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

Lecture- 10
Week - 2
Preparation and Properties of σ - alkyl compounds

Welcome to this course on Transition Metal Organometallic Chemistry from Principles to Applications. In our previous lecture, we were discussing about sigma alkyl complexes and their preparations. These complexes are an important part of organometallic chemistry as they are intermediates for many catalytic processes hence it is of importance that these complexes be synthesized, so that they can be used for various application purposes. In the last class, as far as the synthesis of sigma complexes are concerned, we have discussed four preparative methods for making them. This involved the very common metathesis method, which included reactions of metal halide with organoalkyl compounds.

The second method that we discussed was of insertion reaction, and insertion reaction of an alkyl into metal sigma hydride complexes. The third one was another insertion reaction of carbene into metal sigma hydride complexes. And the last one that we discussed was metallate alkylation reaction in which low valent transition metal organometallic compounds where reduced to form electron rich metallate anions which were then reacted with alkyl halides, so that k was the scope of synthesis of this sigma alkyl complexes. There are few methods remaining which were not discussed in the last class and which we will be discussing in this lecture.

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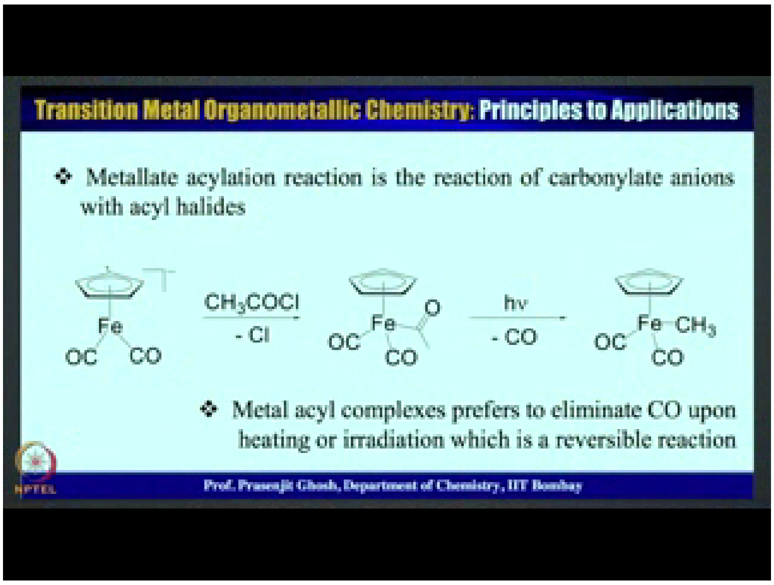

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- Metallate acylation reaction is the reaction of carbonylate anions with acyl halides

- Metal acyl complexes prefers to eliminate CO upon heating or irradiation which is a reversible reaction

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Now, in continuation from the metallate alkylation reaction, there is this variant which is called a metallate acylation reaction. This method is the fifth method that we are discussing on transition metal sigma alkyl complexes.

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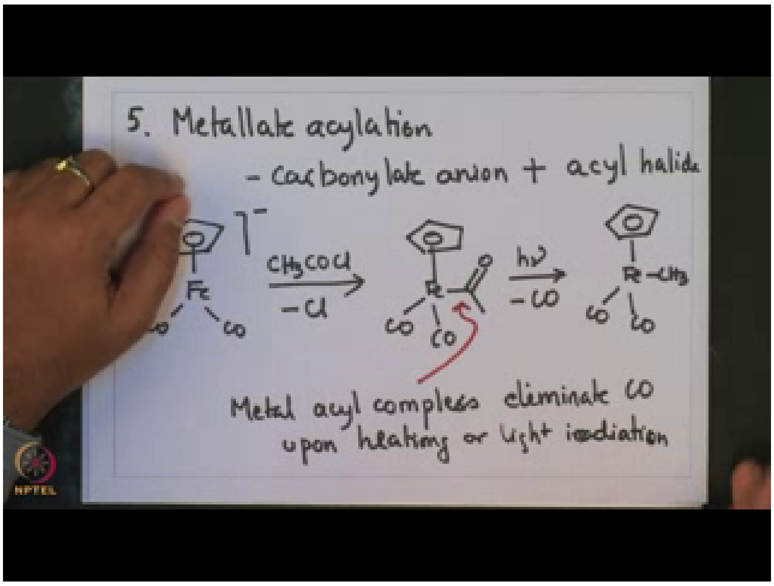

5. Metallate acylation

- carbonylate anion + acyl halide

Metal acyl complexes eliminate CO upon heating or light irradiation

This is called metallate acylation reaction, and involves a reaction between a carbonylate anion and an acyl halide. This reaction is very similar to the last reaction that was discussed in the previous lecture where it was called metallate alkylation reaction; and in this case, it is called metallate acylation reaction. And the reaction is between a carbonylate anion and a acyl halide. I will illustrate this with this following iron metallate complex reacting with CH 3 CO Cl giving minus chloride giving this Fe CO methyl moiety iron cyclopentadienyl dicarbonyl, which in presence of light eliminates CO to form the iron methyl complex. An important characteristic of metal acyl bond is that the metal acyl complex is preferred to eliminate CO in presence of light or heat, heating or light irradiation.

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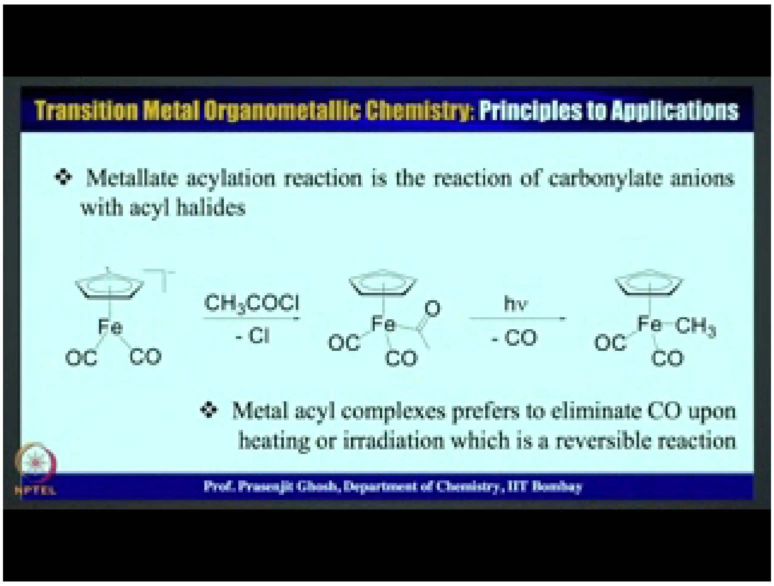

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- Metallate acylation reaction is the reaction of carbonylate anions with acyl halides

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So, this method was very similar to the previously discussed metallate alkylation reaction. Another very important method for preparing metal sigma alkyl complexes is the oxidative addition method.

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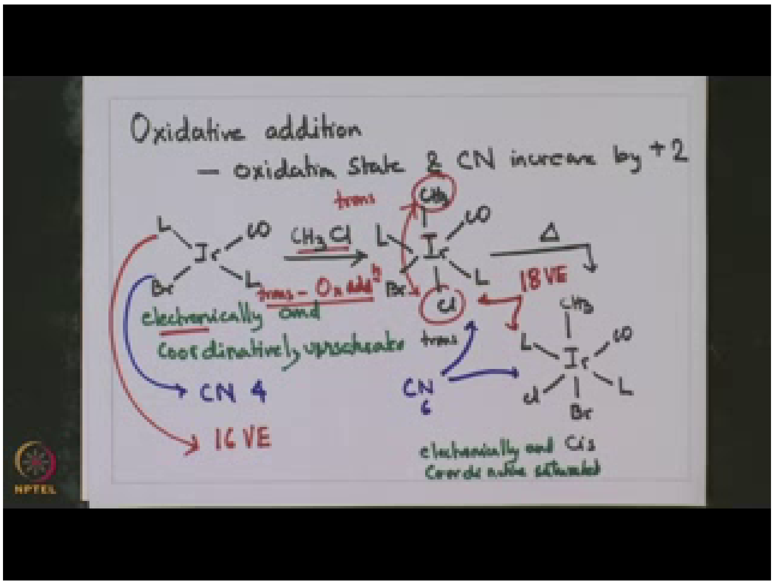

Oxidative addition

— oxidation state & CN increase by +2

Now, oxidative addition is a very important reaction that is encountered frequently in the realm of organometallic chemistry in various catalytic cycles as well as in various synthetic reactions. A hallmark of this reaction is that the oxidation state as well as the coordination number of the metal increases by two. So, as the name suggest that it is a addition of atoms under the metal center. Let me illustrate by this simple iridium complex, which reacts with methyl chloride. Now, for something a metal complex to undergo oxidative addition, in which the oxidation state as well as the coordination number increases by two.

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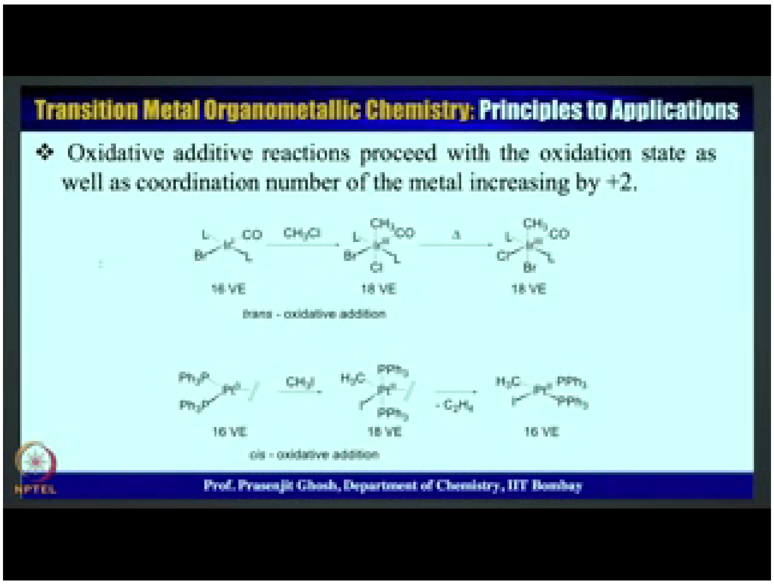

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- Oxidative additive reactions proceed with the oxidation state as well as coordination number of the metal increasing by +2.

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The criteria for such addition is that the complex should be electronically as well as coordinatively unsaturated. So, this iridium complex satisfies both because it has a coordination number of four that means, it can still end up being an octahedral complex having coordination number 6. So, as far as the coordinative unsaturated concerned as mentioned that this square planar complex is coordinatively unsaturated. As far as the electronic saturation is concerned, this complex is electronically unsaturated to as it has 16 valence electron. So, it is also electronically unsaturated. So, this complex which is both electronically and coordinatively unsaturated reacts with methyl iodide to give this electronically and coordinatively saturated iridium complex octahedral complex having the methyl added to it.

Now, the thing to note that this methyl chloride has added in a trans fashion with the methyl a methyl chloride has added in a trans fashion with the methyl and the chlorine occupied transposition, trans to each other. So, this kind of oxidative addition is often referred to as trans oxidative addition. This trans compound upon further heating organises back to the Cis compound as shown over here. So, both the Cis as well as the trans compound are electronically and coordinatively saturated as their coordination number is six and their valence electron are 18.

So, what has been found that this method of oxidative addition required the metal complex undergoing the oxidative addition to be both electronically as well as coordinatively unsaturated. And which upon undergoing oxidative addition would show that the central metal atom has undergone an increase in the oxidation state by plus 2 as well as the coordination number by plus 2. Another example of oxidative addition is been shown now; unlike the past reaction where oxidative addition happened in a trans fashion a cis oxidative addition reaction is shown below.

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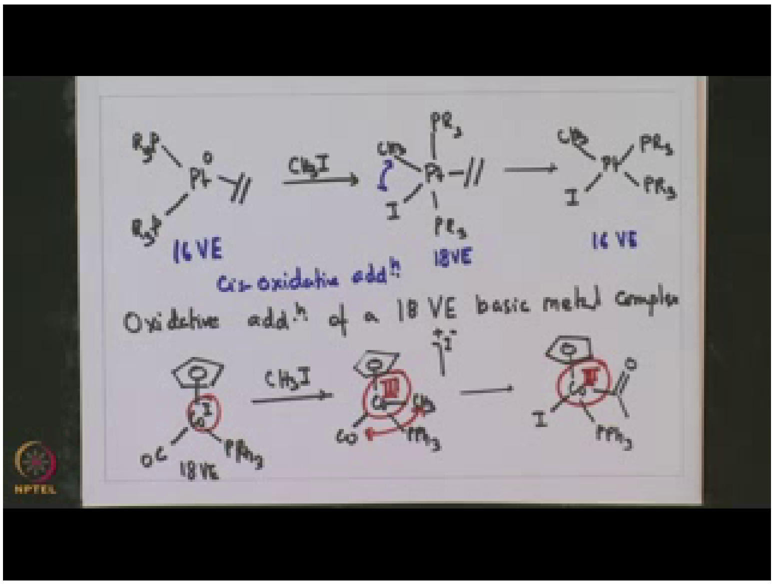

In this platinum zero complexes, methyl iodide undergoes oxidative addition. Here also the complexes both electronically as well as coordinatively unsaturated, its coordination number being occupied by eta 2 alkyl to first (Refer Time: 14:49). And if electronically it has 16 valence electron, it undergoes oxidative addition to give this cis complex, where the methyl and the iodide are in cis disposition to each other, and this is called cis oxidative addition. Now, this t b p complex trigonal bipyramid which is 18 valence electron compound loses this ethylene to give another 16 valence electron square planar platinum complex having cis disposition between the methyl and the iodide moieties. And it is also a 16 valence electron complex. So, oxidative addition requires electronic rich metal centre.

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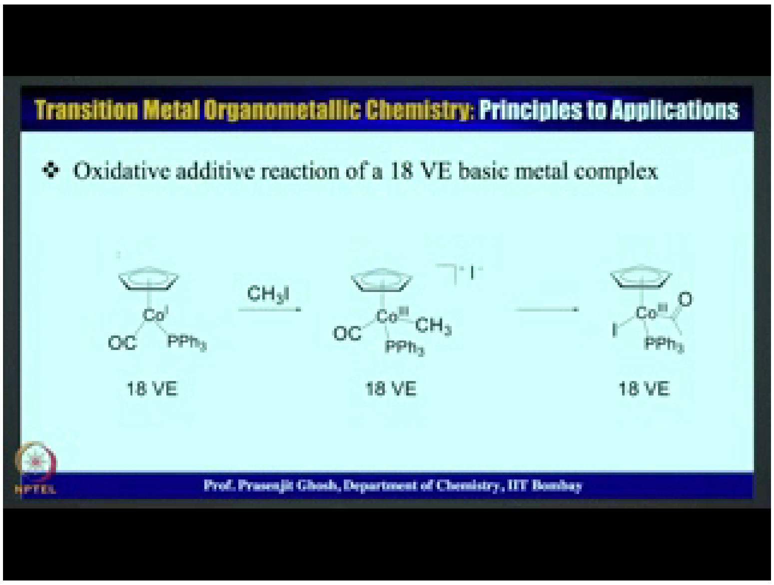

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- Oxidative additive reaction of a 18 VE basic metal complex

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Now, if we look at various examples of oxidative addition, it would same that the complex should have electronic unsaturation that is its total valence electron should be lower than 18 valence electron, at least by two valence electron unit. Now, that would imply that a 18 valence electron might not undergo oxidative addition at all, but this is not true. Oxidative addition may also happen in a 18 valence electron basic metal complex. The metal complex electronically saturated in terms of having 18 valence electron, but should also be electron rich and basic for it to undergo oxidative addition reaction.

For example, for the cobalt compound shown here, cobalt C P, carbonyl PP h 3 which is a 18 valence electron compound undergoes oxidative addition with methyl iodide giving the compound C P cobalt methyl PP h 3 carbonyl. That shows a very characteristic reaction for the such type of compound coleman migratory insertion of CO methyl into the cobalt CO bond giving cobalt acyl compound as shown below. Now, if one were to look at the oxidation at the metal centre then one would notice that over here, cobalt was in plus one oxidation state over here, cobalt is in plus three oxidation state, and over here the cobalt is in again plus three oxidation state. So, this is expected for an oxidative addition reaction that the oxygen state increase by two.

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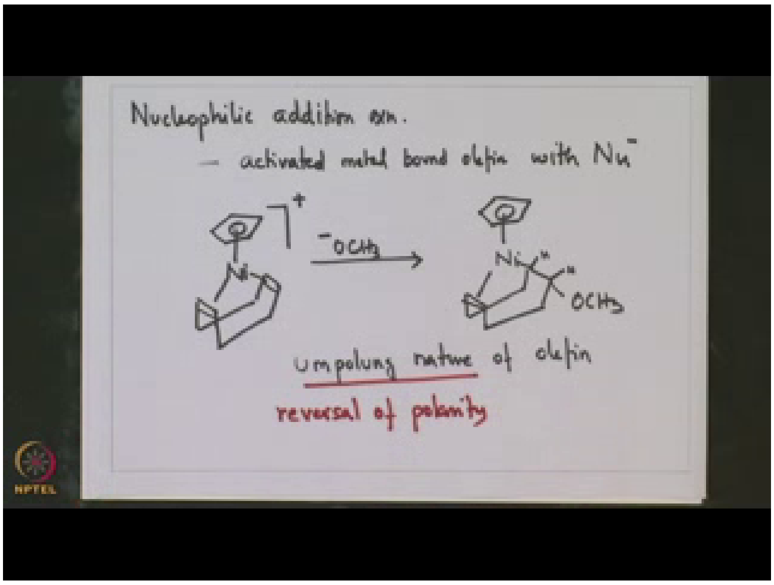

Nucleophilic addition rxn.

– activated metal bond olefin with Nu^-

umpolung nature of olefin

reversal of polarity

Apart from the oxidative addition reaction another important reaction is this nucleophilic addition reaction.

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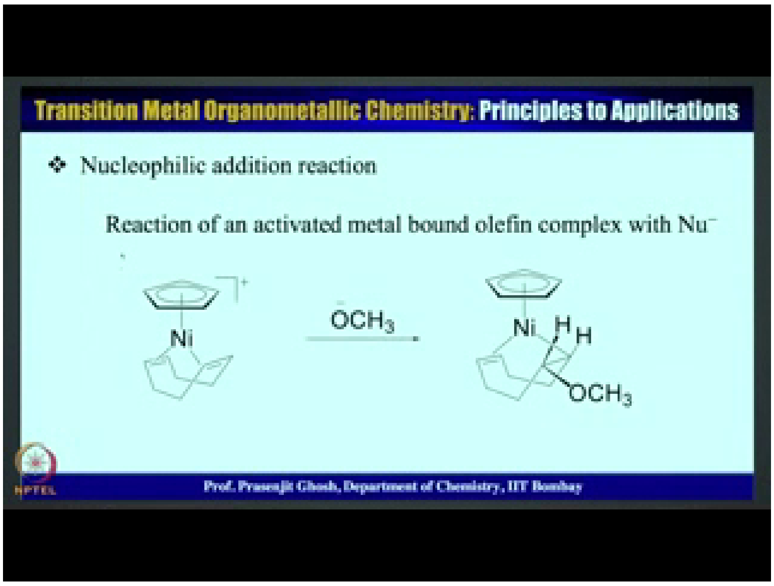

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- Nucleophilic addition reaction

Reaction of an activated metal bound olefin complex with Nu^-

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Nucleophilic addition reaction is very common to certain very specific substrates and mainly involved reaction between activated metal bound olefin with a nucleophile. For example, for this half sandwich CP compound of nickel undergoes nucleophilic attack in presence of methoxide anion to give the following nickel complex as is shown here.

What happens over here is that the methoxide nucleophile attacks on this activated olefin.

The next reaction that we are going to talk about is nucleophilic addition reaction. This reaction is a reaction between activated metal bound olefin with the nucleophile. For example, in this cationic nickel CP star diolefin complex, the olefin being bound to nickel is activated. In the sense the electron density on the olefinic pi cloud gets transferred over to the metal; as a result the olefin become activated and susceptible to a nucleophilic attack. So, a methoxy nucleophile can attack activated olefin giving rise to a complex like this and this talks about the umpolung nature of olefin. So, umpolung reactivity is a very important concept which means reversal of polarity and that has been very cleverly exploited in organometallic chemistry for synthesizing transition metal sigma alkyl complexes.

Now, just a brief discussion on this, olefins when unactivated are very electron rich and would not be attacked by a nucleophile, whereas they would be attacked by normally be attacked by electrophiles. But the same olefin when activated by metal as shown over here can be attacked by a nucleophile and this is what is called reversal of polarity are the umpolung nature.

Another method is ligand sigma pi rearrangement and that is shown over here this is the seventh method of preparing sigma alkyl complexes, sigma pi type rearrangement 5 M n bound to an olefin in presence of sodium borohydride gives the following sigma complex. So, here the borohydride donates a hydride, and the olefinic moiety get reside to a ethyl moiety. With this, we come to the end of various preparative method required for preparing sigma alkyl transition metal complexes. In this lecture, in particular, we have talked about four different kinds of methods; starting with metallate acylation, then going over to oxidative addition, then nucleophilic add addition of activated olefin and lastly sigma pi rearrangement of eta 2 ligands. These four method discussed in this lecture is however, more specialised and more challenging reactions than the somewhat other four reactions which were discussed in the previous lecture.

So, now having covered all of the preparative method transition metal sigma alkyl complexes, we go to a very new exciting segment in the next lecture, particularly talking about the properties of transition metal sigma alkyl complexes and their stability. I hope you have enjoyed this lecture, and look forward to having you in my next lecture, which will be on properties of sigma alkyl transition metal complexes.

Thank you.