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Organometallic Chemistry-I

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Module No. 1

Lecture No. 2

COUNTING OF ELECTRONS

Today we will try to focus on mainly there are 18 electron count rules, and then some of those oxidative addition, reductive elimination if possible we will try to discuss in detail. Before getting into the organometallic chemistry codes I expect all of you to have some background specifically you are expected to read about structure and bonding, also you should have some sort of understanding of counting electrons.

I will briefly go through the counting electrons, well first of all organometallic chemistry is a domain it is a huge domain right at this point anything that metal is having electronegative carbon attached with it, then usually it is called organometallic complex. The essential part of the organometallic chemistry is one must have a metal and then we should have a metal carbon bond with it. Now in order to count the electrons of an organometallic complex we usually follows two method.

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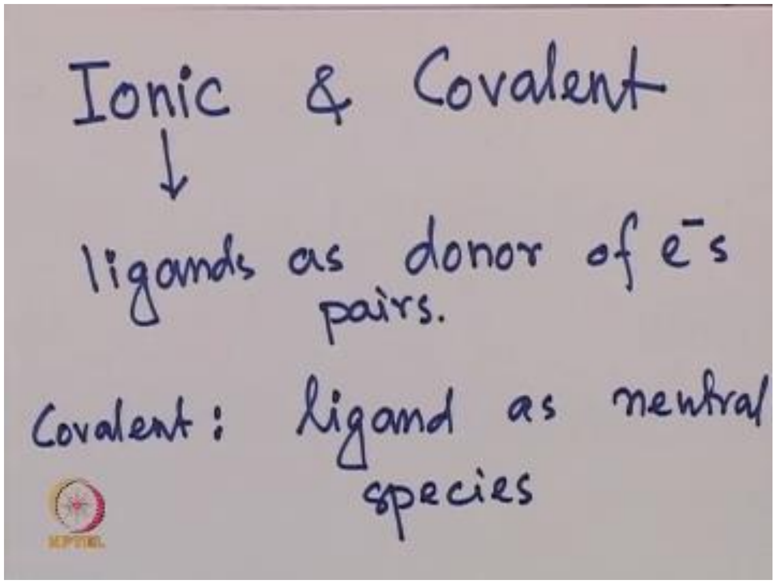

One is ionic and another is the covalent method. In the ionic method we considered ligands as donor of electrons, and in covalent method we consider ligand as neutral species right. Now for example, if we have a metal ligand complex M-L.

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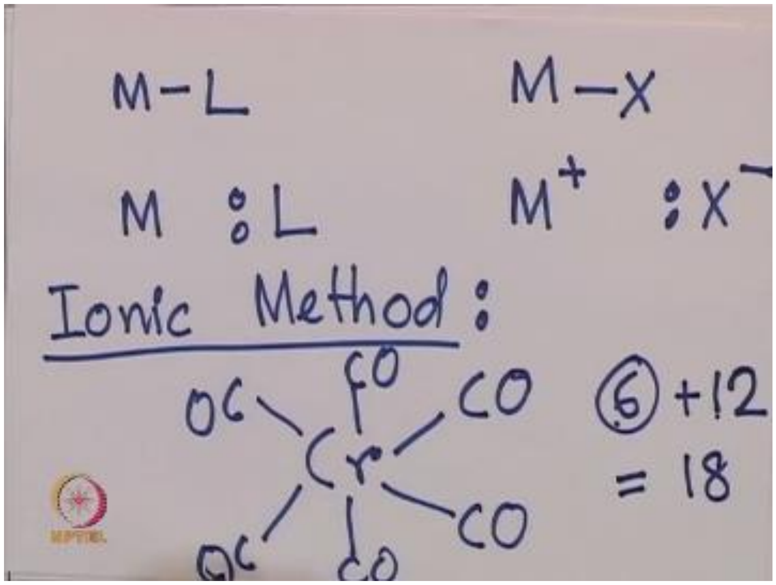

M-L for covalent method we will be considering metal and ligand in this configuration. For example, if we have M-X for ionic method we will be considering M^+ and X^-. Now let us take one example and try to discuss the electron count of it. For the simplicity purpose I will be discussing mainly the ionic method and that electron count of the ionic method. So covalent method those of you who are familiar with and are comfortable with that there is nothing wrong with it you can follow the covalent method as well.

Mainly I will try to have the ionic method as the discussion board for the electron count because that makes things little bit easier. For example, we have chromium complex, chromium hexa carbonyl complex, so it is going to be an octahedral complex as all of you know, it is an octahedral complex. Now if you see in the periodic table scandium, titanium, vanadium, chromium it would be 6 electron for chromium and six of the cobalt's are there sorry six of the carbon monoxides are there.

So each of the carbon monoxide is giving two electron so total electron is becoming six plus 12 18. So this is how usually we try to count the electron. For example, as we shown over here chromium hex carbonyl complex, chromium having six electrons and six of the carbon monoxide giving two electrons each therefore we are having six plus 12 total 18 electrons.

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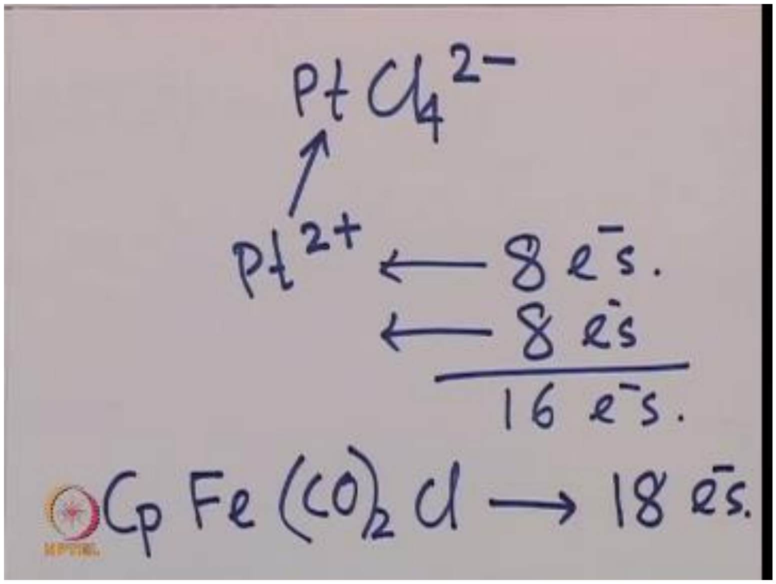

Let us try to take another example Platinum tetrachloride 2^- so the oxidation state of platinum is platinum 2^+ and therefore you can count that electrons of it. So platinum will be, you know OSIRPT osmium, iridium, platinum showed overall 10 electrons. And we will have then therefore on the platinum, platinum 2^+ will be having, you know eight electrons right and four of the chlorine each of them are having two electrons total of eight electrons again.

So overall we will have 16 electrons is that okay, this is what ionic method is where we try to find out the oxidation state of each and every metal involved into the complex. In this case platinum is in + 2 oxidation state each of the chloride will provide two electrons to the complex and thereby we have platinum 2^+ total providing 8 electron into the complex four chloride each giving two electrons into the complex.

So therefore we have another 4 times 2 18 electron overall it is a 16 electrons complex. Similarly something you can work out on your own, cyclopentadienyl, ferrocenyl, dicarbonyl chloride, if you count that electron you will be able to find that it is a 18 electron complex okay, that is something you can try to find out on your own right.

So I think I would expect at this point that you try to take some complex try to count the electrons most often you will get you know 16 or 18 electron complex it is possible to have electron count other than 16 or 18 you just need to count it carefully now let us look at a special case where we do see metal bonding whatever the method you are following either ionic method or coherent method you're expected to add one electron to the electron count and then come up with the total electrons if you are having a metal complex. What is an example of an metal complex let me show you one of them.

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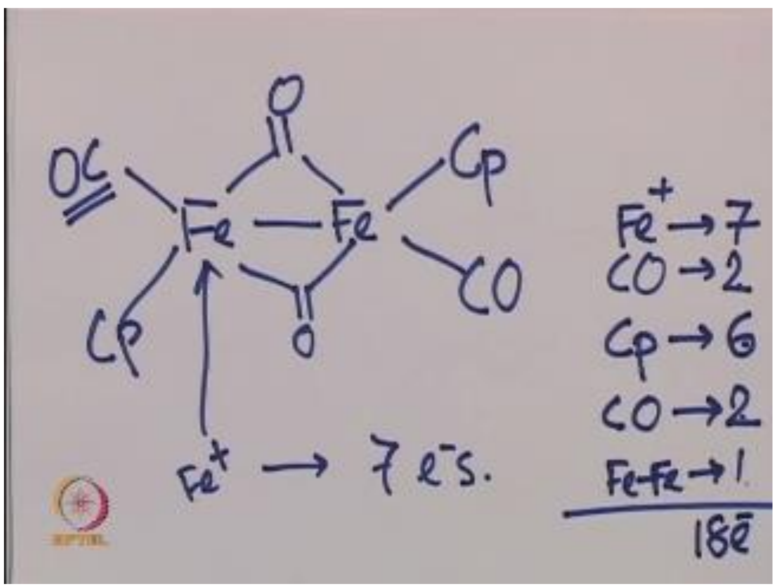

So this is a diagram complex bridged with Cardinal terminal ligands are CP and carbon you say it is a complex where we see that iron is in plus 1 oxidation state right so that electron counts for iron in plus 1 would be totals giving you 7 each 7 electrons right iron electron count for iron atom is B6s2 so total eight electrons RL is in plus 1 oxidation state and therefore we have seven electrons for iron 1 plus now if you look at carbon monoxide it will be giving CO will be giving two electrons as I tried to discuss iron plus seven left one cyclopentadienyl this is in ionic mode so CP minus that means 6 electron bridging carbon monoxide will give you 2 electron and then metal, metal bridge as we say should give you one electron you should count 1electron for metal-metal bond.

Now overall then if you count 7+ 29+6 15 + 2 + 1 so overall you have 18 electrons okay so once again if you had a metal, metal bond in an organometallic complex you are expected to add one electron by either of the ionic method or covalent method let us take another example it is a rhodium complex.

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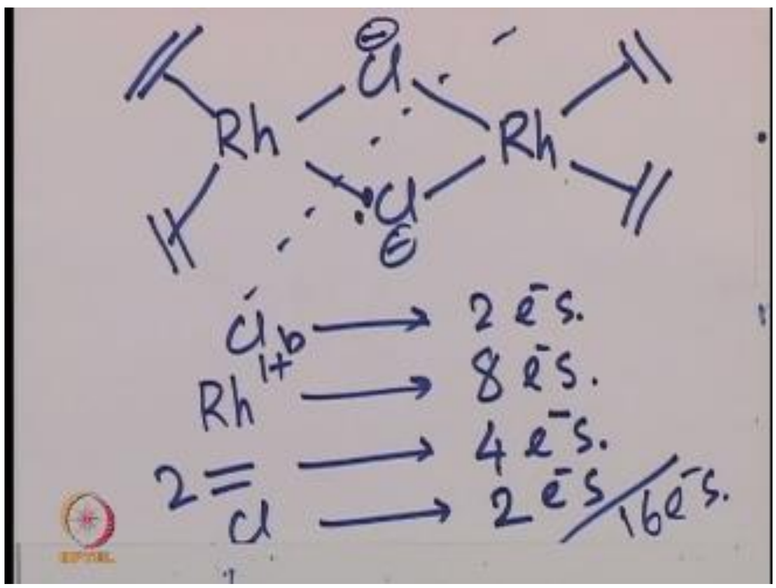

I would like to discuss rhodium chloride bridge complex it is a dinuclear complex terminal ligands are ethylene now if you want you can just you know split the molecule into half what you see is a rhodium 1+ that means it is going to have it is a d7s2 electronic configuration total 9 electrons rhodium 1+ should be giving 8 electrons right everybody got it correct 8 electrons 2 of the ethylene each of them are giving 2 electrons so total of 4 electrons and chloride is giving you 2 electrons one any one of them if you if you pickup.

So it is a 16 electron so far now as you know this bridging chloride both of them in addition of them being in negatively charged they will also give you lone pair to the other rhodium so another two electrons you have to consider for overall electron so bridging electron chloro bridge overall then you will have 10 14 + 2 16 electrons 16 electrons you will have so this complex dirhodium dichloro bridge and diethylene complex where you see that the chloride is the bridging one each chloride are attached with each of those rhodium therefore total electrons coming from two chloride from for any particular rhodium is going to be 2 + s2 total for rhodium is in +1oxidation state that means it is having 8 electrons.

So 8 + 4 from the chloride and 4 from the ethylene overall it is a 16 electron are you all clear with this all right let us move on for the next example now we can have yet another example where we see that.

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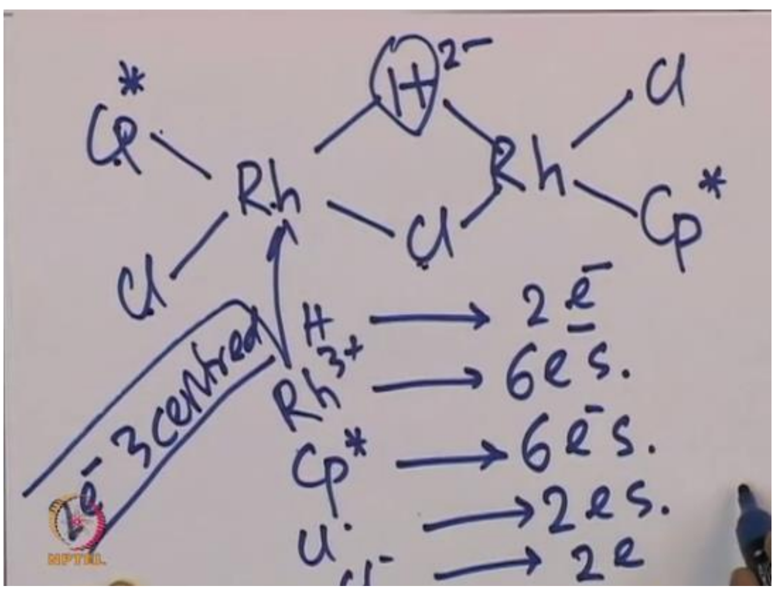

It is a once again it is a rhodium complex dirhodium complex we have hydrogen or hydride and chloride bridged and terminal ligands being chloride and cyclopentadiene now if you try to count that electron for rhodium rhodium here we see that it is rhodium 3+ right now rhodium 3+ will rhodium is d7s2 so total 9 electrons rhodium 3 + will be 6 electrons CP star will again have 6 electrons terminal chloride that will give you 2 electrons now the bridging chloride for each of the rhodium it will give two electrons and the hydride H it will give you 2 electron.

Now this is a special case as you can see the hydride will have overall 2 electron and this is something called 2 electron 3 centered bridging for each of the rhodium then you have to count two electron for the hydride region, so overall for each rhodium we have two electrons from hydride two electrons from chloride so two plus two for another two from this chloride that is 6, 6 from the CP star that is 12 rhodium is three plus that means another 6 electron overall then you have a 18 electron complex.

So I hope it is becoming now clear that the electron count of each of the metal complexes can be done very carefully you can have ionic method or covalent methods for counting that electrons preferably fort his course I will try to stick to the ionic method if any if you are more comfortable with the covalent method there is no problem with it you can follow it as you know in the ionic method will have a Cation and Anion formation.

And in the covalent bond will have a metal and ligand as the ligand two electron donors formation ligand will be deal as a neutral stasis, once again most of the complex you will find will have 18 electron some of them will have 16 electron some rare cases you might will have also 14 electron but whatever it is you should remember few basic thing that it is possible to have a two electron three Center bond that is the last case we have discussed.

Where hydride is bridge between the two rhodium okay, so two electron are shared between the three centers we if there is a metal-metal bond then you have to add one electron more to the total account and otherwise I guess most of the example we have covered so far I expect you to practice on these you know electron count and you should be basically able to count the electron in your almost in your dream and none of the time you should have a wrong calculation because this is going to be very, very effective in terms of discussing the fundamentals of some of the organ metallic chemistry that we will be covering in this course, okay.

Now as we are trying to discuss let us try to see 16 electron complexes and 18 electron complexes and the mode of reaction they undergo, so we will discuss16 electron complexes and 18 electron complexes separately and try to see how they are reacting is the reactivity going to be similar for 16 electron and 18 electron complexes or are they in to differ that is the major question we would like to address.

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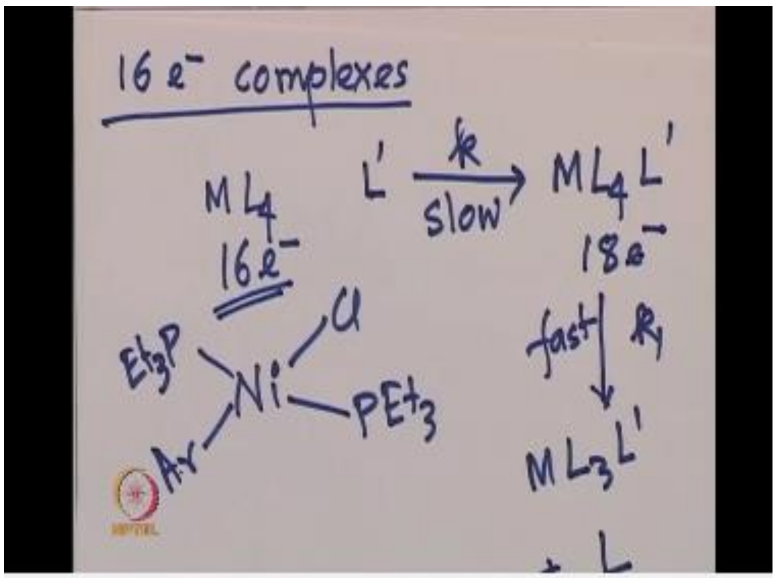

16 electron complex I think a moment ago we have discussed some of them 16 electron complexes, now let us take a simplified example ML_4 and assume that this is 16 electron ligand is each of the ligand are having 2 electron let and you know let us give an example this nickel complex where we have nickel phosphine, aryl fluoride and triethyl phosphine two of them now if you try to count the electron for these complexes.

So what we will find one two three four, four of the ligand that means eight electrons four ligand to each nickel is in plus 2 oxidation state that means it is a eight lecture on count again for it so nickel is d8 s2 total 10 electrons nickel is in plus 2 oxidation state eight electrons total them and ate from the four other ligand total it is a 16 electron complex, usually if it is reacting with another ligand these 16electron complex reacting with another ligand.

And the rate constant is K this is a slow process what we see usually we do see that a 18 electron species formation if L prime is reacting with ML_4 we get ML_4 L prime complex 16 electron complex reacting with two electron donor ligand it is becoming 18 electron complex the next step will be faster it is a first reaction and it will undergo ligand exchange overall will then have ML3 L’ and L will come out of the system.

So a 16 electron complex will undergo associative mechanism this is the one where ligand is getting associated with the 16 electron complex becoming or giving rise to an 18 electron complex this 18 electron complex then will undergo first dissociation you have a ligand exchange and will give rise to ML3 L’along with formation of the ligand L. Now let me give you a practical example that the same one will use the nickel complex,

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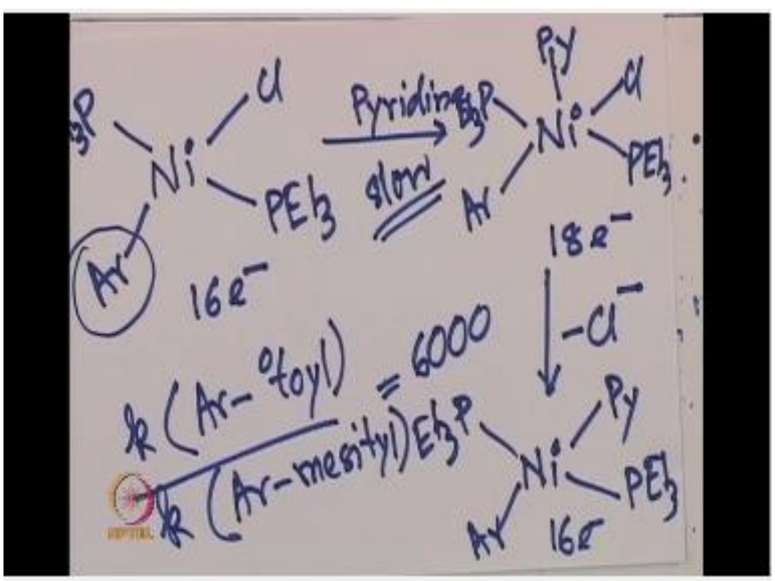

Where we will see that nickel is tetra coordinated, of course it is a square planar complex the same one which we were discussing a moment ago, it is a 16electron complex by now hopefully you will be able to count the electrons very quickly, it reacts with let's a period in, that is the exogenous ligand, overall now from Petra coordinate we have a Penta coordinated nickel complex pyridine is associated with the nickel, along with the other ligand right.

So 16 electron complex going to 18 electron complex, and from here on chloride will come out okay, and we will have a tetra dentate or tetra coordinated nickel complex back, where it will be again square planar, along with formation of the fluoride from the system, just to clarify once again this is a 16 electron complex coming, to give you 18 electron complex while reacting with pyridine, and chloride is coming out from the system to give you back a 16electron complex.
So therefore it is to simplify usually 16 electron complexes, undergo associative mechanism to give you 18 electron intermediate, which will then rapidly be shows here to give you back 16 electron complexes.

Now for this reaction the one we have just discussed where pyridine is exchanging with the chloride, how can of course you can do some experiment to prove that this is what is the trend, now if you are looking at the aryl group, this aryl group if you substitute the aryl in one case if you have if you have toile, okay in another case if you have messy tile, the expected pattern of reactivity or the observed pour pattern of reactivity is aryl if it is toile, such as if it is aryl messy tile, the rate constant varies six thousand times.

So the air I look one when it is toile line that means less technically demanding, that is the one which will react very fast compared to the one with messy tile, which spherically demanding or bulky, and thereby will be preventing the pyridine coordination this is the one which is the slow step, period in coordination will be hindered if this aryl, messy tile one that means ethically demanding one the reaction will be slow.

If the iron is less technically demanding, then this step will be faster and then their pie depending on the aryl whether it is a toile or messy tile, we can have a significant difference in the rate constant and do it constant if you compare the toile one in six thousand times faster compared to the messy tile one.

So a deuce just see these complexes nickel, complexes underwent an associative mechanism we're starting nickel complex one 16 electron, and then the ligand came in give rise to 18 electron complex which then rapidly dissociate to give you the 16 electron complex, overall it is a 16 electron complex undergoing an associative mechanism, to give you an18 electron complex which then dissociates to give you 16 electron compact.

So 16 electron complex starting out resultant is also a 16 electron complex in between you have an 18electron complex.

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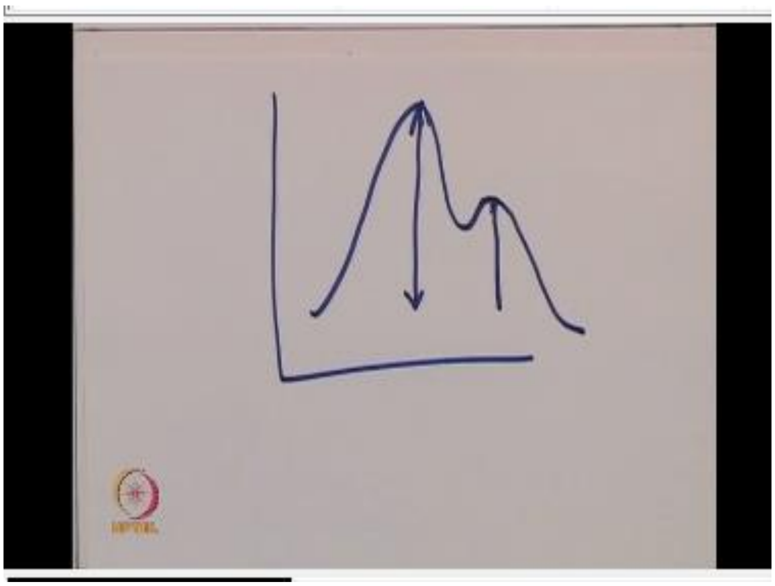

If you try to draw them, you know the energy profile of this reaction it should somewhat looks like, this is the first step which is the slow step, and then the next step is the very first one first one to give you the product okay with this we'll meet again shown in the next class, thank you all and I expect you will be studying on the electron count mainly, and look at the 16electron complexes as well, I hope all of you will be able to do the electron count very easily, so that we can discuss at the same space have a nice one see you bye.

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