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

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Lecture 16

Properties and Unique Reactivities of parallel and bent Metallocenes

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Lecture 16: Properties and Unique Reactivities of parallel and bent Metallocenes

Welcome once again. So today we will be continuing the properties and unique reactivities of some of the common metallocenes parallel and the bent. In the last class, we have discussed extensively the synthetic protocols of the bent metallocenes and also some common general synthetic protocols for parallel metallocenes.

So, today, we will be discussing some of its unique reactivities and then we will try to understand that how the electronic factors and the molecular orbitals dictates the reactivities of the bent metallocenes and you will be very excited that how and the interesting you very unique and very uncommon reactions you can do with these kind of bent metallocenes compounds which are not possible with common organic compounds or even the parallel metallocenes compounds. So, let us enjoy the class today.

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CONCEPTS COVERED

Properties and unique reactivities of common

- Parallel metallocenes
- Bent metallocenes

So the concepts we will cover here today will mainly will focus on the unique properties of the, and reactivities of common parallel metallocenes and the bent metallocenes.

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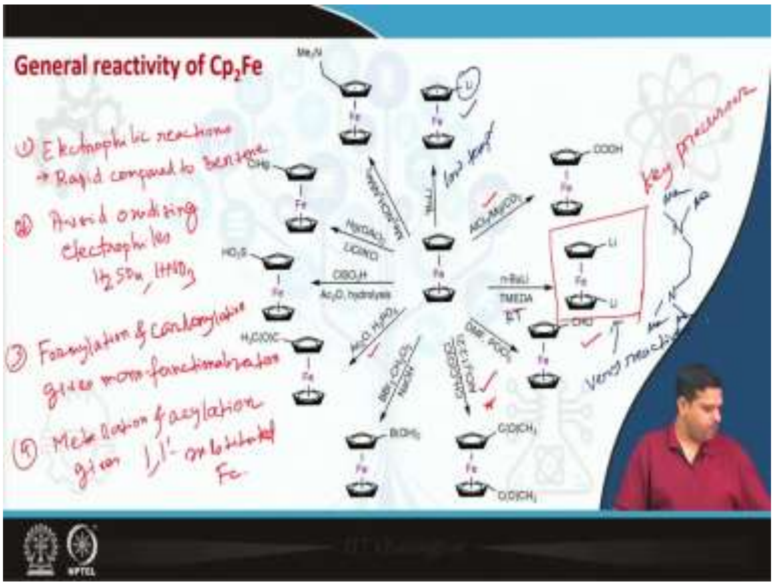

General reactivity of Cp_2Fe

① Electrophilic reactions
→ Rapid compared to benzene

② Avoid oxidizing electrophiles
H_2SO_4, HNO_3

③ Formylation & carbonylation gives mono-functionalization

④ Metalation & acylation gives 1,1'-substituted Fc

So, you know that this is the ferrocene, so we will try to understand first with the most popular and simple metallocenes that is the ferrocene. And you see that there are a lot of reactivities it can undergo the ferrocene and it is you are very familiar that the ferrocene undergoes the electrophilic reactions as the aromatic rings does as example for benzene and most interesting is that the electrophilic reactions is rapid compared to the benzene. Because there is involvement of metal centers, so basically the electrophile first interact with the iron centre and then after that it actually attacks to the Cp rings.

So, this electrophilic reaction is through the metal centre and this actually enhances the electrophilic reactions compared to the benzene. However, this you have to be careful that there should not be any oxidising electrophile because ferrocene is redox activate and undergoes the iron 2, iron 3. So, you should not use any electrophile which is oxidising in nature. So, you have to avoid oxidising electrophile, as example H 2 SO 4, H NO 3 like that.

But in other cases you will see most of the reactions what benzene does as example you see the acylation, the ferryl cupped alkylation's, all you see the this is the ferryl cupped reactions. So, all the reactions whatever the benzene does the same reactions you can also do here. So, this is very common and you are familiar, I will not explain in more detail here, but these are the few points interesting points for the ferrocene reactivities you should point out.

So, this is 2 and 3 that in here you see that formylation reactions like this one this formylation reactions that most of the formylation and carboxylation gives mono-functionalization. And very interesting that acylation reactions as example you see this one or metallation reactions as example you see this one it gives the 1-1 substituted, metallation and acylation. So, these are the basically key features that is why I am just listing out, give 1, 1-substituted ferrocene derivatives.

You are quite familiar with these kind of compounds these kinds reactivities. I am more interested like for this delithiation, because you will see this can be used as a key precursor for many useful ferrocene derivatives. As example, if you and you know that for to get delithio you have to use the Tmeda because these actually stabilize, I am just writing in a different colour so that you can more easily understand. So, this is Tmeda is basically a chelating ligand, it actually favours the delithiation by chelating the delithiated compounds.

So, you know that making dianine of a single compound is difficult, so that is why if you use this chelating ligand it favours the dilatation and you can make it very easily that delithiated ferrocene, if you do not use you will see you will get the mono-lithiation here, if you use the Tmeda you will get the delithiated. However condition is little different here we have to use low temperature 0 degree centigrade and here you this room temperature is good enough no need to do any extra precaution. But you have to be careful this one is very reactive, this is very reactive and actually pyrophoric in nature, I am sure you know what is pyrophoric, which spontaneously catches fire.

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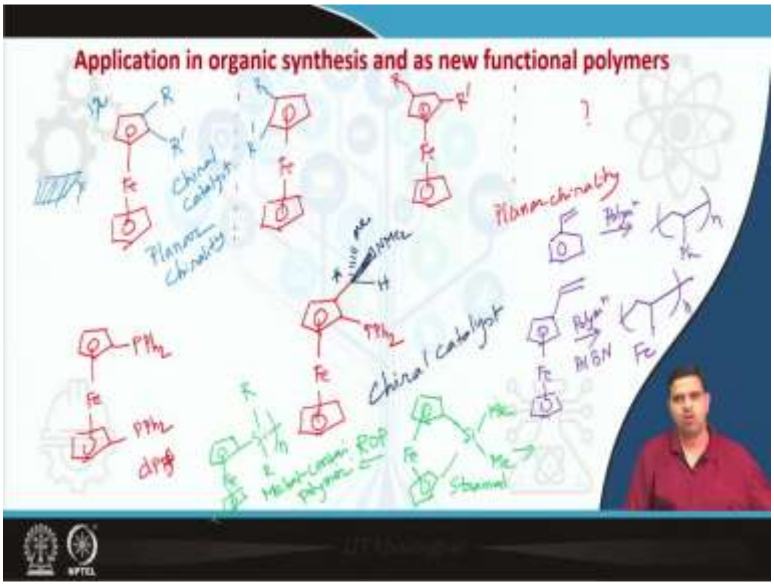
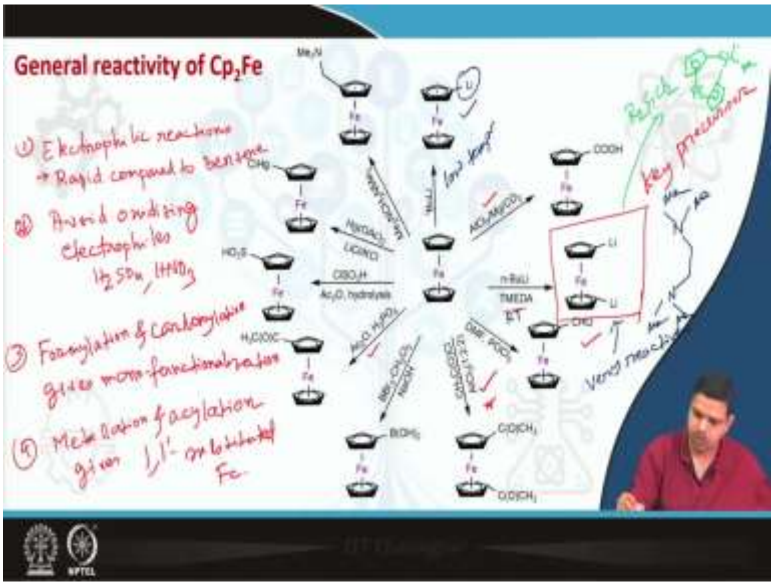


Application in organic synthesis and as new functional polymers



General reactivity of Cp$_2$Fe

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H_2SO_4, HNO_3
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④ Metalation & acylation gives 1,1'-substituted Fc

So, I will just very briefly discuss that the application in organic synthesis and as a new functional polymers, you know that ferrocene is one of the very popular organometallic compounds which are used extensively in organometallic chemistry, synthesis, synthetic chemistry, material chemistry, and polymer chemistry domain. And you know why I just give some test I not discuss it elaborately for the ferrocene but I just want to give the strategy.

So, here you see suppose, this one I am writing let us say d 5 H. So, here you see that it has the plane of symmetry, so it is no chiral. Now what will happen if I put let us say this is R, and let us say this is another different R. Now what I am doing, I am basically destroying the plane of symmetry. So, initially there is a plane of symmetry here now, this is not there. So, if it will have a non-superimposable mirror image and how does it look like? So, it will look like…

So what we are inducing? We are basically inducing the planar chirality and this kind of compounds will have lots of applications in asymmetric synthesis as a chiral catalyst, so chiral catalyst. So, if you put the if you design your ferrocene catalyst in this way you can induce the chirality and this is called the planar chirality. So, not only this is the 1, 1 substituted you can also make the one, sorry this is the 1, 2 substituted and you can also induce the similar chirality by 1, 3 substituted.

So, you will get the very similar here, so let us just draw it you can also draw with me. So, here you will see that if I have a R and here R prime, so you will have also the same. So, this is also non superimposable here also planar chirality you can draw yourself what will. So, one of the famous and very useful although it is non chiral is PPh 2, we call dpp, sorry dpf, diphenylphosphino ferrocene dppf. And you can also induce the planar chirality and the central chirality by designing your ligands further, as example like aminophosphino derivative of the ferrocene.

As example, here I am showing one representative examples. So yes, and here you will see, so, this one is the chiral and you have a R and R prime. So, you have also the planar chirality, both central chirality and planar chirality. So, this kind of chirality catalyst are very popular in asymmetric synthesis, so use applications. So, not only that you know that polystyrene, and if you do the polymerization what you will get? You will get like this one.

So, similarly, if you get, what polymer you will get? The similar polymer here it is ferrocene. So, you will see metal containing polymers you can get by control radical polymerization or anionic polymerization using the AIBN or the other anionic polymerization. Not only that a very interesting ferrocene derivatives which is actually strained in nature and these are you can make it from the delithiated ferrocene. So, this one you can actually you can prepare from this one.

So, if you react with the R 2 Si Cl 2 you will get like this one. So, this is again you will see this is a strained metal ring and this is called the silicone based ferrocene of n. And this actually undergoes the ring opening polymerization and you can get this kind of metal containing polymer like this one. So, here you will see that this is the metal containing polymer a new type of metal polymers which have very interesting properties and applications. So, there you will see that these metallocenes compounds, the parallel metallocenes compounds like ferrocene has a lot of applications, although in this course, there is no scope to discuss all we will be focusing on the bent metallocenes.

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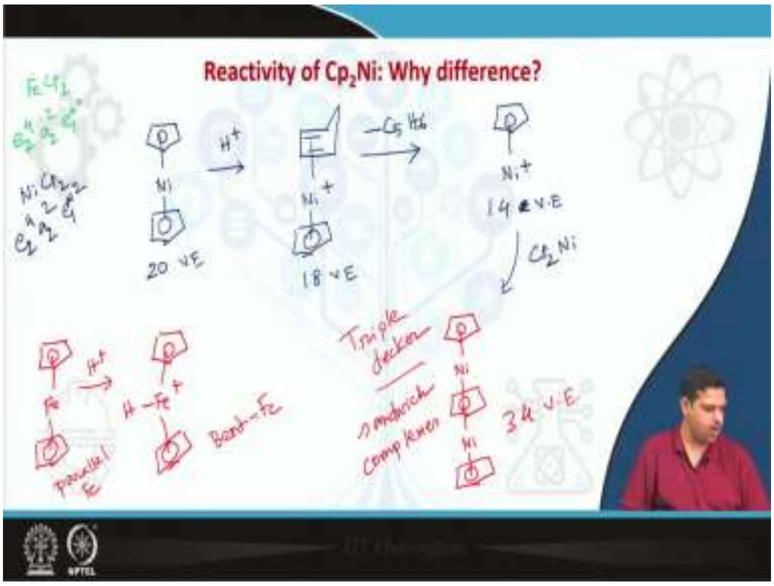

Reactivity of Cp_2Ni: Why difference?

So now, we know that what are the common reactivities of the metallocenes, we are very familiar. I will give one example how the electronic factor dictates the reactivity of the metallocenes. You know that for ferrocene we have the e 2 4, a 2 2 and e 1 star 0. Now, you come to the nickelocene that is the Cp 2 Ni. So, here what will be you have a total eight electrons, because it is a d 8 system.

So, for nickelocene what will happen you will have e 2 4 the electronic arrangement, a 2 2 and e 1 star 2, that means in anti-bonding orbital you have a 2 electrons. So, who will be more reactive than? Yes, obviously the nickelocene will be more reactive. So, in ferrocene what we saw? That ferrocene moiety is intact and you do the electrophilic substitution reactions very easily, there is no degradation of the ferrocene or there are no breaking of the metal Cp bond, but here you will see there will be breaking of metal Cp bond because your electrons is in the anti-bonding orbital.

Now, due to that one, you will see some interesting reactions which are not observed for metallocenes, what are they let us see. Like that, if you to take proton what will happen? You will have like this. So you see that one Cp ligands is now is basically now it will act as a butadiene cyclic butadiene, you have a Ni plus. So, it was it this one is 20 electron system, electron total if you calculate 20 valence electron and it is now 18 valence electrons I should write the valence electron, in short I will write the VE, otherwise it will be confusing. So, I will write the 18 this the valence electron, this is the 20 valence electrons.

Now, there is an interesting reaction happens. So, this one will come out see C 5 H 6 and then what will happen? You will happen is so, this is Ni plus and this is actually now how many electron? 14 electron, 14 valence electron, fine. Now what will happen it will react with the another Cp 2 nickel and you will get a very interesting compounds which is very fascinating structure like that. So, you will get now again 34 valence electron and this kind of called, triple decker because you see the triple decker. So, it is like a 2 bread sandwich initially it was and now basically three layer of sandwich. So, you will see this is called triple decker sandwich complexes and this is very unique reactivities.

If you use the ferrocene and if you add the H plus what happens, it will be protonated but very interestingly you bond does not degrade but here so, you get the parallel to bent ferrocene parallel ferrocene and here the bent ferrocene, but for nickel you see that reactivity is totally different. So, the electronic nature what I want to tell or give the message that electronic nature of the metallocenes will dictate the reactivity. So, it is very important to understand the electronic nature of the metallocenes.

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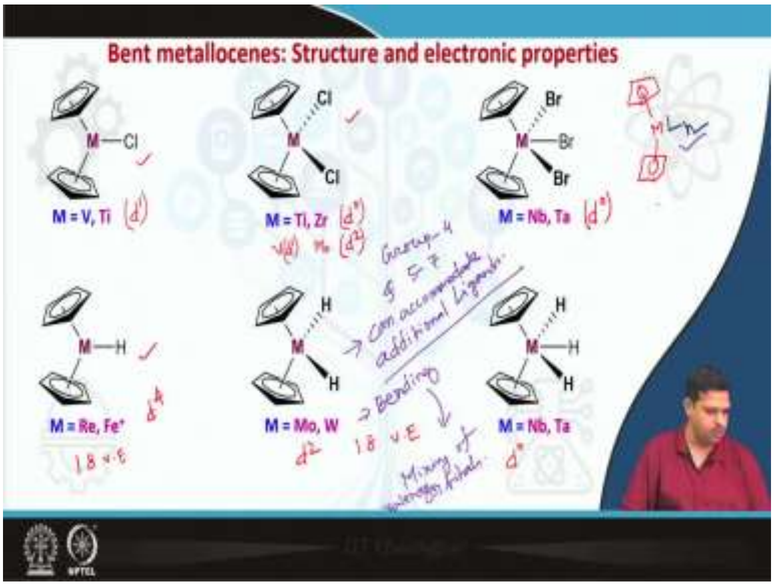
Bent metallocenes: Structure and electronic properties

M = V, Ti

M = Ti, Zr

M = Nb, Ta

M = Re, Fe+

M = Mo, W

M = Nb, Ta

So, that is why you see here this slide this one we partly discussed in our previous classes I just want to refresh. So, here you will see that this is Cp 2, two Cp ligands the first one this one and this is vanadium, titanium, is quite common and it has d 1 electron, this is very important to understand that how many electrons are there in the d orbitals and also total that

that is the valence electrons both are very important to understand. Now this one the next one is 2 Cp ligands and 2 chloride, so this is basically the category of like M and here I am just writing as MLn, where L can varied and also n can be varied.

So in this case, you see that for titanium, zirconium case it is, again the d 0. So, and if you have vanadium and molybdenum what we will have? You will have the d 2 for the vanadium and molybdenum for sorry for vanadium it will be d 1 sorry. So, if it is vanadium it will be d 1 and for molybdenum it will be d 2. Now, you will see that for the next one that is you have 3 bromo-bonds 3 methyl bromide the metals maybe niobium and tantalum and this case it is d 0.

Now, here the next one that is the this case where metal hydride bond so, it is metals maybe rhenium or iron plus. So, here it is the 18 electron system valence electron and these cases for it is rhenium it is d 4. Next one the molybdenum and tungsten this is d 2, here again 18 valence electron. And next one that is the niobium tantalum obviously, it is d 0. So, why these variations? Because the group 4 and group 5 metallation compounds, group 4 and 5 to 7 can accommodate additional ligands which is not possible for the 3d transition metals.

So, this is the I was telling that here there are possibilities up in keeping more bonds metal ligand bonds and that is possible for group 4 and some of the group 5 to 7 metals and that actually dictates the properties by modifying the molecular orbital due to the mixing, the bending and which actually causes the mixing of orbitals. Mainly here the valence I am telling the orbital means the valence orbitals, the mainly d orbitals. So, due to the extra ligands here these metallocenes are forced to bend and due to this one there is a mixing of the valence orbitals and you see the different electronic arrangement compared to the parallel metallocenes. So, this one will be useful to understand the electronic properties of the bent metallocenes and to understand the reactivities.

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So, in the last class, we discussed extensively that how some of the bent metallocenes have a lone pairs, some of no have not, and what will be the difference in this reactivity studies. So here what I will be doing, I will be taking like this one here too. If you take the e 2 a 1, or e 1, this is actually anti-bonding in nature. Now, let us say this is for the Cp 2, I am just trying to discuss with one specific example. Let us say this is Cp 2 Ti and I am not ignoring the 2 chloride bonds, Cp two Ti. So, Cp 2 Ti is the d 2 system and 14 electron.

Now, if I have 2 chlorides, so what will look like? So, here I have the 2 chlorides, 2 Cl minus. Now, I have 2 electrons here so that is this one and for 2 Cl like this one. So, now if I do the simplified molecular orbital, so what will happen? So, this is your so 1, 2, 3, 4, so, now your electrons will be here and you see that this is empty, vacant, fine. So, this is my Cp 2 Ti Cl 2. If you recall we discussed in the previous classes more extensively. So, here what we will have empty orbital, so this is the empty orbitals and empty orbitals. So, if it is empty then it will be electron deficient.

Now, let us take another example, this is a very simplified molecular orbitals approach to understand. So, similarly, if you take another metallocene compounds and you will see this I am taking Cp 2 Mo fragment, and Cp 2 Mo fragment how many d electrons are there? Any idea, we discussed yes this is d 4. Now, you arrange the d 4, 1, 2, 3, 4, like. Now, you will see here now, I am 2 chlorides and for 2 chlorides there is 1 electron and 1 electron. Now, if you form the simple molecular orbitals in a very simple way now, what you will get? You will get here one and this is like this one. So, d 4 like this one.

So, actually in Cp 2 Mo electron is it is in triplet, so, I should write triplet here like a triplet. So, what will happen here, so you will see that 1, 2, 3, 4, 5, 6, so, 2 electrons from the 2 chlorides and here d 4 as I told that Cp 2 Mo moiety has a triplet, so, there are 2 unpaired electrons and then you just fill up like this. So, what you see that there is a this is my nonbonding orbital, so this is the nonbonding orbital and here you will see that this is the filled orbital.

So, in this case, you saw the last case in titanium case, you saw that this is electron deficient because this is vacant in Cp 2 Ti Cl 2 and in this case in Cp 2 Mo Cl 2, in this case you will see that orbital is not vacant there is a lone pair. So, this is the metal of group 4 and this is the metal of the group 6 understand, so that is why the 2 electron difference to one case d 2 one case d 4. So, what I want to tell that depending on the metal centre you will see the similar composition Cp 2 Ti Cl 2 and Cp 2 Mo Cl 2 you will see that how different the electronic nature, and what will be the effect of this one?

So, this one can act as a Lewis acid and this one will act as a Lewis base, why it is Lewis base? Because this one is contents one lone pair. So, this as it is vacant so, this also can accept the electron from even from the like let us say for any alkene like ethylene so, that is why the group 4 transition metals reactivities is quite different then the group 6 or group 5 or group 7, due to the, of course it also depends on the oxidation state that is the, this is the plus oxidation state is the plus 4 here, although here it is also 4. And you see that depending on the electronic arrangement the properties is also very different.

So, here you can say that there is a striking difference in chemistry of different metallocenes. So, this thing you have to understand very clearly the electronic nature then it will be very easy to understand its properties, so no need to remember them. So very easy, and it is very logical.

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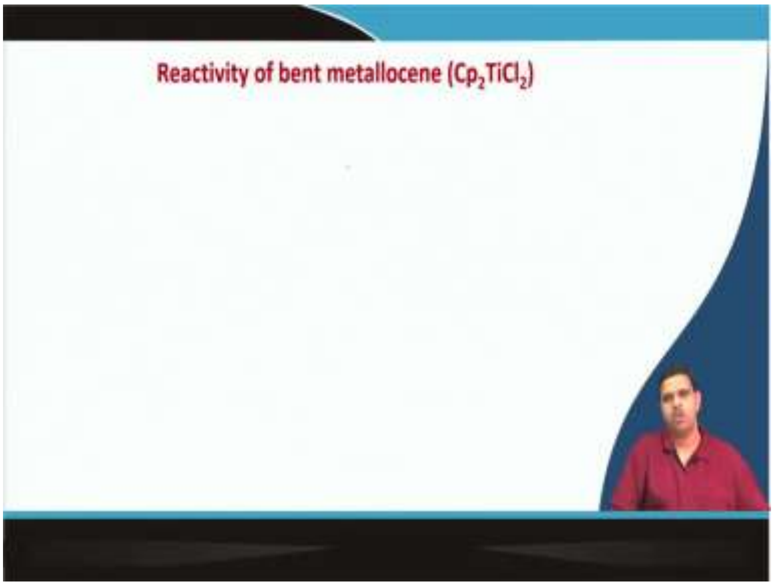
Bent metallocene (Cp_2TaH_3) as Catalyst


Reactivity of bent metallocene (Cp_2TiCl_2)

So, in the next class, I will continue to discuss the unique properties of the other bent metallocene as example like this one or Cp 2 Ti Cl 2 in more detail and will try to explain by the simple molecular orbitals of the bent metallocenes. So, till then, thank you and see you in the next class.