Advanced Transition Metal Chemistry
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Lecture - 41
Oxidative Addition and Reductive Elimination Reactions

Hello everyone, it is my pleasure once again to welcome you all to MSB lecture series on transition metal chemistry. This lecture is 41st lecture in the series of 60 lectures. Today I shall discuss about two important reactions which are very, very vital when you want to use coordination compounds or organometallic compounds in homogeneous catalysis for a variety of organic transformations.

If you are a inorganic chemist or if you are an organic chemist, if you are working in an industry. Or if you are planning for doing doctoral research, understanding these two reactions are very important. From that point of view, I shall start discussion on two important reactions, that is oxidative addition and reductive elimination reactions. Let me tell you some general information before, that let me write a general reaction that represents oxidative addition.

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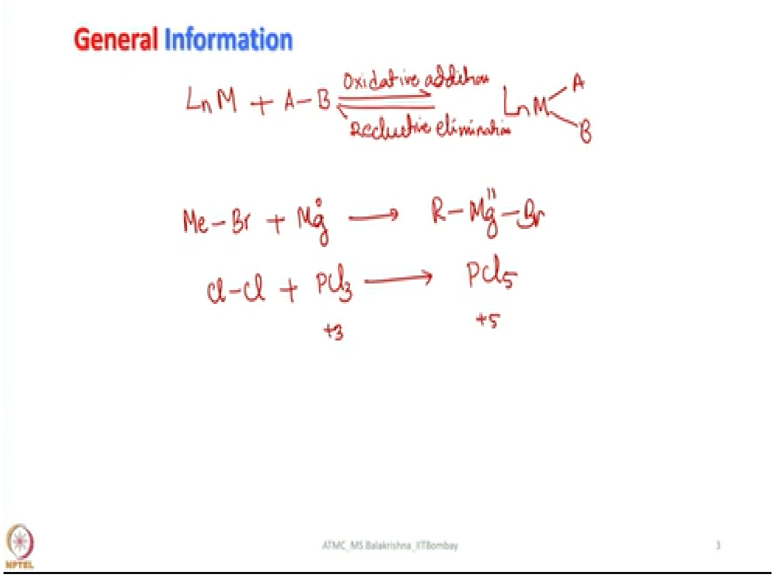

General Information

$$L_nM + A{-}B \underset{\text{Reductive elimination}}{\overset{\text{Oxidative addition}}{\rightleftharpoons}} L_nM\begin{smallmatrix}A\\B\end{smallmatrix}$$

$$Me{-}Br + \overset{0}{Mg} \longrightarrow R{-}\overset{II}{Mg}{-}Br$$

$$Cl{-}Cl + \underset{+3}{PCl_3} \longrightarrow \underset{+5}{PCl_5}$$

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Let us take a typical metal complex. I shall tell you what kind of complex and conditions and all those things later. Let us consider a substrate molecule AB, my interest is to show you oxidative addition reactions which are reversible in nature, at least in some cases. So, if I reverse this reaction that is called reductive elimination. So, that means there should be an equilibrium between oxidative addition reaction and reductive elimination reaction.

And if the rate at which oxidative addition reaction happens to the same extent reductive elimination happens then that is called microscopic reversibility. And we will discuss more about those things as we progress with that one. And now let us consider what kind of metal complexes we should look for. Before we go for that one let us try to recall our understanding of main group chemistry and let us try to recall whether we have come across any similar reactions when we studied main group chemistry.

So, let me write one reaction that you are all familiar with. For example, you take methyl bromide and treat with magnesium what you get is methyl magnesium bromide. So, if you see this one this is a typical oxidative addition reaction magnesium. To begin with the zero oxidation state and it goes to plus two. And another reaction I will show you let us take chlorine and treat with PCl_3 at appropriate reaction condition what we get is PCl_5.

So, again here phosphorus from plus three state to go to plus five state, and its coordination number if you say it was three now it has become five. So, remember these things now that means an element having two accessible oxidation states with a difference of two electrons is a must to perform oxidative addition reaction. Before I write point by point, the conditions, the nature of the ligands, and nature of the metal, let us look into a few more reactions.

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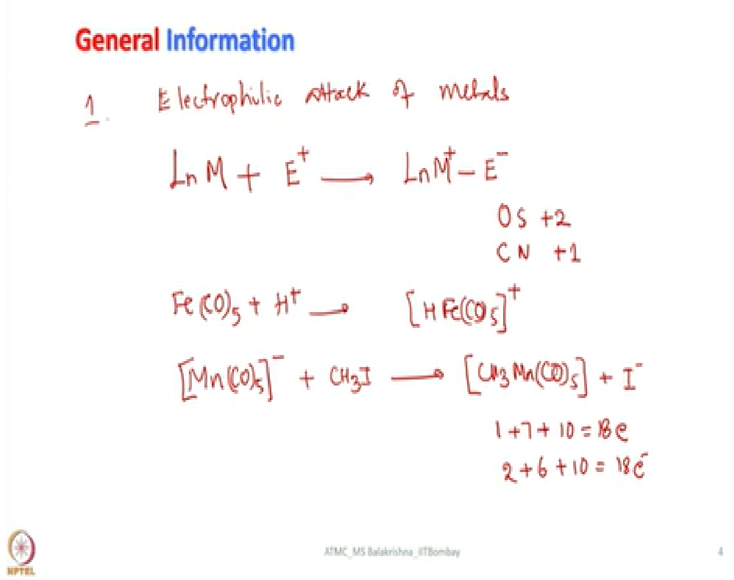

General Information

1. Electrophilic attack of metals

$L_nM + E^+ \longrightarrow L_nM^+-E^-$

OS +2

CN +1

$Fe(CO)_5 + H^+ \longrightarrow [HFe(CO)_5]^+$

$[Mn(CO)_5]^- + CH_3I \longrightarrow [CH_3Mn(CO)_5] + I^-$

$1+7+10 = 18e$

$2+6+10 = 18e^-$

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So, let us consider a general equation here. Ancillary ligands L_n means, we have “n” number of ancillary ligands plus the electrophile comes and then we have a reaction something like this. So, in this also, if you see oxidation state increases by plus two and coordination number increases by plus one in this case. So, this is a typical electrophilic attack of metals.

Another specific example, I will give you, let us consider $Fe(CO)_5$ and treat this one with H^+ what we get is $[HFe(CO)_5]^+$. And then another, one let us consider $[Mn(CO)_5]^-$ and add methyl iodide. So, if you see this one, of course you can also try to write whether it follows eighteen electron rule or not by counting of electrons. So, here let us go with neutral method 1 + 7 + 10 = 18, so eighteen electrons.

If you go by ionic method 2 + 6 (manganese(I)) + 10 = eighteen electrons. So, if you think if it is oxidative addition, why iodide was not added to the metal, because then it becomes 20 electron species. So, you can understand why anion comes out. So, these are about mononuclear reactions. Is it possible to perform a binuclear oxidative addition? Yes, there are examples.

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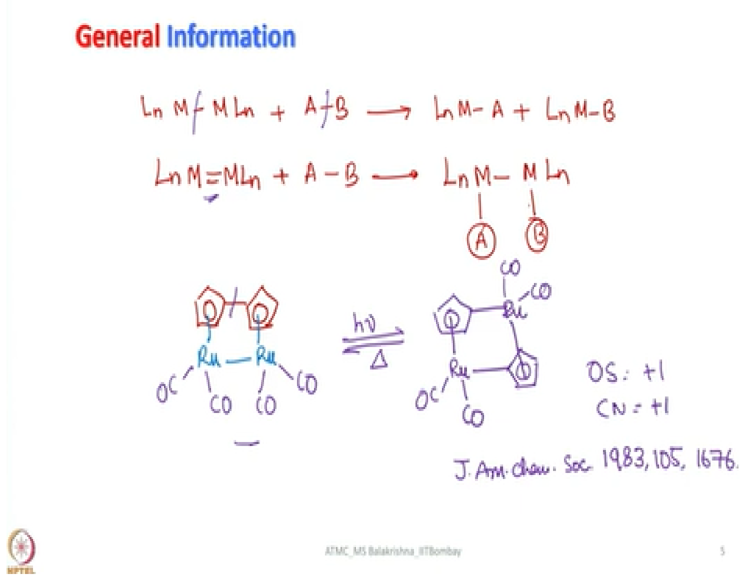

General Information

$$L_nM-ML_n + A-B \longrightarrow L_nM-A + L_nM-B$$

$$L_nM{=}ML_n + A-B \longrightarrow \underset{\underset{A}{|}}{L_nM}-\underset{\underset{B}{|}}{ML_n}$$

OS: +1

CN: +1

J. Am. Chem. Soc. 1983, 105, 1676.

So, let us consider a bimetallic complex having a metal-metal bond and again add a substrate molecule AB. So, in this case what we get is a product where A and B are added to two different metal ions. Of course, if you consider having metal to metal double bond, reaction follows the sequence. One bond will be broken and now they will be added separately to two independent metal ions retaining one of the metal-metal bond.

So, for this one I will give you very nice example. For example, if we shine UV light to this molecule, what happens, the C—C bond is activated. So, now if you see here oxidation state increases by plus one and coordination number increases by plus one for each metal centre. If you heat it, it can revert back to the starting compound.

So, in this case if you see now this is broken and this is also broken of course that is the thing that happens in a neutral molecule that splits into two anionic ligands and both of them are added oxidatively. Since it is a bimolecular process, they are added to two different metal atoms. Whereas here also same thing happens. But initially we had two bonds one of the bonds is broken and then one of the bonds is retained, so that it remains as a binuclear species.

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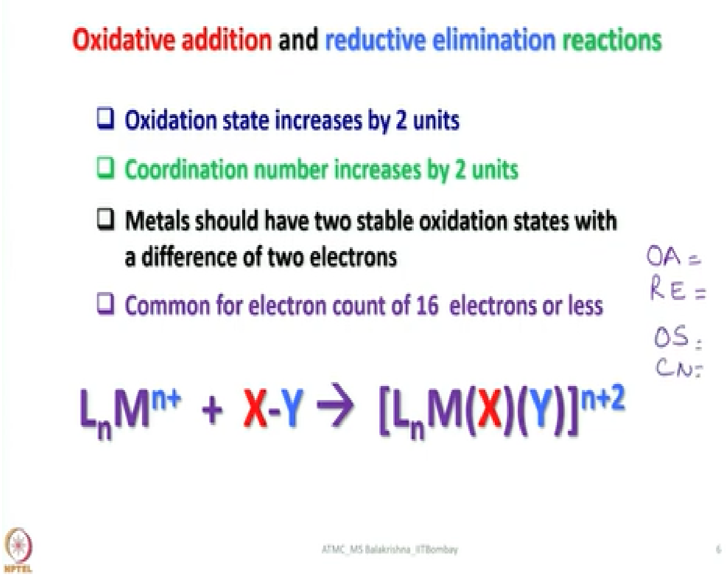

Oxidative addition and reductive elimination reactions

- ☐ Oxidation state increases by 2 units
- ☐ Coordination number increases by 2 units
- ☐ Metals should have two stable oxidation states with a difference of two electrons
- ☐ Common for electron count of 16 electrons or less

OA =
RE =
OS :
CN:

$$L_nM^{n+} + X\text{-}Y \rightarrow [L_nM(X)(Y)]^{n+2}$$

Now with this information, let us try to understand more and the definition of this reaction. Let us try to understand and what are the prerequisite in order to perform an oxidative action reaction or reductive elimination reaction. So, during this process of oxidative addition, the oxygen state of a metal increases by two units. If you take a metal in zero valent state, it becomes plus two state, if I we take metal in plus one state it becomes plus three, if you take plus two it becomes plus four.

Or if you take plus three it should become plus five. So, that means a metal should have two stable oxidation states with a difference of two electrons. At least we should have two accessible oxidation states with a difference of two electrons and in this process coordination number increases by two units. For example, you take four coordinated component it becomes six coordinated compound, if you take five coordinated, it can become seven coordinated or if you take three coordinated it become five coordinated.

The most common and important aspect is this should not be 18 electron saturated system. Of course, one can also perform oxidative addition on a saturated system having six coordination number and 18 electron that I can tell you but in general, in order to perform an oxidative addition reaction, a metal should have 16 electrons or less.

And it should be coordinatively unsaturated. I am going to show you some special cases also. So, this is the typical reaction here I have shown. Take a $[\text{complex}]^{n+}$ and then after oxidative addition $[\text{complex}]^{n+2}$, increased by 2 units and we have taken XY. And now this is a neutral molecule this breaks into two anionic ligands and they will be added as a result coordination number increases by two..

If I write OA, it is understood that it is oxidative addition and reductive elimination will be RE. Please remember I may not be expanding. Now let us look into what kind of ligands or substrate molecules we come across which are capable of performing oxidative addition reaction on a given metal.

So, there are three main classes of molecules that we can think of to perform oxidative addition reaction with metal centres: They are non-electrophilic intact and electrophilic. What is non-electrophilic means? These molecules neither contain electronegative atoms or themselves function as good oxidizing agents. That means they are neither oxidizing agents nor contain electronegative atoms. Except for H_2 they are often considered to be non-reactive substrates.

These molecules generally require the presence of an empty orbital on the metal centre for coordination prior to being activated for oxidative addition by breaking the bond to generate two anionic ligands. For example, H2, CH bond, SiH bond, SH bond, BH bond, NH bond, SS bond and also CC bond. And if you consider among all these substrate, molecules H_2 is by far the most important for catalytic applications.

And followed by SiH bond and then BH, NH and SH bonds. Of course, hydroxylation, hydroboration, hydro amination when we talk about this kind of reactions, we have to look for SiH bond, BH bond, NH bond etcetera. And of course, CH bond activation and functionalization is very important and every group working in organic chemistry methodology try to look for a better method for CH activation.

However, this method using homogeneous catalysis is not really practical because of various reasons attached to utilizing these kinds of catalysts for CH activation. Most of these findings are confined to synthesis in small scale under laboratory conditions. So, now what is non-electrophilic intact type of molecules? These molecules may or may not contain again electronegative atoms but certainly they contain a double bond or a triple bond.

So, that means one needs a metal centre with an empty orbital with having 16 electron count or even lower is much better in order to pre-coordinate the ligand. If it is a double bond it should coordinate prior to undergoing oxidative addition or a triple bond it should coordinate something like this. Most of the other substrate molecules break a single bond between those two entities to generate two separate anionic ligands upon oxidative addition.

These ligands, I am talking about non-electrophilic intact ligands, always have a double or triple bond and only one of the pi bonds is broken leaving the sigma bond intact or another pi bond along with the sigma bond intact in case of alkyne molecules. So, the ligand does pick up two electrons from the metal and becomes a dianionic ligand. Typical intact ligands that can perform an oxidative addition without fragmenting are alkenes and alkynes.

If we have electron withdrawing functional groups on the alkenes or alkynes that would enhance their electron withdrawing ability so that the transfer of electrons from the metal to the ligand is very facile, that means oxidative addition reaction will be much faster. So, the third class is electrophilic, next one is non-electrophilic intact, the third class of substrate molecules are electrophilic.

These molecules do contain electronegative atoms and are good oxidizing agents. They are often considered to be reactive substrates and these molecules do not require the presence of an empty orbital, even 18 electron count is also ok and as I mentioned they do not require an empty orbital on the metal centre in order to perform the oxidative addition reaction. For example, all halogens dimeric X_2 where Cl_2, Br_2, I_2 or we can think of polar molecules like RX, alkyl halides, aryl halides or HX and O_2 also.

The most common substrates used here are alkyl or aryl halides and also HX, whenever we perform reaction when it comes to the coupling reactions. So, that means the common substrates used in general are alkyl halides or aryl halides when it comes to the application of these metal complexes for cross coupling reactions. Let us consider a simple 16 electron platinum complex and see how an oxidative addition reaction happens and what kind of ligands we are considering, you should be able to tell.

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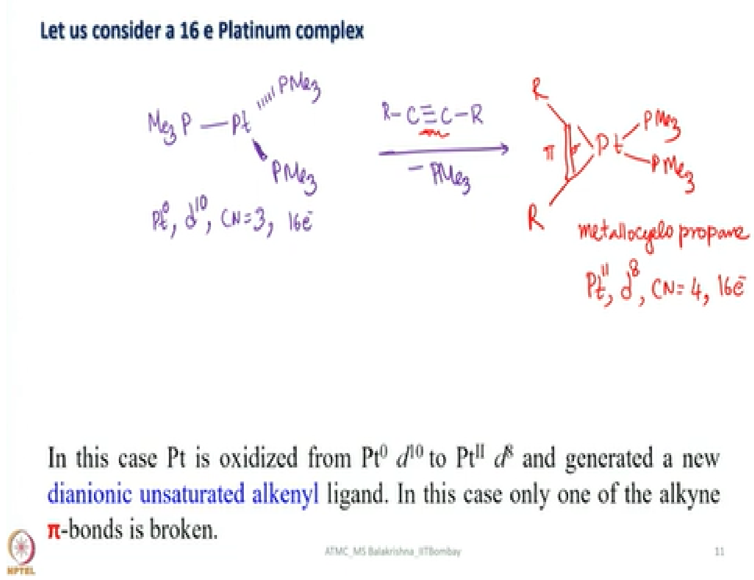

Let us consider a 16 e Platinum complex

In this case Pt is oxidized from Pt^0 d^{10} to Pt^{II} d^8 and generated a new dianionic unsaturated alkenyl ligand. In this case only one of the alkyne π-bonds is broken.

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You can see here platinum is in zero oxygen state because all are neutral ligands and of course now it is a d^{10} system and coordination number is three and next electron is 16, 10 + 6. It is better to write down all these points. So, when you perform a reaction so that understanding would be very better. Now let us consider an alkyne; so during oxidative addition reaction one of the phosphine ligands comes out.

So, now you can see one of the triple bonds is broken here and then it becomes di anionic unlike electrophilic ligands, here the bond between these two dianionic sides that are going to metal through oxidative addition are retained by a single bond and a double bond. So, we have still a sigma bond and a pi bond. One of the pi bonds is broken. This is called metallocyclo propane and now let us do electron count.

So, platinum is in plus two state so it is a d^8 system and coordination number is four and now it is a 16 electron species. So, in this case platinum is oxidized from platinum(0) to platinum(II), the d-electronic configuration changes from d^{10} to d^8 and generated a new dianionic unsaturated alkyne ligand. In this case only one of the alkyne pi bonds is broken. If you take an alkene then since we have only one pi bond, that will be broken and carbon-carbon sigma bond is retained.

Now the question is, is it possible to perform oxidative addition on any 18 electron complex. I mentioned that we can also perform oxidative addition reaction on 18 electron complex, how? Let us look into it by taking a right and appropriate example.

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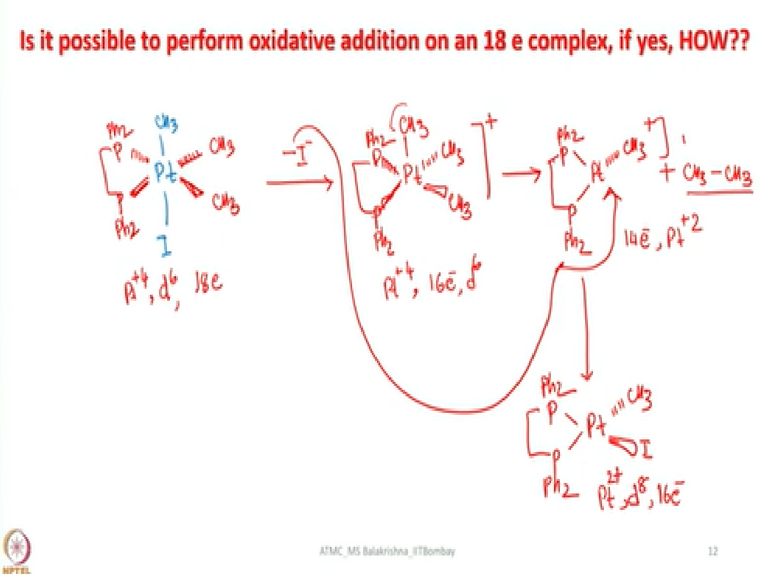

Is it possible to perform oxidative addition on an 18 e complex, if yes, HOW??

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I am choosing again a platinum complex. Of course, one can also show like this, here I am taking a bidentate ligand such as dppe. Look into this one here, four anionic ligands are there as a result platinum is in plus 4 state. If it is in plus 4 state, it has to be a d^6 system and then if you do electron counting, we have 12 + 6, 18 electrons. By ionic method you can do quickly platinum(IV) gives six and all are two electron donors.

Now 12 + 6 18. Now what would happen? Does it appears like oxidation is happening. So, now what happens is if you heat it, one of the iodide comes out and then platinum will be going to plus 4 state. So, here already written, no need to write here. Now if you see here, this is platinum now in plus 4 state and then it is a 16 electron species and still d^6 system. So, 5 x 2 = 10 + 6, 16. Now if you see this one this is a 14 electron species and a platinum is in plus 2 state so 8 + 6.

So, now this iodide which was here of course this will be added to here. So, now oxidation is completed it is a d^8 system and 16 electron species. You can see we started with 8 electron species and one of the ionic ligand was eliminated to generate a cationic complex here and there is a 16 electron species and then in this process reductive elimination happens and ethane molecule is coming out and then now electrophilic attack happens here, and hence the oxidation is completed.

So, yes, it is possible to perform oxidative addition reaction on an 18 electron complex also and this is how one should be able to understand the sequence of reactions. So, let me give a couple of more examples in my next lecture. I am sure you are very attentive listening to my lecture. Thank you for your kind attention, see you in my next lecture you.