# Advanced Transition Metal Organometallic Chemistry
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## Lecture – 13
## Transition Metal Cyclopentadiene Complexes: Reactivity of Metallocene

Welcome to today's lecture on, Advanced Transition Metal Organometallic Chemistry. We are discussing an important topic particularly reactivity of metallocene in thisseries of lectures on transition metal cyclopentadienyl complexes to help explain the various reactivity patterns that are shown by metallocenes. In our previous class, we have looked into the metal a transition metal cyclo pentadienyl inter, interaction particularly from their molecular orbitalpoint of view.

The electronic structure of the transition metal cyclo pentadieneligand interaction explained a lot about the electronic fillingof thesecomplexes. Also he take itself explain, how the orbitals are arranged with respect to the energy, what are the conditions for their homo, and the LUMO orbitals, and also greatly it helped explain the magnetic properties that arise from unpaired electrons present in the valence outer orbitals of this transition metal cyclopentadienyl complexes.

Continuing furtherwe are going to discuss in detail more on the reactivity of transition metal cyclopentadienyl complexes, andthe thing that stands out is theirextremely a facile reactivity with electrophiles.

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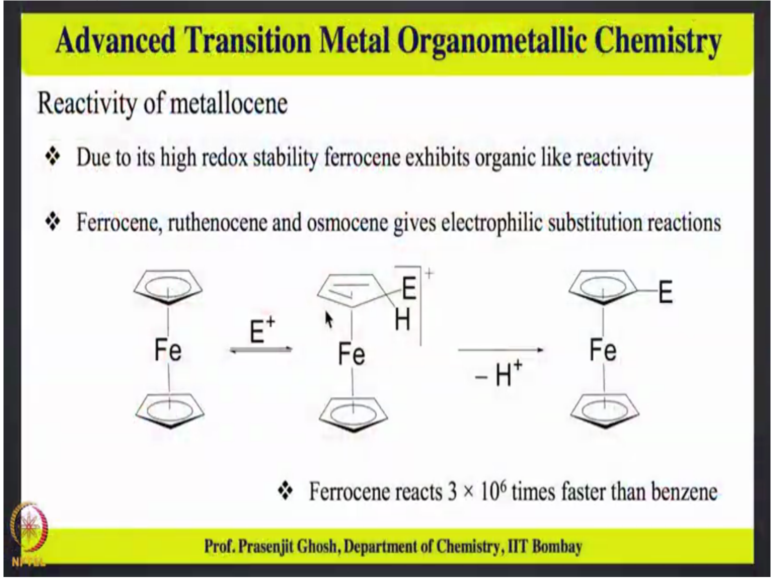

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Reactivity of metallocene

- Due to its high redox stability ferrocene exhibits organic like reactivity
- Ferrocene, ruthenocene and osmocene gives electrophilic substitution reactions

- Ferrocene reacts 3 × $10^6$ times faster than benzene

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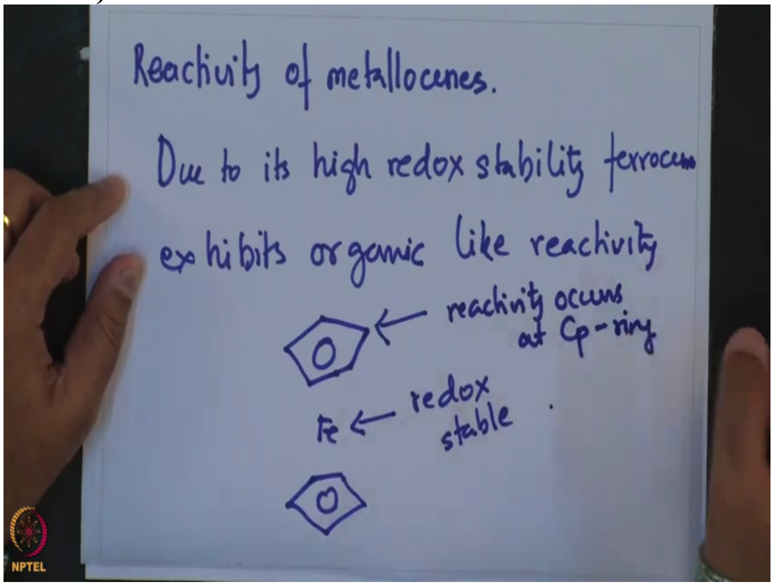

Reactivity of metallocenes.

Due to its high redox stability ferrocene exhibits organic like reactivity

So, today we are going to talk about metallocenes and to begin withlet us justfocus on ferrocene one particularly exempt ferrocene like one particular type of metallocene before we expand on the reactivity of metallocenes in general. Now as far as the ferrocene is concerned, it is highly a redox stable, that means that in ferrocene, iron is in plus 2 oxidation state and does not really undergo, redox reactions to +3 or +4 oxidation states.

So, this high, high redox stability, a ferrocene exhibits organic like reactivity, by this it means that, this iron center is redox stable, as a result the reactivity occurs atthe CP ring, and that is whyit gives this organic like reactivity.

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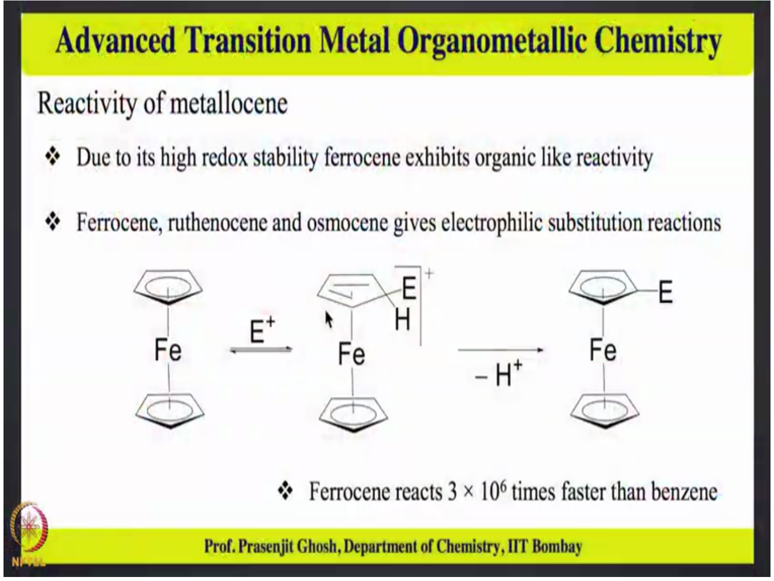

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So to help explain thispoint further we are going to look at the reactivity of ferrocene ruthenocene on osmocene, towards various electrophilic substitution reactions.

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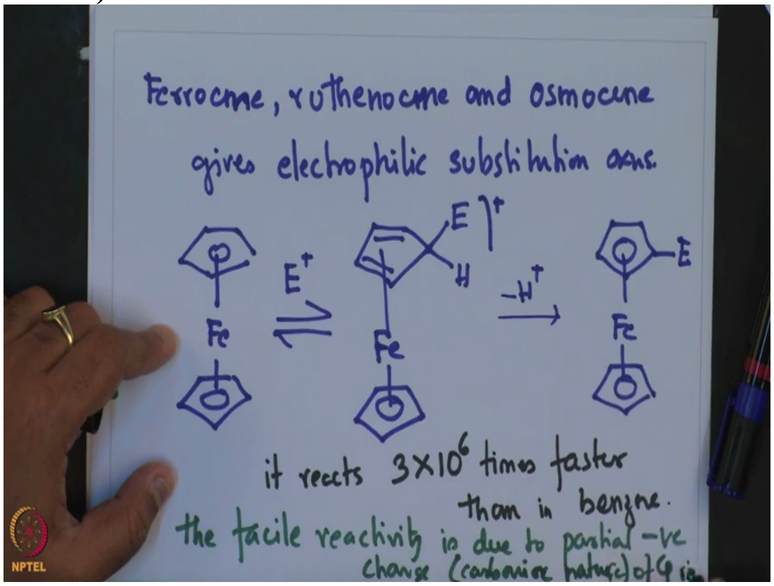
Ferrocene, ruthenocene and osmocene gives electrophilic substitution rxns.

it reacts $3 \times 10^6$ times faster than in benzene.

the facile reactivity is due to partial −ve charge (carbanionic nature) of Cp ri

So, reactions, that is illustrate this, in presence of an electrophile, the electrophile goes and attacks the CP ring, giving this cationic complex, thiswhich eventuallylosesthis proton, leading to electrophilic substitution on the CP ring. Now this reaction is so facile that it reacts 3 into 10 to power times 6 faster than in benzene, andthe reason, the reason for extremely highnature, reactivity nature of ferrocene, ferrocenyl CP ring towards electrophilic substitution is primarily due to its carbon ionic nature.

The facile reactivity is due to partial negative charge or carbonic nature of CP ring, okay. Soyou knowthese aresort of partially negative in charge because of its carbonic nature of the CP ring that is what it makes ferrocene so vulnerable, to electrophilic substitution reaction. So, this is an important reaction which distinguishes the ferrocene from othertransition metal complexes or other even organic compounds is the fact that these reacts extremely fast with electrophiles that is due to carbonic nature of the CP ring.

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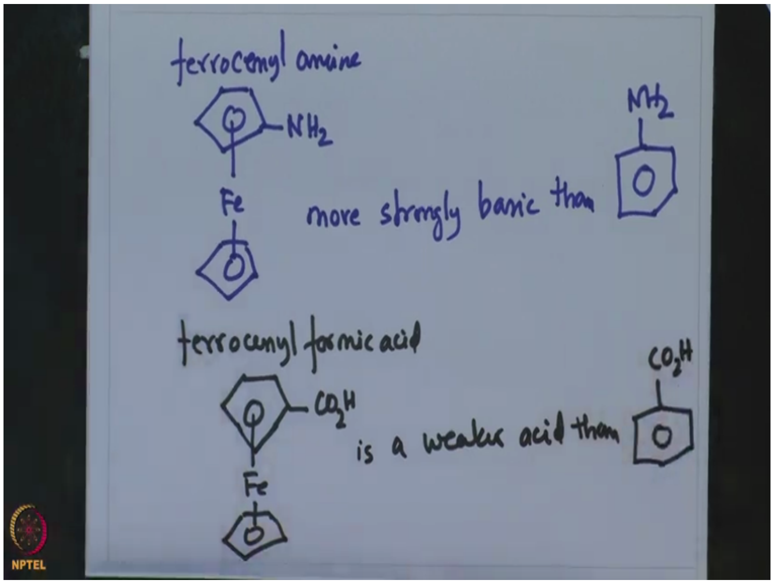

So,as a result this ferrocenyl amine, ferrocenyl amine is a more strongly basic than aniline. Sothis carbonic nature makes this ferrocenyl amine more basic,significantly more basic thananiline. Similarly a ferrocenyl formic acid, this is called ferrocenyl amine. Similarly ferrocenyl formic acid, which is a weaker acid, than, again benzoic acid so all, it confers is the fact that, these cyclopentadiene moiety arequite electron rich, they have this partial negative charge or an ionic character as a result they makevery strong bases and weak acids and also they undergo electrophilic substitution reactions at a  much faster pace than that of the organic molecules.

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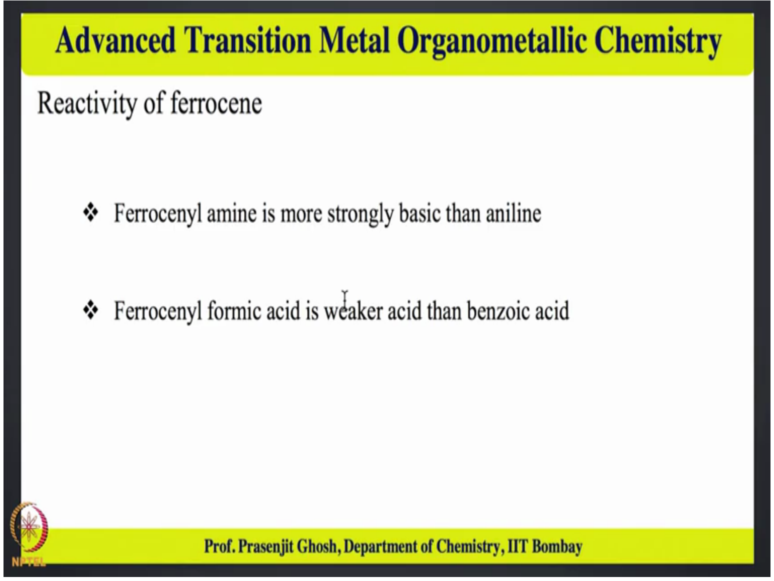

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Reactivity of ferrocene

- Ferrocenyl amine is more strongly basic than aniline
- Ferrocenyl formic acid is weaker acid than benzoic acid

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Now an importantmarker of this electrophilic substitution reaction of course, is this Friedel-Crafts reaction the Friedel-Crafts reactions sort ofare taken to be a benchmark reaction for any kind of electrophilic substitution reactions and no wonder that ferrocenyl compounds, also exist exhibit Friedel-Crafts oscillation reactions.

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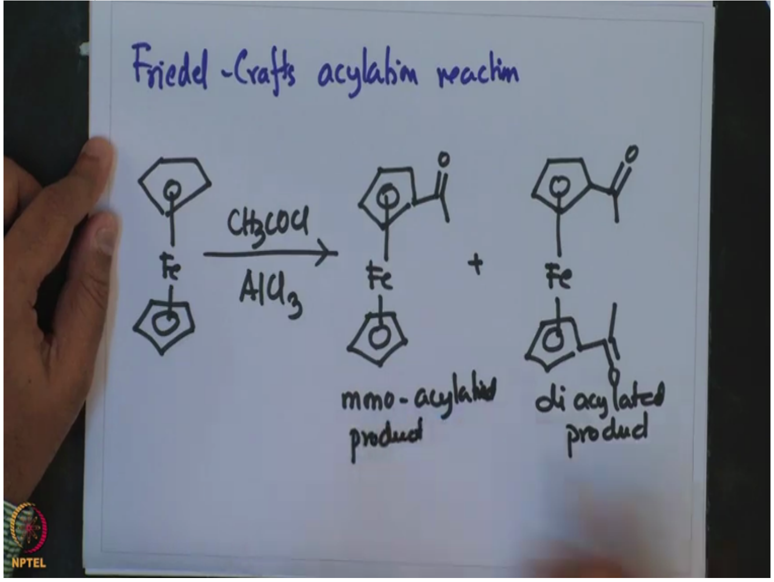

So, ferrocene reacts with acetyl chloride in presence of Alcl3, giving both mono acylated, this is mono acylated product and well as di acylated product. Please note that the di acylated product occurs on the second ring, and does not occuron the first ring, where the mono acylated product has happened. One thing whichsort of is an important point to consider, that these electrophiles there should not be acting as an oxidizing agent.

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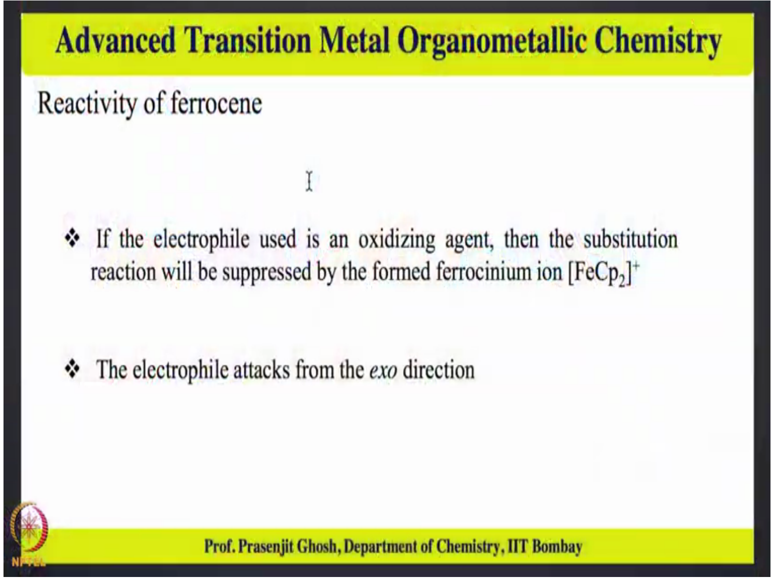

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Reactivity of ferrocene

- If the electrophile used is an oxidizing agent, then the substitution reaction will be suppressed by the formed ferrocinium ion $[FeCp_2]^+$
- The electrophile attacks from the *exo* direction

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When undergoing electrophilic substitution reaction because, if it does, then that would oxidize, ferrocene to ferrocenium ion.

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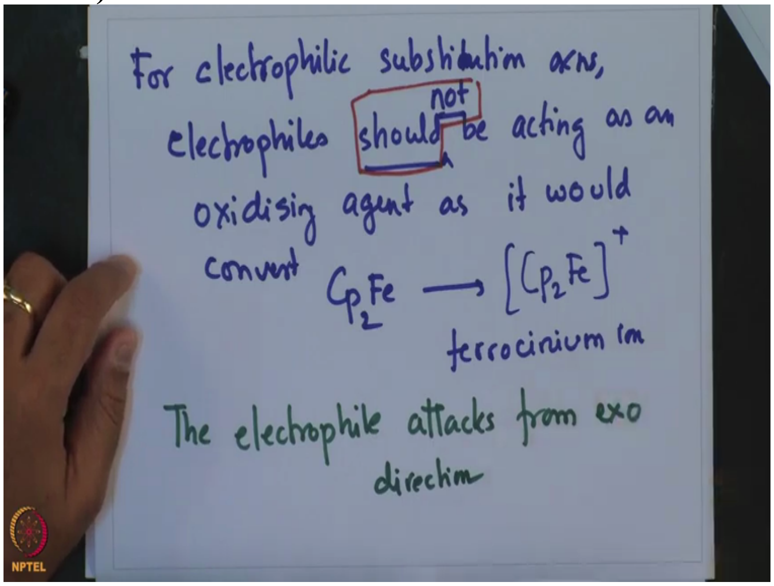

For electrophilic substitution rxns, electrophiles should not be acting as an oxidising agent as it would convert $Cp_2Fe \longrightarrow [Cp_2Fe]^+$

ferrocinium ion

The electrophile attacks from exo direction

So, one important criteria is for electrophilic substitution reaction, fusion reaction, electrophiles should not be acting as an oxidizing agent, should not, should not be acting as an oxidizing agent, as it would convert CP2Fe to CP2Fe+ or ferrocenium ion. So, this is an importantcriteriathat has to be followed or that has to be made when these electrophilic substitution reactions are covered that they should not be acting as an oxidizing agent, because if it does then ferrocene itself would get oxidized.

So, if it does not act as an oxidizing agent then obviously the electrophilic substitution reaction would occur and then the question comes,that, where would the electrophile attack from? Whether it will be an exo oh, from the exo direction or from theendo direction. A common convention would however, suggest an exo attack, because of simple easier approach, due to historic reasons.

And indeed there are several experiments which does conclude thesame insight or include the same attack. So exo electrophile attacks occur in the exo direction, the electrophile. Now this is bestexplained through thesevery sophisticated intra molecular acylation reaction.

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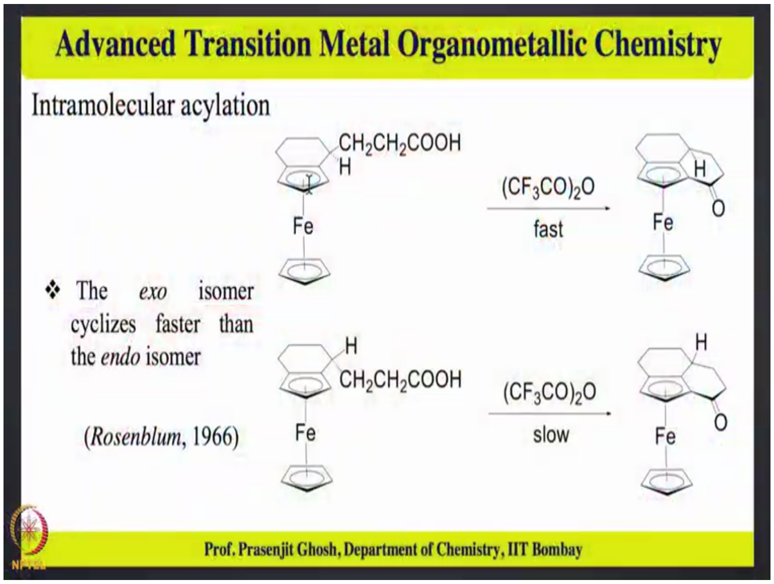

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Intramolecular acylation

- The *exo* isomer cyclizes faster than the *endo* isomer

(*Rosenblum*, 1966)

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Which further corroborates this EXO attack in the electrophilicsubstitution reaction;

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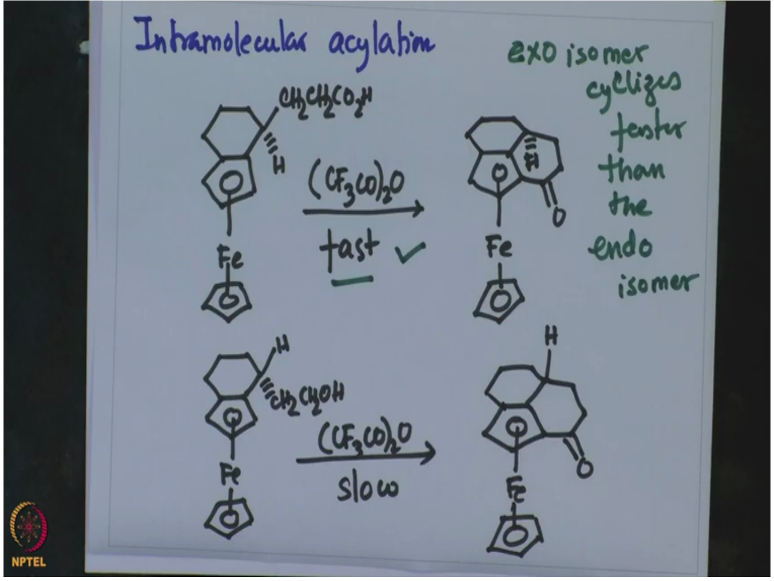

Intramolecular acylation

exo isomer cyclizes faster than the endo isomer

So, that isbeautifully illustrated in this particular example which contain six-membered cyclohexane ring attached to our CP ring, containing CH2, CH2, CO2H, this when treated with CF3 CO whole to O, reacts readily to give the product which is from the exo direction and that is reflected by this hydrogen in the endo position, whereas endo attack has depicted by this reaction which is extremely slow so,the exo isomer cycles faster than the Endomer isomer.

And this is shown over here, so this is a beautifulexperiment which was done to prove thefacial in a selectivity of the electrophilic attack and it has shown that the XY isomer is from faster, suggesting that the electrophile attacks from the extra direction and which is also theconventional wisdom because of steric reasons, one may suggest that these exo isomer would attack much faster from the outer face of the CP ring than endo isomer.

Another interesting reaction that we have been going to be talking about is,for the formation of iron hydride complex because of this electrophilic reaction, but in this case, the substitution reaction, does not eliminate the proton but in case, results in the formation of either a hydride moiety. So this is a nice variation of our nice variant of electrophilic substitution reaction which is predominantly seen for ferrocene.

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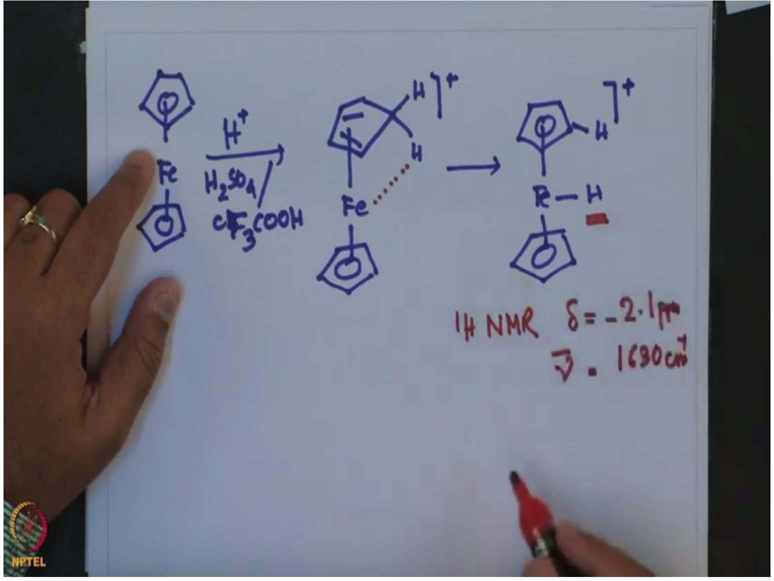

So, for example the treatment offerrocene with H+ of sulfuric acid and acetic acid, CF3 trifluoroacetic acid gives this expected protonated hydrogen complex. So this is similar to theelectrophile attacking the CP ring from exo direction, however, what is interesting over here, that one of the endo hydrogen of the CP ring, shows an interaction with the transition metal which eventually will lead to the formation of iron hydride complex and this is a beautiful experiment in which, this eliminating the H+ is actually grabbed by the iron resulting in the iron hydride complex.

This hydride complex has been characterized by proton NMR spectroscopy, where it appears often shifted at minus 2.1 ppm and also characterized it by IR where it appears as 1630 centimeter inverse,this iron hydride moiety. So this is an interesting example that showed that this proton when treated with acid, that had indeed, happens from the that of the H+ indeed happens from the extra moiety, but the di in cyclopentadienyl cation, so form the proton on the endo side get abstracted by the iron to form these iron hydride speciesand the CPD gets aromanticized andelectrophilic substitution occurs.

So, this is a nice demonstration of the fact that iron hydride can be formed through these electrophilic substitution reaction and the hydride moiety has been characterized by proton NMR where it appears off field shifted at minus 2.1 ppm as well as by IR where it appears at 1630 a centimeter inverse.

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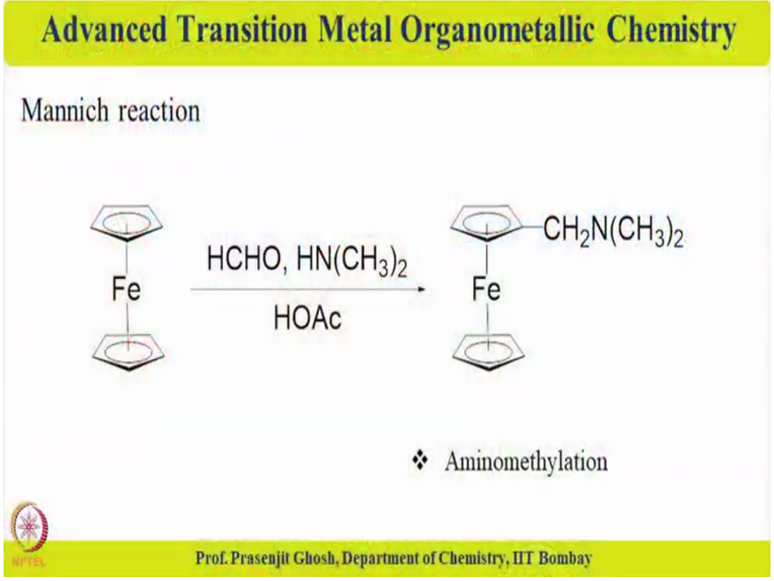

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Mannich reaction

❖ Aminomethylation

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Another important reaction again the hallmark of ferrocene chemistry is, Mannich reaction.

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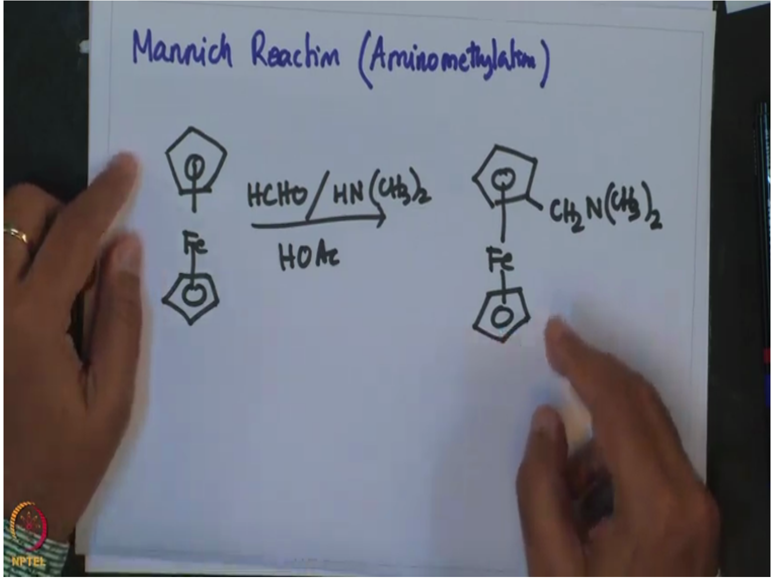

Mannich Reaction (Aminomethylation)

And these are also popularly called as Amino methylation relation reaction.the reaction is done under standard Mannich condition, which is treatment of ferrocene with formaldehyde, and a primary, a secondary amine, in presence of acetic acid which results in Amino calculation or Amino methylation of one of the ferrocenyl CP rings giving CH2 and CH3 whole2.

So, thisagain is an interesting reaction whichoccurs on the CP ring by rooting ferrocene with formaldehyde and di methyl amine in presence of acetic acid, and this reaction as mentioned is called Amino methylation reaction. So, with this I would like to conclude today's lecture, we have been talking about, various reactivity patterns of ferrocenyl complexes, and what comes to the fore is their extremepropensity to undergo electrophilic substitution reaction.

And that is primarily due to the fact of its carbon anionic nature which has results in a partial negative charge on the CP ring which allows it to readily undergo, these electrophilic substitution reactions, these reactions are so fast about 3 into 10 to the power 6 faster than that of conventional benzene,exhibiting similar electrophilic substitution reactions. Also because of its electron richness and a carbon ionic or partial negative charge and the CP ring, these amino ferrocenyl complexes are extremely basic than aniline.

Whereas ferrocenyl formic acid complexes, are even weaker acids than benzoic acid, having said that, that these ferrocenyl complexes undergo facile electrophilic substitutions, there are however certain restrictions though, the restrictions being that these electrophile should not be interfering with the iron center, that means that electrophile cannot be acting as an oxidizing agent,which might convert feriss ferrocene to ferrocenyl cation, and if it does, then this electrophilic substitution reaction would not occur.

So, the primary conditions are restrictions on the electrophilic substitution reaction is that the electrophile should not be acting as an oxidizing agent. The second thing that we learned about this electrophilic substitution reaction is the approach of the electrophile or attack of the electrophile and the CP is primarily from the exo phase of the CP that is from outside of the CP or external phase of the CP that also is a conventional wisdom.

Because the end of X is more sterically crowded and the approach of the electrophile from the end of phase is notfacilitated, and that is shown by two beautiful experiments by Rosenthal where it was experimentally proven that the exo cyclisation occurs at a faster pace than the end reaction. And lastly we have seen as fallout of this electrophilic substitution reaction formation of iron hydride complex as well as these amino methylation or the Mannich reaction occurring readily on ferrocenyl complex.

So, with this I would like to conclude today's discussion and some more of the reactivity of transition metal cyclopentadienyl complexes will dwell upon in the next lecture, till then goodbye and thank you.