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Organometallic Chemistry-I

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Module No. 1

Lecture No. 5

OXIDATIVE ADDITION
[2. SN2 MECHANISM]

Hello everyone today we will discuss oxidative addition and in particular SN2 mechanism in the last class we have finished oxidative addition concerted mechanism and we started discussing just little bit on SN2 mechanism let us get into the details of SN2 mechanism today SN2 mechanism involves the nucleophilic attack on the substrate right in the organic chemistry also

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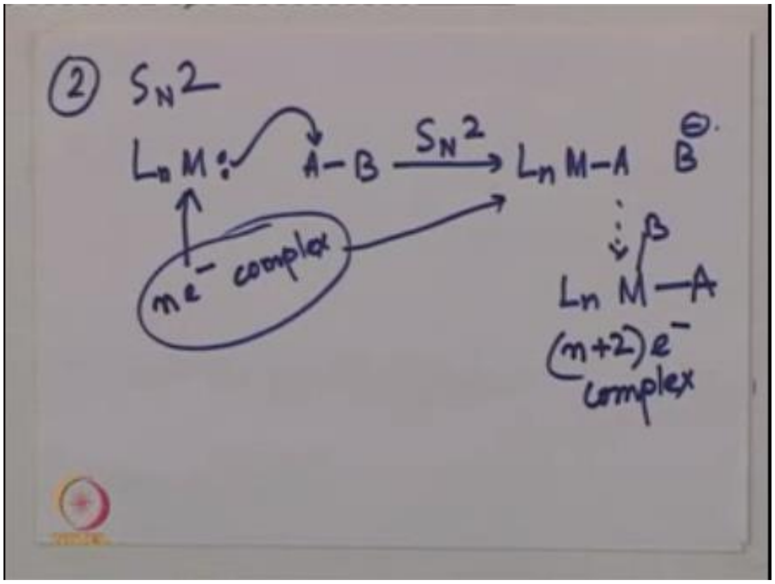

We do see that ligand metal complex will attack the substrate AB where metal lone pair or negative charge will attack on the A and B overall you will get a LnM A complex and the B- will be sitting around now next step obviously will be recombination or combination of D with the metal to give rise to LnM AB this is the one which we are calling the oxidative addition complex now the starting material LnM if it is n electron species n electron complex the same will be true for the LnM A complex it will be all Ln M electron complex finally we will get n+ 2electron complex.

So up on oxidative addition total electron count will go up by2 so if the 16 electron species we are seeing then upon oxidative addition the complex will have 18 electron count often we do see let us say palladium catalysis where palladium is in let us say 14 or16 electron count after oxidative addition with Aaron halide we are going to have 18 electron count for the oxidative addition complex the famous substrate.

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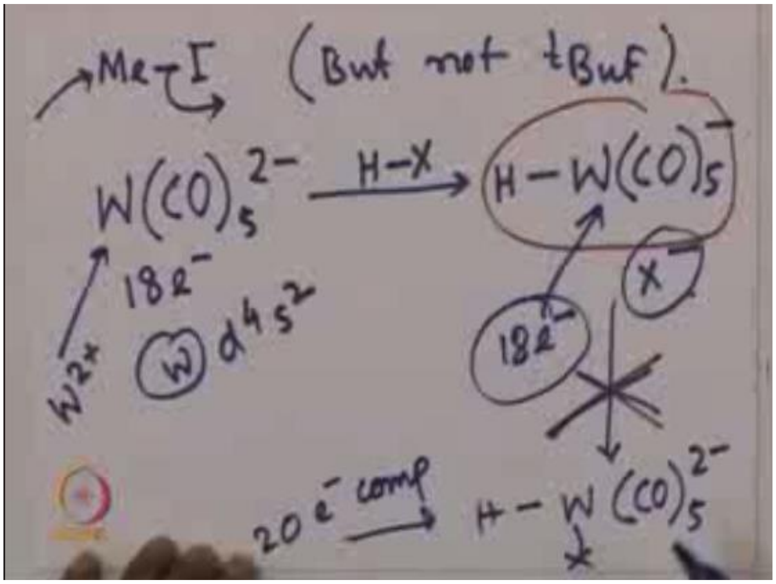

Which usually people discuss for oxidative addition is methyl iodide of course methyl iodide you can have nucleophilic attack on the CH$_3$ group and the iodide can go out you cannot do such thing with let us say tertiary butyl fluoride the SN2 reaction will not be feasible now if we would like to discuss one of the complex we will be discussing1,2 such cases one of the complex let us say tungsten complex tungsten pentacarbonyl die and ionic species it is having 18 electron count all of you are familiar by now about the electron count.

So this is the 18 electron species tungsten is in +2 oxidation state tungsten electronic configuration is D4 tungsten is D4 s^2 electronic configuration now the total electron count becomes 18 electron if you are adding H-x to this tungsten pentacarbonyl die and ionic species overall will have H protonation of this basically H-W(CO)$^-$ now you will have X- going out of this right.

Now in this case we are still having 18 electron complex as we are trying to discuss while the nucleophilic attack is happening both the starting material and the species generated upon nucleophilic attack will have the same electron count then the recombination of the anion will give rise to the you know increase of electron count multiplied plus 2.

In this case since it is already 18 electron count will not see the recombination or the combination of x minus with tungsten this process will not be feasible so we will have overall the final species as this one as the final spaces, right. So the final species one may expect as this one but this one is not going to happen because it is going to be 20 electron complexes, so tungsten tetra carbonyl species di-anionic species upon oxidative addition of HX.

Will overall see a protonation of the of the Penta carbonyl species to give it H-W(CO)$_5$ minus the X minus will not combined with the tungsten so therefore will not get the 20 electron complex finally we will get the 18 electron complain. Now we will try to discuss another complex for its oxidative addition, famous complex is the Vasquez complex right it is a iridium complex we have discussed I guess previously also the Vasquez complex is the Iridium complex.

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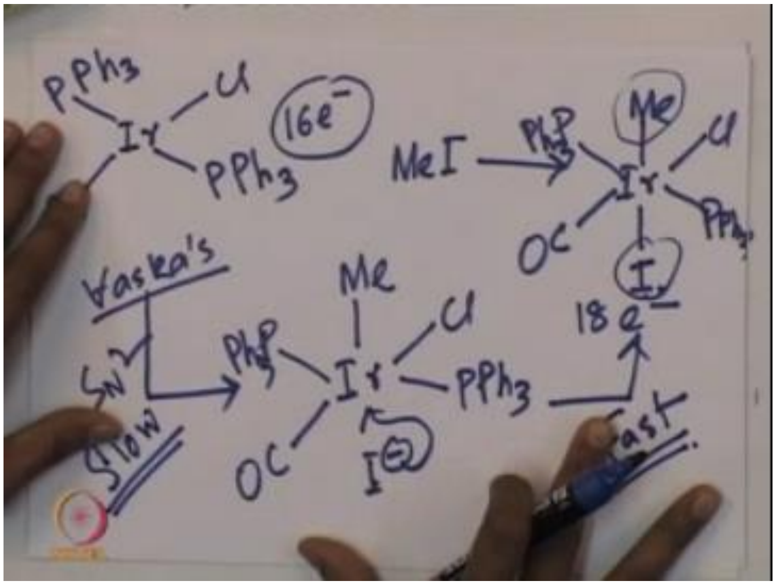

It is a trans geometry for let us say PPH$_3$ if you are drawing or you can write as PR$_3$ with the chloro and the carbonyl species this is called as Vasquez complex, okay. Now if you do the electron count for this species you will find that it is a 16 electron species, now if we are having methyl iodide addition with it the species that we are going to get is iridium methyl iodide addition complex.

Now this piece is overall will have again 18 electron count for the species now the Vasquez complex which is a 16 electron species reacting with methyl iodide to give the 18 electron species few things are to be noted first of all this is you can see the trans addition type of thing where methyl is on the transude of the iodine, right but usually for concerted mechanism we have previously seen.

For concerted mechanism we can have first the Seas addition but for SMT reaction as you know backside attack is favorable we will usually get a trans addition complex in this case the Vasquez complex which is a 16 electron complex undergoing oxidative addition with methyl iodide to give the18 electron complex where methyl and iodide are trans to each other, if we try to analyze this reaction little bit in detail.

We will see of course the first form intermediate will be the one where methyl is attached with the Iridium complex iodide is a anion counter anion rather and we have overall a five-coordinate and complex as an intermediate, this complex will then bind with the iridium that iodide will then bind with the Iridium to give the final 18 electron complex.

Now the first step which is the attack of methyl iodide this is the one which is the slow step and this is where it is the SN^2 reaction the second step where iodide is combining with the metal centre this is the one that is going to be the first one so traditional SN^2 type of reaction mechanism will follow and if you follow that reaction kinetics for this reaction you will get a reproducible kinetics for this reaction, reaction of baskin complex with methyl iodide will get reproducible kinetics data that invariably means that we are not having a radical mechanism right so the experimental observation for these reactions include.

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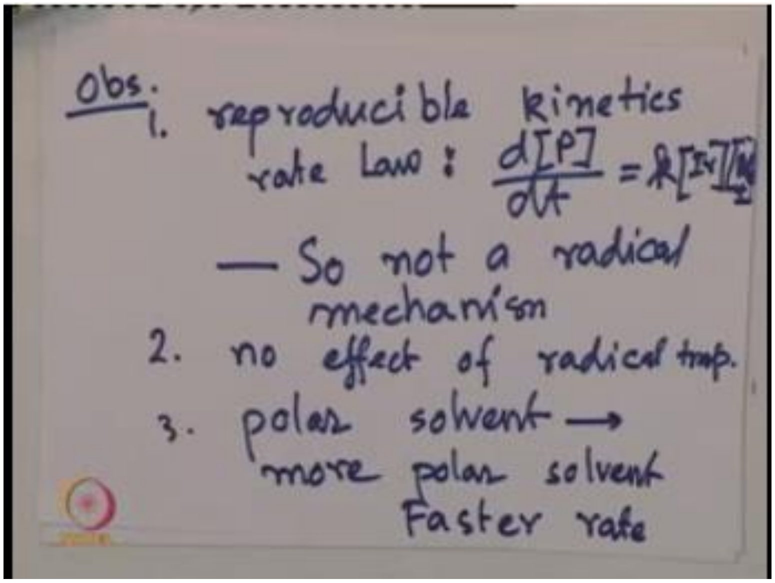

Obs.

1. reproducible kinetics
   rate law : $\frac{d[P]}{dt} = k[Ir][$
   — So not a radical mechanism
2. no effect of radical trap.
3. polar solvent →
   more polar solvent
   Faster rate

First of all as I told it is reproducible kinetics reproducible kinetics means, if you keep on doing the kinetic studies the data will be reliable and it will not differ too much the rate law for these reactions will be essentially the product formation by DTDP DT will be at constant times iridium complex and methyl iodide complex. So it will be first order with respect to iridium and first order with respect to the methyl iodide this confirms that this is not a radical mechanism that is essential to understand that it is not a radical mechanism and the rate, rate law will follow first order with respect to the iridium complex and first order with respect to methyl iodide essentially.

Since it is not a radical mechanism the other way to prove this is to add various radical traps for this reaction you know there are plenty of radical traps available depending on the reaction condition we can we can discuss about the different radical traps but essentially no matter what radical trap you use you will see that the you know the reaction is not getting stopped so radical trap will not have any effect on the reaction rate again verifying that it is not a radical mechanism for, for the reaction so no effect of radical trap now as you have seen the reaction intermediate involves the attack off of methyl iodide or attack on methyl iodide to give a cationic and ionic species.

Therefore if you take a polar solvent you will see a lot of solvent effect if you change the solvent from polar to non-polar the reaction rate variation you will be able to say so polar solvent will end up effective effect the reaction condition as you see for the concerted reaction the solvent will not have much effect overall in the reaction rate but in this case we will see that the polar solvent will have strong effect on the reaction outcome or so to speak the rate of the reaction.

So polar solvent will we can add as an observation polar solvent we can we can have a lot of reaction effect by polar solvent more polar solvent, more polar solvent that means we will have further faster rate, more polar solvent will have faster rate. Of course another feature of this reaction will be that the intermediate species which where methyl iodide is getting adapt that species is going to be the one where we can see that it is a kinetically fable favored product.

Once again it is confirming that it is not a radical mechanism and not definitely a concerted mechanism if it was a concerted mechanism that you know the first form intermediate will not be seen there by this SN2 reaction these observation can rule out the formation of a concerted mechanism or radical step. So once again just to repeat what we usually expect for SN2 reaction is it is a first order with respect to both the component that means the organo metallic species and the methyl iodide in the inch case and the first form intermediate is the one which is the kinetically favored pathway or kinetically favored intermediate that involves the slowest step the first step is going to be the slowest step.

Second step is going to be the faster one and therefore we will see overall the oxidative addition of methyl iodide from 16 electron complex to 18 electron complex. The kinetics is completely reproducible that tells us that it is not a radical mechanism if we add various radical traps for this reaction we will not see any effect. Since the reaction involves a polar intermediate we can expect the polar solvent various polar solvent like DMF DMA so we can take and polar solvent will have great effect on this reaction, more polar the solvent will get a faster rate.

Of course you know then as the research progresses we have to design the reaction to probe the nature of this reaction thereby in the Vaska’s complex if we are not having triphenylphosphine if we take simple PR_3 and then the R group of the PR_3 is varied we can then perhaps get more idea about the reaction specifically the mechanism of the reaction.

Let us see take one systematic example of such PR_3 groups on the Vaska's complex and see how the reaction varies or how the relative rate varies when R is varying. We will draw the Vaska's complex again that is again your iridium complex.

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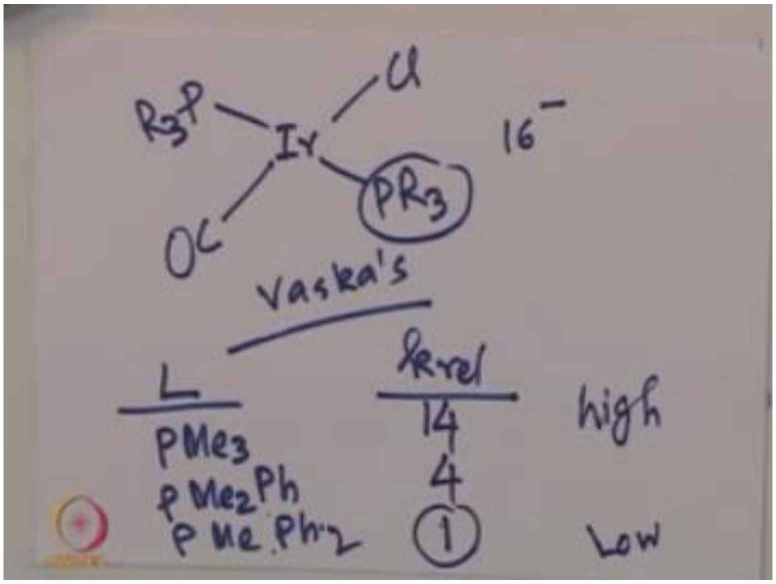

L	k_{rel}	
PMe_3	14	high
$P Me_2 Ph$	4	
$P Me Ph_2$	①	Low

In this case we are not defining the R it is PR_3 this is CO chloride again 16 electron complex this is Vaska's complex, if we have ligand so this PR_3 ligand and various ligand such as PMe_3 PMe_2Ph, $Pmeph_2$ and if we measure the relative rate,okay, in this case what we can expect and this is what usually researcher looks at as a problem to solve or to get more idea we can prove different are and try to gather information about the reaction. Now since it is a nucleophilic attack you would agree with me that if we increase the electron density on the metal center without crowding the metal center too much then the nucleophilic attack on the methyl iodide will be expedient it will be faster right.

Now these three different ligands we have taken one is tri methyl phosphine one is dim ethyl phenyl phosphine another is methyl di-phenyl phosphate if you just measure the relative reaction rate no need to go for the absolute one we will see that the relative reaction rate will be the fastest when we have tri methyl phosphate because tri methyl phosphine is the smallest one and the most electron rich one therefore electron density on the tri methyl phosphine will be the maximum out of these three ligands and also try methyl fasting is least bulky.

So the nucleophilic attack will be preferred by the Iridium complex in caves of tri methyl phosphine and the kinetic study will show that the pme3 kinetics data is the maximum if you just put one to pull the value for example we are discussing about p me3 p me2ph and p me.ph if you set the last one as one will get this is the highest 14 and these are again relative value so from top to bottom will get that it is high value to low value this value once again can be explained by the by the size of the ligand and also by the electron richness of the ligand.

In this case tri methyl phosphine is the smallest in size and also most electron rich and therefore the relative rate constant is the highest in case of tri methyl phosphine step, now in terms of oxidative addition some time what we see is the oxidative the addition can be made faster by adding a number of additives if you look at the research papers often we do see that you know the researcher are using a number of additives sometime you know from distance we may not be able to judge the proper reason behind adding a particular additive.

Sometime you say molecular shapes some time you see let us say in these cases they will add potassium iodide or any other iodide source when oxidative addition is going on with let us say methyl iodide they will add potassium iodide as an additive but our the researcher just adding this for fun or there is a scientific ground scientific explanation or observation behind this so this is what we are going to discuss next and that is what is called Anion accelerated oxidative addition.

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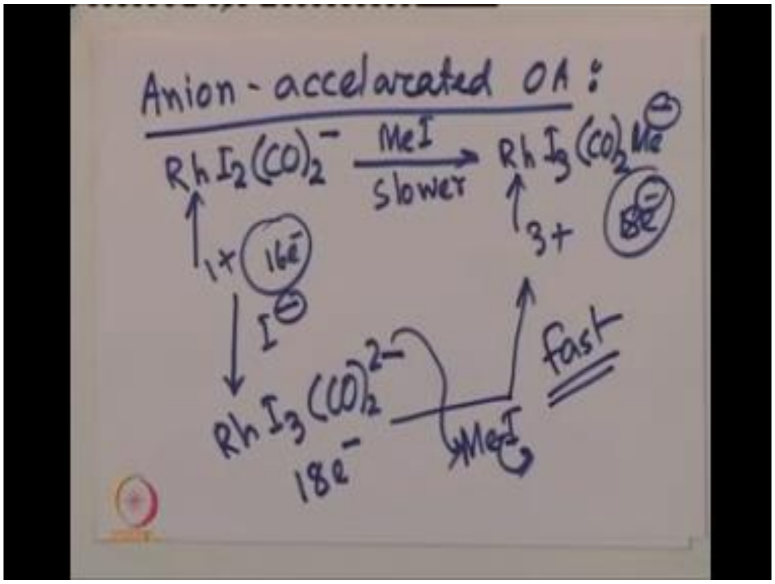

It is a part of oxidative addition, it is called anion accelerated, oxidative addition. Now if you take the rhodium complex di-hydro complex, di-hydro carbonyl complex, you want to do the addition with methyl iodide. You will get a very slow reaction, to get the oxidative addition RhI_3 (CO_2) me^- right.

Now the starting complex rhodium is 1+, as you know the final complex it will have 3 +, now the first complex is 16 electron complex, of course the first complex starting complex is 16 e^- complex, and the final complex is going to be the18 e^- complex, now this is a slow reaction indeed a very slow reaction, how can you make it fast? If you look at the literature if you look at the research papers, they have done is very simply added some iodide shows with it.

If you add the iodide shows immediately what will get is the, first form intermediate that is rhodium I_3 CO_2 $^{2-}$, now this is what is going to be the 18 e^- complex, now essentially what we are trying to do is? In addition to methyl iodide we are adding let us say potassium iodide with it, or sodium iodide with it any iodide salt can be added with methyl iodide, and in this particular case a slow reaction can be accelerated.

If we add an iodine source, iodine salt will get fast a I_{32-} complex rhodium I_3 di carbonyl 2- complex, now that species is going to be much more nucleophilic compared to the starting 1 minus basis, with that species if we now have methyl iodide since we have methyl iodide and is iodide salt together, after formation of that to minus species that are RHI_3 species will then attack on methyl iodide quite faster.

This species will add two methyl iodide quite faster, to give the product formation so overall if we see simply methyl iodide will give a slower reaction, by addition of iodide I minus will get a very fast reaction, this is what is usually known as a non accelerated oxidative addition, we do not need to add the iodide salt in large quantity.

A catalytic amount of iodide salt will be good enough, because we are having catalytic amount of iodide salt and methyl iodide let us say instoichiometric amount, therefore the iodide that is coming out from methyl iodide, will be acting as a next catalyst okay, that is why initiation of the action is important with a salt iodide salt, but once the reaction is initiated methyl iodide, iodide from methyl iodide will take care of the reaction and the reaction will be going very fast.

So what we have learnt today is a SN2 to mechanism of oxidative addition, we have seen the protonation first and then we have seen the Vasquez complex where the iridium complex we have discussed, is going undergoing oxidative addition with methyl iodide to give the species or the final product in the trans geometry methyl is trans to the iodide.

And we have seen the characteristic of an SN2 reaction which is distinct from radical mechanism and the concerted mechanism, we have subsequently discussed the oxidative addition, one example where the reaction itself is not fast enough it is rather very sluggish methyl iodide in addition, if we have some other iodide salt such as potassium iodide or sodium iodide, pinch of it catalytic amount we can make that reaction faster, because it forms an intermediate species which is more nucleophilic in nature by virtue of having more charge density or more charge on the organic intermediate.

Now this is the species which is the doubly charged intermediate or more negatively charged intermediate will then undergo SN2 reaction on methyl iodide this is what is known as an ion accelerated oxidative addition. So today we will conclude over here the oxidative addition of SN2 reaction in the next class we will discuss oxidative addition by radical mechanism. Thank you, keep studying and of course please study from standard textbook as we have mentioned at the beginning of the class, okay bye-bye

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