Transition Metal Organometallic Chemistry: Principles to Applications

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Week – 04
Lecture – 16
C-H activation

Welcome to this lecture on transition metal organometallic chemistry from principles to applications over the last few lectures. We have been discussing some an interesting topic, which is on C H activation. C H activation is a leading area of interest in organometallic chemistry, because it has significant utility in both academic as well as industrial world. An important drawback to this reaction the this problem is that this problem is very challenging and not a very simple one and that arises primarily due to strong C H bonds.

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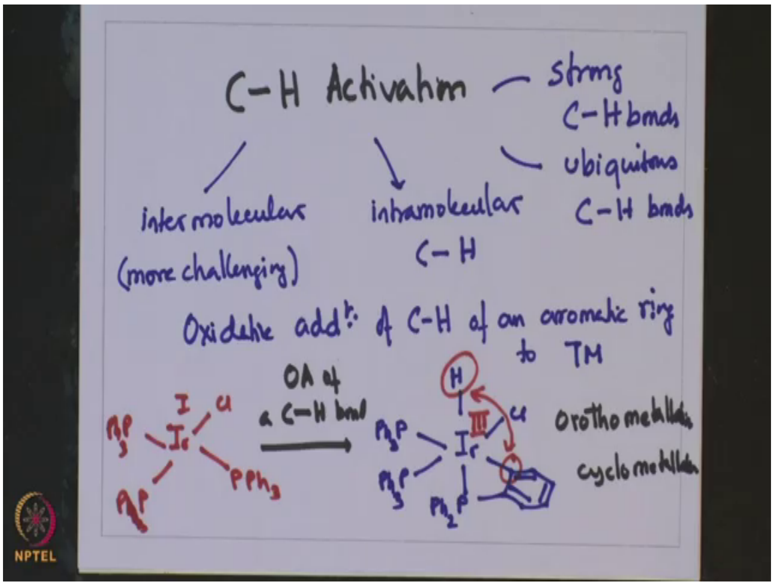

C-H Activation – strong C-H bonds

ubiquitous C-H bonds

intermolecular (more challenging)

intramolecular C-H

Oxidative add^n: of C-H of an aromatic ring to TM

And, also because of large number of C H bond present in several compounds. They are ubiquitousness also poses a selectivity problem in C H activation chemistry. So, these bonds are difficult to break and also very difficult to selectively a perform the cleavage of these. We have also discussed in the last lecture about various methods or various types of C H bond activation chemistry that has been practiced and what one comes around is there are both kinds of C H activation possible, one is intermolecular the other is intramolecular of these two types of C H activation that is a possible. The intramolecular C H activation is less challenging whereas, intermolecular C H activation is more challenging to attempt.

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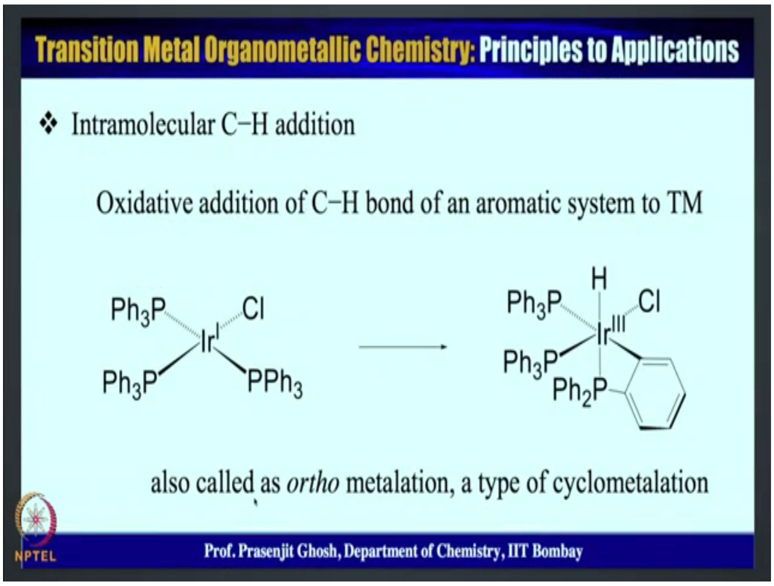

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- Intramolecular C–H addition

Oxidative addition of C–H bond of an aromatic system to TM

also called as *ortho* metalation, a type of cyclometalation

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Now, in our discussion on C H activation, in the last lecture, in our discussion on C H activation in the last lecture, we have started off with looking at intramolecular C H activation reactions and one example that we looked at was that oxidative addition of a C H bond of an aromatic ring on to our transition metal and that resulted in complex iridium, complex shown here, where these hydrogen and this carbon has undergone oxidative addition. So, this method involves the C H activation of this aromatic ring across iridium and as a result the oxygen state of iridium increased and in the current complex, it is iridium 3 whereas, it started off from iridium 1 complex.

So, because of this oxidative addition of a C H bond, the iridium 1, center increased its oxidation from iridium 1 to iridium 3 as a result, both coordination number increased by 2 as an oxidation state, also increases by 2 and this type of reaction that we discussed are called ortho methylation or cyclo methylation. Ortho methylation, because the C H bond ortho to the aryl ring gets activated and make a metal carbon bond and cyclo methylation is because there is a cyclic ring structure that is formed, that contains a metal carbon bond as a part of the cyclic ring.

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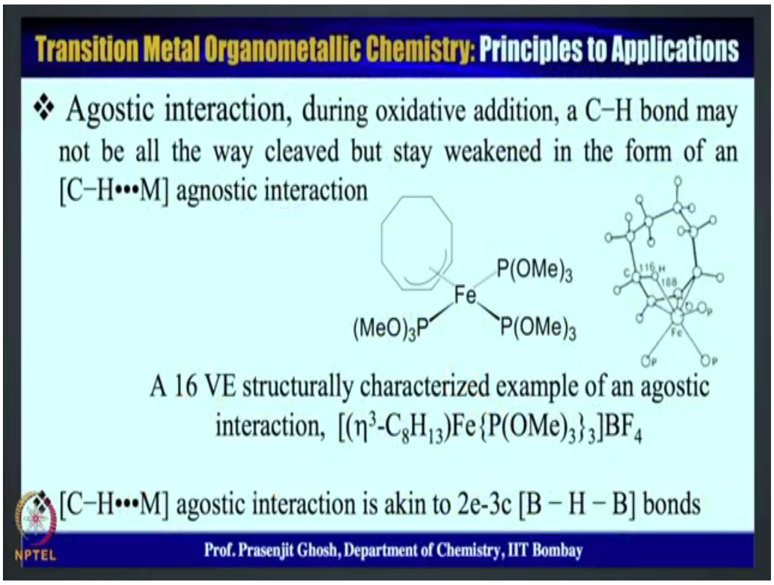

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- Agostic interaction, during oxidative addition, a C–H bond may not be all the way cleaved but stay weakened in the form of an [C–H•••M] agostic interaction

A 16 VE structurally characterized example of an agostic interaction, $[(\eta^3\text{-}C_8H_{13})Fe\{P(OMe)_3\}_3]BF_4$

- [C–H•••M] agostic interaction is akin to 2e-3c [B – H – B] bonds

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So, one has to then look at various methods or the mechanism in which this C H activation proceeded, whether in case of intermolecular or intra molecular reactions, careful probe into this C H activation reaction shows that C H activation occurs via interesting interaction called agostic interaction that precedes C H activation during this oxidative addition process.

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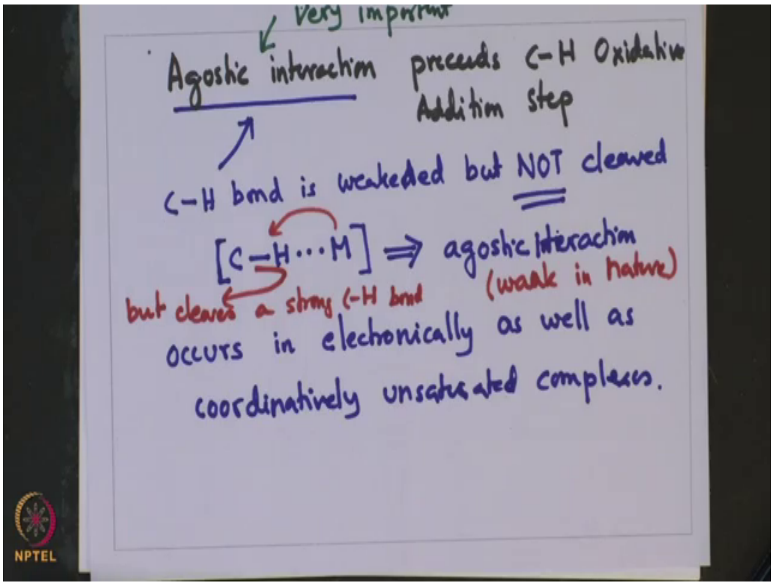

Very important

Agostic interaction precedes C–H Oxidative Addition step

C–H bond is weakened but NOT cleaved

[C–H•••M] ⇒ agostic interaction (weak in nature)

but cleaves a strong C–H bond

occurs in electronically as well as coordinatively unsaturated complexes.

So, that sort of implies that, agostic interaction initiates the C H activation mechanism or agostic interaction triggers the C H activation pathway and what it turns out that, in this agostic interaction, the C H bond is weakened is weakened considerably, but not cleaved. So, this is a very interesting interaction, which weakens the C H bond and not cleave it completely and hence, acoustic interaction is often represented by the following implying agostic interaction.

Usually agostic interaction occurs in electronically as well as co ordinatively unsaturated complexes and what one needs to look at is how does this metal center influences or facilitates the C H bond activation through this weak interaction, even though the weak interaction is kind of weak, but it has very significant impact in clearing a very strong bond, agostic interaction may be weak in nature, but cleaves strong C H bond and that sort of puts or that sort of makes this agostic important interaction, very important.

So, if one were to understand C H activation, one should begin by understanding agostic interaction and one finds that agostic interaction occurs for complexes, which are electronically as well as coordinatively unsaturated. So, this unsaturation is a hallmark of complexes that would show agostic interaction. Let us illustrate this, with the example shown here.

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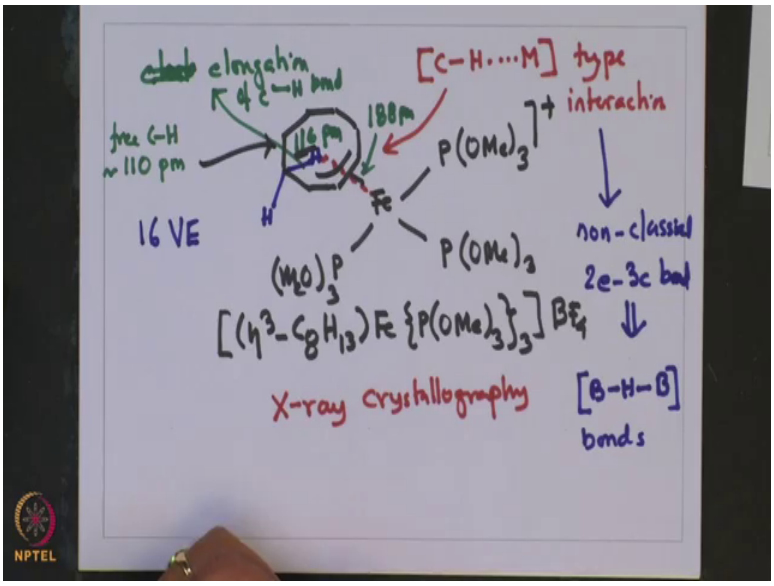

For this complex eta 3 C 8 8 13 F e P O M e 3 whole 3 B F for the structure is given here, it has 3 P O M e 3 moieties bound to this 8 membered ring. Now, this is 16 valence electron complex and what it has is an agostic interaction occurring between the hydrogen at this position. So, one of these hydrogen interacts with the iron center in an agostic fashion, which is M type interaction. Now, the evidence for the existence of this interaction came from X-ray crystallography.

As this compound was structurally characterized and what came out from that is; that this C H bond interacts and has considerably elongated and this distance is, which is hydrogen to Aaron is about 188 picometer and this carbon to hydrogen is about 116 picometer. Now, the these interaction of the C H bond with the metal leading to elongation of the C H bond to 116 to p m whereas, free C H bond, which is not involved in agostic interaction that have a distance of about 110 picometer.

So, a free C H bond, which does not have a agostic interaction is around 110 picometer whereas, in this complex as it shows C H M agostic interaction. This bond has increased from 110 picometer to 116 picometer as a result of this agostic interaction. So, what we see that, these kind of agostic interaction is of a non classical to electron 3 center bond and similar to the B 8 B bonds, that we are familiar with displaying such non classical 3 center to electron bonds.

So, the extra structure of these compounds to prove the presence of agostic interaction, it also showed that as a result of agostic interaction that the C H bond undergoing the agostic interaction has increased his length to 116 to p m with respect to let us say a C H which does not under grow agnostic interaction, which would have a average bond length of 110 p p m, not only there was an increase C H bond length, the hydrogen is seen interacting with iron kind of designated by H dot M. This is the weak interaction and has a distance of about 188 picometer.

Now, this structural characterization of this complex does establishes the fact that 18 C H activation is prevalent in this particular complex and many other complexes, for both electronically as well as coordinatively unsaturated metal centers. Now, X-ray is not the only way to ascertain the presence of C H activation.

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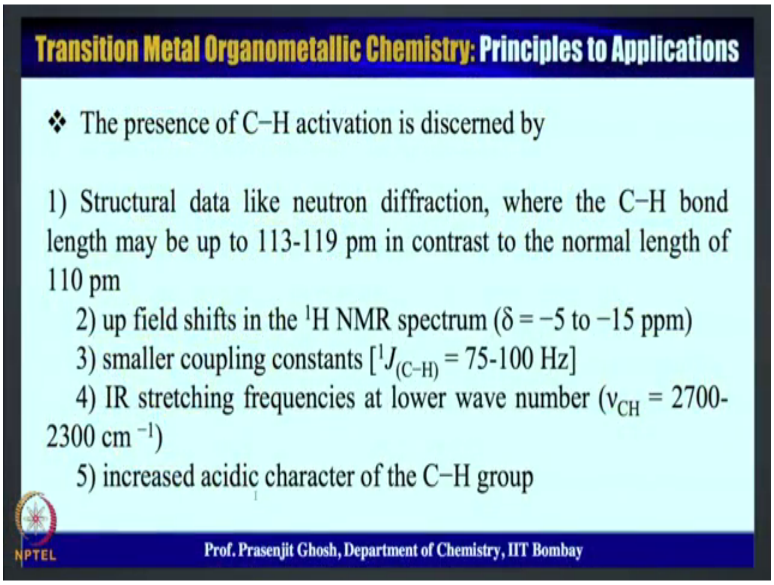

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- The presence of C–H activation is discerned by

1) Structural data like neutron diffraction, where the C–H bond length may be up to 113-119 pm in contrast to the normal length of 110 pm
2) up field shifts in the ^{1}H NMR spectrum ($\delta = -5$ to -15 ppm)
3) smaller coupling constants [$^1J_{(C-H)} = 75\text{-}100$ Hz]
4) IR stretching frequencies at lower wave number ($\nu_{CH} = 2700\text{-}2300\ \text{cm}^{-1}$)
5) increased acidic character of the C–H group

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Sometimes in X-ray it is difficult to obtain the data for hydrogen atom and hence, neutral diffraction becomes more useful than X-ray for discerning C H activations. And there are other spectroscopic techniques, which will allow us to understand the presence of C H activation.

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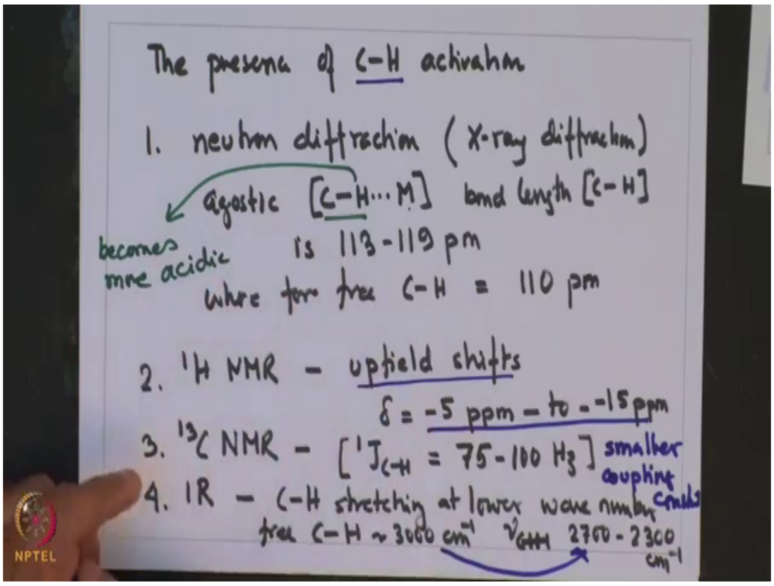

The presence of C–H activation

1. neutron diffraction (X-ray diffraction)
agostic [C–H⋯M] bond length [C–H] is 113-119 pm
where for free C–H = 110 pm
becomes more acidic

2. ^{1}H NMR – upfield shifts
$\delta = -5$ ppm – to – -15 ppm

3. ^{13}C NMR – [$^1J_{C-H} = 75\text{-}100$ Hz] smaller coupling consts

4. IR – C–H stretching at lower wave number
free C–H ~ 3000 cm^{-1} ν_{C-H} 2700 - 2300 cm^{-1}

So, hence one can say, the presence of C H activation can be established by let us say, neutron diffraction to be more precise. Sometimes X-ray diffraction as well, where hydrogen is located, where agostic C H bond length is around 113 to 119 picometer where, for free C H. This is about 110 picometer. Similarly, plutonium N M R is a useful method, spectroscopic technique for identifying C H agostic interactions and they show up; fill shapes in the region from del minus 5 p p m to minus 15 p p m. So, this is really very up shield, up shielded proton resonance, which can be easily picked up in proton N M R as most of the other proton resonances they appear from between 0 to 10 p p m.

Furthermore, in carbon 13 N M R, the presence of agostic interaction is also prominent as mentioned earlier that, agostic interaction leads to weakening in C H bond, which results in lowering of the coupling constants and that can be observed in carbon 13 N M R, where 1 J C H coupling constant. The reduced coupling constant can be something around 75 to 100 hertz. Similarly, infrared spectroscopy would also take up this agostic interaction, where it shows C H stretching at lower wave number, energy wave number. New C H is between 2700 to 2300 centimeter inverse as opposed to free C H, which is around 3000 centimeter inverse.

So, the weakening of C H interaction as a result of the agostic interaction can be reflected in I R C H stretching, where the free C H stretching that comes at higher energy of about 3000 gets reduced to that of 2700 to 2300, because of the presence of agostic interaction, the same can be seen in lowering of coupling constant. In carbon 13 N M R and proton N M R showed up field shifts in the region from minus 5 to minus 15 p p m as a result of this C H interacting with metal center, the hydrogen in the C H becomes acidic and it shows increased acidic character.

Now, let me summarize the points that we have discussed in this particular lecture. We began by looking at various types of C H activation, examples that are known in the start. We looked at intramolecular C H activation, which was ortho metallation type C H activation, in which ortho hydrogen of aryl ring oxidatively added on to the metal center. We also looked at the mechanism, how the C H activation proceeded and found that C H activation initiates with an important interaction, which is agostic C H M type interaction. This agostic C H M type interaction is a weak one, but it has significant implication as this result in cleaving of a very strong C H bond.

So, even though by itself it is a weak interaction, the agostic interaction, but it has tremendous implication and significance in terms of being able to play a very strong C H bond. We also discussed about the criteria, that are required for the existence of agostic interaction and what was discussed is, that metal complexes have to be electronically as well as coordinatively unsaturated to exhibit. See agostic type interaction, the presence of an agostic interaction in metal complexes can be confirmed by X-ray, single crystal diffraction studies, where the complex exhibiting agostic interaction can be structurally characterized as mentioned.

Agostic interaction weakens our C H bond, but does not cleave it all the way and this weakening of C H bond is reflected in increase in C H bond length, with respect to free C H that is not undergoing the agostic interaction, and we had seen in the particular example that the bond length increased to about 116 picometer as opposed to 110 picometer for non-interacting C H bonds. The weakening of C H bonds can also be picked up in proton N M R spectroscopy, where these protons appears in highly up field shifted region between minus 5 to minus 15 p p m. The weakening of bond also is reflected in carbon 13 N M R spectroscopy, where a smaller coupling constant is visible.

And this coupling constant arise between 75 to 100 hertz and the same can be picked up in infrared spectroscopy, where these agostically interacting, C H appears as the much lower energy at 2700 to 2300 wave numbers as opposed to the free C H appearing at 3000 centimeter inverse and, because of this increased interaction of C H 2 metal centered in an agostic type interaction. The C H becomes increasingly acidic in nature and this interaction increases the acidity of the C H group. So, with this, we sort of looked at the mechanism or mode of action of the C H activation, which originates with an important interaction called agostic interaction, which we have learned in this lecture and looked at how it manifests in different spectroscopic techniques, that allows us to characterize interaction.

We are going to look a bit more detail in this C H activation as well as agostic interaction and in various kinds of intermolecular as well as intramolecular C H activation process. What are their implications? How good they are and how people are utilizing all this interaction in carrying out C H activation followed by C H functionalization in subsequent lecture. So, I look forward to the next lecture that will have this elaborate discussion on C H activation particularly of intermolecular type and also their implication in various catalytic processes. So, with this thank you for being with me in this lecture and I look forward to being with you in next lecture.