Advanced Transition Metal Organometallic Chemistry
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Lecture – 04
Transition Metal Allyl and Enyl complexes: Reactivity and Transition Metal Sandwich Complexes

Welcome to today's lecture on advanced transition metal organometallic chemistry. This lecture we are going to talk about an interest as interesting aspect of transition metal allyl and in enyl complexes that we have been discussing about in the last few lectures. These allyl and enyl ligands are very interesting type of ligands in the subclasses of various ligands that exists for transition metal organometallic complexes.

Their uniqueness of arise primarily for their Sigma donor as well as Pi acceptor behavior. So, unlike the very simple alkyl or hydride donor which are or methyl donor, methyl ligand which are simple Sigma donor ligand or like olefins these allyl and enyl ligands can have both Sigma donor and Pi acceptor properties. From that perspective we have looked into in the beginning of the course looked into various kind of interactions that occurs between the molecular orbitals of transition metal as well as that of the allyl and enyl ligand and try to understand how the interaction of Sigma relation and PI acceptor kind of interaction originated from the overlap of these molecular orbitals or atomic orbitals of transition metals and then enyl and allyl ligands.

We have also looked in the last lecture about different methods that are available in preparing the transition metal allyl and enyl complexes. By and large what we saw there are various repetitive methods that are available for preparing this transition metal allyl and enyl complexes all of them can be classified into two or three main type of reactions where most of the different examples would belong to.

However apart from that there are a few unique methods and unique strategies which also lead to the formation of transition metal allyl and enyl complexes. So, in today's lecture we are going to finish up on this topic of transition metal allyl and enyl complexes by looking into the reactivity are the kind of reactions these transition metal allyl and enyl exhibit. And then we are going to move on to another interesting topic which are transition metals sandwich complexes.

Now these sandwich complexes actually started with the origin of ferrocene in and then gradually expanded on to various combinations and various type of sandwich complexes we are going to explore those in details as a part of this lecture. So, to begin with let me just look into some of the reactivity of transition metal allyl complexes.

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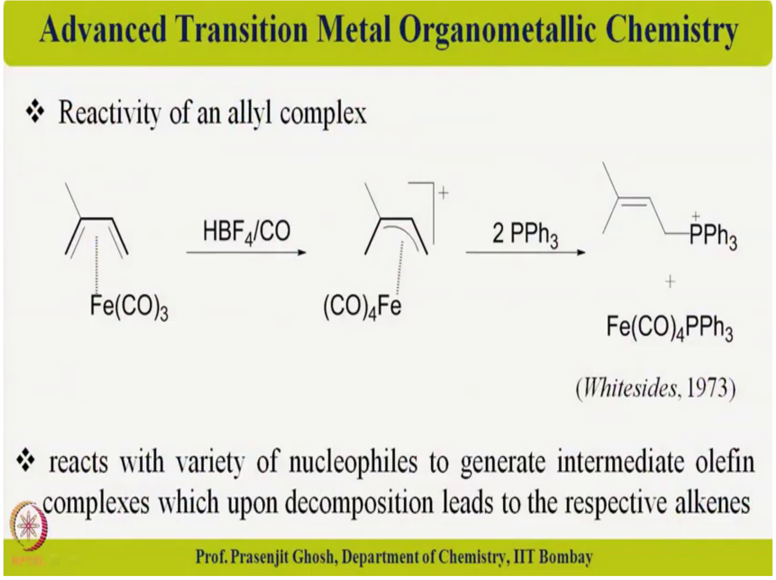

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- Reactivity of an allyl complex

(*Whitesides*, 1973)

- reacts with variety of nucleophiles to generate intermediate olefin complexes which upon decomposition leads to the respective alkenes

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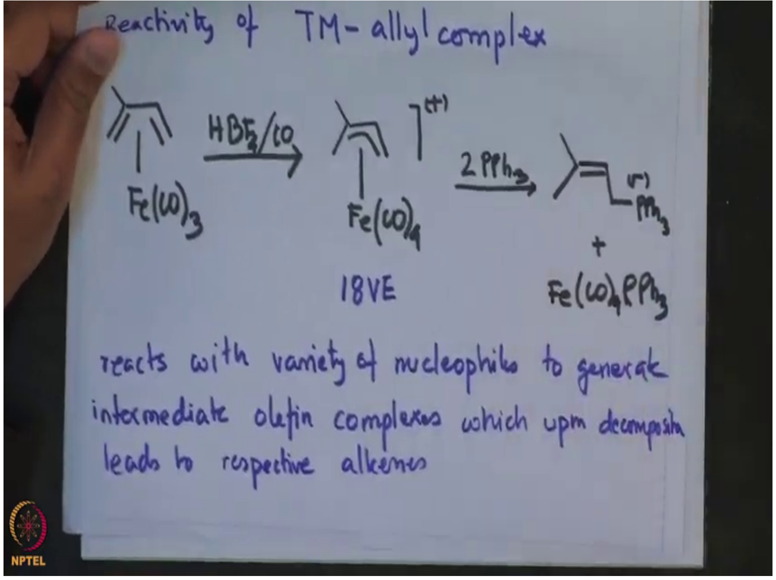

Reactivity of TM-allyl complex

reacts with variety of nucleophiles to generate intermediate olefin complexes which upon decomposition leads to respective alkenes

The particular example starts off reacting diluting complex of iron resulting in formation of this transition metal allyl complex of iron and then exploring the reactivity of the same. So, the reaction goes as this diluting complex of iron carbonyl reacting with HB a4 and carbon monoxide giving this allyl complex of iron which is cationic in nature. Now include in the context of our earlier methods that existed on preparation of this Eta 3 bound allyl transition metal complex.

This particular method thus is electrophilic attack electrophile being the proton on the dilutin complex of the iron resulting in Eta 3-bound allyl iron complex in presence of donor ligands like CO and the vacant space that is created as a result of the protonation and as a result of conversion of Eta 4 bound dilutin to Eta 3 bound allyl is occupied by then this carbon monoxide and does the iron goes from becoming Fe CO 3 to Fe CO4. Overall this is also 18 electron complex this is 4 CO that means 8 electron iron 8, 16 + 3 a from the allyl 19 over all these being a positive charge.

So, this is a 18 valence electron complex so the reactivity of these complex stems from the reaction of this Eta 3 allyl by triphenylphosphine resulting in the attack of the phosphine moiety onto this olefin with the formation of these olefinic compound and iron tetra carbonyl phosphine the way it is shown over here. So, this reaction is not only limited to triphenyl phosphene but it is generic to a variety of nucleophiles and as a result large number of compounds can be obtained through this method.

So, reacts with variety of nucleophiles to generate intermediate olefin complexes which upon decomposition leads to respective alkenes. So, this is a interesting example where by Eta 3 bound transition metal compound is formed by electrophilic addition to a delivery complex and subsequently the reaction of this Eta 3 bound iron compound to various nucleophiles like the phosphine occur at this Eta 3 bound allyl ligand resulting in the formation of the olefins.

So, we would now look at a different reaction in which instead of the nucleophiles attacking Eta 3 bound allyl transition metal complex we are going to look at electrophile attacking similar Eta 3 bound transition metal allyl complex.

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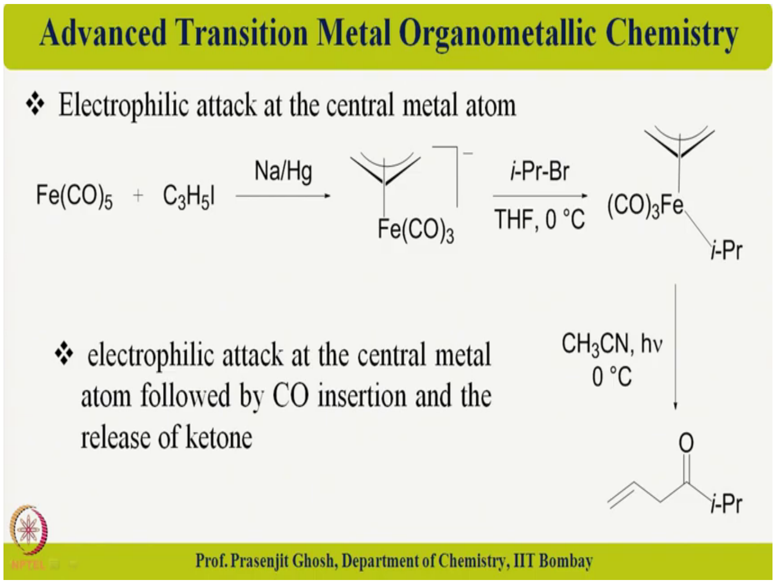

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- ❖ Electrophilic attack at the central metal atom

- ❖ electrophilic attack at the central metal atom followed by CO insertion and the release of ketone

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Now here there is a certain catch in terms of the complex even though these are transition metal allyl complex in which in the previous example electrophile attack was considered whereas the example which I am going to talk about is also a Eta 3 bound transmittal compound but here and electrophile attack would occur. So, one I must note that in the beginning I must note in the beginning that these Eta 3 bound transition metal compound however are different in these two cases.

For example in the former where a nucleophilic attack happened on the Eta 3 bound transition metal compound it was cationic in nature and in the present case where a electrophilic attack would occur on to another transition but will it three bound allyl complex this complex would be a as expected and ionic in nature to facilitate the electrophilic attack.

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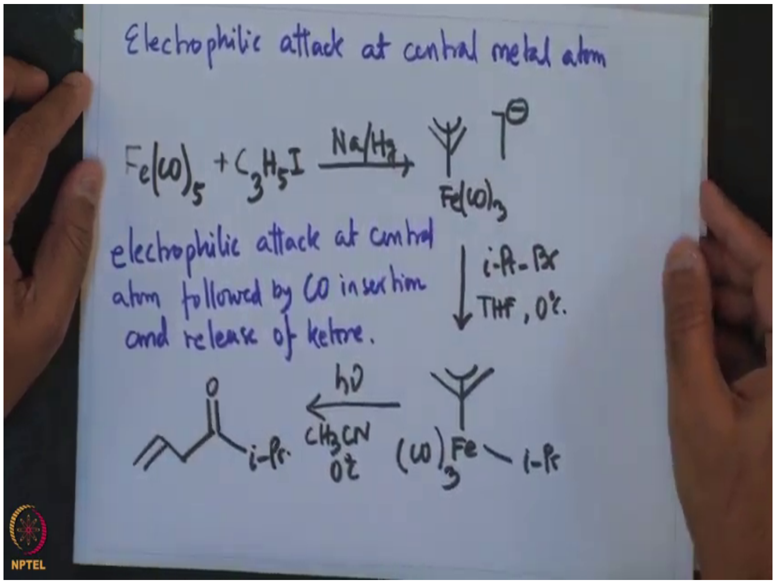

Electrophilic attack at central metal atom

electrophilic attack at central atom followed by CO insertion and release of ketone.

So, let us take a look at the specific example that involves electrophilic attack at central metal atom and is again governed by the formation of Eta 3 bound transition metal allyl complex as is shown here from Fe CO5 plus allyl iodide in presence of sodium amalgam giving this Eta 3 allyl iron tricarbonal anion which can then reacts with isopropyl bromide in THF at 0 degree centigrade resulting in this eta 3 bound iron isopropyl moiety and CO3.

So, to note over here the electrophile is this isopropyl a cataion that is attacking on this Eta 3 bound allyl iron tricarbonal anion. Then subsequently in presence of light and in acetonitrile at zero degree centigrade to you insertion occur along with the formation of these ketone. This is an interesting alpha beta unsaturated compound and is a useful precursor for many sentence in organic synthesis.

So, the take-home message is the electrophilic attack at central atom followed by CO insertion and release of ketone, so what we see that in this particular reactivity that one can generate ketone by CO migratory insertion and that in the preceding step one can undergo an electrophilic attack on to a Eta 3 bound transition metal allyl anion and which subsequently can also be generated by the reaction of iron pentacarbonyl with allyl iodide.

So, let us take a look at this a little radical and C4 H4 particularly with respect to their molecular orbital as that will explain some of the reactivity issues that we are discussing.

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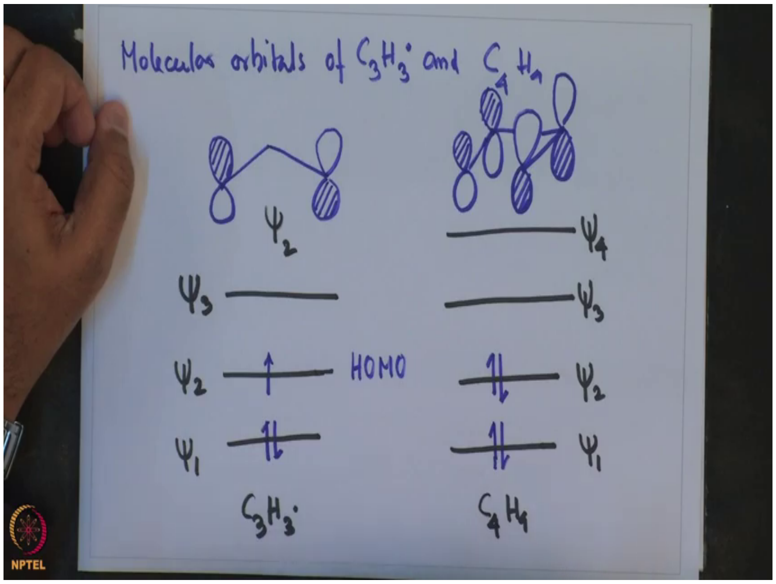

So, molecular orbitals of C3 H3 dot and C4 H4 so one can see for C3 H3 dot there will be 3 PI type orbitals and there will be a 3 emos resulting from 3 arrows which are Psi 1, Psi 2 and Psi 3. In our earlier discussion we have discussed in details the various molecular orbital combinations that are formed for this allyl radical. Now allyl radical has three electrons. So. Psi 1, bond is paired and populated. Psi 2 is unpaired single electron so it has a radical nature and this is the highest occupied molecular orbital or homo.

Thus the reactivity of C3 H3 dot radical is very much dependent on this unpaired electron available at the Psi 2 orbital. Now the Psi 2 molecular orbital would resemble or would look like this now in the same context let us look at how the molecular orbital of C4 H4 would be like. So, C4 H4 could also have 4 PI orbitals and then it would have 4 emos which was which will go from Psi 1 to Psi 4 and each of these would have two electrons.

So, in this case the highest occupied molecular orbital is paired up and it is occupied by two electrons of opposite spin. Now if we look at the molecular orbital diagram of Psi 2 of the homo that would resemble something like this. So, these two molecular orbital clearly depicts the reason for extremely high reactivity of allyl or enyl kind of ligands because these ligands allyl or enyl kind of ligands have odd number of carbon atoms and these are unsaturated compounds.

And also by the because of the fact that in the neutral form they are homo just contains one single electron which makes these polygons very reactive in their neutral form particularly going to their radical nature. And hence these further highlights the importance or challenges that are associated with their stabilization.

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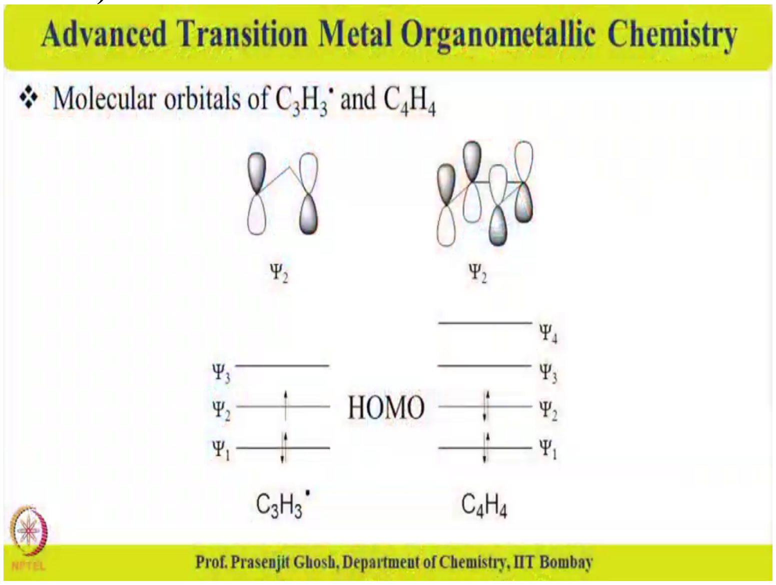

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- Molecular orbitals of $C_3H_3^\bullet$ and C_4H_4

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As well as their isolation and also sort of highlights the importance of their stability being achieved through complexation with transition metals leading to their isolation. So, with that I would finish off this discussion or transition metal allyl complexes and then move on to another very interesting topic which are the sandwich complexes.

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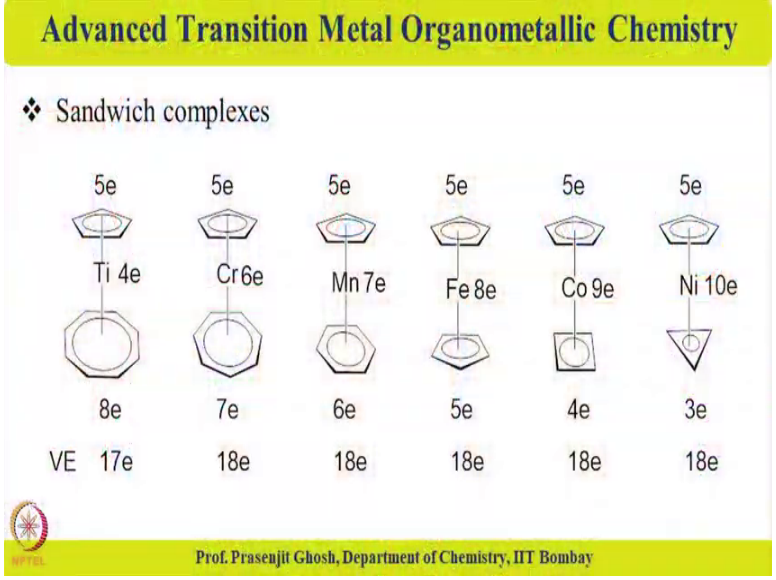

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- Sandwich complexes

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As the name suggests that these sandwich complexes are complexes of cyclo pentadienyl or other ligands of transition metals cyclic ligands of transition metals and these are mainly a homo elliptic or hetro elliptic complexes of transition metals and transition metal is bound to the CP or the other cyclopentadienyl or Cyclohexane, hexadynl, Optitrondynl beings through Pi electron.

Now I must say that the curiosity on these kind of complexes and which complexes sort of originates from that of the studies with respect to ferrocene.

Where two cyclopentadienyl ring was found bound to iron and it aroused the tremendous interest in 1950-60's particularly from the standpoint of understanding the nature of bonding that exists between transition metal and the cyclopentadienyl ring. Now one of the unique feature about the cyclopentadienyl interaction with transition metal is the fact that CP ligand interacts with transition metal through the Pi electron cloud and that what led people to try to rationalize and understand such interaction.

Because it was mainly thought that these ligands are very different from simple Sigma type ligands that people were used to before and they were not sure as to how P type orbital can engage with transition metal in a Sigma type fashion. So, having said that a lot of research went into studying and understanding sandwich complexes and what turned out at the end that sandwich complexes are not are not limited to are restricted to only ferrocene or metallocene various combinations of homo elliptic or heterolytic transition metal by a real and of complexes are known there having different static as well as electronic demands.

So, to illustrate this example I am going to present to you a various kind of sandwich complexes and their total valence electron count just to give you a feel for as to what kind of different varieties they exist upon. For example these CP titanium cyclooctatetraene, so this is 5 electron, 4 electron, 8 electron overall 17 valence electron species. The next comes CP chromium cyclohexatriene.

Now this is 5 electron, 6 electron, 7 electron overall 18 electron. The next one is CP manganese benzine so 5 electron, 7 electron, 6 electron resulting in 18 little species. Then comes ferrocene 5 electron iron so this is 5, 8 electron, 5 electron overall 18 electron. We also have this CP cobalt cyclobutadiene. So, this is also a 5 electron, 9 electron, 4 electron overall 18 valence electron compound. Last one is also a very interesting one which is CP nickel cyclopropane.

So this is 5 electron, 10 electron and 3 electron overall 18 electron species. So, one can see that there is with the CP remains the same there is a steady increase in electron density on the metal and similarly there is a steady decrease in the electron density or the other cyclic ligand of the sandwich complex. However over such that the overall valence electron of these compounds he means the a team the that these compounds as 18 electrons means that they are kind of stable compounds and that there at least electronically saturated.

And because of the presence of true planner CP or other cyclic ligands the metal is kind of shielded from both ends and hence that also imparts the stability to these transition metal sandwich complexes. So, what comes to the fore is the fact that sandwich complexes are not just the ones which are restricted to the central ferrocene atom from where the interest sort of arose. But one can see that it expands in both the direction in terms of diversity not only and the ligand but also at the metal center.

So, with this I will conclude this particular discussion in this lecture fourth lecture in particular we have been looking at two interesting aspects of transition metal compounds particularly in the reactivity of Eta 3 bound transition metal allyl complexes in which we have seen that these compounds transition metal compounds can be a reacting with electrophile as well as nucleophile and as a result they can be used to produce olefins or ketones because of their reactivity.

We have also looked into the property of their neutral compound being extremely reactive as compared to the C4 H4 or the even number carbon containing unsaturated compound the reason being there allyl or enyl multi containing unsaturated odd number of carbon atoms are radical in nature with their homo containing and unpaired electron which results in their tremendous reactivity.

In the next the second half of our discussion we have initiated a new topic which are sandwich complexes and in that aspect what we saw that those sandwich complexes has its Genesis from ferrocene or be cyclopentadienyl CP complexes but it sort of diversified into various kinds of combinations of various cps and other type of cyclic ligands and also it has huge amount of versatility or diversity arising from the various kinds of transition metal that can form these sandwich complex.

So, with this I would like to conclude today's lecture and we are going to take up the sandwich complex in much more detail in the next lecture looking into various forms of sandwich complexes are there what are their diversity, what are their classifications, how they are prepared and what are the interesting aspects or characteristics are associated with the sandwich compounds.

So, with that I once again thank you for being with me and patiently listening to this lecture on advanced transition metal organometallic chemistry and also look forward to being with you in the next lecture which will talk in more details about sandwich complexes, thank you.