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Organometallic Chemistry-I

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Module No. 1

Lecture No. 4

OXIDATION ADDITION
[1. CONCERTED MECHANISM]

Hello every one welcome today's class today we will discuss oxidative addition in the last class we have seen the 16 electron and 18 electron complexes and the way they react today we will discusses one of the most interesting topic organometallic complexes that is there oxidative addition now how the oxidative addition occurs and what are the criteria's and how the complexes are varying that is what is the topic of today's discussion.

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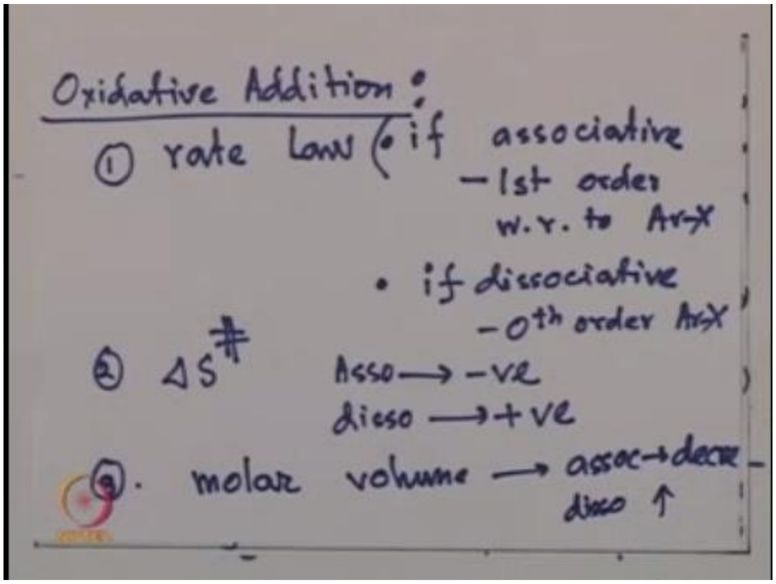
\ 

Oxidative Addition:

① rate law
- if associative
  - 1st order w.r. to Ar-X
- if dissociative
  - 0^{th} order Ar-X

② $\Delta S^{\#}$ Asso → -ve
disso → +ve

③. molar volume → assoc → decre
disso ↑

Now if you look at the oxidative addition and if you try to deal with their rate law then you will see if it is associative if associative then we will have first order with respect to Ar- x oxidative addition is happening in Ar- x if it is dissociative then we will have 0^{th} order with respect to Ar- x that is the first thing we will see now if you look at based on the associative and dissociate mechanism if you look at $\Delta s^{\#}$ the we will see associative case will give you negative Δs and dissociative case will give positive Δs.

Most importantly also you are molar volume in case of associative it will be decreasing and in case of dissociative it will be increasing right well before getting into discussion of the rate law Δs and the molar volume let us try to discuss with some real example first now let us take a generic example.

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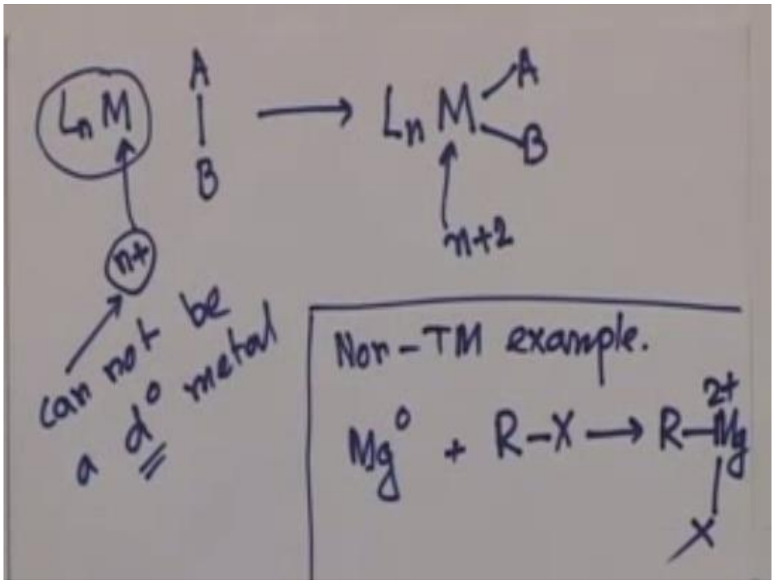

And that is L_nM it is a organometallic complex that will form and you want to have oxidative addition of this ligand metal complex into AB this is once again it is a generic example you will end up getting L_nM A and B if the oxidation state of this one was n+ at the end of the reaction you will have n+2 so change in oxidation state is +2 change in overall electron count from the starring material is again +2 so total 2 electron count increasing if this is a 16 electron complex this one will be an 18 electron complex so overall now if the metal was having n+ oxidation state it will then have n+2 oxidation state, now if that is true what you would understand is that this cannot be a d^0 metal because if it is a d^0 metal then n+2 oxidation state will not be attain.

So it has to have more than two electron mode than or equal to 2d electron, now before going into the real example let us try to take a non transition metal equivalent or non transition metal example, we have seen magnesium 0 reacting with any R-X organic halide to give you R-Mg-X this is magnesium 2+0 oxidation state giving you =2 overall this is an oxidative addition example of an oxidative addition complex, right. Now let us try to get back to this A and B we are trying to discuss the generic reactions of.

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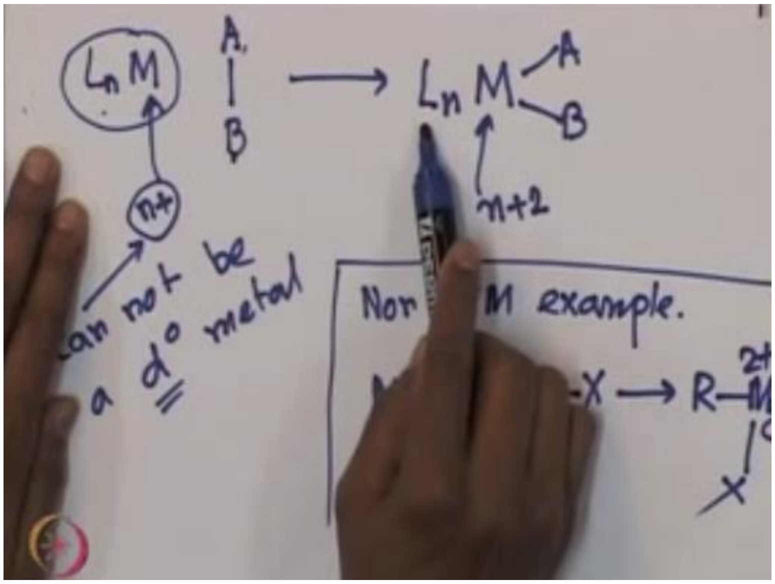

Ligand metal complex reacting with A and B complex or A-B organic spaces to give you ligand metal A-B complex, now need to discuss what are the different variations of A and B so classes.

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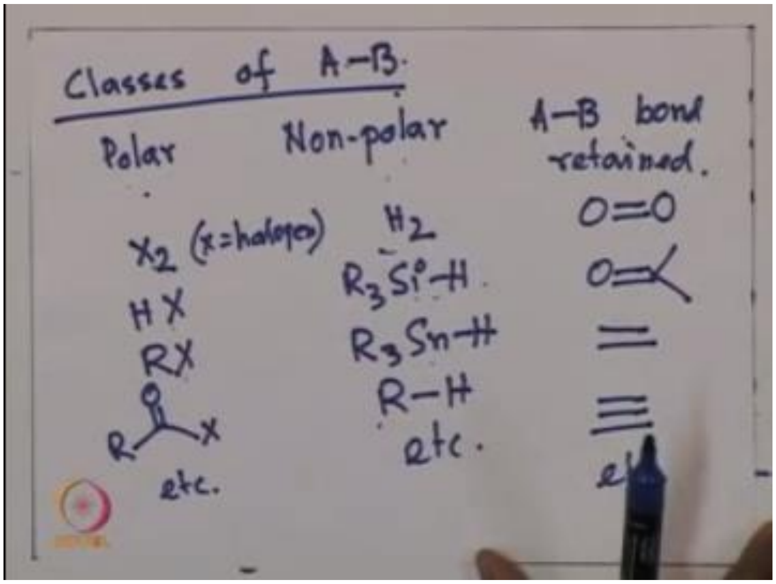

Classes of A-B.

Polar	Non-polar	A-B bond retained.
X_2 (X=halogen)	H_2	$O{=}O$
HX	$R_3Si{-}H$	$O{=}C{<}$
RX	$R_3Sn{-}H$	$=$
$RC(O)X$	R-H	$\equiv$
etc.	etc.	etc.

A and B we can have a polar A-B or a non polar A-B and we can have something where we have multiple bond where A-B bond will be retained, let me give to an example it will be clear, so polar compound would be X2, X equals halogens or could be HX could be RX could be RCOX etc, these are polar A-B non polar A-B would be hydrogen silyl hydride various silyl hydride Tin hydride and simple alkaline so on.

A-B bond can be written in oxygen during oxidative addition or if it is a carbonyl of or it is an olefin or if it is an alkyne etc, so three different classes of A-B is possible A-B could be polar, non-polar or A-B could be the one where after oxidative additions still A and B bond will be retained in the polar and non polar example we have seen that the bond between A and B will be broken.

But in these case atleast one bond will be retained, again the polar are X_2 HX RX or RCOX acetyl, chloride and so on, hydrogen Si-H, Sn-H, R-H all these are non polar and you can see oxygen or carbonyl spaces, olefin or alkyne if you are having oxidative addition then A and B bond will be retain now there are three common path ways by which oxidative addition can occur three different path which let me write them down.

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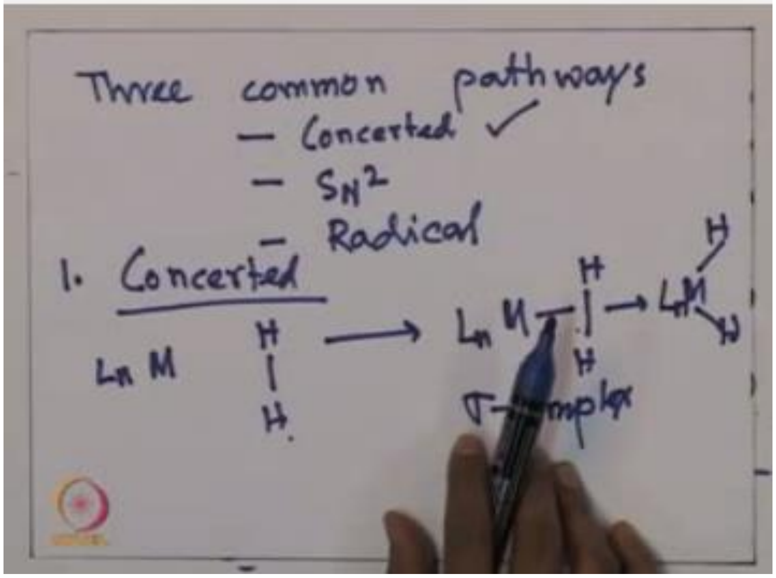

Three common pathways

- Concerted ✓
- S_N2
- Radical

1. Concerted

Three common path ways we see for oxidative addition what are this one could be concerted and another could SN2 of course the final one could be radical one right, three different path ways exist let us take an example or the first example we would like to discuss is the concerted one concerted path way so today’s class slowly will discuss this different mode of oxidative addition the first one is the concerted one now you can take one second a generic example L_n M reacting with hydrogen.

To give you first a L_n M σ complex with hydrogen finally it will gives raise to L_n M H H so oxidative addition into hydrogen is happening you will see the bond between the two hydrogen atom is broken in the final complex intermediate will be a σ complex now would like to discuss one of them real example rather than defining or keeping the M as one of the non variant.

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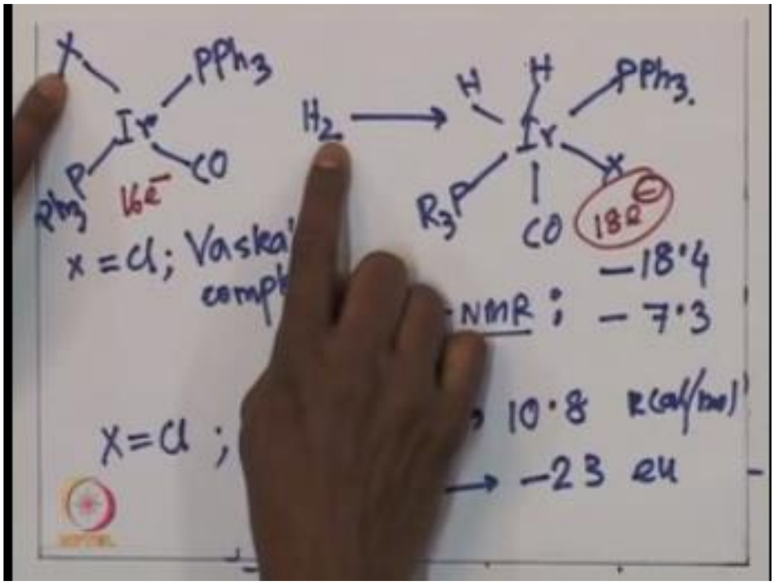

Let us discuss this complex iridium complex I think you are quite familiar with this complex iridium triphenylphosphine carbonyl allied now if it is x = chloro I think you might will know this complex and that is known as Vaska’s complex now this Vaska’s complex if x = chloro can react with hydrogen okay overall it can give you from a Itra complex to a exha coordinated complex right so what we see here is this is iridium triphenylphosphine complex reacts with hydrogen to give you the hydrogen, hydrogen bond broken species that is now it is a hydrate how can you prove that it is a hydrate.

If you take the 1H Nm of this complex you will see two picks 1 – 18.4 PPM another case at – 7.3 PPM thereby this is again showing that this is a hydrate in hydride c in nature this hydrogen and hydride in nature and if you have x = chloro that is again the Vaska’s complex ΔH for this reaction is found to be 10.8 K cal/mol and ΔS double diagonal for this reaction will be – 23 again this is conforming the fact at this 16 electron.

Vaska’s complex undergoing an associative mechanism to give you this 18 electron complex final complex further how can you prove that these Vaska’s complex or Vaska’s type of complex where x is varying x=chloro in Vaska's complex is really the one which is giving you the oxidative addition in a way you are looking at in here.

To figure that out what you can do is you can vary the x, x could be your ido bromochloro extra, should an electronic properties of x will change and thereby you will see the relative rate of this Iridium complex with respect to the hydrogen whether x=ido what is the rate of the relative rate of the reaction to bromo to chloro what is the relative rate of the reactions now in order to do that you can design the experiment where x is varying.

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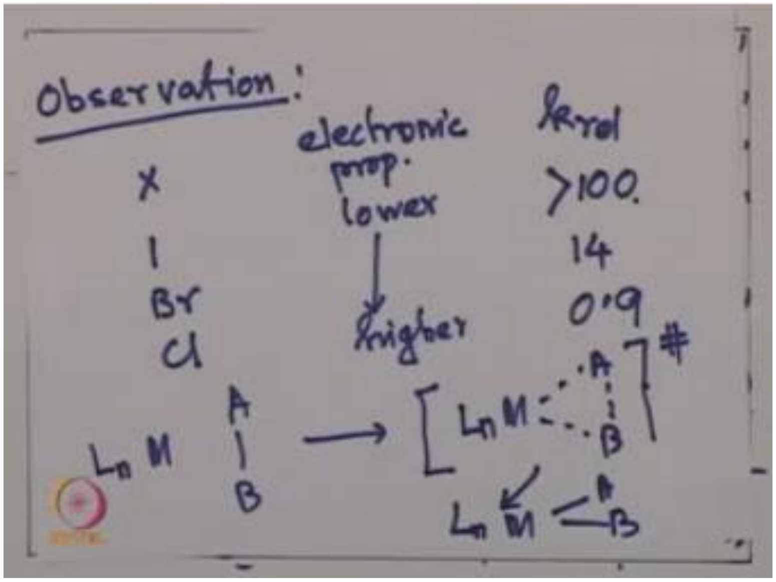

Observation:

x	electronic prop.	krel
I	lower	>100.
Br		14
Cl	higher	0.9

Observation wise experimental observation wise you can see when x equals ido bromo or chloro of course electronic properties or electronic properties you can see that it is lower in this case this is higher for chloride and the relative rate or relative reaction rate is great with respect to ido and bromo is little bit slower and chloride is the slowest one. What it is telling you is the Vaska's complex that is the cholor complex will react with hydrogen the slowest and the x when it is ido it will be the fastest reaction, right.

Now again we will get back to this concept of L_n M reacting with AB in this case it was hydrogen. If it is undergoing this interaction the transition state you will find is something like this from which you will get L_n M AB formation, now if this intermediate or the transition state is not really a cationic or ionic in nature then you would expect that solvent polarity will have little effect on the rate of the reaction.

For the consorted reaction the type of reaction we have drawn over here is a consorted one for consorted reaction this transition state will have little effect or little bearing on the solvent polarity. So if you change the solvent from polar to non polar your reaction rate will not vary too much in case of a consorted mechanism, so this is one way to determine whether a reaction is undergoing a consorted reaction or not to probe that once again you can change the solvent if the reaction rate is not varying too much that will indicate that the oxidative addition is undergoing a consorted mechanism.

Of course the mechanism you cannot proof it can suggest only you have to do other implements to further prove ant mechanism now let us try to take an example where in the plash case we have seen a 16 electron complex is you are staring material you see an association of hydrogen with the 16 electron complex so hydrogen is coming and guess thing associated with your worst cage complex or the 16 electron complex iridium complex.

Now what happens when you have an 18n electron complex can you have a consorted mechanism for an 18 electron complex and what would be one of the example let us try to give one of the example oxidative addition.

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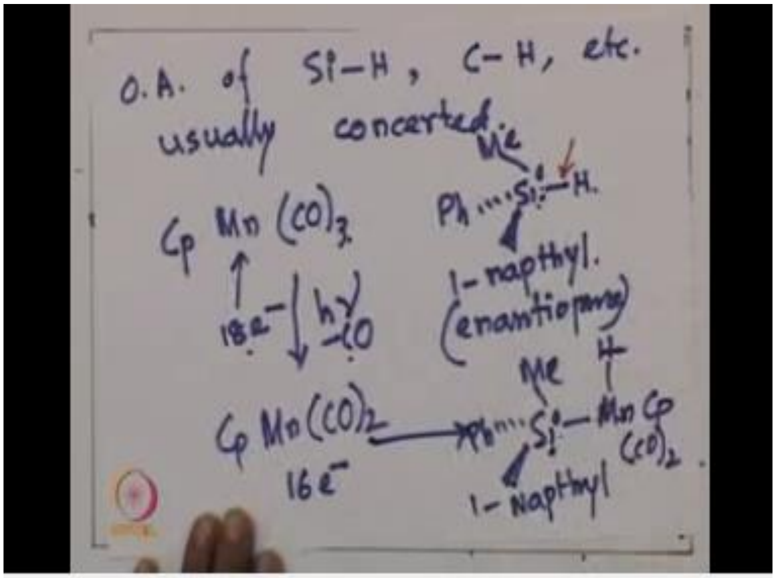
O.A. of Si–H, C–H, etc.
usually concerted.

Which you can write down as O A of different Silyl hydride different Halkan etc usually can undergo concerted mechanism one let us take example of a Mn complex (CO) try canonical Mn complex this is once again an 18 electron complex we would like to react this with the silyl hydride a idyll one I will come in a movement let us say this is the Kidul silyl hydride enantio pure, now this 18 electron Mn complex we would like to react with this silyl hydride.

Of course you know if you want to directly do oxidative addition into the silyl hydride bond then the complex you will get is 20 electrons which is unfavorable, the first step then for would like to do is would like to treat this with light we can expect and elimination of CO to give us Cp Mn Co spaces from it is trace carbonyl spaces we now have a di-carbonyl spaces okay from an 18 electron complex we now have a 16 electron complex which can then undergo oxidative addition in to this silyl hydride bond to eventually give us this silyl complex where you will get the silyl metal bond formation.

With the hydride being there and Cp CO so we have manganese complex with cyclopentadiene two carbonyl one carbonyl went out during treatment with light and now thus manganese is instated in between the silyl and hydride bond okay. So we have manganese hydride complex with silyl bond with manganese most importantly what you will see is they are it is undergoing a retention of configuration the final complex will retain the stereo chemistry of the starting silyl hydride. So consorted mechanism in this case a manganese complex which is an 18 electron complex reacting with sililie hydride, enhance a pure sililie hydride, to give finally the $18e^-$ complex, it doesn't react via associated path, rather it undergoes dissociative mechanism, where the starting manganese complex, looses one of the carbon monoxide, during treatment of light, to give you manganese di-carbonyl cyclo penta dyne species.

Which then react with sililie hydride, to give you sililie hydride oxidative intermediate with manganese, where we have the final complex once again manganese with cyclo penta dyne, two carbonyl, one hydride and one sililie point, most importantly this oxidative addition complex retain the stereo chemistry, of the starting material.

So stereo chemistry can be retain during the oxidative addition, if it is undergoing a consorted mechanism, will come to the other example which are Sn2 in nature, or radical in nature, then in those cases we able to see what happen with the stereo chemistry of the AB that is the organic species square we will undergo, the oxidative addition.

Now as you see there is one example we have shown, how light can be used to remove carbon monoxide, so the un saturation or the coordinative un saturation is promoted by shining light on the metal complex, so the un saturation was not there in to the organ metallic spaces, un saturation is created by the mean of an extra ordinal shows in this cases light, is it possible to create this coordinative un saturation, to the metal complex by the other means, answer is yes! It is possible we can have various approaches or various chemical reactions for these cases, for example.

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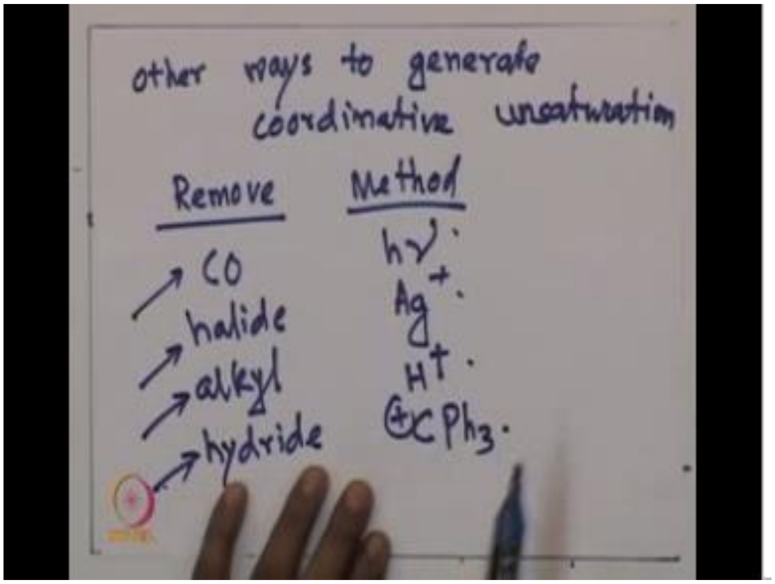

other ways to generate
coordinative unsaturation

Remove	Method
CO	$h\nu$
halide	Ag^+
alkyl	H^+
hydride	$^{\oplus}CPh_3$

If you want to remove various other, groups, then we can have various other ways to generate coordinative un saturation, okay. For example you have seen if you want to remove carbon monoxide, the method you are using is light, if you want to use or halide you can of course use the famous silvers cat-ion.

If you want to remove alkyl, you can use proton, if you want to remove hydride you can use this one, right so there are four different ways for example, of course there are many more clearly you can removed a particular group from an organ metallic intermediate.

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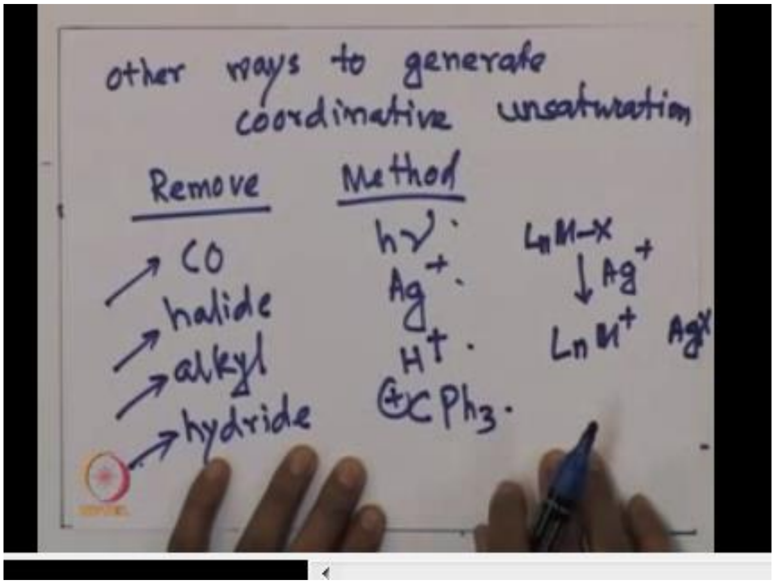

other ways to generate coordinative unsaturation

Remove	Method
CO	$h\nu$
halide	Ag^+
alkyl	H^+
hydride	$^{\oplus}CPh_3$

$$L_nM{-}X \xrightarrow{Ag^+} L_nM^+ \; AgX$$

These are the usual practices. For example, if you have, you know I think it is very clear if you have LnM-x, you can react with silver + to get LnM+ and silver alloy and ore, okay. So what we have seen so far is a concerted mechanism and these concerted mechanisms have seen, one example each of 16 electron complex and 18 electron complex. How that AB the organic species is undergoing oxidative addition with 16 electron and 18 electron complex?

Next briefly will discuss, S_N2 mechanism of oxidative addition, of course will discuss both V and radical mechanism. Today in next five minutes also, I will they to briefly discuss S_N2 mechanism, will come back to the topic again in the next class, S_N2 mechanism as you would know, the elegant metal of complex can react with A and your B in a way, w have n traditional organic reaction of S_N2 type to give you Ln M-A, which is now an n electronic complex.

Let say, it was also an n electron complex, of course you are having B-generated from this species, n electron complex undergoing reaction with A,B in S_N2 fashion, where Ln M-A bonding did form and B- comes out, finally you can have overall LnMAB and A complex. So A, B is now incorporated with the metal to give you n+2 electron complex, the first step as you see n electron complex will form the n electron complex. Now we have interaction with M and A, then eventually this B- will coordinate with M to give you Ln M BA complex which is now n+2 electron complex.

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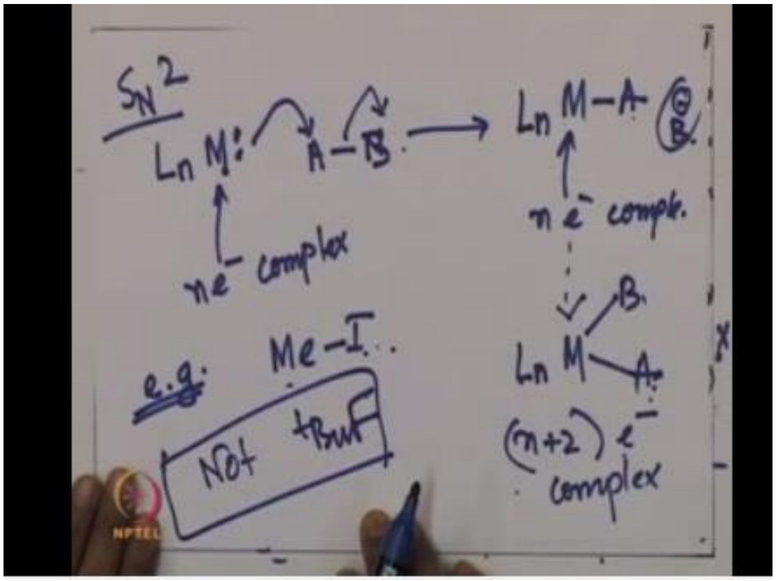

So you can imagine, that such examples will be easy with something like methyl with iodine, If A and B is methyl and iodide, respectively or methyl iodide will have such oxidative addition where S_N2 reaction mechanism will be followed. Of course you know, if you have tertiary butyl fluoride, these will not undergo the S_N2 mechanism.

Well in the next class will discuss much more about the S_N2 reaction, their reactivity pattern will give you the organometallic complex, the real complex in their example and discuss the mechanism of S_N2 complex, will also discuss in the next class the concerted mechanism or just S_N2 mechanism and radical mechanism, once again the oxidative addition can be of three different type, concerted, the one which w discussed today, S_N2, which we were discussing right now and will continue in the next class. Again in the next class will try to discuss the radical mechanism for oxidative addition reactions. Okay, see you in the next one, till then bye, bye.

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