Transition Metal Organometallic Chemistry : Principles to Applications
Prof. Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology, Bombay

Week - 12
Lecture – 58
Transition Metal Alkyne Complexes: Reactivity

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. We have been discussing a very important topic particularly these transition metal alkyne complexes over the last few lectures.

And in the previous lecture we had seen about the techniques which are often used for characterizing these transition metal alkyne complexes and what we have seen is that transition metal alkyne complexes can have two forms of structure a one is a complex and the other is a metallo cycle propane kind of structure.

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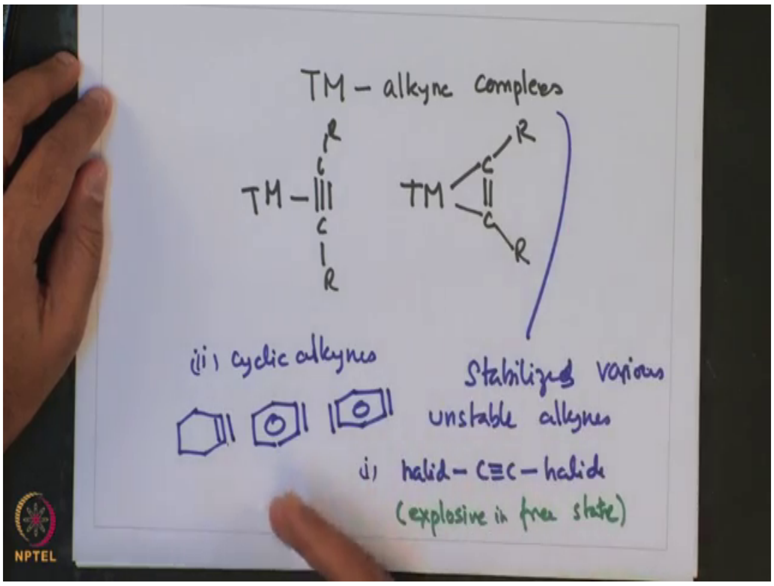

And then these can be distinguished by various spectroscopic a techniques like I R NMR as well as by x rays single crystal diffraction techniques.

So, these transition metal complexes have two kinds of structures one is something of a linear pi complex type or the other can be something of a cyclo propane kind of type and that they have two structures which can be distinguished by various spectroscopic techniques.

What we have also seen that these coordination or transition metal alkyne complexes lead to stabilization of various unstable alkyne for example, a these transition metal alkyne complexes stabilizes stabilizes various unstable alkynes like halide substituted alkyne, which are explosive in twisted, but stabilized when coordinated to metal.

So, this is one the others are a kind of it also stabilizes cyclic alkynes, and in this category falls the cyclohexane which is stabilized when a coordinated to transition metal and the stabilization comes from release of ring strain which this unstable cyclo hexane process. The same can be extended from cyclohexene to benzene and then ultimately even further the same can be extended to benzidine.

So, what we see that these transition metal alkyne complexes we had discussed in our previous lecture has a several utility and among them one of the most useful utility is this type of complex a stabilizes unstable alkynes like the ones which are halogen substituted acetylenes which are explosive in nature, but still got stabilized when coordinate transition metal as well as the cyclicoric cyclic alkynes like hexane benzene, or benzidine which two are stabilized when in this transition metal complexes and the stabilization arises from relief of ring strain which the free cyclic alkyne are subjected to.

So, with that discussion we had in the last lecture we are going to discuss an important aspect of these transition metal alkyne complexes particularly their reactivity in this lecture.

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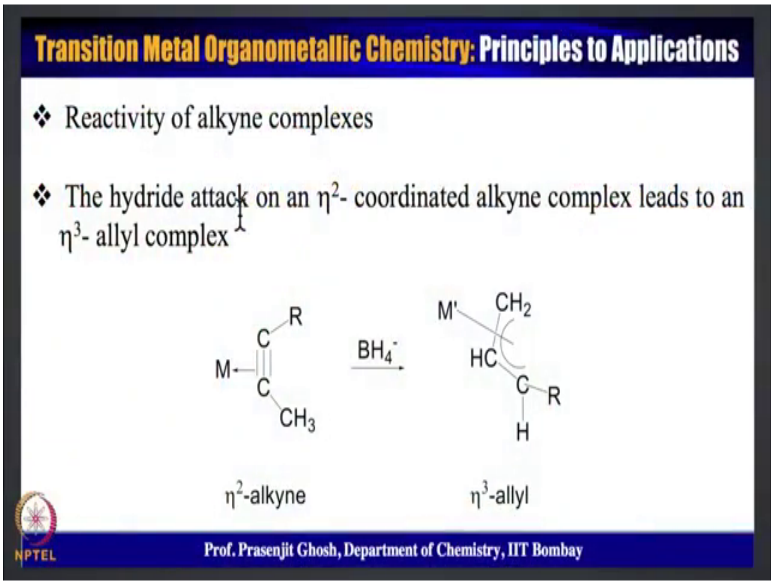

Transition Metal Organometallic Chemistry: Principles to Applications

- Reactivity of alkyne complexes
- The hydride attack on an η²- coordinated alkyne complex leads to an η³- allyl complex

η²-alkyne η³-allyl

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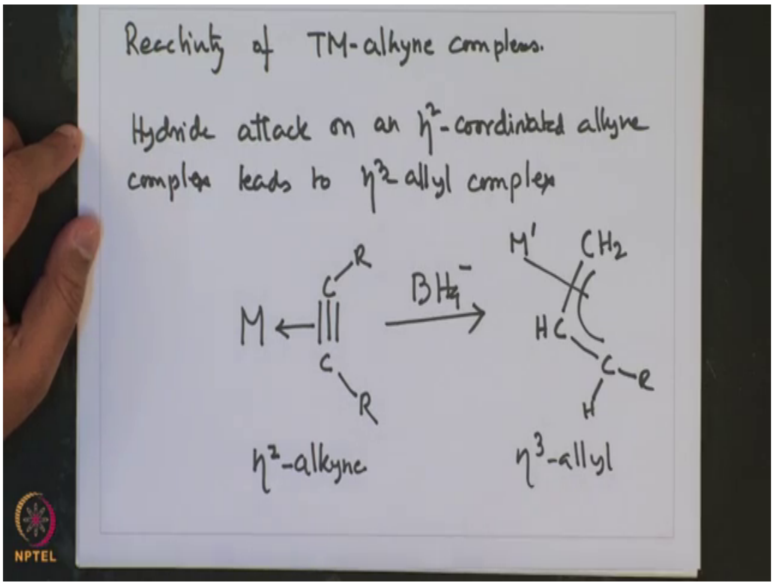

Reactivity of TM-alkyne complexes.

Hydride attack on an η²-coordinated alkyne complex leads to η³-allyl complex

η²-alkyne η³-allyl

Now, of the reactivity aspect of transition metal alkyne complexes and one important to reaction is the hydride attack on an eta 2 coordinated alkyne complex leads to eta eta 3 allyl complex.

So, it is sort of like a hydride complex going to an allyl complex and the transformation is given over here where alkyne complex which is eta 2 alkyne when treated with B H 4 minus gives this eta 3 allyl complex which is kind of extremely interesting as to how does a this conversion proceed M dash. So, these conversion is proceed process through a sequence of rearrangement and intermediate steps resulting in such conversion.

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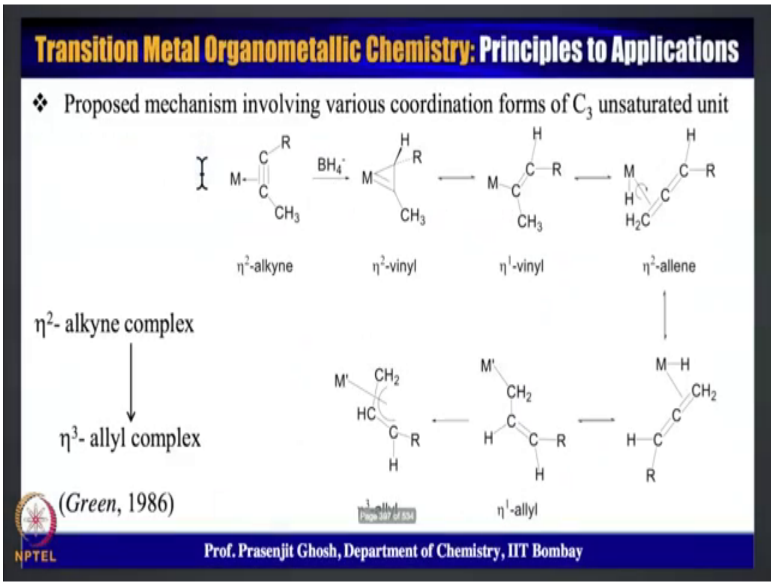

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❖ Proposed mechanism involving various coordination forms of C_3 unsaturated unit

η^2- alkyne complex

η^3- allyl complex

(*Green*, 1986)

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And we are going to look a the proposed mechanism for conversion of this eta 2 alkyne to eta 3 allyl in more details.

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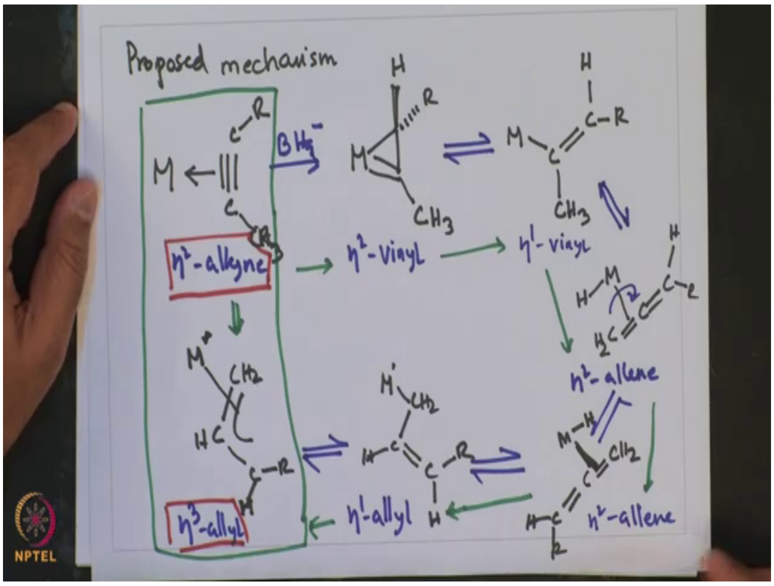

So, let us take a look at the proposed mechanism that has been given for the conversion of eta 2 alkyne to eta 3 allyl. So, R this is is 3 and this is eta 2 alkyne when treated with

B H 4 minus the hydride attacks at this carbon and gives a C C H 3 H. So, this is a eta 2 vinyl complex.

Now, that undergoes a rearrangement to give this eta 1 vinyl; So, eta 2 going to eta 1 vinyl which undergoes another rearrangement to give metal hydride so this becomes eta 2 allene. Now, this eta 2 allene undergoes a rotation along this M C bond to give to give this C H R H R complex which undergoes again.

So, this also is a eta 2 allene which is undergoes a rearrangement to give M dash C H 2 C H C R H. So, this is eta 1 allyl finally, to give this C H 2, C H, C R H M dash which is a eta 3 allyl complex. What one can see that these conversion of an eta 2 alkyne to an eta 3 allene proceeds by several rearrangement and several step eta 2 alkyne going to eta 2 vinyl, going to eta 1 vinyl, going to eta 2 allene.

Then that goes to another eta 2 allene from there it goes to eta eta 1 allyl eta 1 allyl to eta 3 allyl. So, for these are a very a complicated series of manoeuvre that sort of eventually gets the conversion of eta 2 alkyne to eta 3 allyl and this a reaction is unique a for transition metal alkyne complexes.

Now, this is a very common phenomenon and there are a lot of applications arise out of these a arrangements and then we are going to take a look at this particular intermediate which is a how does data 1 vinyl, and eta 2 vinyl compounds they sort of interchange among each other. So, we are going to now take a look more closely at this eta 1 vinyl, and eta 2 vinyl complexes and they are chemical forms.

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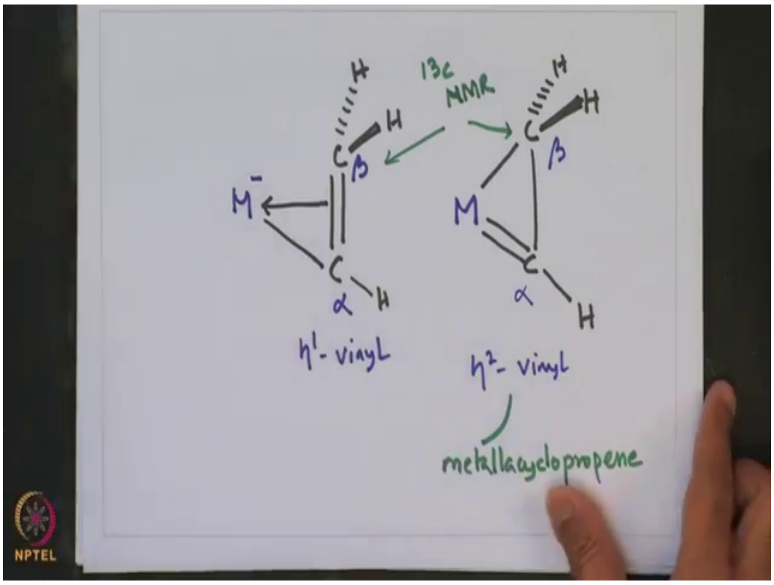

So, C H C H this is a eta 1 vinyl, alpha and beta carbon and the corresponding eta 2 vinyl structure can be given as M C hydrogen, C this is a alpha beta eta 2 vinyl. This structure eta 2 vinyl is formed from the metallocyclo or called metallo cyclopropane, propane structure where this is formed can from the metal to ligand back back donation and that results in significant downfield shift of the carbon centre.

So, these the difference between these to form can be a assigned based on 13 C NMR, the spectroscopy and the assignments. And so this is the eta 2 vinyl form is more like a metallocyclopropane intermediate which is formed by back donation of the metal electron on to the pi star orbital resulting in this eta 2 vinyl a intermediate.

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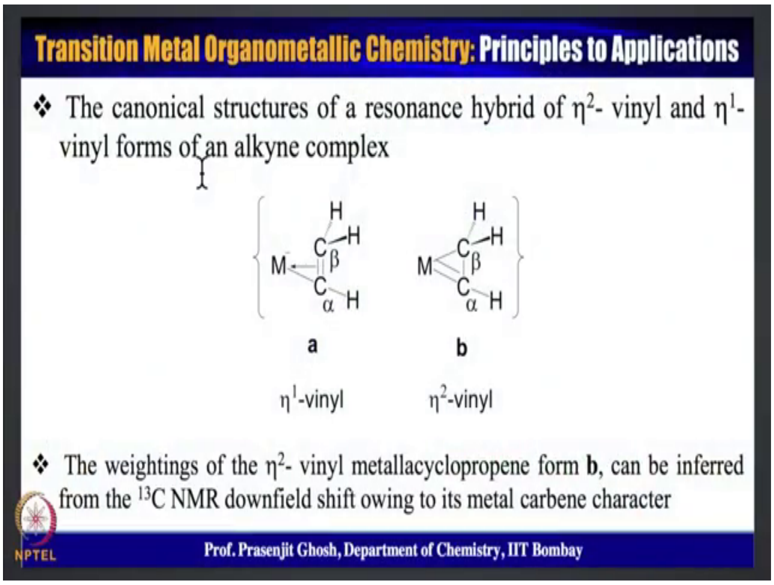

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- The canonical structures of a resonance hybrid of η^2- vinyl and η^1- vinyl forms of an alkyne complex

- The weightings of the η^2- vinyl metallacyclopropene form **b**, can be inferred from the ^{13}C NMR downfield shift owing to its metal carbene character

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Now, this eta 2 vinyl intermediate is a very important intermediate in the conversion of a eta 2 alkyne to eta 3 allyl as we had seen in the earlier transformation.

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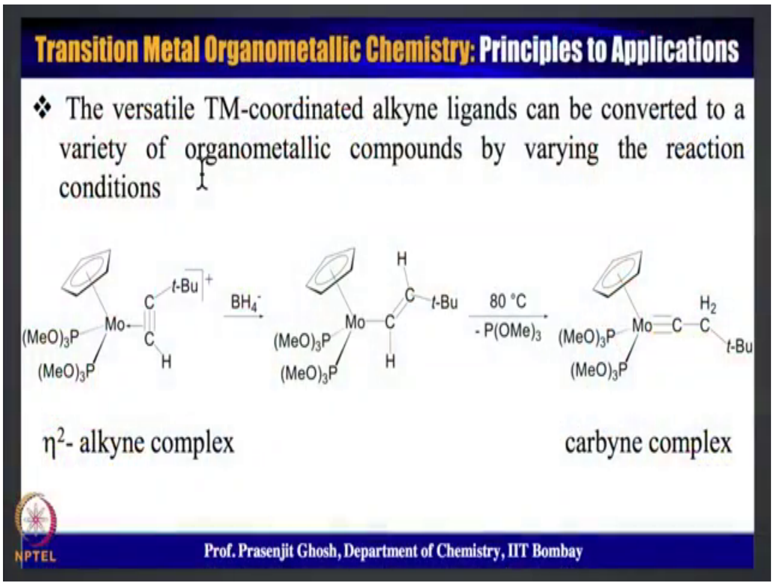

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- The versatile TM-coordinated alkyne ligands can be converted to a variety of organometallic compounds by varying the reaction conditions

η^2- alkyne complex

carbyne complex

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These transition metal alkyne complexes can be converted to a various kinds of compound depending on the reaction and a very nice example is given T M alkyne can be converted to converted to eta 1 vinyl, and also T M carbine complex depending upon conditions that the example of this is given below.

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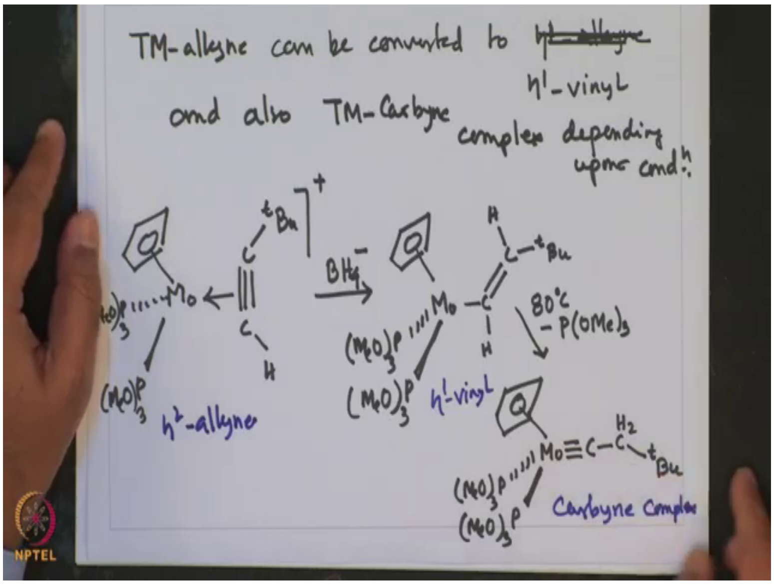

TM-alkyne can be converted to ~~η¹-alkyne~~ η¹-vinyl and also TM-Carbyne complex depending upon cond^n.

So, C p molybdenum P o M e 3 3 P o M e 3 alkyne C hydrogen t B u plus B H 4 minus gives this molybdenum C p P o M e 3 3 o M e 3, this is eta 1 vinyl complex H t B u which at 80 degree centigrade eliminates P o M e 3 giving the carbine complex M o P o M e 3 P o M e 3 C H 2 t B u which is the carbine complex this one is eta 1 vinyl complex, and this one is eta 2 alkyne complex.

So, what one can see is that depending on the reaction condition one can go from eta 2 alkyne complex eta 1 vinyl complex to carbine complex and here is a very nice example how a the same is formed with the elimination of P M e 3.

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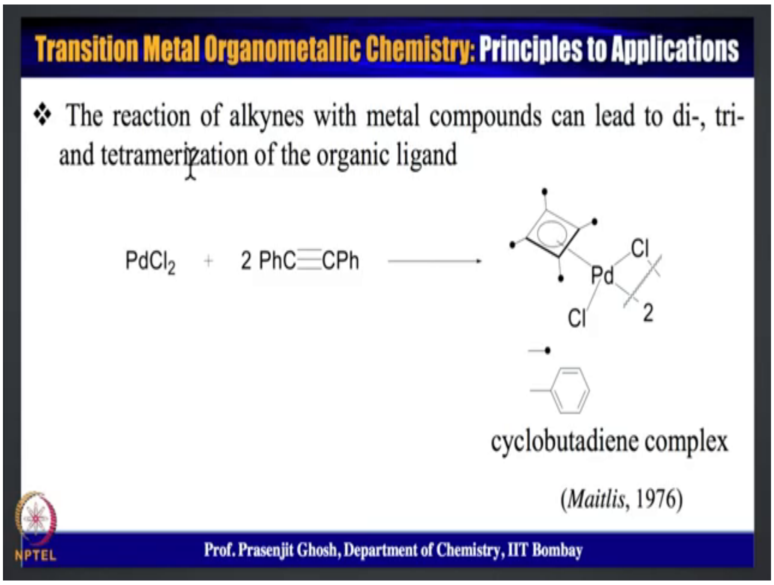

Transition Metal Organometallic Chemistry: Principles to Applications

❖ The reaction of alkynes with metal compounds can lead to di-, tri- and tetramerization of the organic ligand

$PdCl_2 + 2\ PhC{\equiv}CPh \longrightarrow$

cyclobutadiene complex

(*Maitlis*, 1976)

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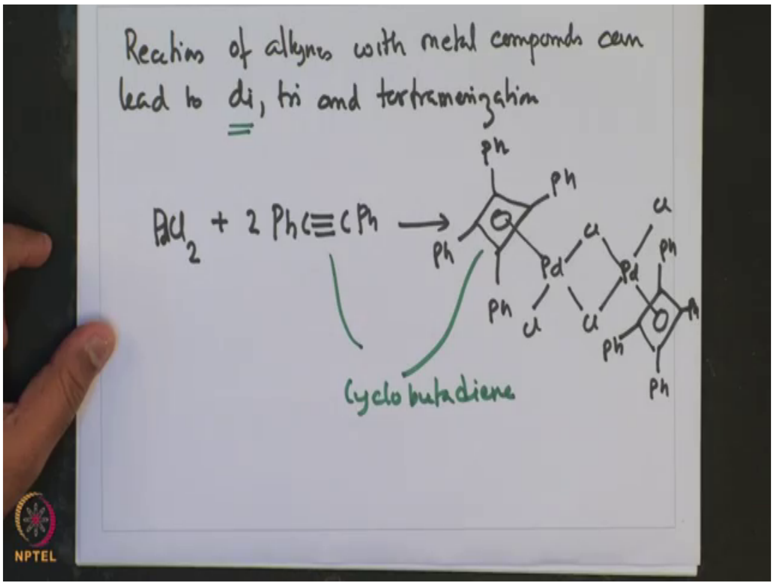

Reaction of alkynes with metal compounds can lead to di, tri and tetramerization

$PdCl_2 + 2\ PhC{\equiv}CPh \longrightarrow$

We going to take look at examples of this reactivity of transition metal alkyne complexes and reactions of alkynes with metal compounds can lead to di tri and tetramerization of the acetylene moiety.

A very good example of this is P d C l 2 plus 2 P h C C p h this cyclo butane with P h, P h, P h, P h, P d C l, P d, C l, C l, P d, C l, P h, P h, P h, P h complex.

So, this is the cyclo butadiene fragment is formed cyclo butadiene is fragment is from two of these acetylene moiety. And this represents an example of dimerization of the acetylene in the reaction in presence of a P d C l 2. So, let us a take a look at some more examples where this oligomerization a take place and here is an example of trimerization reaction of alkynes.

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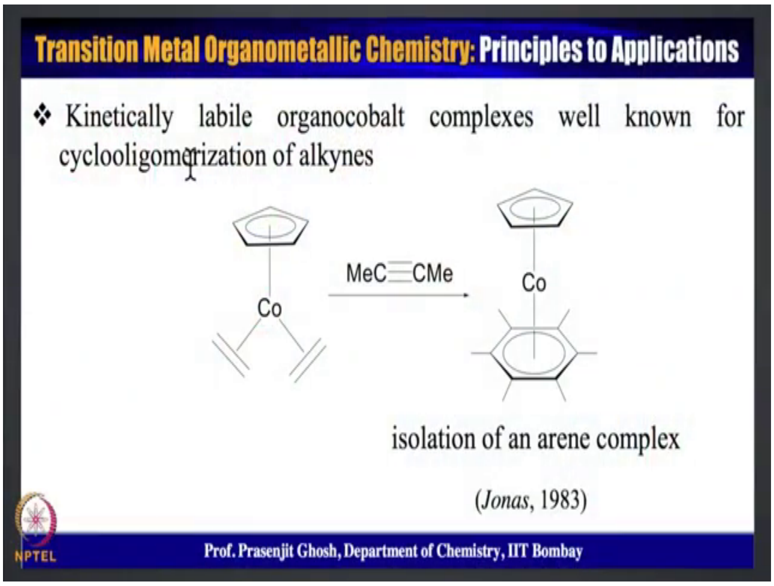

Transition Metal Organometallic Chemistry: Principles to Applications

- Kinetically labile organocobalt complexes well known for cyclooligomerization of alkynes

isolation of an arene complex

(*Jonas*, 1983)

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And a this has been achieved by from kinetically labile cobalt complexes.

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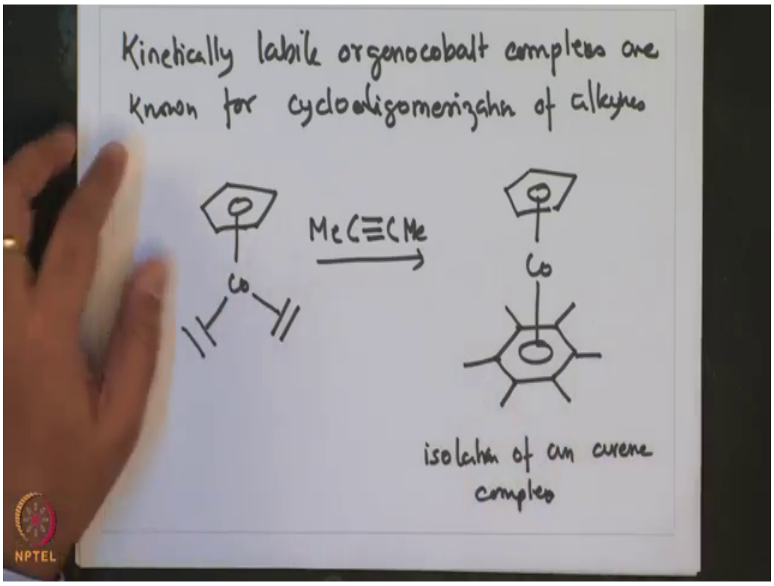

Kinetically labile organocobalt complexes are known for cyclooligomerizahn of alkynes

isolahn of an arene complex

So, kinetically labile cobalt complexes are known for cyclo oligomerization of alkynes.

So, here is a C p cobalt olefin olefin. So, this ethylene is the labile ligand which when reactor with the methicillin C M e gives this a ring complex cobalt with methyl methyl, methyl, methyl, methyl, meythl it is a mytheyl complex.

So, this is a very nice example whereby this trimerization of methicillin to give this a ring complex, complex is achieved a when methicillin reacted with kinetically labile organo cobalt compound where the labile ligand is this these the olefinic moiety.

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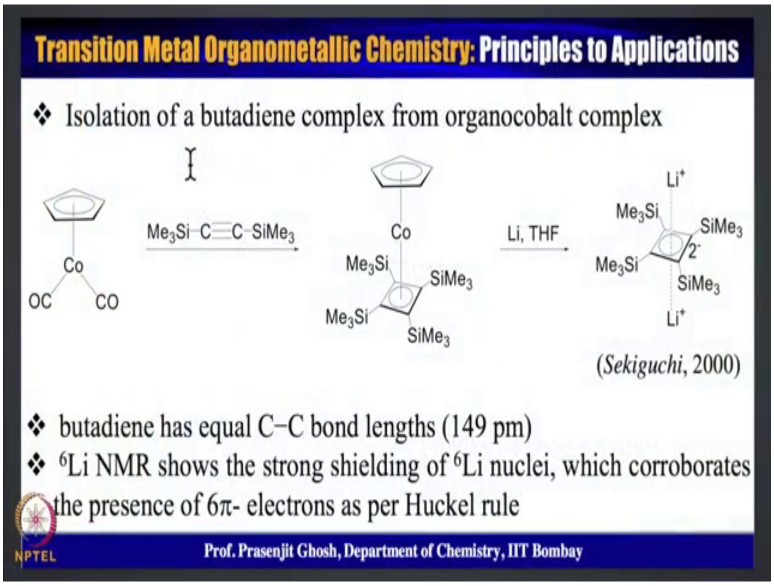

Transition Metal Organometallic Chemistry: Principles to Applications

- Isolation of a butadiene complex from organocobalt complex

(*Sekiguchi*, 2000)

- butadiene has equal C–C bond lengths (149 pm)
- ^{6}Li NMR shows the strong shielding of ^{6}Li nuclei, which corroborates the presence of 6π- electrons as per Huckel rule

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Let us a take a look at another set example of cyclo butadiene intermediate.

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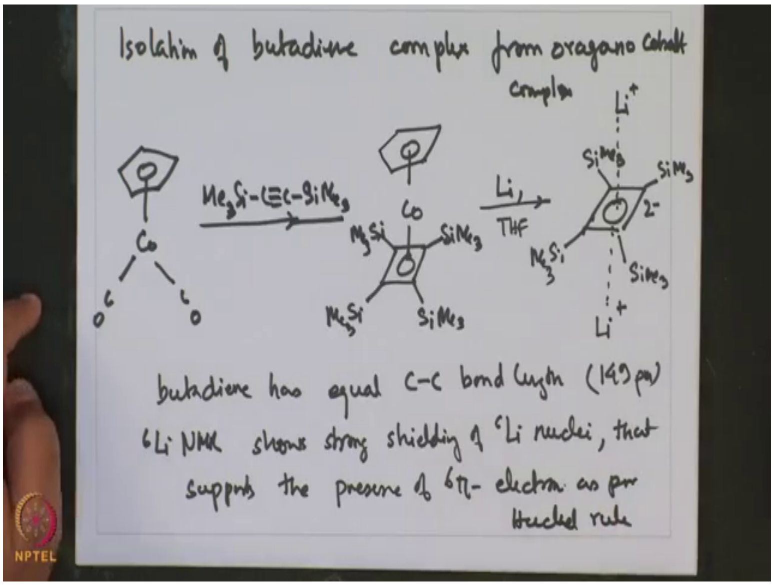

Isolation of butadiene complex from oragano cobalt complex

butadiene has equal C-C bond length (149 pm)

^{6}Li NMR shows strong shielding of ^{6}Li nuclei, that supports the presence of 6π- electron as per Huckel rule

So, isolation of butadiene complex from organo cobult complex; So, here it is a cobalt carbonyl reacting with M e 3 S i S i M e 3 giving this cyclo butadiene complex of cobalt S i M e 3, S i M e 3, S i M e 3, and S i M R 3 which in presence of lithium in T H f gives this anion di anion S i M e 3, M e 3, M e 3 3.

This is the di anion with 2 lithium I am coordinated at the top as well as at the bottom stabilizing this and this butadiene has equal has equal C C bond length 149 picometer and 6 lithium NMR shows strong shielding of 6 lithium nuclei that supports the presence of 6 pi electron as per Huckel rule.

So, this is a very nice example where this aromatic 6 pi electron have been constructed from to acclaim by making the cyclo butadiene and then reducing and put more electron on this 4 pi system to make this 6 pi electron and to stabilize that by lithium cation not only by the x-ray, but also a lithium a NMR such a characterization has been done.

So, with that let me conclude a what we have been discussing and the part of the reactivity in today's lecture a we have started off by looking at these eta 2 alkyne transition metal complexes getting converted through the series of steps to give the eta 3 a allyl complexes and we have seen how that it goes through vinyl and allyl intermediates.

And then we have looked into how these can be used a for transition metal alkyne complexes can be used for preparing other organo transition metal complexes for example, transition metal carbine complexes as well as done transition metal eta 1 vinyl complexes and how they mutually can be converted a one to another.

We have also seen examples of a isolation of cyclic aluminized product like from dimerization, trimerization to even the formation of aromatic cyclo butadiene two minus ligands having 6 pi electron by proper manipulation of the acetylene a moiety by reaction with kinetically labiled organo cobalt complexes.

So, we have seen many examples of that and that shows that these transition metal alkyne complexes are extremely versatile in being able to produce a several other important and otherwise very challenging compounds for example, this butadiene two minus having 6 pi electrons through proper manipulation.

So, with that I would conclude today’s lecture and we are going to be a talking a bit more detail in transition metal alkyne complexes particularly their reactivity. The logical conclusion is the transition metal complexes are extremely important they not only can stabilize various unstable alkynes by coordination to a transition metal, but they can also participate in the very important reactions of oligomerization, and dimerization, trimerization, or even all oligomerization of substituted acetylenes to give products which otherwise are very difficult to a synthesize as well as isolate.

So, with that let me thank you for being with me in this lecture. And I am going to take up these transition metal alkyne complexes in more detail in the next lecture until then goodbye.

Thank you.