Advanced Transition Metal Organometallic Chemistry

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Lecture – 14

Transition Metal Cyclopentadiene Complexes: Reactivity of Ferrocene

Welcome to the 14th lecture of this course entitled, Advanced Transition Metal Organometallic Chemistry. We have been looking at various kinds of transition metal complexes they are synthetic protocols, their structure and bonding as well as their reactivity, particularly, from the perspective of their utility in various kinds of catalytic reactions. From that standpoint, we have been discussingimportant type of organo metallic compounds.

And these are transition metal cyclopentadienyl complexes, particularly various kind of metallocene compounds. These compoundsare not onlyunique in terms of their bondingfeaturesbut also they showunique reactivity when it comes to their property studies. And of the various metallocenes, we have focused on ferrocene, usual suspect of metals in chemistry in great detail, to look at its bonding, structure, reactivity and propertyis.

Now in that perspective we have looked into various reactivities of ferrocene in the previous class. Particularly in the previous lecture we have looked at various reactivitiesthe one that stands out is the extremely facile reactivity of ferrocene towards electrophiles. Now the reason for this extremely facile reactivity of ferrocene towards electrophile, arises because of the carbon ionic nature of the cyclopentadienyl ligands which when bound to iron in ferrocene are stillpartially negatively charged and hencethey react extremely fast with electrophiles.

Now it seems very simple, conventional, as well as expected, and this reaction is so fast in ferrocenile complexes, that they are about 3 into 10 to power 6 times faster than that of benzene,such kind of electrophilic substitution reactions, ferrocene ambience correspondingly are more basic than aniline and ferrocenial formic acid also is a weaker acid than benzoic acid. One of the condition though for this electrophilic substitution reaction to occur is that, the electrophile in anyway should not be acting as an oxidizing agent.

So, that electrophilic substitution reaction on the ferrocenial ring takes place, and if it doesotherwise, that means it acts as an oxidizing agent, then ferrocene will be oxidized to ferrocene in cation, and then the electrophilic substitution reaction wouldn't be happening and the last thing that we had discussed in the previous lecture, is the approach of the electrophile and it hasbeen proven by elegant experiments in which it was convincingly showed, in a try cyclicCP system, that this approach of the electrophile occurs from the exo phase in a facile manner as opposed to the end of phase.

And this also again is the conventional wisdom because of steric reasons there as attack from the facile faceis morefavored. Nowin today's lecture we are able to or discuss something very intriguingwe have seen that these electrophilic attack occurs,but of able to dwell on another interesting aspect of ferrocenyl chemistry, particularly lithiation reactions of the ferrocenyl ring.Now these lithiation reactions of ferrocenyl ring,is kind of challenging, becausethese lithiation reactionsoccurs uncontrolled and as a result there aremono di lithiation or even tried nucleation of lithiation that occurs.

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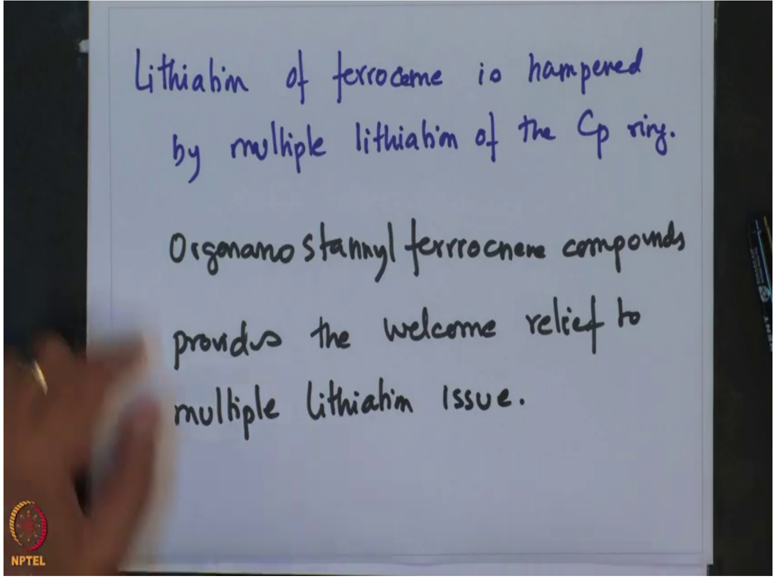

Lithiation of ferrocene is hampered by multiple lithiation of the Cp ring.

Organano stannyl ferrocnene compounds provids the welcome relief to multiple lithiation issue.

So, the lithiation of ferrocene is hampered by multiple lithiation of the CPring. Now lithiation is an important reactionbecause lithiation gives rise to a various other kind of substitutionon the CP ring so uncontrolled lithiation of the CP ring, make the normal conventional lithiation of ferrocene ring, kind ofnot very useful. So,in this perspective, finding a controlled lithiation of the CP ring was of utmost interest and that was the need of the day, and the solution arises to this is, by anion derivative, now which is shown over here.

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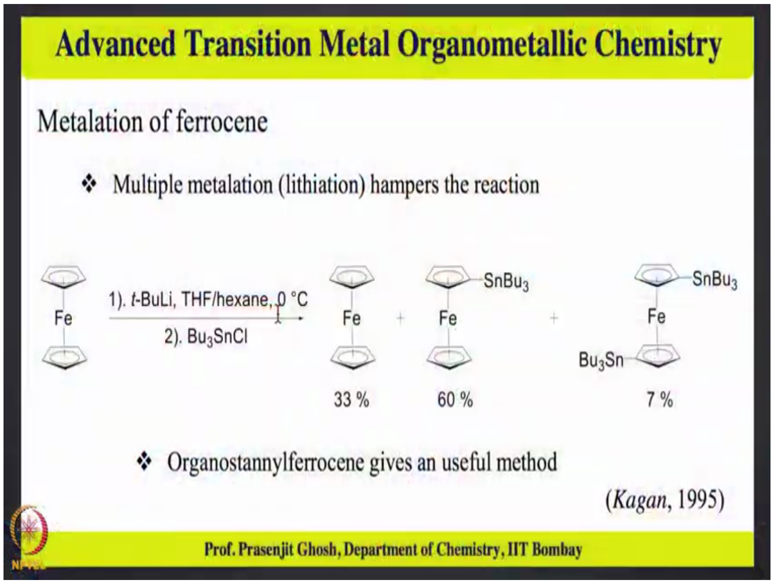

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Metalation of ferrocene

- ❖ Multiple metalation (lithiation) hampers the reaction

- ❖ Organostannylferrocene gives an useful method

(*Kagan*, 1995)

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So, the metalation of the ferrocene is hampered by multiple lithiation and as a result as a request to this organostannyl ferrocynl compounds are often used. So organano stannyl ferrocene compounds provides the welcome relief to multiple lithiation issue. So, this is kind of a very useful method for putting various kinds of substitutions on the ferrocene ring, which otherwisecould be easily achieved by lithiation in other organic compounds, so I am going to illustrate this in much more details in next few minutes of our discussion.

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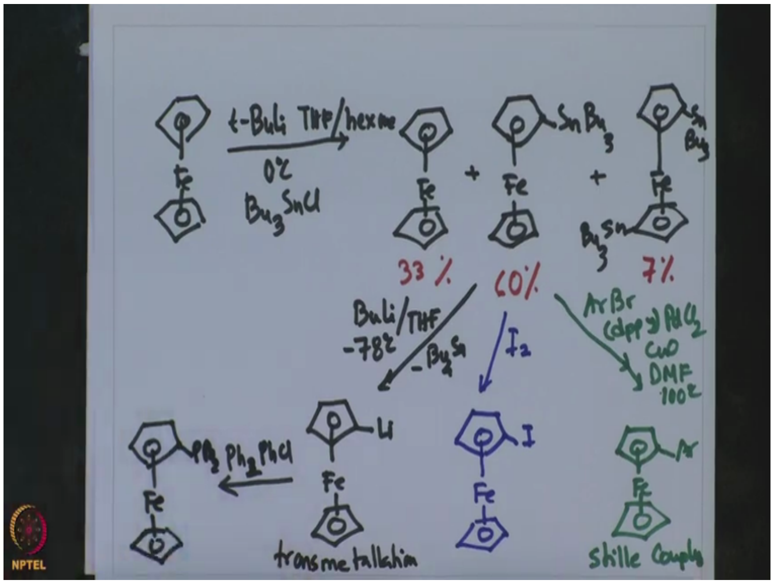

For example the treatment of ferrocene with t butilellithium in THP hexme at zero degree centigrade and in presence of tributyltin chloride gives a mixture of compound which is, some unreacted ferrocene plus ferrocene with tributyltin and plus double standard tributyltin compounds. Now the reaction, this mixtureis like the mono or stannyl ferrocene compound, is the major product, so this is about 66%.

And the di stannyl compound is variable little, which is about 7% and the unreacted ferrocene is about 33%. Now the reaction of this mono strannyl compound withvariousregions, for example, aryl bromide in presence of DPP y pd CL 2,copper oxide DMF 100 degree centigrade, so this is nothing but the stille reaction out of CC cross coupling reaction gives this aryl substituted ferrocenyl compound.

So, stille coupling similarly the mono tributyl stannyl ferrocenyl compound, reacting with iodine gives the hygiene substituted ferrocenyl compound as well as the organo stannyl derivative with butyl lithium in THF at -78 degree centigrade eliminates the tributyl tin giving the much desired monolith iated compound. So, thisis the simple transmetalation reaction. And that when treated with triphenyl phosphine chloride, diphenyl phosphine chloride would give the phosphinated ferrocene compound.

So, what we see is a nice example of beautiful chemistry laid out over here. As we saw that lithiation or multiple lithiation wasthe problem with ferrocene if ferrocene is treated with simple butyl lithium, however that problem is circumvented by treating this with tributyl tin chloride as an electrophile and then preparingmono substituted tributyl tin ferrocenyl compound in major amount.

And then subsequent treatment of this mono tributyl ferrocenyl compound with aryl bromide in presence of palladium doing a regular stille coupling resulting in the aryl substitution of the same.

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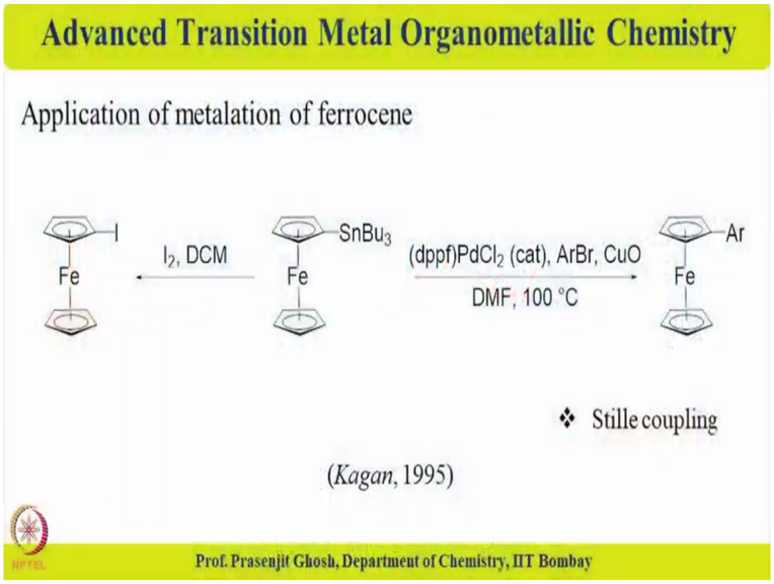

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Application of metalation of ferrocene

- Stille coupling

(*Kagan*, 1995)

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Treating that withnormal iodine as an ear profile will give the iodide compound as well as treating this tributyl stannyl ferrocenyl compound with butyl lithium exclusively gives the monolithiated product which when treated with pH to be phosphorus chloride pH to PCL. This is pH 2 PCLgave the diphenyl phosphine derivative of the ferrocenyl compound. So,this organostannyl ferrocene provides a useful route to so many different compounds andthat solve the issue of multiplelithiation which usually plaguing the normal litigation chemistry of ferrocene.

So this is where one can see that how chemists primarily a circumvent many complicated issues not only by making a derivative and then successfully making what really it wants it to make, for example in this case,the chemistshave found a method to really make this monolithiated product successfully even though they had to go make it via this organo stannyl ferrocene derivative which they made from ferrocene. So this is the way you can see that one can avert or avoidissuesby coming out with a novel approachin making them.

So here we find the example a beautiful demonstration of chemistry,and alsovarious protocols including the one to make the monolithium, lithiation of ferrocene in a successful manner.

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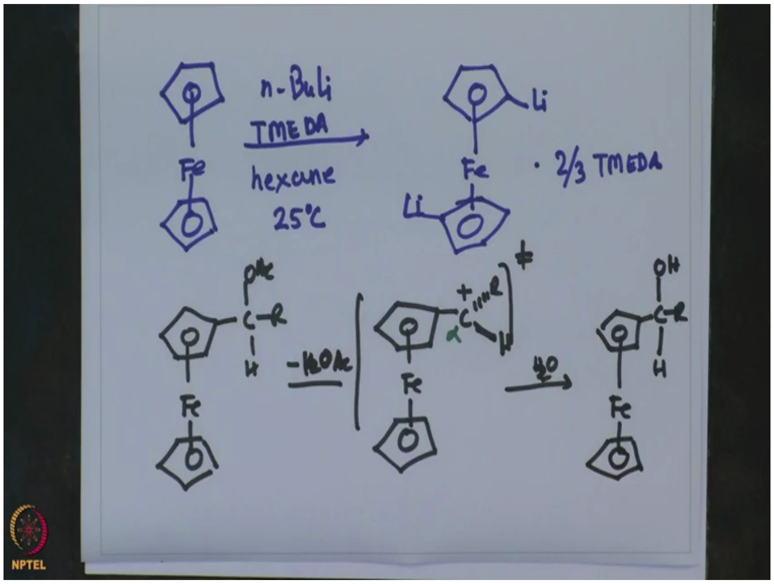

Similarlythe dilithiationin a selective manner of ferrocene has been achieved andthis has been donein presence of by doing the reaction in presence of TM EDA in hexane at 25 degree centigrade gives exclusively the desired diluted product plus 2/3rd. Okay. Now another important feature about ferrocene is that it stabilizescarbo cationwhich is adjacent to it, I will illustrate that with the example over here now.

For example, so this alpha carbon cation issort of stabilized, as a result of loss of thisacetic acid moietyand that can pick upwater to give this is sort ofthe transition state to give the alcohol. Now it is important to note that there are like this transition state which is cationic alpha carbo cation has been successfully characterized by expect dystrophy by putting various substituent's where it sort of explains the fact that this cationic charge is highly stabilized by this CP ring.

And that also again is an obvious conclusion given the fact that the CP rings are carbionic nature so if there is a positive charge in the alpha position so that gets stabilized readily and this has been done even using x-ray crystallography. So with this we are going to move on tosome important variants of transition metal cyclopentadienyl complexes, particularly the cyclopentadienyl carbonyl complexes.

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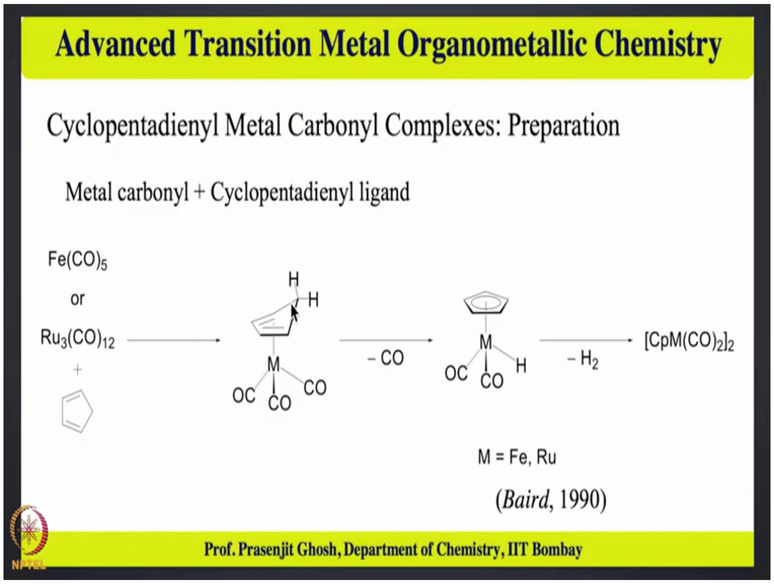

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Cyclopentadienyl Metal Carbonyl Complexes: Preparation

Metal carbonyl + Cyclopentadienyl ligand

M = Fe, Ru

(*Baird*, 1990)

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So, we are just moving away from binary cyclopentadienyl transition metal complexes like metal OC in CP to m the which are homoleptic complexes to heteroleptic cyclopentadienyl metal carbonyl complexes.

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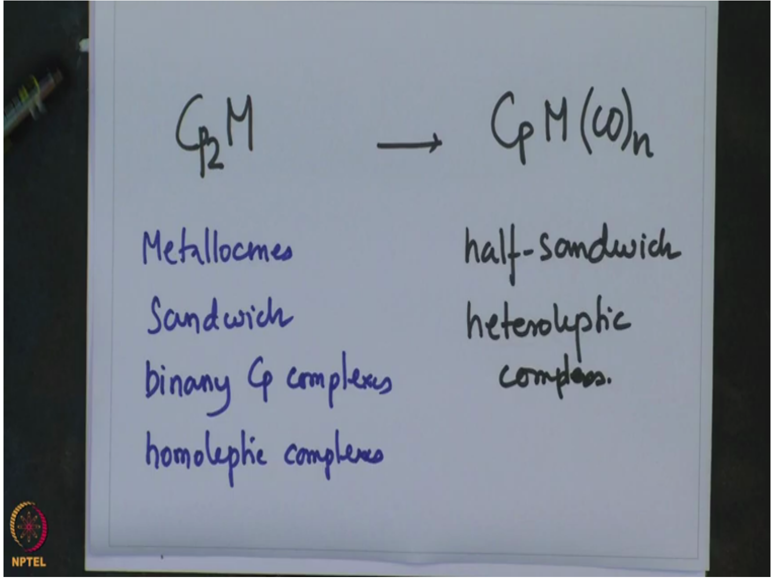

$Cp_2M \rightarrow CpM(CO)_n$

Metallocenes	half-sandwich
Sandwich	heteroleptic complexes.
binary Cp complexes	
homoleptic complexes	

So, far in the lastfew lectures we have been discussing aboutCP 2 M type of complexes which are, which are, called metallocenes or sandwich complexes. These are binary, binary CP complexes or even homoleptic complexes. From these we are going to move to CPM CO n type of complexes these are cyclopentadienyl metal carbonyl complexeswhich are no longer metallocene,they are called half sandwich complexes.

And also there are no longer binary complexes because now there are more than two different kinds of ligands so these are called heteroleptic leptic complexes, so these are particular special kinds of variations of BCP iron complexes in the sense that one of the CP ring has been removed and is andis placed replaced by carbonyl metal complexes. So, the next part of this lecture we are going to talk about various synthetic air methods that are available for preparation of cyclo pentadienyl metal carbonyl complexes.

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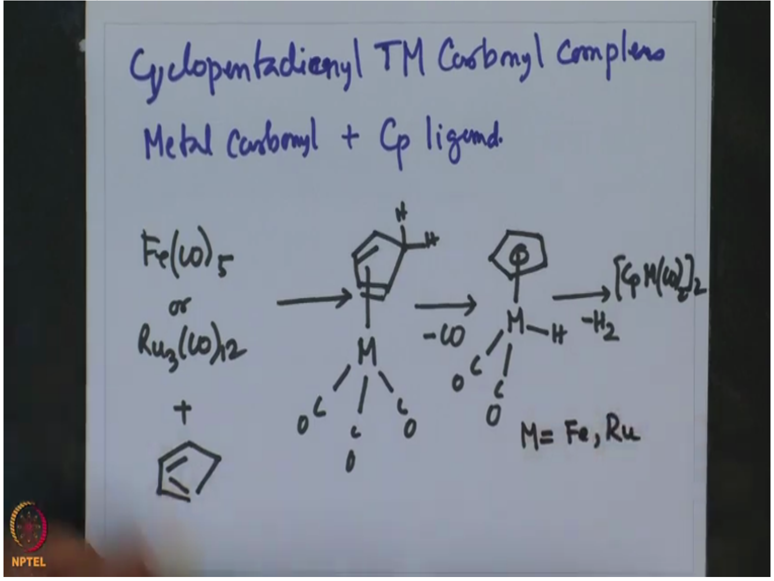

Cyclopentadienyl TM Carbonyl Complexes

Metal Carbonyl + Cp ligand

The first and the foremost at the cyclopentadienyl metal carbonyl complexes are directly prepared. Cyclopentadienyl transition metal carbonyl complexes are prepared by metal carbonyl and the CP ligand. This is illustrated by the reaction of fe CO5 or ruthenium CO12 and cyclo pentadiene, giving the cyclo pentadiene complex, of metal tricarbonal, which loses a carbon monoxide, followed by this aromatization of the cyclo butadiene, pentadiene ring, resulting in a metal hydride complex and which eventually eliminates hydrogen to give the dimeric compound, and over here the metal is equals iron and ruthenium.

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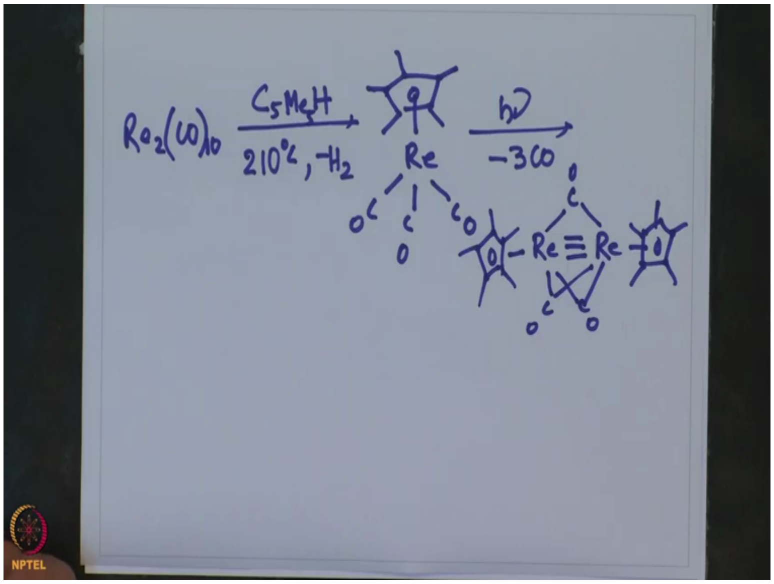

Similarly along the same line the reaction proceeds for the CP star derivative for example the reaction of CO 10 its C5 Me5 hydrogen, this is occurs at very high temperature give CP star rhenium, uses to give this beautiful compound, containing rhenium, rhenium, triple bond, with bridgingcarbonyl okay. So, this is avery elegant compound which is prepared for from the reaction of di rhenium to take a carbonyl with CP, CP star Penta methyl cyclo pentadieneby hitting them at 200 degree centigrade at very high temperature it cause if CP star rhenium tri carbonyl which in presence of light loses these three a carbonyl moiety, to give this rhenium, rhenium, triple bond, with three bridging carbonylatoms.

So, with this I would like to draw conclusion to today's lecture. Today's lecture had been on looking at thereactivity of transition metal cyclopentadienyl complexesandwith the main emphasis and today's reaction, he, was on trying to look at the challenges that lied with a simple metal lithiation chemistry of ferrocene aryl compounds and the ways and means to come around it.

The primary challenge that we have discussed about the lithiation chemistry of ferrocenyl compounds, is the fact that, it would undergo, multiple lithiation,which would hamperthis process of lithiation without giving any selectivity to the lithiater product, and that was deviously overcome by preparing a mono organo stannyl ferrocenyl compound which was predominantly form.

And subsequentlythen converting this organostannyl ferrocenyl compound to various other derivative through simple stille coupling or various kind of electrophiles or even by treating with butyl lithium successfully converting it to a monolithiated compound, which again can be reacted with, various electrophiles to get that. We had also seen in our discussion that, under certain conditions, particularly in presence of TM EDA, one could successfully isolated the di ethylated product where the litigation had occurred on each of the the two rings.

We have alsocome upon the discussion onthe stabilization of cationic charge at the alpha position of the cyclopentadienyl ring and that we had seen, had been used in making alcohol substituted ferrocene aryl compounds,the reason for successful stabilization of the alpha carbon cation and adjacent to the ferrocenyl ring is kind ofdue to the obvious resonance that arise out of this highly conjugated electron rich carbon ionic nature of the cyclopentadienyl ring.
Now having discussed the reactivity of cyclopentadienyl transition metal complexes we moved on to one of its variant which are these half-sandwich heteroleptic transition metalcarbonyl complexes and looked into various methods for preparing this compound. The methods that we have today discussed upon is, the radical reaction of metal carbonate carbonyl with the cyclo pentadieneolefin compoundsresulting inthis half sandwich cyclopentadinyl carbonyl compounds.

So, this is pretty useful method and kind of generic method and resultsin the expected compound. We had seen the formation of beautiful metal, metal, triple bond, particularly in case of rhenium, appropriately stabilized by CP star ligand. So, with this I am going to conclude today's lecture, we are going to discuss in more details about various property as well as reactivity patternsthat remains to be discussed for transition metal cyclopentadinyl carbonyl complexes.

And then move on to some other variants of each particle with the nitro cell compounds in the next lecture or the subsequent lectures. So, with this, I once again thank you for patiently listening to this lecture and I look forward to being with you in the next lecture. Till then goodbye and thank you.