Transition Metal Organometallic Chemistry: Principles to Applications
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Lecture – 22
C – C Bond activation

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. In the last lecture we have talked about a very interesting kind of activation reaction particularly the C-C bond activation reaction, which is very challenging in the sense that it is much more difficult than C-H activation reaction or, as well as H H activation reactions in the last class with regard to C-C activation reaction.

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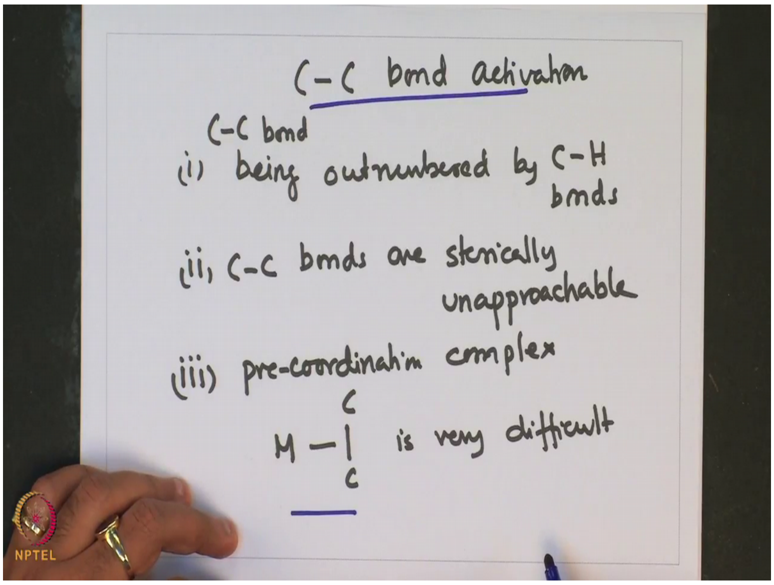

C-C bond activation

C-C bond
(i) being outnumbered by C-H bonds

(ii) C-C bonds are sterically unapproachable

(iii) pre-coordination complex

$M - \overset{C}{\underset{C}{|}}$ is very difficult

We have seen that this reaction is challenging, because of being out numbered C-C bond being outnumbered by C-H bonds. Secondly, that C-C bonds are sterically unapproachable, and lastly the formation of pre coordination complex of the type is very difficult as this C-C bond is under sterically unapproachable.

Now, this is an important point for the difficulty in achieving C-C bond activation because with our knowledge in C-H bond activation, what has been what we have found that C-H bond activation is always active initiated by initial coordination of a C-H bond to the metal center. And that is a prerequisite for the occurrence of a C - H bond activation.

Now, in case of C-C bond activation analogous pre coordination of C-C bond to metal becomes very challenging, because of the steric unapproachability around a C-C bond as a result this will lead to difficulty in achieving C-C bond activation. The way it is done in case of H H or C - H bond activation reactions. In this regard it is worth noting that despite C-C bonds in fact, being weaker than C-H bonds. As well as H H bonds because of the occurrence of all these 3 different factors C-C bond activation become very challenging. We have also seen in our previous lecture that the C-C bond activation has been primarily attained by using loss of ring strain.

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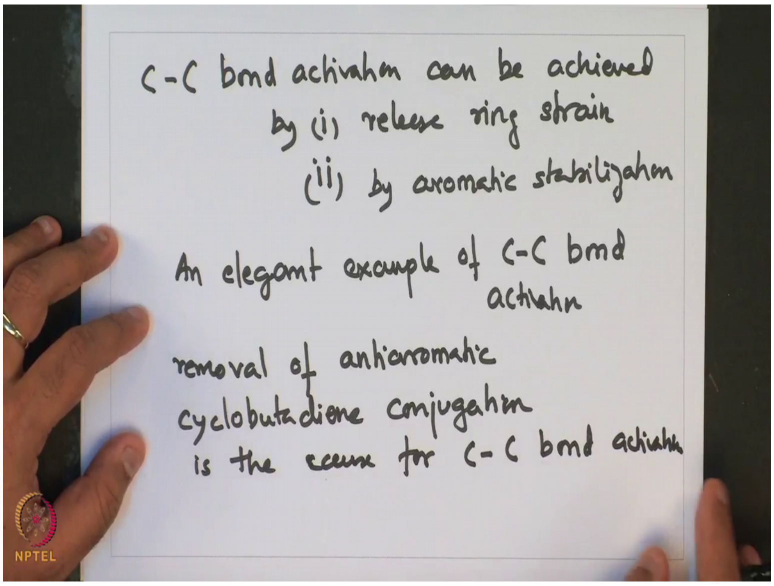

C-C bond activation can be achieved
by (i) release ring strain
(ii) by aromatic stabilization

An elegant example of C-C bond activation

removal of antiaromatic
cyclobutadiene conjugation
is the reason for C-C bond activation

So, C-C bond activation can be achieved by release of ring strain. As well as by aromatic stabilization, and we have seen 2 examples pertaining ah to these ways of attaining C-C bond activation.

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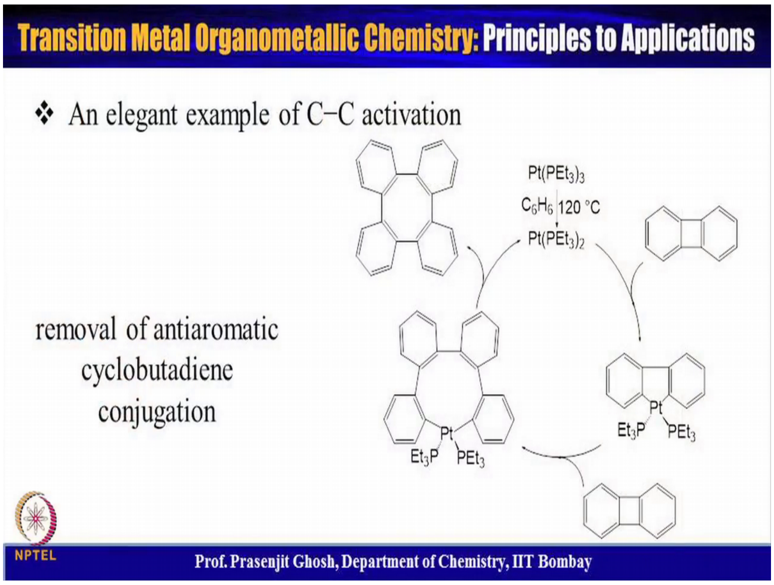

Transition Metal Organometallic Chemistry: Principles to Applications

- An elegant example of C–C activation

removal of antiaromatic cyclobutadiene conjugation

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Here is another example that we are going to take up which is also an elegant example of C-C bond activation. And in this case removal of anti-aromatic cyclobutadiene conjugation is the source cause for C-C bond activation; this can be or is illustrated using this example.

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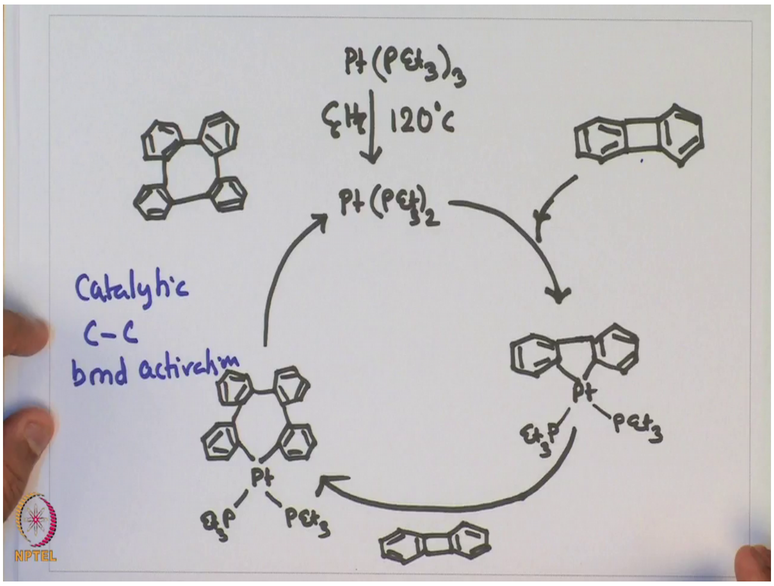

So, a platinum complex of the formula platinum triethyl phosphine, in presence of benzene at 120 degree centigrade gives this platinum complex. To that reacts with this compound which has this highly strained cyclo butadiene rain, and that undergoes oxidative aeration on this platinum giving this compound.

That reacts with another molecule of this compound where there is a ring strain, and that adds against one of these platinum carbon bond resulting in this micro cyclic compound. And these undergoes reductive elimination to give this huge micro cyclic compound containing 4 aromatic rings.

So, what we see is an elegant example that comprised of C-C bond activation, this particular bond. As well as this particular bond and as a result huge macro cyclic compound containing 4 benzene rings are obtained, and that too these have been obtained in a catalytic fashion. From that perspective this is a very nice example in which catalytic C-C bond activation has taken place, and all of this has been achieved without metal pre ordination to the C-C bond, and this all has been achieved because of release of ring strain. As well as removal of anti aromatic cyclo butadiene conjugation to give something which is a more stable nature.

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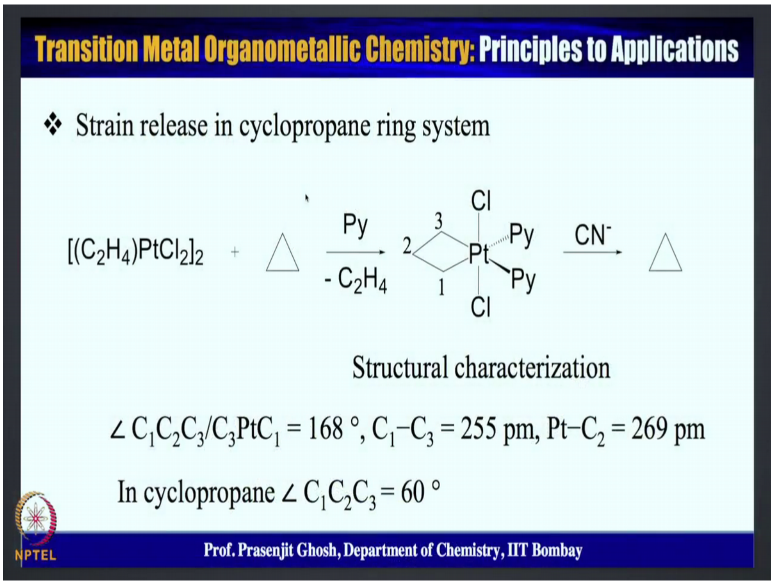

Transition Metal Organometallic Chemistry: Principles to Applications

- Strain release in cyclopropane ring system

Structural characterization

$\angle C_1C_2C_3/C_3PtC_1 = 168\,°$, $C_1–C_3 = 255$ pm, $Pt–C_2 = 269$ pm

In cyclopropane $\angle C_1C_2C_3 = 60\,°$

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Another strain release of strain in cyclopropane ring also gives, similar C-C bond activated compounds.

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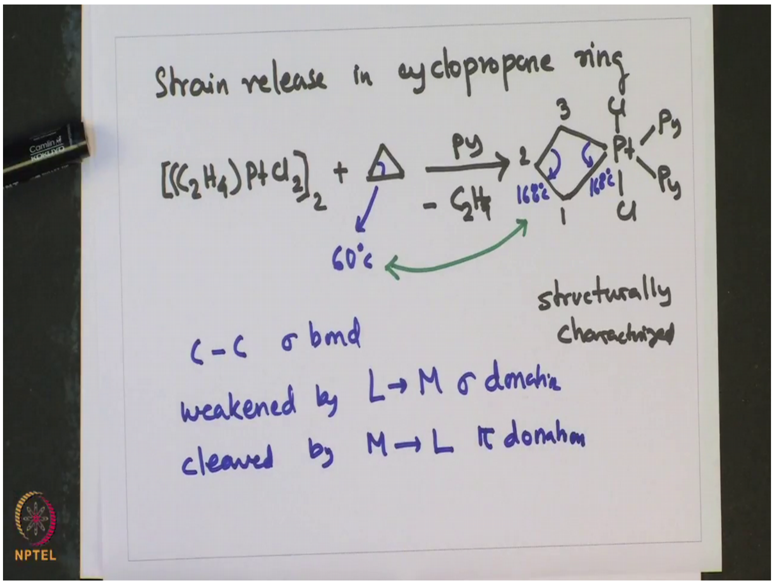

Strain release in cyclopropane ring

structurally characterized

C-C σ bond

weakened by L→M σ donation

cleaved by M→L π donation

For example for this platinum complex, reacts with cyclopropane in pyridine and that eliminates a molecule of C 2 H 4 giving this platinum metano cycle with 2 chlorine and 2 pyridine ligands, here this complex is also structurally characterized and the release of strain is prominent from, this angle which is 60 degrees in cyclopropane becoming 168 degrees C 1, C 2, C 3 or C 3 platinum C 1.

So, what 1 sees that there is a increased release of ring strain on going from 60 degree to 160 as a result of this metala cycle formation. And this compound has also been structurally characterized. So, the main aspect of C-C bond sigma bond is that this is weakened by ligand to metal sigma donation, and cleaved by metal to ligand pi donation.

So, here it is interesting to know how does this forward donation and backward donation, when a C-C bond interacts with a metal center occur. And these are can be particularly seen from the cyclopropane ring system.

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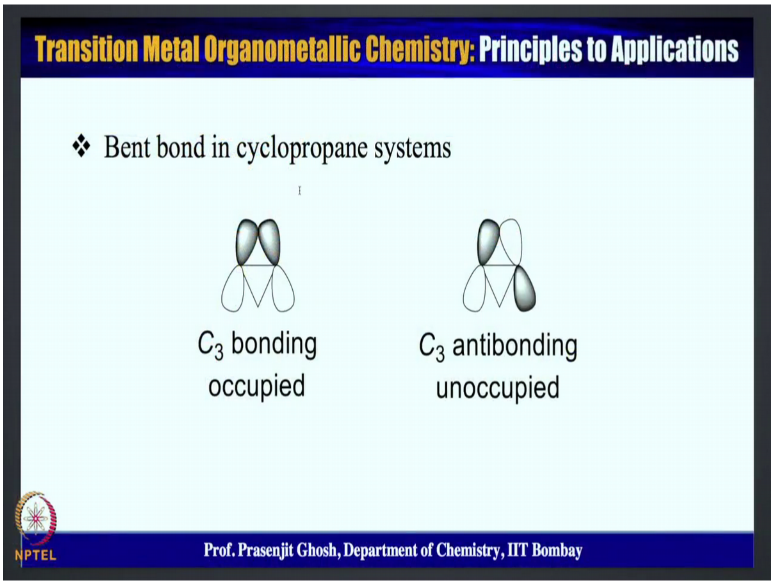

Transition Metal Organometallic Chemistry: Principles to Applications

- Bent bond in cyclopropane systems

C_3 bonding occupied

C_3 antibonding unoccupied

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Where the ring is very constrained for example, for the cyclo propene ring.

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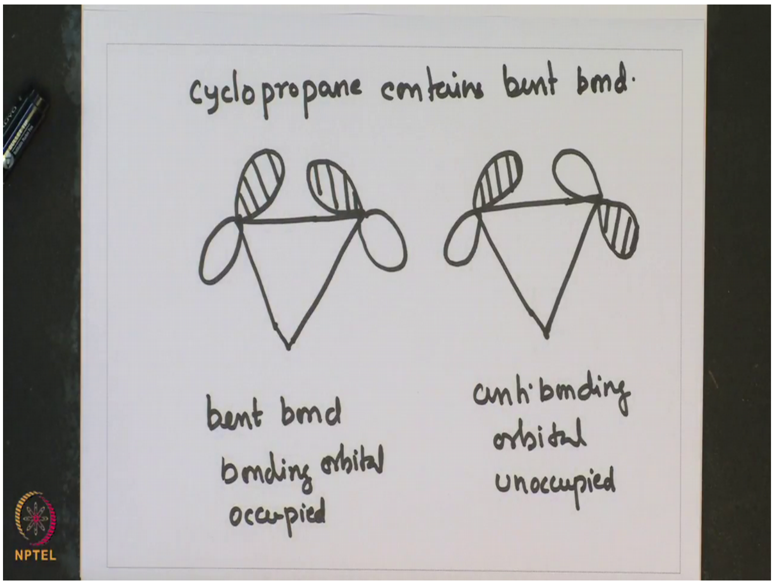

Cyclopropane contains bent bond.

bent bond
bonding orbital
occupied

anti bonding
orbital
unoccupied

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The sigma bond is bent for example, and the bonding orbitals are given as something like this, where of the lobes of the same face are constructively overlapping. So, this bent bond bonding orbital are occupied. Similarly the antibonding orbital is given by so, here also anti bonding orbital remains unoccupied and thing which stands out is that cyclopropane contains bent bonds. And this bonds being bent has very little sigma overlap, if they were to be head on overlap between 2 sigma orbitals. As a result cyclopropane bonds are under lot of strain, and hence not very stable if they were to be fully head on sigma bond type overlap.

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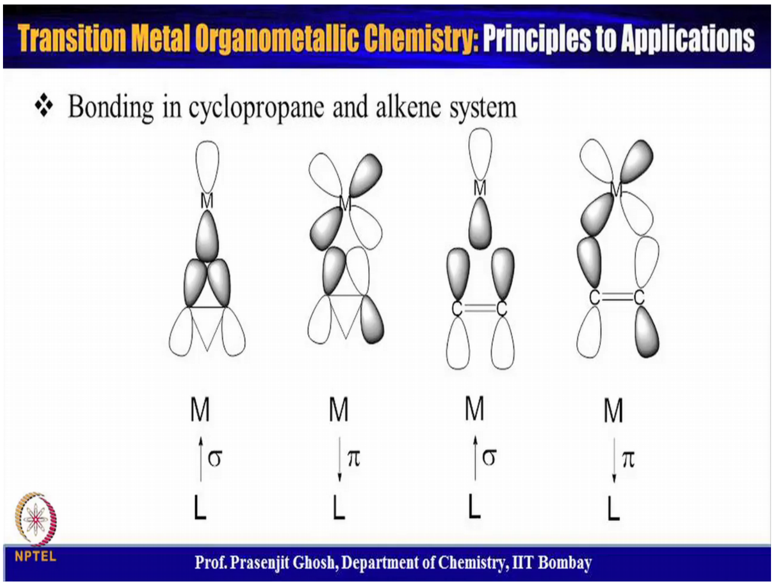

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- Bonding in cyclopropane and alkene system

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Now, there is a difference between an alkene metal interaction, as well as cyclopropane C-C sigma bond interacting with the metal. The difference between being that in an alkene metal interaction the C-C sigma bond remains unaffected whereas, in a cyclopropane C-C sigma bond metal interaction the sigma bond becomes affected.

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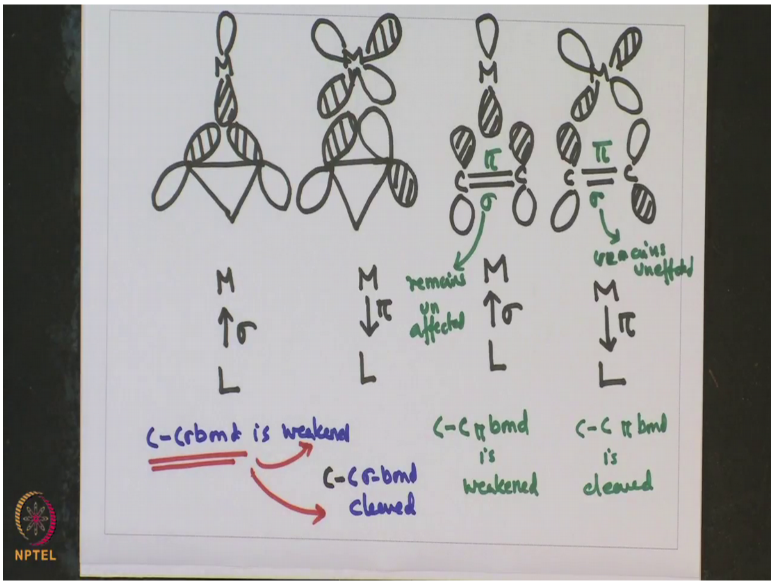

I am going to illustrate this with respect to following diagrams for example, in cyclopropane bonding orbital, which interacts favorably with another metal orbital of suitable symmetry and this is designated by L to M sigma bonding.

So, as a result of L to M sigma bonding, this C-C bond is weakened whereas, in M 2 L pi back donation, and that is given by a vacant sigma star orbital interacting with a filled metal orbital as the donation happens this way C-C sigma bond is cleaved .

Now, compared to these let us take a look of look at the scenario in which an olefin for example, C double bond C having a pi cloud, interacting with metal orbital of similar symmetry. Now this is designated as legan to metal sigma bonding. Now the difference with regard to the cyclopropane case is that in the olefinic case the C-C sigma bond remains unaffected whereas, C-C pi bond is weekend.

The olefinic pi bond is weakened as a result of these donation of this pi electron onto an vacant metal orbital. And similarly when the electron donation occurs from the metal to the pi star orbital the sigma bond C-C sigma bond remains unaffected whereas, the back donation results in cleaving of the pi bond. And that is given by metal to ligand pi back donation and C-C pi bond is cleaved, because of metal to ligand pi back donation and what it says that in cyclopropane system the C - C sigma bonds gets affected it either gets weakened, because of forward sigma donation and then because of further back donation it gets cleaved. Whereas, in a olefin under analogous kind of bonding only the C-C pi bond gets weakened and the C-C pi bond gets cleaved.

So, with this let me summarize the topics that has been covered today we have looked into various examples of C-C activation which mainly dwelt around the fact of achieving this C-C bond activation through release of ring strain. We have looked into various example, and then we have looked in details about the C-C bond activation in cyclopropane ring system.

Particularly with regard to molecular orbital interaction between the metal orbital and the cyclopropane orbitals, and the analysis of the metal ligand interaction in cyclopropane orbital along with the metal ligand interaction in the olefinic orbital, shows that this metal ligand interaction in the cyclopropane orbital directly affect the carbon carbon sigma bond. Whereas, the metal ligand orbital in an olefinic system under analogous situation affect only the carbon carbon pi bond.

We have also discussed that this cyclo propane ring being under tremendous strain is bent, because of the bent due to the overlap of the orbitals resulting in bent bond. And with this we are going to discuss in much more details about various C-C bond activation. As well as other kind of perfluoro alkane complexes with regard to C-C bond activation in the next lecture. So, I thank you for being with me in this particular lecture, and I look forward to being with you in the next lecture discussing the topic of C-C bond activation in more detail, and looking into various other compounds which shows such reactivity till then goodbye.

Thank you.