloride and you will get your metallocenes. So, this is C 1 bridged, so this one is the C 1 bridged, so this will be quite high strain. And in the last here you will see this is the C 2 bridged.

(Refer Slide Time: 29:52)



Synthetic strategies to construct bent metallocene

☐ Formation of bridge followed by Metalation to obtain bent metallocene

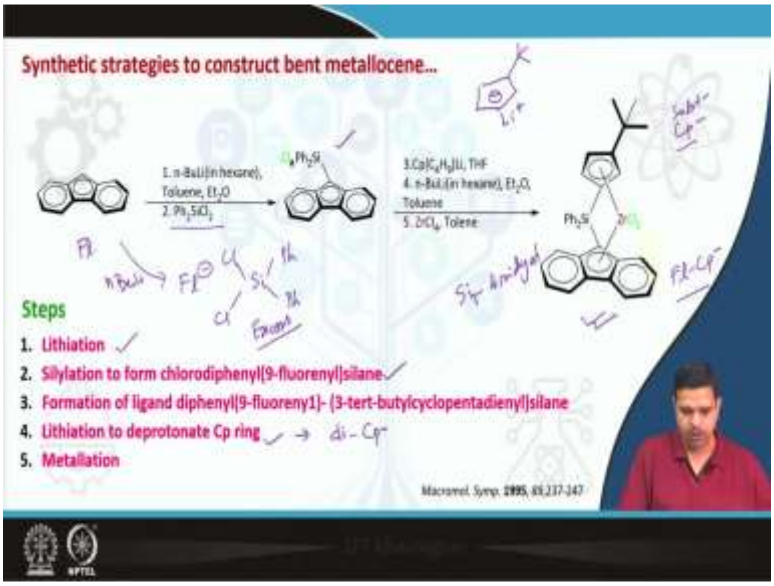
1. n-BuLi (in hexane), Toluene, THF
2. $Si_2(CH_3)_4Cl_2$
3. n-BuLi (in hexane), Toluene
4. $ZrCl_2$

Steps
1. Lithiation
2. Silylation
3. Deprotonation of Cp ring
4. Metallation

Macromol. Symp. 1995, 89,237-247

So, there are similarly you make your different types of. So here all are here different types of Cp ligands is basically to induce the different chirality, the different symmetry. I will we will discuss the relation between the symmetry and the polymerization that is actually our all of the main objective of this course, we will discuss later, but, today you try to understand that how we can synthesize because this is important, unless you synthesize and characterize then you cannot go further for the applications and polymerizations. So, here you will see this is again this is basically here the silicone two bridged metallocenes. Synthetic procedures are similar, so instead of the mono sealant you have to use the dye sealants like this one, so like this one.

(Refer Slide Time: 31:04)



Synthetic strategies to construct bent metallocene...

1. n-BuLi(in hexane), Toluene, $Et_2O$
2. $Ph_2SiCl_2$

3. $Cp(C_4H_9)Li$, THF
4. n-BuLi (in hexane), $Et_2O$, Toluene
5. $ZrCl_4$, Tolene

Steps
1. Lithiation ✓
2. Silylation to form chlorodiphenyl(9-fluorenyl)silane ✓
3. Formation of ligand diphenyl(9-fluoreny1)- (3-tert-butylcyclopentadienyl)silane
4. Lithiation to deprotonate Cp ring ✓ → di-Cp⁻
5. Metallation

Macromol. Symp. 1995, 89,237-247

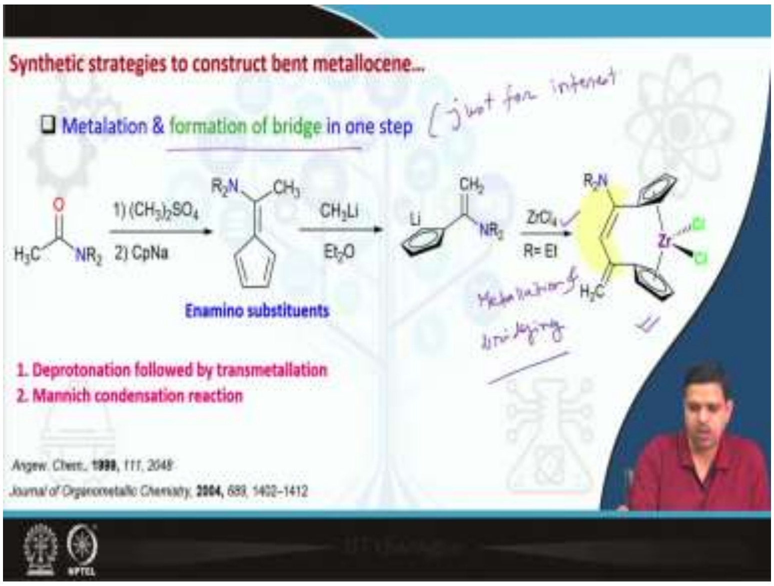
So, similarly, here similarly, here you see that you can make the silicone 1 bridged. So, in the earlier case it is silicone 2 bridged and this case silicone 1 bridged. So, again you see that you take the fluorenyl, this is the fluorenyl and you treat with butyl lithium and then you react with Ph 2 Si Cl 2. One thing you have to remember that once you react with the, so this is happening and if you n-butyl lithium, now, you have to you are reacting with the Cl Ph. So, here what we are doing, we are so, here basically there is a mistake there will be one chloride.

So, what we are doing here you see that we are substituting only one chloride. So, that means, this one you have to take excess these remember. If you take these one stoichiometric, then what will happen that the both the chlorides they are maybe substituted and you will not get this desired product. So, you have to take this one is excess when you want to substitute only one chloride. So, now, then again you see that if this react with this another Cp and this case it was is butyl substituted Cp minus is basically here all we are doing to break the symmetry that is why you are doing the hetero not homo di-Cp ligands, hetero di-Cp ligands, this is you see, this is the fluorenyl Cp and this is the Cp but substituted Cp, substituted Cp minus.

So, now, this is actually Li plus and then if you react you are you will be getting this one and then you do the n-BuLi to deprotonation and you will get your desired zirconium metallocene compound. So, here you will see the steps you follow. So, you did the lithiation and then the silylation as I told the controlled silylation you have to take excess silanes. Then, you got the neutral form of this ligand and then you do the lithiation to deprotonate to get your di Cp minus. And in this case two Cp are different, one is the substituted Cp, one is the fluorenyl Cp and last is you do the metallation.

So, you see, and of course, these reactions are quite sensitive because you are using the butyl lithium and you know that butyl lithium is very sensitive, you have to properly follow the silane conditions, silane condition mean you have to do the all the reactions in a silane flask and under inert atmosphere avoiding moisture and oxygen. And of course, most of the your metallation compounds are sensitive, so that also you have to take care and you have to store after synthesising in a silane condition, you have to store these kind of metallocene compounds in a proper way.

(Refer Slide Time: 35:09)



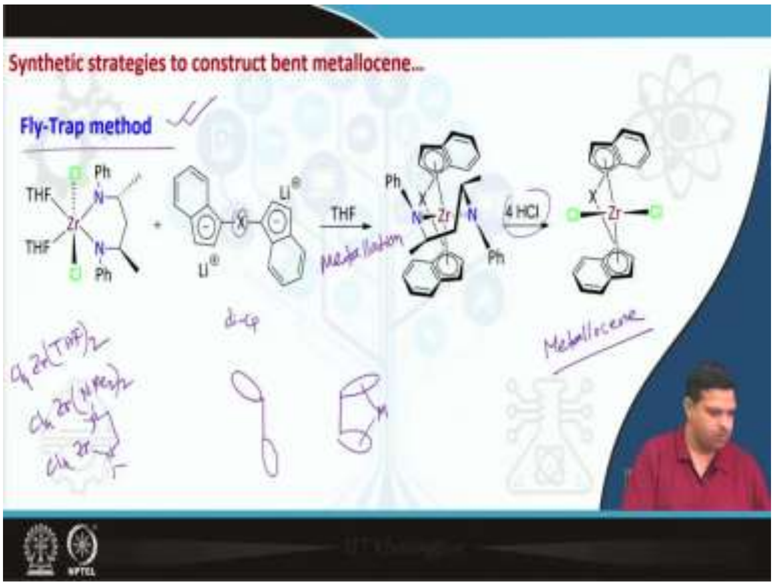
## Synthetic strategies to construct bent metallocene...

☐ Metalation & formation of bridge in one step

1. Deprotonation followed by transmetallation
2. Mannich condensation reaction

Angew. Chem., 1999, 111, 2048

Journal of Organometallic Chemistry, 2004, 689, 1402–1412



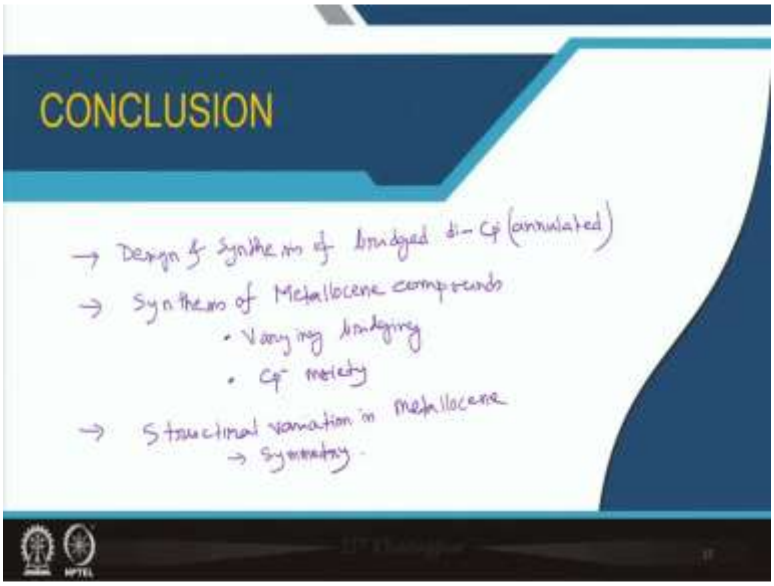
## Synthetic strategies to construct bent metallocene...

Fly-Trap method

So, another example you see here this one metallation and formation of bridge in one step. So, here you will see, we do the many conditions condensation reaction to get this in enamino substituents of the Cp. And you here you see this interesting is that here the bridging the metallation and bridging. So, in the earlier all the cases you so that bridging we did first and then at the last step after deprotonation we are doing the metallation and here is basically in one step for metallation and formation. So, here you see that we are litigating this one and then if you charge with tetrachloro zirconium and you will get that these kinds of metallocene compounds.

So, this is just for your information actually the list this step, this is not very general this is just for interest, this is not a general synthetic protocols, but you have to really be understand these general synthetic protocols what we have discussed mainly this one. So, I think now, it is very clear that how we can engineer our ligands to make a different metallocenes compounds and to induce the symmetry.

(Refer Slide Time: 36:48)



CONCLUSION

→ Design & Synthesis of bridged di-Cp (annulated)

→ Synthesis of Metallocene compounds
  - Varying bridging
  - $Cp^-$ moiety

→ Structural variation in metallocene
  → Symmetry.

So, what we have learnt in today's class that we learnt about design and synthesis of bridged annulated di-CP ligands. So, this is annulated, we are more interested on the annulated and then the synthesis of metallocene of course, mainly we concentrated on group 4 because we our main interest or is on zirconium, titanium based metallocenes compounds for polymerization.

Synthesis of metallocenes compounds by varying the bridging, by varying the Cp minus moiety and you saw that structural variation in metallocenes and why we are doing you will understand later is basically to induce different symmetry which has relation with the polymerization to get the different tacticity. So, as a summary we have discussed the general synthetic strategy for different metallocene compounds mainly for the group 4 transition metals.

(Refer Slide Time: 39:21)

## 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
- Polyolefins: 50 years after Ziegler and Natta II by Walter Kaminsky, Springer, 2013

And as a reference, you can read these are the books, which (())(39:27) discussion is available. In the next classes we will discuss the reactivities of some of the parallel metallocenes the unique reactivities and the reactivities unique reactivities of the bent metallocenes compounds with the help of the molecular orbital theory or the electric nature of the orbitals molecular orbitals discussed in the last classes. So see you in the next class, thank you.