Advanced Transition Metal Organometallic Chemistry
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Lecture – 02
Transition Metal Allyl and Enyl complexes: Preparation

So, welcome to this lecture on Advanced Transition metal Organometallic chemistry, today is second lecture. In our first lecture, we had briefly spoken about various kinds of Allyl and Enyl ligands offer a wide role range of electron donating capacities, in terms of electron that they donate, while binding to transition metals, and this range can go from 2 electron donor to 8 electron donor. Another interesting feature about this Allyl and Enyl in ligands is the fact that this ligands can bind neutral, anionic and cationic forms.

Now ligand, binding to metal in neutral and anionic form however ligand binding to metal in cationic form is kind of counter intuitive. The reason being, ligands are supposedly thought of as something which is electron reach whereas metals are supposedly thought of as something which is electron deficiency, so the metal ligand interaction is an interaction that involves electron rich species with that of electron deficiency species.

Now Cationic ligand in this context is kind of counter intuitive, now in cationic the ligand no longer will be thought of as something which is electron rich and hence it is kind of not so easy to conceive the fact that how cationic ligands bind to transition metals. Now one of the versatility of these Allyl and Enyl ligands is the fact that they can bind both in radical anionic and cationic forms. In our last lecture we have also looked at, the transition metal Allyl and Enyl ligand interaction,

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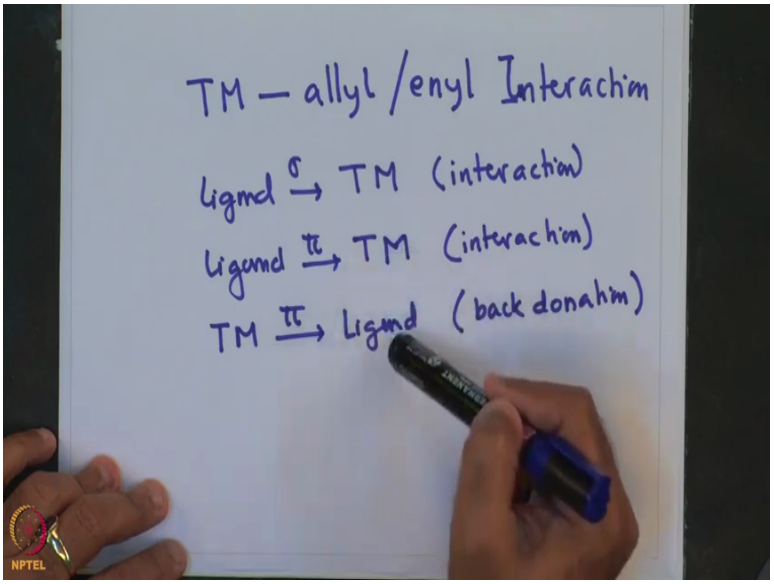

TM — allyl /enyl Interaction

ligand $\xrightarrow{\sigma}$ TM (interaction)

ligand $\xrightarrow{\pi}$ TM (interaction)

TM $\xrightarrow{\pi}$ ligand (back donation)

And what we saw is that it contains two kinds of ligands to transition metal sigma and pi interactions, sigma interaction as well as ligand to transition metal Pi type interaction, and lastly there is also a transition metal to ligand interaction which is of Pi type and they are called as back donation, because the obvious donation of electron density happens from ligand to metal, ligand to metal and in back donation there is reversal of donation that offers from transition metal to ligand.

Now these three interactions constitute, in transition metal interaction we have discussed this, in our previous lecture and these forward donation, the first two are called forward donation and the second one, the third one is called backward donation. These two interaction sort of define transition metal allyl ligands or ligand bond. Now that said with this lecture, what we intend to do is to look at various preparative methods which are out there for preparing transition metal allyl complexes.

Now obviously there are several methods which are available for synthesizing this transition metal allyl type complexes, and depending on the nature of synthesis, this preparative methods can be classified into 3 classes or sub classes.

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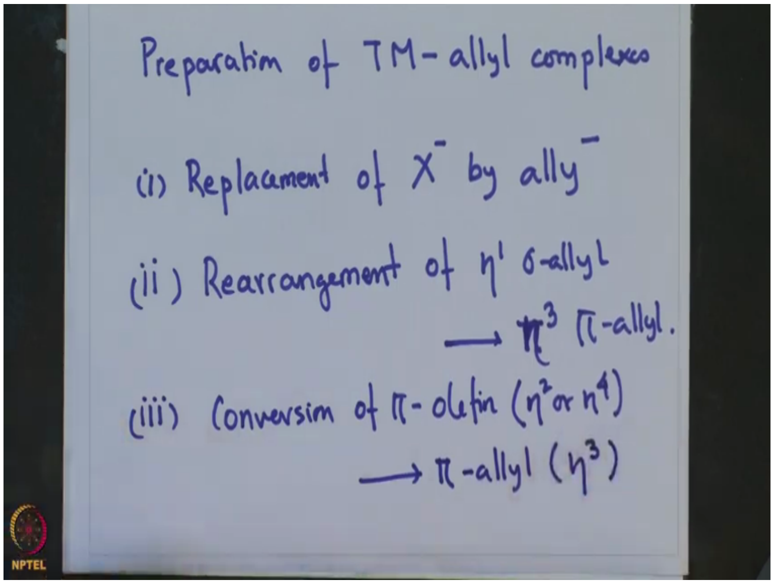

Preparation of TM-allyl complexes

(i) Replacement of X^- by ally$^-$

(ii) Rearrangement of η^1 σ-allyl

$\longrightarrow \eta^3$ π-allyl.

(iii) Conversion of π-olefin (η^2 or η^4)

$\longrightarrow$ π-allyl (η^3)

So, this preparation of transition metal allyl complexes can be classified into 3 sub classes, and first one is replacement of allyl on a metal by an allyl moiety or allyl enyl. So this is simple similar to salt metaphysics exchange where there is an allyl in the metal precursor and allyl-enyl goes and replaces the allyl, resulting in transition metal allyl bond. The second method is a rearrangement action of eta one bound sigma allyl bond to a Pi bound it has 3 bounds, Pi allyl bond.

So over here the hapticity changes from eta 1 to eta 3 and as a result a sigma allyl ligand becomes a Pi allyl ligand. We will take a look at various examples which belongs to this category. Now the third one is a conversion of Pi olefin, now olefin usually is bound in a eta 2 or eta 4 fashion to a Pi allyl ligand which is bound in a eta 3 fashion. So, to summarize what we see is, that there are various methods available for the synthesis of transition allyl metal complexes and all of these methods can be further classified into 3 main type of preparations.

First of all main simple replacement of halide ion on the metal by a allyl anion, and the second one is the rearrangement of the allyl moiety from eta one bound sigma allyl ligand to a eta 3 bound Pi allyl ligand, and third one is the conversion of Pi olefin ligand which has bound eta 2 or eta 4 to transition metal to a Pi allyl ligand which is the eta 3 bound. These are the 3 sub classes of methods which are available for transition metal allyl complexes. Now let us look at these sub classes individual sub classes in much more details.

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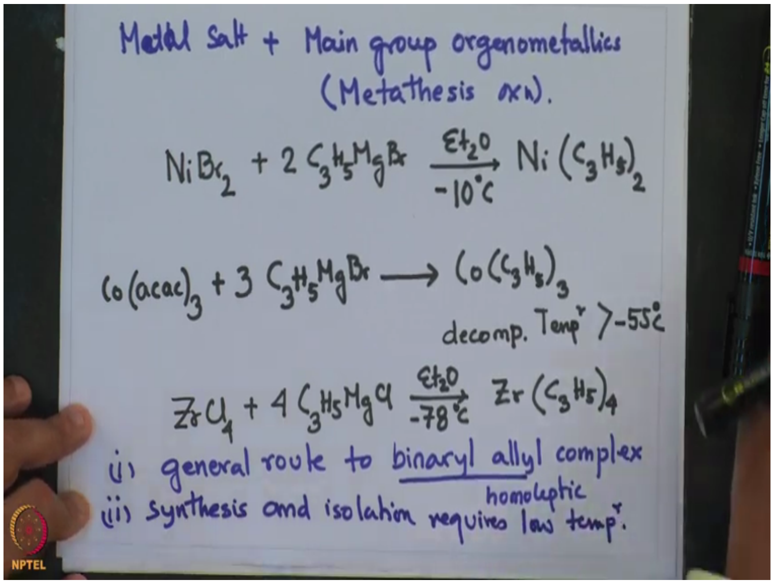

Metal Salt + Main group organometallics (Metathesis rxn).

$$NiBr_2 + 2\,C_3H_5MgBr \xrightarrow[-10^{\circ}C]{Et_2O} Ni(C_3H_5)_2$$

$$Co(acac)_3 + 3\,C_3H_5MgBr \longrightarrow Co(C_3H_5)_3$$

decomp. Temp^{r} $> -55^{\circ}C$

$$ZrCl_4 + 4\,C_3H_5MgCl \xrightarrow[-78^{\circ}C]{Et_2O} Zr(C_3H_5)_4$$

(i) general route to binaryl allyl complex

homoleptic

(ii) synthesis and isolation requires low temp^{r}.

The first one obviously as I have said is reaction of metal salt plus main group orgenometallics, this reaction is popularly called as metathesis reaction. For example, nickel bromide reacting with 2 equivalence of allyl magnesium bromide, in ether at mean temperature -10 degree centigrade produces nickel this allyl, similarly cobalt acetyl acetolyt thrice reacting with 3 equivalence of allyl magnesium bromide produces cobalt thrice allyl.

Now this compound is highly unstable and its decomposition temperature is about -55 degree centigrade. So, in order to stimulize this cobalt this allyl compound one has to be for attain a temperature range below -55 degree centigrade. Similarly zirconium tetra chloride reacting with 4 equivalence of allyl magnesium chloride again in ether at -78 degree centigrade, produces zirconium tetra allyl complex.

Now one important feature which stands out is the utility of ligand reagent in these metaphysics reactions. And second thing that stands out is that, these method is that represents the general method for synthesizing binary allyl complex. General route to binary allyl complexes, now these binary allyl complexes are also called homoleptic complexes because they are made of one kind of ligands.

If a transition metal organometallic compounds is made of two kinds of ligands or more than one type of ligands, these are can also be referred to as being heteroleptic complexes. So, over here, transition metal by binary allyl complexes it can be synthesized very easily using this general route. Now, one intersting thing about organometallic compound, particularly with respect to binary allyl complex is that these complexes are supposedly very reactive and this reactivity is primarily due to their catalytic ability rather than that of thermodynamic origin.

And from that perspective, preparation of pure binary allyl binary allyl complexes or any binary homoleptic organometallic complexes remains the challenge. And from that perspective, these particular route which exclusively gives binary allyl complex is particular importance. Now, as mentioned that these binary allyl compounds are extrermely reactive and because of this reason, the synthesis and isolation are to be done at low temperature, requires low temperature as these ligands are thermolabile.

So, now let us look at the next method available for synthesizing the transition metal allyl complexes.

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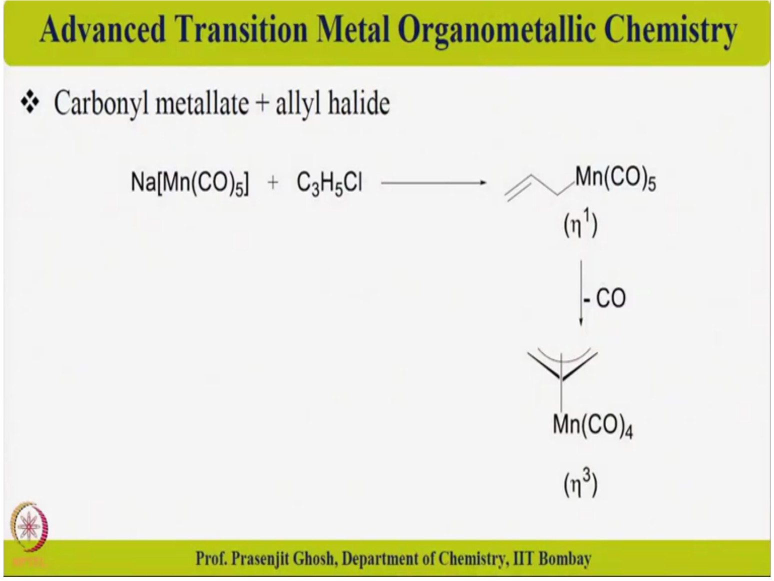

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- Carbonyl metallate + allyl halide

$Na[Mn(CO)_5] + C_3H_5Cl \longrightarrow$

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And these particular methods involves reaction of carbonyl metallate anion with allyl halide.

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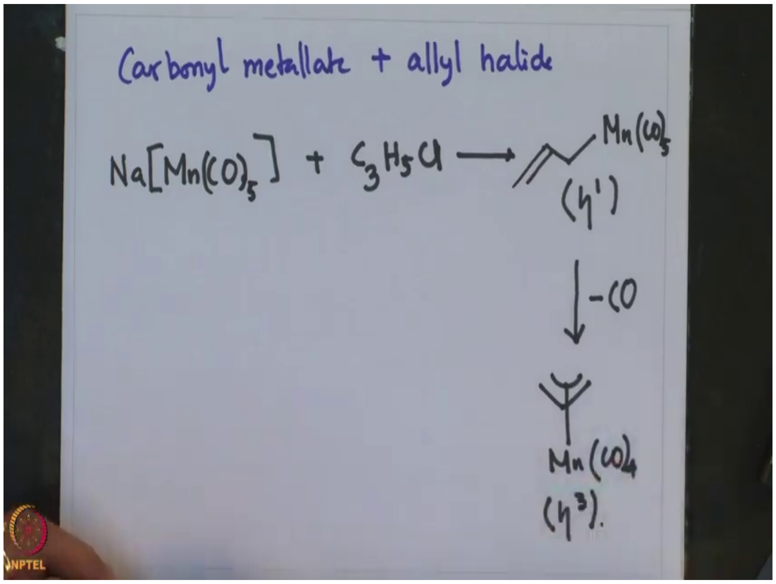

Carbonyl metallate + allyl halide

So, the reaction is given as 5 + C5 H5 Cl giving allyl Mn(Co)5 which is eta 1 and this using carbon monoxide giving eta 3 Mn(Co)4 . In the earlier reaction, where allyl did not was used the allyl ligand was used in its anionic form whereas in allyl chloride is being used in this reaction then the allyl moiety is used in its partially electron deficient cationic form because chlorine being more electronegative than carbon bound to the chlorine will be more well positively in charged.

And from that perspective, for this for this reactions to happen, one needs to have metal species which is highly electron rich and this can be none other than this metallate anion. So, in the mettalate anion there is sodium positively charged sodium bound to Mn(Co)5 minus. So, metal is being highly electron rich and it attacks this allyl chloride giving rise to eta 1 allyl Mn(Co)5 then subsequently loses carbon monoxide resulting in eta 3 Mn CO4 allyl complex.

So, here, we see an example of the second method we spoke which involve a rearrangement of eta 1 to eta 3 allyl moiety.

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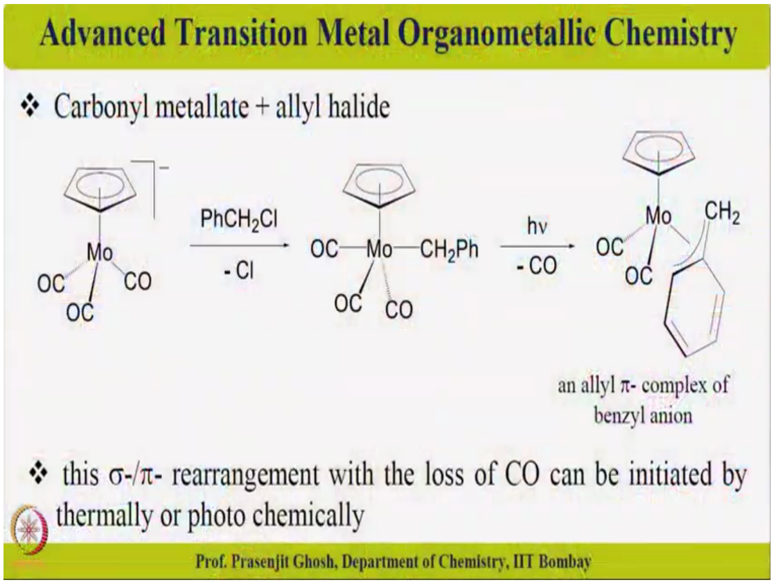

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- Carbonyl metallate + allyl halide

an allyl π- complex of benzyl anion

- this σ-/π- rearrangement with the loss of CO can be initiated by thermally or photo chemically

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So, the second example of this also involves a reaction, another reaction of a CP tricarbonyl molybdenite.

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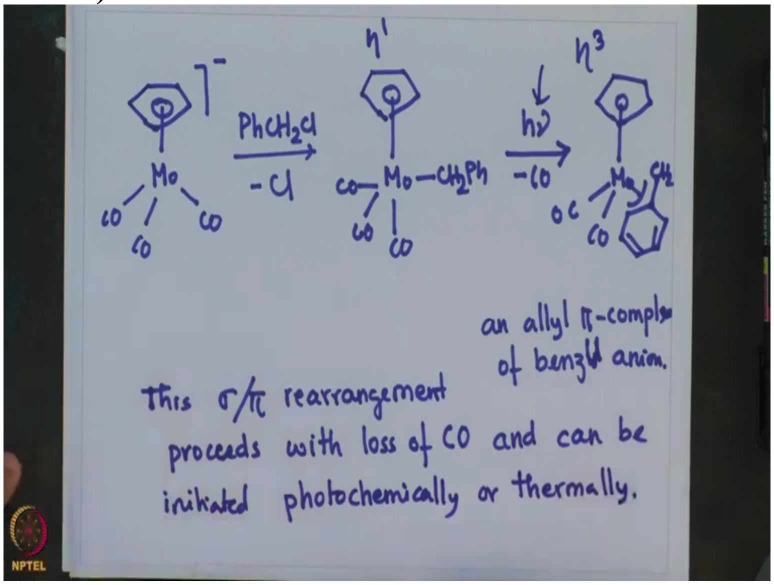

an allyl π-complex of benzyl anion.

This σ/π rearrangement proceeds with loss of CO and can be initiated photochemically or thermally.

Anion, so this is again a metal plate this reacts with benzene chloride uses the chlorine to give eta bound molecular alkenes complex which uses carbon monoxide to give a eta 3 bound allyl complex. So, this is an allyl Pi complex benzyl anion. And so over here it is eta 3 and over here it is eta 1. And this, sigma/Pi rearrangement, this is called a , sigma/Pi rearrangement, takes place with the loss of CO, and can be initiated photochemically that has been down over here with the with this slide or thermally.

Now this photo chemical disassociation of carbon monoxide as well as thermal, thermal disassociation of carbon monoxide are delivered to temperatures have been reported or are known for a long time. And such can be systematically utilised in preparation of eta 3 allyl complexes from eta 1 allyl complex using this sigma/Pi rearrangement reaction.

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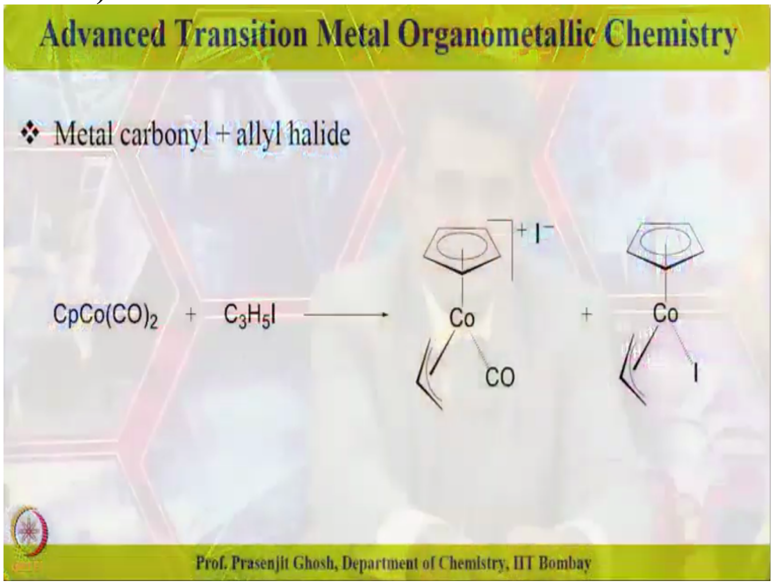

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- Metal carbonyl + allyl halide

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Another example of this metal allyl complex synthesis involves the reactions of metal carbonyls with allyl halide.

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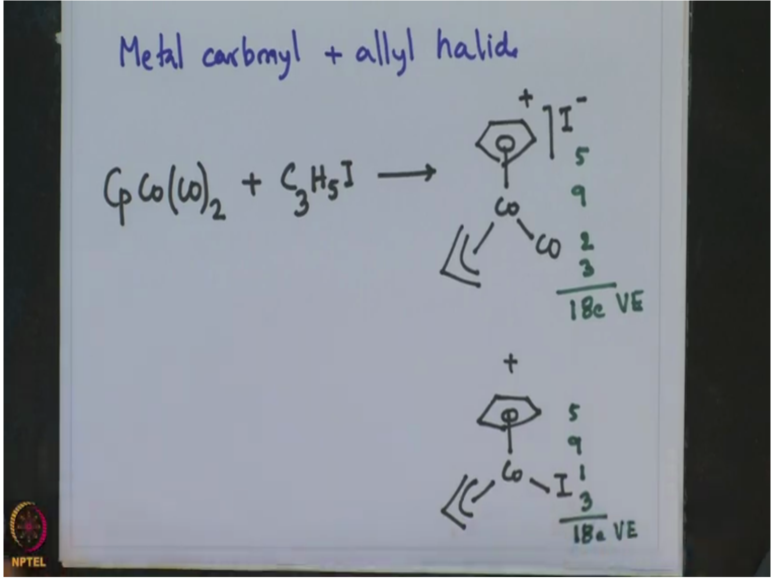

Metal carbonyl + allyl halide

For example reaction of Cp cobalt di carbonyl with allyl iodide gives this cationic Cp cobalt allyl carbonyl compound with an iodide anion, plus a neutral Cp cobalt allyl iodide. To note that these two, both the species are 18 electron compounds, for example 5 from Cp, 9 from cobalt, 2 from carbonyl and 3 from allyl, this resulting in cationic charge over to that resulting in overall 18 valence electron compounds.

The same can be done in other compound, 5 for Cp, 9 for cobalt, 1 for iodide and 3, so this also gives 18 electrons, valence electron compound. So the other metal for preparation of transition metal allyl complexes is from the transition metal olefin compounds.

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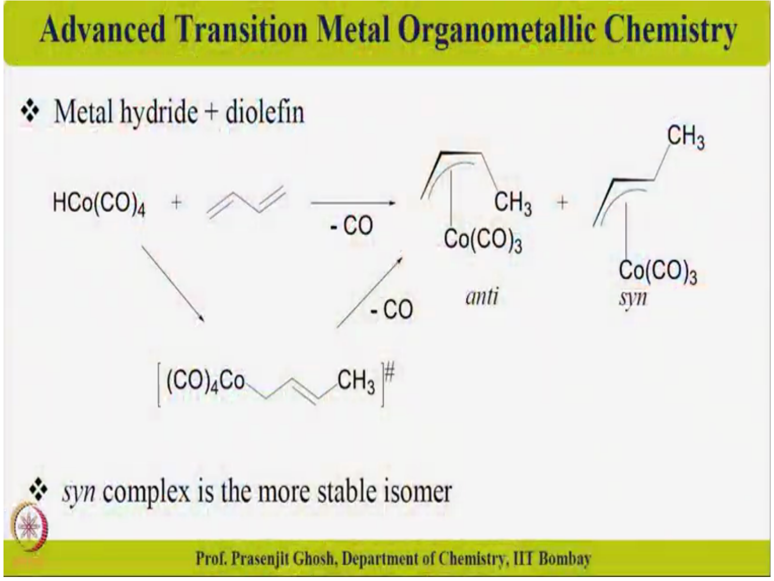

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- Metal hydride + diolefin

- *syn* complex is the more stable isomer

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This is the example which belongs to the third category and the starts with the reaction of the metal hydride with diolefin.

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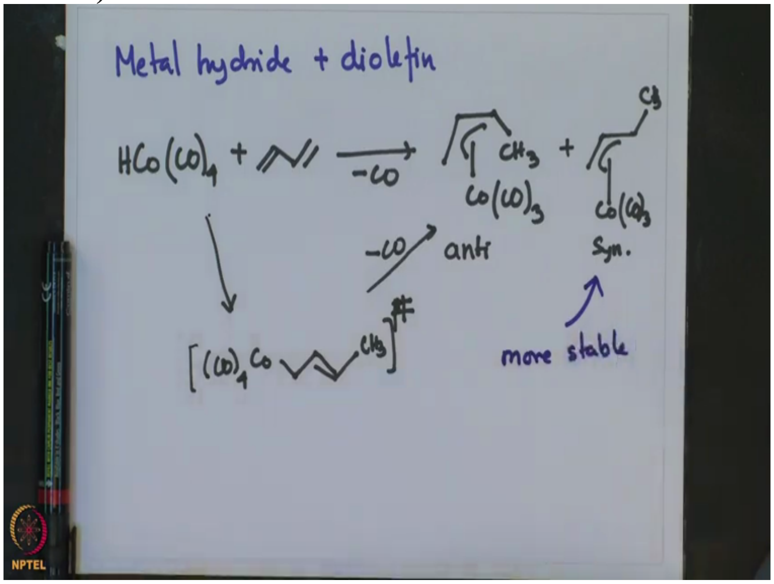

Metal hydride + diolefin

Cobalt tetra carbonyl hydride reacting with butadiene loses a carbonyl to gives this allyl cobalt tri carbonyl and mixture of this isomer, this one is anti and the other one is same. This reaction proceeds by a transition state which involves this cobalt hydride adding against this conjugated double bond and the transition state is that carbonyl cobalt methyl complex which then subsequently loses a carbon monoxide to give this syn and the isomers.

Of the two, the syn, a syn from the geometry, a syn isomer is more stable, so, with this account to the end up this lecture in which we have spoken about various methods which are available for preparation of transition metal allyl complexes. Now the methods that are available, they all can be classified into 3 sub groups, one is simple metaphysics type where, a metal prepares allyl is replaced with allyl anion.

The second one is a transition metal allyl eta 1 bound sigma allyl complex rendering to transition metal bound eta 3 allyl complex and the third one is a conversion of the, a transition metal bound olefin, complex, to a transition metal allyl complex. Now for the first examples it is very simple. It is simple metathesis of metal halide precusers, with allyl anions, these are usually derived from grimness like allyl magnesium bromide and chloride.

And these methods are very useful method for preparing the challenging transition metal binary allyl complexes. This normally take transition metal organometallic complexes are extremely reactive, and difficult to synthesize, from that prospective this metathesis reaction producing binary transition metal allyl complex, is note worthy. And one has to be aware of the fact that these compounds are unstable, and hence the synthesis and isolation of this tri transition metal allyl complex results have to be undertaken at a very low temperature. Now the second method, that is the sub method involved conversion of sigma, transition method sigma allyl complex to eta 3 bound transition method 3 complex.

This reactions primarily involve formation of this compounds, from transition metallate complexes with allyl halides and subsequently a re-coordination of carbon monoxide resulting in eta 3 bound transition metal allyl complex. So, there are 2 and 3, 2 or 3 different methods which utilises the syn principle where a eta bound sigma allyl complex is converted to eta 3 bound transition metal allyl complex.

And lastly the third sub class involve the conversion reaction of transition metal hydride with diolefins and in the process generating eta 3 bound allyl complexes, the reaction that we have looked at is cobalt hydride tetra carbonyl reacting with butadiene giving a mixture of syn and anti isomer of allyl cobalt tri carbonyl compound. And of the two syn and anti isomer, the syn isomer is more stable, than the other isomer.

So with these I conclude today's discussion on transition metal allyl complexes as for today the more some more of the primitive methods still remains, and which will be in the subject of discussion in the next lecture and able to also look at the reactivity of these kinds of tansition metal allyl complexes before we move to other enyl-allyl ligands, so with that thank you for being patiently listening to this lecture and I look forward to taking up this topic in more details when we meet soon, thank you.