

Advanced Transition Metal Organometallic Chemistry
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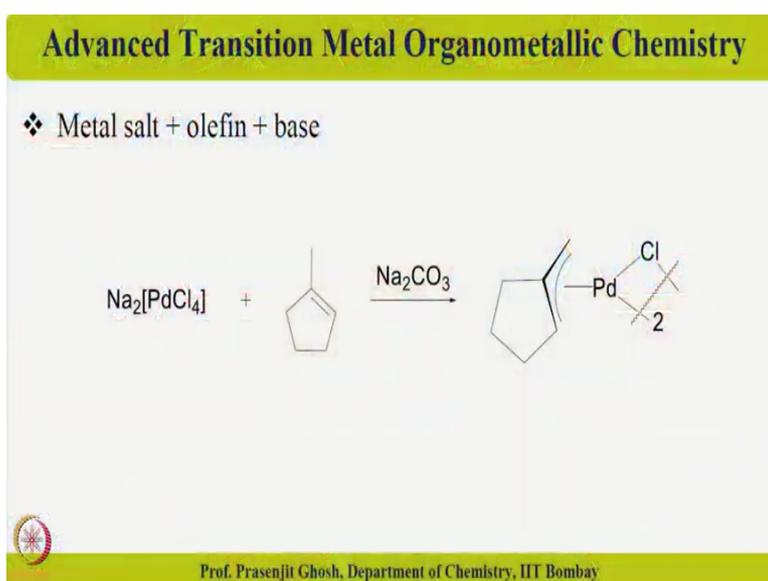
Lecture no- 3
Transition Metal Allyl and Enyl Complexes: Preparation

Welcome to the third lecture of the course, Advanced Transition Metal Organometallic Chemistry. The topics that we have been discussing over the past two lectures have been about allyl and enyl ligands and their complexes of transition metals. We had looked in the last class about various preparative methods that are used for preparing this transition metal allyl and enyl complexes.

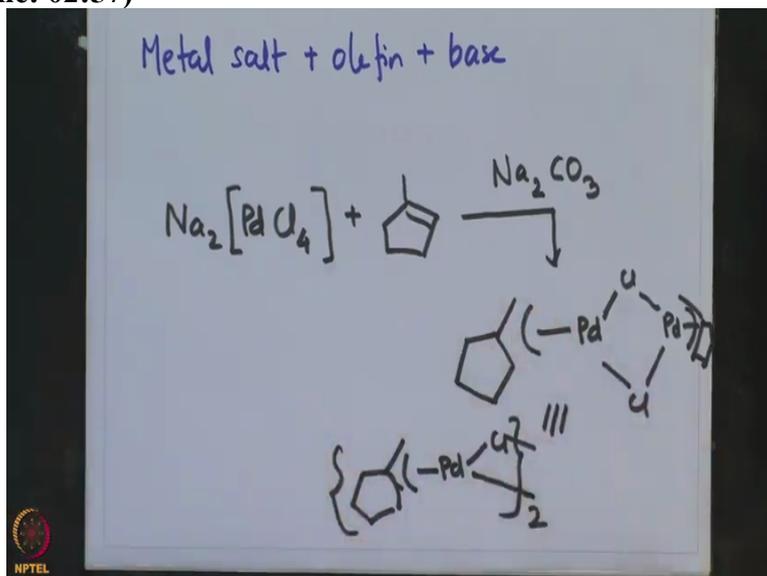
We have also looked at unique features that are prevalent between interactions that exist between transition metals and allyl and enyl ligands. Of the various synthetic methods that we have discussed about in the last lecture, all of them have been classified into 3 main subclasses. The first one is more of a meta; metaphysics type reactions in which the metal allyl precursors are critically allyl enyl.

The second sub class, the examples of which we discussed belong to conversion of transition metal sigma allyl enyl complexes to transition metal sigma eta 3 type allyl complexes. Last type that we discussed was about conversion of transition metal olefin or diolefin complexes to their sigma eta bound transition metal allyl complexes. Now in this discussion proceeding further, able to look at various other preparative methods which are available for making this transition metal allyl and enyl complexes and this would form the topic of today's lecture.

So, starting from where we left about conversion of metal olefin complex to the corresponding transition metal eta 3 allyl type complexes
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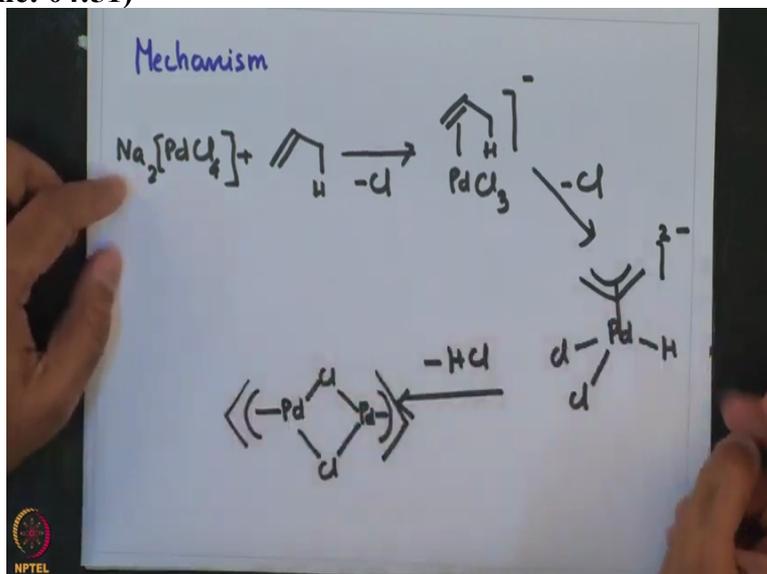


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Another example of such reaction involves the reaction between a metal salt and an olefin in presence of base. For example, reaction of disodium PdCl_4 with this olefin in presence of sodium carbonate gives the corresponding allyl complex, so this is a dimer of type this. So, in this reaction of a metal metal palladium tetrachloride dainties with this olefin in presence of base gives this forming eta 3 bound allyl ligand.

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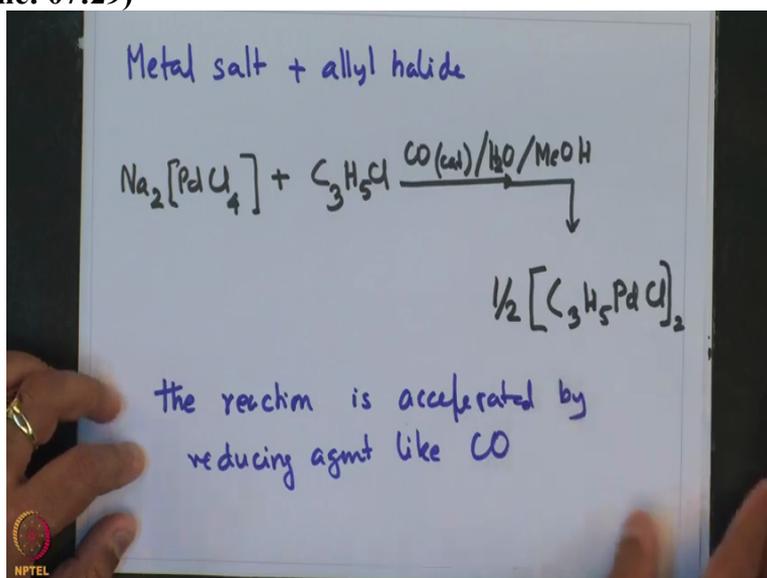


A possible mechanism of this is shown over here so first, this sodium, disodium PdCl_4 reacts with the olefin with the elimination of chloride anion resulting in this olefin bound PdCl_3 species which is mono anionic in nature, this species further loses another chloride, chloride anion as a migration of this hydrogen from olefinic moiety onto palladium leading to the

formation of a palladium hydride complex of the type, shown over here that loses HCl to give this palladium allyl dimer.

So the reaction to say in two steps in which the first palladium chloride is lost giving a monine, and subsequently the second chloride is lost. And further loss of HCl results in this palladium allyl di chloride. Another strategy involves the reaction of metal salt with allyl halide.

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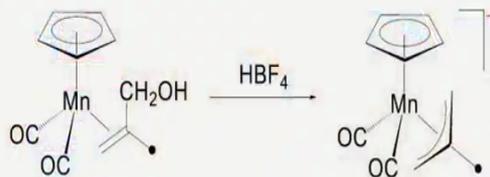
The reaction is given as follows, $\text{Na}_2 \text{Pd Cl}_4 + \text{C}_3 \text{H}_5 \text{Cl}$ in presence of Co catalytic amount and H_2O and Methanol gives rise to this palladium allyl chloride dimer. This reaction is accelerated by reducing agent like CO. So in this, one has to know that this is a disproportionation reaction, in which this, carbo cation, that the carbo, allyl chloride carbon is positively charged, hence to become, allyl anion, and the reducing agent for that species is this CO.

Whereas palladium remains in plus two state on the way, so this is a interesting reaction whereby palladium allyl chloride dimer can be formed. This palladium allyl chloride dimer can also be directly obtained by the reaction of palladium allyl chloride with palladium zero species, simply by following oxidation rule.

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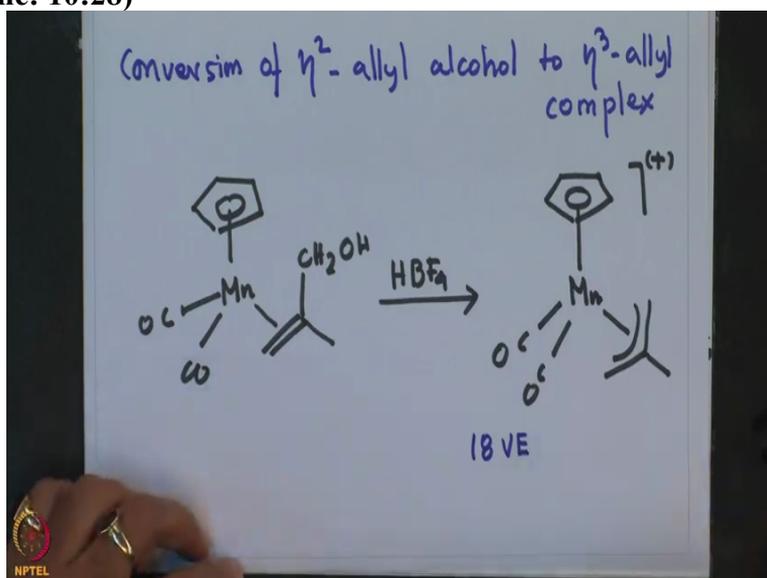
❖ Conversion of η^2 - allyl alcohol to η^3 - allyl complex



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There is another example in which one of the conversion of eta 2 bond allyl alcohol to eta 3 bound allyl complex, the reaction is shown over here.

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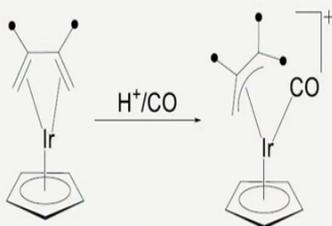
In particular the reaction of CP, manganese, CO, CO, Olifen, CH₂OH when reacted with protonating agent like HBF₄, actually protnets is alcohol, and eliminates water presenting in the formation of eta 3 bound, of allyl manganese complex. So, these is again a 18 valence electron complex, and that arrives from 5 of the CP, 7 manganese, 12, plus 3 allyl, 15 plus 2 CO₄ electrons that means 19, and since this cationic complex, so overall which is 18 valence electron complex which means that it is more cognitively as well as electronically saturated.

Along the same line formation of eta 3 allyl complex can also be observed by simple electrophilic addition to an activated diolefin complex.

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❖ Electrophilic addition to diolefin complex



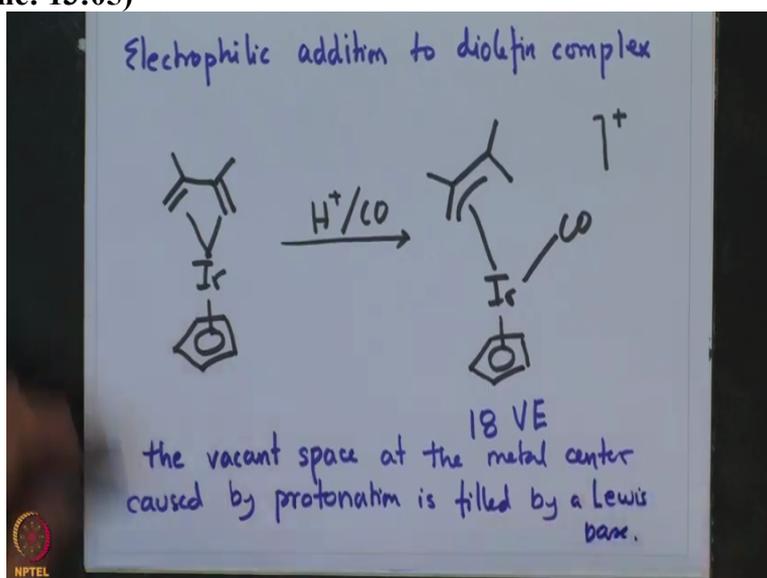
- ❖ the electron gap at the metal center caused by the protonation is filled by a Lewis base



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This is a very interesting reaction and this you seen as an electrophilic attack on an activated diolefin complex.

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This is specifically given as reaction of diolefin complex of Iridium bound to CP ligand, which when treated with a proton, in presence of co-ordinating ligands like carbon monoxide, results in cognition of one of the olefinic bonds giving rise to the formation of methyl methylene like this like this alongside the formation of a allyl eta 3 bound allyl ligand, similar to what we have seen in case of manganese in previous example, this one also is a 18 valence electron complex.

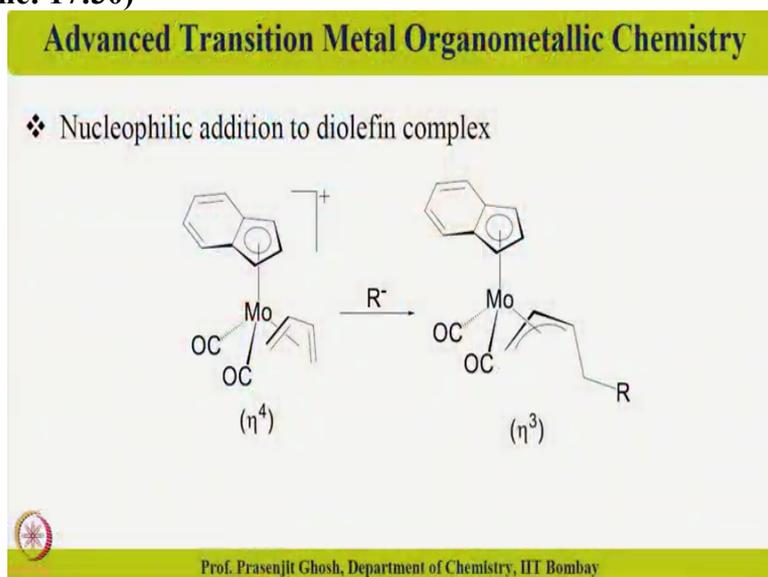
And can be seen from the electron counting as follows, 3 for the allyl, 9 for the iridium 12, and 2 gives 14, and 5 19 having an overall cationic charge which makes the 18 valence electron. So the important strategy that has been used is that the coordinative on saturation or

the vacant space created by the protonation of diolefin resulting in η^3 allyl is then filled by a Lewis base or donor ligand like carbon monoxide, caused by the protonation, is filled by a Lewis base.

We have observed in the course of this, this discussion about various ways of making this η^3 bound allyl transition metal complexes. We have observed that these can be converted from the olefin complexes or diolefin complexes by electrophilic additions where we have seen the examples in our previous discussions. Now able to take another example where it will be a nucleophilic addition to an activated diolefinic complex.

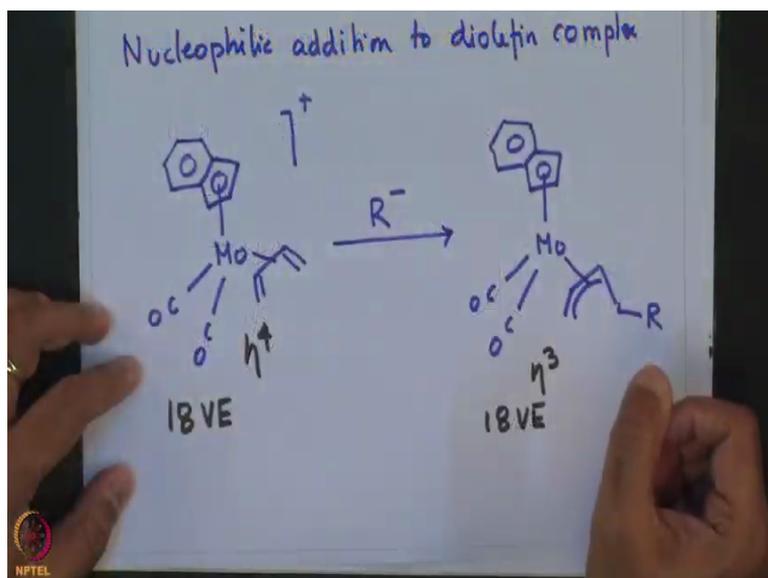
So this is exactly opposite to what we had discussed in our previous example, where a diolefin complex was in fact protonated resulting in η^3 bound transition metal complex, and in this case we will see the opposite, we will see the diolefin, diolefinic complex of transition metal being attacked by a nucleophile resulting in again the same η^3 bound transition metal allyl complex.

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So this is a very interesting reaction from that perspective and sort of encashes on the umpolung reactivity of olefin when they bind to transition metals.

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So, here we have a molybdenum complex, bound to a diolefin as it is shown, these also is a eta 4 bound diolefin complex and also is a 18 valence electron compound, $5+6, 11, 11+4, 15+4, 19$ having a cationic charge so overall that makes it to a 18 valence electron compound and it is eta 4 bound or diolefin complex of molybdenum. That when fitted with a nucleophile results in attack of the nucleophile on this diolefin yielding eta 3 bound allyl complex as it is shown over here.

Now these has become eta 3 bound allyl complex, again it is 18 valence electron compound. $5+6, 11+3, 14$ and 2 carbonyl $+4, 18$. And what we see that this attack of nucleophile anion on to these cationic molybdenum diolefin complex results in the formation of these neutral compounds having eta 3 allyl bound to these molybdenum. Now there are two interesting aspects of this particular reaction, one is this umpolung reactivity of this diolefin.

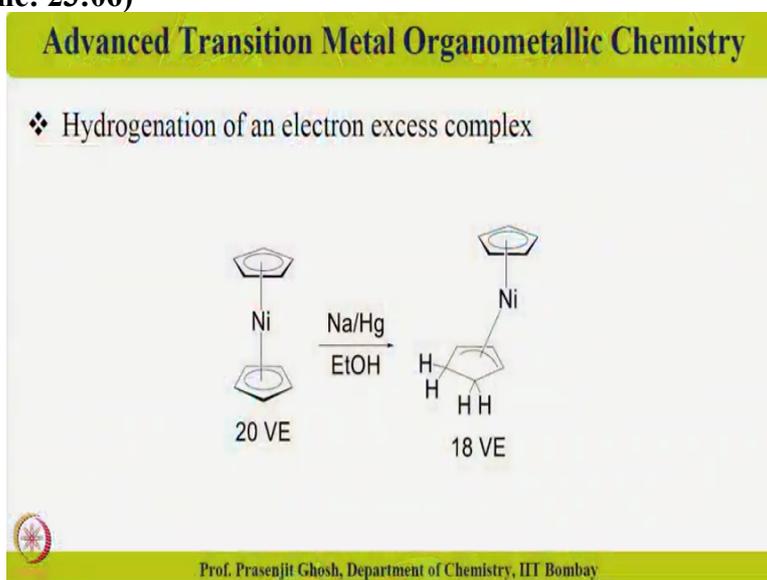
Usually free olefins are extremely electro rich and they do not get attacked by another electron region it is like the nucleophile of carbonyl, now these free olefins when they get bound to the metal particularly they get activated particularly when they are in a cationic metal complex, they are even further activated which can be seated of the attack of this carbonyl on to the olefin resulting in the exhibition of the umploung activity that is so famously called, and that attack happens at the olefinic carbon with the addition of the R group at the terminal carbon resulting in the formation, simultaneous formation of eta 3 allyl ligand.

So, here is another very interesting example in which the nucleophilic addition to diolefin complex has been discussed, and these reactions as well as the earlier one reactions where electrophilic addition to the diolefin complex was discussed. These two reactions together

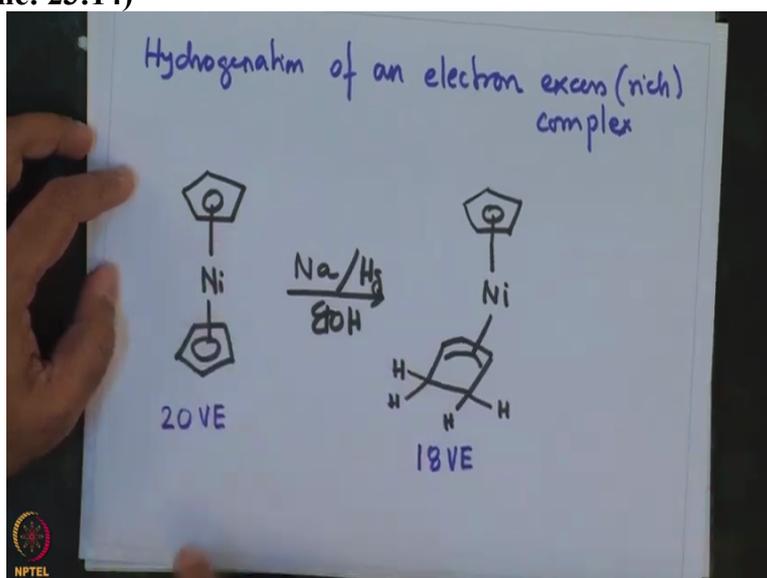
forming the third sub category of the methods which are used available for preparation of this transition metal eta 3 allyl complex, and this third category involved because of reactions which converts, diolefin complex on to the eta 3 allyl counter parts by the addition of various electrophiles and nucleophiles.

Next comes another interesting reaction and these reactions makes use of too much electron density present in a metal, resulting ah, in the unstability, which if used or exploited in a very clever manner, one can live to the formation of this eta 3 allyl transition metal complex. So the reaction or this particular example is titled as Hydrogenation of an electron excess or electron rich complex.

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Let us take a look at this complex, this electron rich or electron excess complex, is none other than sandwich or nickelosin or sandwich complex of nickel having two cyclopentadienyl

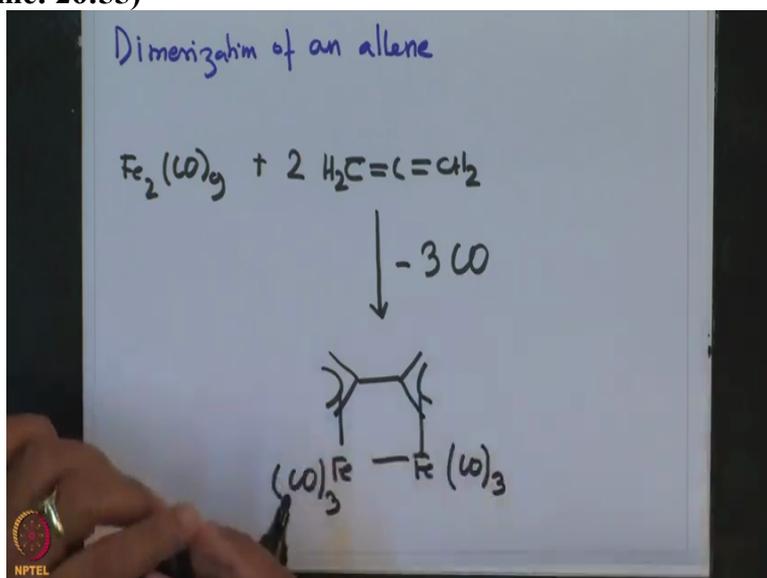
ligand.. Now the electron richness, or an electron excessness of these nickelosines is very much evident by counting the valence electron of this nickel complex, which is 20 valence electron compound, because 10, 5 each from two cyclopentadienyl anions and nickel having 10 valence electrons.

So, that makes a 20 valence electron complex, which sort of is not very stable, or relatively more unstable, as compared to the 18 valence electron compound, and hence also this nickelosin is much more electron rich, having 20 valence electron as opposed to the more inner or the more stable 18 valence electron configuration of other transition metal complexes. So the treatment of these nickelosin in presence of sodium, mercury and ethanol results in hydrogenation of one of the cyclopentadienyl ring along with the simultaneous formation of a sandwich complex of nickel which contains one cyclopentadienyl ring being Ni.

And the other cyclopentadienyl ring converted to eta 3 allyl ligand having been hydrogenated on the ring carbons. So, overall this complex ends up being 18 valence electron species. So, 18 can come from 5 nickel, 8, 5 cyclopentadienyl 8 10 nickel 15 + 3 allyl ligands becoming 18 valence electrons compound and the source of hydrogen for this hydrogenation arise from this ethanol and sodium, mercury amalgam which results in the formation of sodium ethoxide along with the generation of hydrogen.

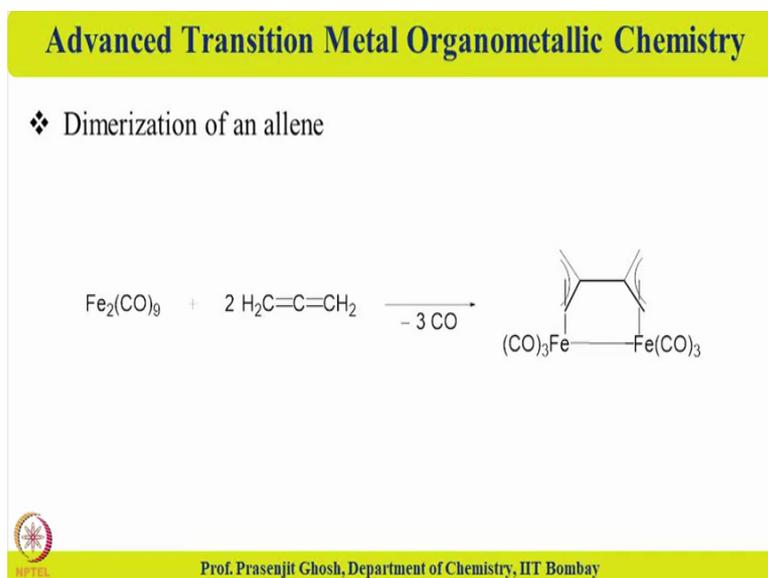
This hydrogen then further hydrogenates this electron excess nickelosin compound and cleverly makes this eta 3 cyclopentadienyl nickelosin sandwich compound as shown over here.

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Another very interesting reaction involved dimerization of allene. Now this is a distinct reaction and this type of reaction has not does not following to one of the three classes sub classes.

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That we have spoken about where this diolefins are activated, this is just direct reaction of Fe₂(CO)₉ the di-nickel iodine carbonyl, with 2 allyl moiety's resulting in elimination of 3 carbonyl molecules and formation of this dimer ring di allene iron di nuclear compound as is shown over here. So this is a very elegant way of generating a dinuclear diallene complex of iron starting from this dinuclear dicarbonyl compound of iron.

And that involves the dimerization of an allene molecule. So, with this I would conclude today's discussion on various preparative methods that are available out there for preparing this very important eta 3 bound transition metal allyl complexes, so most of the reactions today that we have discussed, fell in the third category, which involve this conversion of activated or metal bound diolefin ligands to the eta 3 transition metals allyl complex.

And these conversion of diolefin transition metal allyl ligands can be achieved by reactions with electrophile as well as nucleophile on the activated diolefin compound to give the product of eta 3 transition metal allyl compounds. Now we have also seen that apart from these there are two other methods, one is that, simple hydrogenation of electron rich nickelosin complex in presence of sodium amalgam and ethanol which resulted in hydrogenation of part of the cyclopentadienyl ring resulting in eta 3 bound cyclopentane.

So, eta 3 bound allyl type ligand to nickel under Cp ring bound to a nickel resulting in the sandwich allyl cyclopentadienyl complex the other method also was quite distinct in the

sense that involved the formation of dinuclear di allyl eta 3 bound iron carbonyl complex which was achieved by direct reactions of 2 equivalent of allene in presence of di iron $\text{Fe}_2(\text{CO})_9$ resulting in elimination of 3 molecules of carbon monoxide along with the formation of dinuclear di allyl eta 3 bound iron complex.

So, with that I would like to conclude on today's discussion that we are talking about various synthetic methods available for transition for transition metal eta 3 allyl compounds and then well in subsequent lectures we will pursue this topic in much more detail particularly looking at various kinds of re-activities these transition metal allyl compounds usually show and their and the reasons behind exhibiting such re-activities.

So with this again I would like to reiterate my thanks for patiently listening to today's lecture and I look forward to deliver next lecture on various reactivity aspects of transition metal allyl enyl compounds. So with that, thank you, I look forward to being with you in the next lecture.