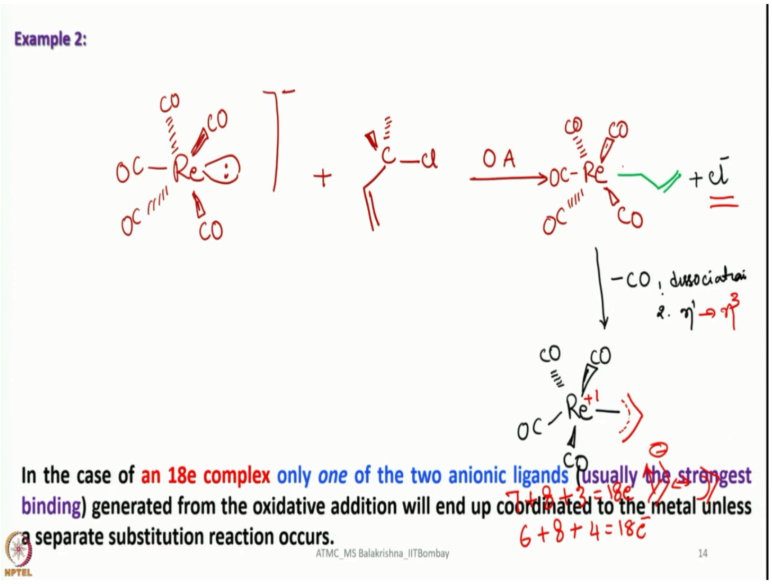
Advanced Transition Metal Chemistry
Prof. M.S Balakrishna
Indian Institute of Technology, Bombay

Lecture - 42
Oxidative Addition and Reductive Elimination Reactions

Hello everyone, I welcome you all once again to MSB lecture series on transition metal chemistry. I am sure you are enjoying the topics that I am discussing since previous lecture that is, oxidative addition and reductive elimination reactions. And in my previous lecture I showed you even with an 18 electron species having coordination number 6 we can perform oxidative action reaction.

And also showed you how in case of a trimethyl-bisphosphine-iodo complex undergoes sequence of reactions to end up with an oxidatively added product having platinum in plus 2 state and 16 electrons. So, now let us discuss another example, a very interesting example.

(Refer Slide Time: 01:14)



Example 2:

In the case of an 18e complex only *one* of the two anionic ligands (usually the strongest binding) generated from the oxidative addition will end up coordinated to the metal unless a separate substitution reaction occurs.

ATMC_MS Balakrishna_IITBombay 14

Let us consider a rhenium complex for a change. This is anionic, if it is anionic, you should remember that we have a pair of electrons so that can be readily abstracted by a ligand that is entering, the ligand chosen is this one. So, now oxidative addition reaction happens; chloride comes out. So now this species lose a carbon monoxide that means CO dissociation happens.

And second point is now you can see what would happen to this η^1 ligand. Negative charge is there and this also comes, means it can be shown something like, now η^1 is changed to η^3. So, now we if we do electron count for this one rhenium is in plus 1 state and now it is an 18 electron species, we can count. If you go with neutral method, where rhenium has 7 + 8 + 3 = 18.

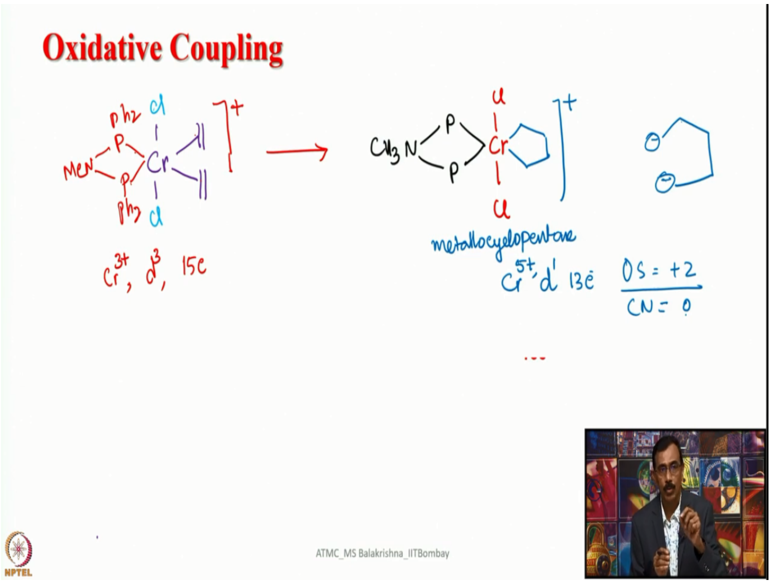
Because this double bond two electron and one this in neutral method 1 electron; 3 is 18 electron species in neutral method. In ionic method this is 6, 4 ligands are giving 8 and now this is 4 electron donor allyl group anion alive so it is 8 electron species so this is another example.

So, in the case of an 18 electron complex, only one of the two ionic ligands. You can see here this is also an anion ligand and this also anionic ligand usually the strongest binding generated from the oxidation will end up coordinated to the metal unless a separate substitution reaction occurs. Why this one? Because rhenium has a pair of electrons and now if the electron is taken it becomes carbo cation you should remember it becomes carbo cation and carbanion.

So, that is the reason that immediately abstract the pair of electrons at the end it appears like both of them are anionic and both of them are taking one electron each from the metal centre. So, these are typical examples where you can see how 18 electron complex undergoes oxidative addition reaction to give the desired product. Another interesting reaction is that, that is called oxidative coupling.

What is this oxidative coupling? Let me write a specific chemical equation so that you can understand.

(Refer Slide Time: 05:44)



Oxidative Coupling

Let me consider a chromium complex. I am considering two ethylene ligands and two chlorides and my favourite a bisphosphine. Now let us do electron count for this one, this is cationic, if it is cationic obviously you can tell chromium is in plus 3 state yes, if chromium is in plus 3 state we have d^4s^2 so we left with three electrons this is a d^3 system and if you count electrons now we have total of 15 electrons here.

So, you consider all of them 10 2 4 6 8 10 12, 12 + 3, 15 electron species this is. What would happen to this one? Here this is not the ligand actually, this is methylaminobis(diphenylphosphine), my favourite ligand. I am very fond of aminobisphosphines. Of course, this bidentate coordination mode remains intact and these two chlorides also remain intact.

Then what is happening here? You can see here what is this, one metallocyclopentane, earlier I showed a metallocyclopropane now we ended up with a metallocyclopentane. And now let us do electron count before we try to understand this reaction. Chromium is in plus 5 oxygen state because positive charge is there 4 anionic ligands are there. Chromium is in plus 5 oxygen state as a result it is a d^1 system now 6 x 12 + 1 = 13, 13 electron system.

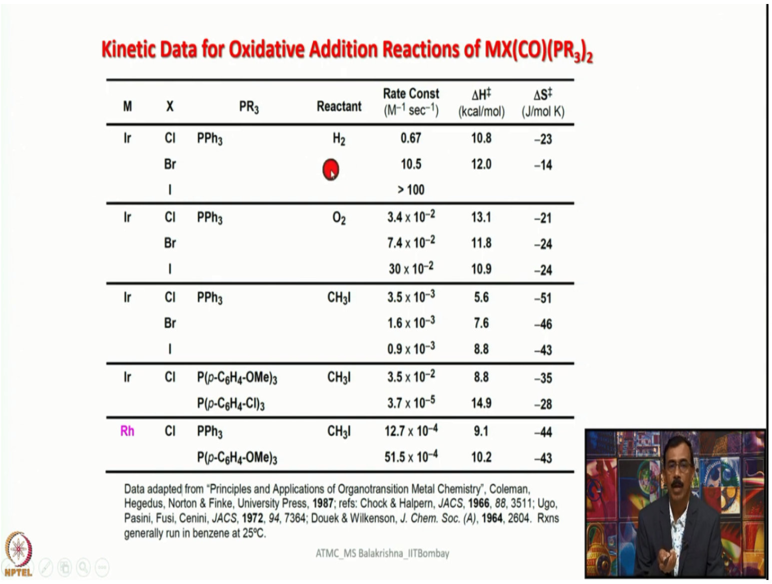
So, what is the prerequisite for an oxidation reaction? Oxygen state should increase by plus 2 and coordination number yes can change and come back, does not matter, not that important here. oxidation state plus 3 become plus 1. So, this is a again an oxidative reaction but here we had two independent ethylene molecules are there and we lost a pi bond on each of them and in the place of two pi bonds what we have seen is a C-C bond formation is there.

And that resulted in again dianionic ligand so for this one if you consider, so this is anionic this is anionic. Only thing is compared to other molecules, we are not ending up with two independent anionic ligands, whereas here we have a dianionic ligand. And now these binds to the metal to complete the metallocyclopentane formation and in this process, we can see metal oxidation state increases by plus 2 and coordination number does not change, it does not matter.

So, this is also a typical oxidative addition reaction but here since two independent ligands are coupled, we call it as oxidative coupling. This oxidative coupling is happening with non-electrophilic intact ligand, we are taking two alkenes. So, oxidative coupling can be anticipated when you are considering non-electrophilic intact ligands such as alkenes and alkynes. And of course, it goes with your imagination.

And if you think of such reactions in some organic transformation and organic synthesis certainly you can succeed and of course you have to choose right kind of ligands as anchoring ligands and also how they nicely control the steric and electronic properties of metal, on which you are performing oxidative addition reaction.

(Refer Slide Time: 10:34)



Kinetic Data for Oxidative Addition Reactions of $MX(CO)(PR_3)_2$

M	X	PR_3	Reactant	Rate Const (M^{-1} sec^{-1})	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (J/mol K)
Ir	Cl	PPh_3	H_2	0.67	10.8	–23
	Br			10.5	12.0	–14
	I			> 100		
Ir	Cl	PPh_3	O_2	3.4×10^{-2}	13.1	–21
	Br			7.4×10^{-2}	11.8	–24
	I			30×10^{-2}	10.9	–24
Ir	Cl	PPh_3	CH_3I	3.5×10^{-3}	5.6	–51
	Br			1.6×10^{-3}	7.6	–46
	I			0.9×10^{-3}	8.8	–43
Ir	Cl	$P(p\text{-}C_6H_4\text{-}OMe)_3$	CH_3I	3.5×10^{-2}	8.8	–35
		$P(p\text{-}C_6H_4\text{-}Cl)_3$		3.7×10^{-5}	14.9	–28
Rh	Cl	PPh_3	CH_3I	12.7×10^{-4}	9.1	–44
		$P(p\text{-}C_6H_4\text{-}OMe)_3$		51.5×10^{-4}	10.2	–43

Data adapted from "Principles and Applications of Organotransition Metal Chemistry", Coleman, Hegedus, Norton & Finke, University Press, **1987**; refs: Chock & Halpern, *JACS*, **1966**, *88*, 3511; Ugo, Pasini, Fusi, Cenini, *JACS*, **1972**, *94*, 7364; Douek & Wilkenson, *J. Chem. Soc. (A)*, **1964**, 2604. Rxns generally run in benzene at 25ºC.

ATMC_MS Balakrishna_IITBombay

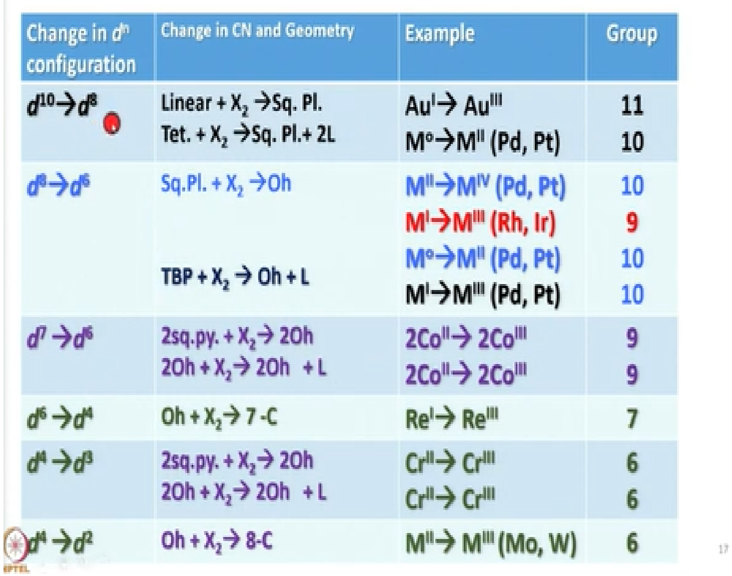
Now let us look into some kinetic data that is obtained from studies that have mentioned here. Just look into the type of ligands we have and type of reagents and also what kind of rate we are seeing and what is happening to ΔH and ΔS. These are very important and especially when you are considering electrophilic reagents or non-electrophilic reagents. One such example, I am going to show you in one of my lectures.

Now let us consider here reactant is H_2 and in this case O_2 and in this case methyl iodide and in all these cases methyl iodide and also you can see phosphines have been changed here we have in first three cases phosphines are there. We have a different kind of phosphine. And if you just look into the rate what would happen is, the rate is quite high for electron rich species, you can see the rate is very high.

If you just look into this case here, when you go from chlorine to bromine to iodide what happens the rate is decreasing. It is because of steric effect. When this CH_3 comes out as carbo cation, is added on to the iridium through axial position targeting d_z^2 orbital. Since iodine relatively bulkier and it prevents the free access of d_z^2 to methyl cation.

As a result, what happens in this case it readily decreases with increasing the size of the anion. Otherwise, it is very interesting data we have. Always you can just look into these things and also try to analyse this. Later I will show you how one can assess a reaction through thermodynamic aspects whether that reaction can undergo oxidative addition or not. In case if it undergoes oxidative addition, whether we can use it in a catalytic reaction. Some of these things I shall tell you as we progress.

(Refer Slide Time: 12:37)



Change in d^n configuration	Change in CN and Geometry	Example	Group
$d^{10} \rightarrow d^8$	Linear + X_2 → Sq. Pl. Tet. + X_2 → Sq. Pl.+ 2L	$Au^I \rightarrow Au^{III}$ $M^o \rightarrow M^{II}$ (Pd, Pt)	11 10
$d^8 \rightarrow d^6$	Sq.Pl. + X_2 → Oh TBP + X_2 → Oh + L	$M^{II} \rightarrow M^{IV}$ (Pd, Pt) $M^I \rightarrow M^{III}$ (Rh, Ir) $M^o \rightarrow M^{II}$ (Pd, Pt) $M^I \rightarrow M^{III}$ (Pd, Pt)	10 9 10 10
$d^7 \rightarrow d^6$	2sq.py. + X_2 → 2Oh 2Oh + X_2 → 2Oh + L	$2Co^{II} \rightarrow 2Co^{III}$ $2Co^{II} \rightarrow 2Co^{III}$	9 9
$d^6 \rightarrow d^4$	Oh + X_2 → 7-C	$Re^I \rightarrow Re^{III}$	7
$d^4 \rightarrow d^3$	2sq.py. + X_2 → 2Oh 2Oh + X_2 → 2Oh + L	$Cr^{II} \rightarrow Cr^{III}$ $Cr^{II} \rightarrow Cr^{III}$	6 6
$d^4 \rightarrow d^2$	Oh + X_2 → 8-C	$M^{II} \rightarrow M^{III}$ (Mo, W)	6

Now I have given another chart here. Here I have shown: if you perform oxidative addition reaction with metals having different electronic configuration what would happen after oxidative addition. And also, what would happen to geometry and specific examples and to which group these metals belongs all these details I have given here. For example, if you take a d^{10} species, group 11 copper, gold or silver. I have considered gold(I) to gold(III).

When you perform oxidative addition reaction, what happens, to start with linear geometry is there that should change to square planar and, in some cases, even, they can have tetrahedral geometry, that can also change to square planar. And two ligands would come out in that case because we started with four and we end up with four so the two ligands that were present on metal should come out.

A typical example is $[Pd(PPh_3)_4]$ or $[Pt(PPh_3)_4]$, in that one, before oxidative addition happens, two ligands would dissociate to generate a 14 electron species. To which this substrate molecule is added that result in the formation of again a square planer complex and two ligands would come out, example metal(0) to metal(II). Similarly, when you consider d^8 species that changes to d^6; two electrons.

And if you consider Vaska's compound or group 10 species with plus 2 state nickel palladium and platinum or group 9 metals in their plus 1 state (rhodium or iridium) what happens is d^8 to d^6

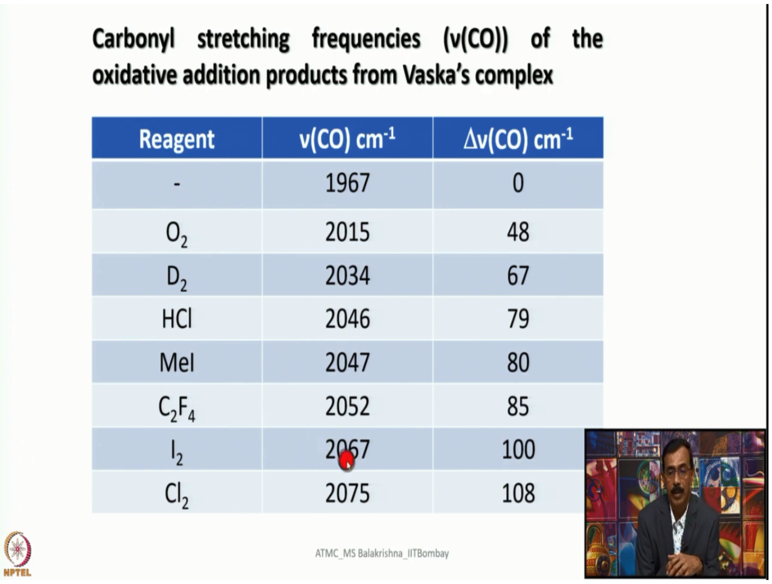
16 electron species, becomes 18 electron species. And then they will be having octahedral geometry one such is palladium or platinum going from plus 2 to plus 4; or rhodium and iridium going from plus 1 to plus 3 or palladium and platinum going from 0 to 2 also quite possible. Many square planar complexes of platinum and palladium in plus two state show this kind of oxidative addition. And if you have trigonal bipyramidal geometry five in that case, what happens one of the ligand has to leave so that it would attain octahedral geometry after oxidative addition. And in those cases, one can think of palladium(I) and going to palladium(III) or platinum(I) going to platinum(III) again group 10 metals.

And d^7 to d^6, in this case what happens, you can see this is one electron process since metal has two stable oxidation states with a difference of one electron. In that case a typical oxidative addition reaction cannot be performed. On the other hand we can consider dimeric species, as I showed you, in that case you can perform. For example, if you consider cobalt case cobalt 2 to cobalt 3 and square pyramidal geometry changes to octahedral geometry.

And now square pyramidal geometry when it changes to octahedral, of course, a bridging ligand will be there and then geometry would change to octahedral. In that case one ligand has to come out; a common bridging ligand. And there are examples of oxidative addition with metals having d^6 in that case they become d^4. For example, octahedral and then go to 7 coordinated complexes and then with losing one ligand or it may be anionic.

So, example: rhenium(I) to rhenium(III), 7 group and d^4 to d^3 again chromium(II) to chromium(III) again octahedral to octahedral; chromium 2 to chromium 3. And also, there are examples with the metals having d^4 they can change to d^2 for molybdenum and tungsten. That is the reason to make you familiar I chose examples having different metal ions and having different ligands on them. Just go through all these reactions I wrote for better understanding of oxidative division reaction.

(Refer Slide Time: 16:44)



Carbonyl stretching frequencies (ν(CO)) of the oxidative addition products from Vaska's complex

Reagent	ν(CO) cm^{-1}	Δν(CO) cm^{-1}
-	1967	0
O_2	2015	48
D_2	2034	67
HCl	2046	79
MeI	2047	80
C_2F_4	2052	85
I_2	2067	100
Cl_2	2075	108

ATMC_MS Balakrishna_IITBombay

Now I have given another interesting data here this is about Vaska's compound which is undergoing oxidative addition with various substrate molecules here. And of course, stretching frequency given in the first one is for a neutral starting compound. That is a typical rhodium trans-$[RhCl(CO)(PPh_3)_2]$ that is similar to Vaska's compound, for that one stretching frequency for CO appears at 1967 cm^{-1}.

After performing oxidative addition in case of oxygen, it changes to 2015 cm^{-1}. This is the difference in the stretching frequency with respect to this one. So, that means, stretching frequency is increasing for carbon monoxide after we perform oxidative addition and also it is increasing in this order when you are changing O_2 to D_2, D_2 to HCl, HCl to methyl iodide, methyl iodide to tetrafluoroethylene to iodine to chlorine.

So, that means you should try to understand how these ligands differ in terms of sigma donor abilities or electron pulling abilities. It is always anticipated that stretching frequency should increase when a particular complex having carbon monoxide undergoes oxidative addition. Here in case of Vaska's compound what happens here. In this case the it appears like back bonding is very extensive.

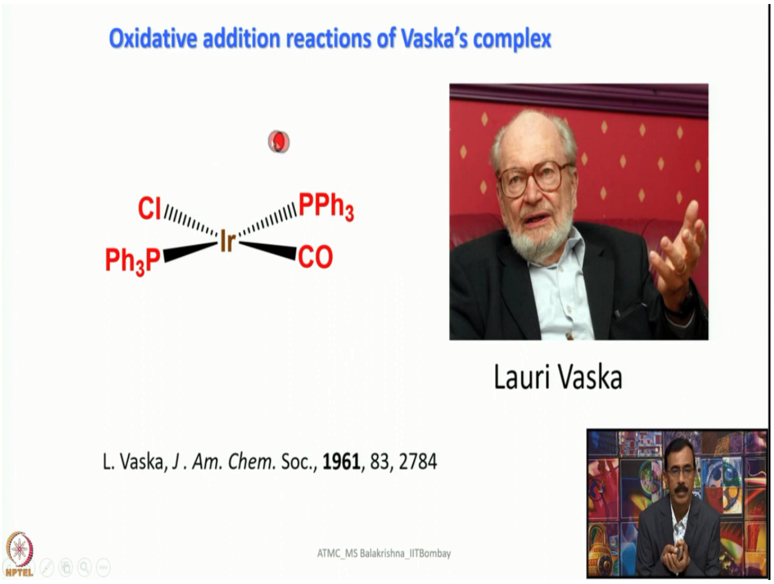
When the back bonding is very extensive what happens CO bond becomes weakened as a result stretching frequency decreases. You recall the free carbon monoxide frequency that comes around 2170 cm^{-1}. Now it is 1967 cm^{-1} you can see a considerable back bonding is there from iridium to carbon monoxide pi star. So, as a result setting frequency is 1967 cm^{-1}, now metal become electro positive. So, metal has lost two electrons because of oxidative addition.

In that case what happens metal is not a good pi donor or it reluctantly gives electrons to the pi star of CO through back bonding. As a result, what happens it is increasing and if you see here, they are more electronegative and thy are anionic ligands, when they are anionic ligands what happens they pull more electron density as a result less and less electrons are available for back bonding.

As a result, consistently you can see here in the same sequence, stretching frequency is increasing here. So, least back bonding is there in case of chlorine because it is a more electronegative group. And it pulls electron density and you may ask me, cannot they give electrons through sigma donor and pi donors, not in this case especially with early metals which are not really oxophilic. Late metals which are not really oxophilic that is not going to happen here.

So, in these compounds, you should remember, these are mere sigma donors but not pi-acceptors. But when they pull the electrons, they pull electron density. Because of their electronegativity generate Cl minus, you should remember Cl_2 we are taking it becomes two Cl minus when it becomes 2 Cl minus 2 electrons are pulled out very strongly from the metal. As a result, less electron density is left on the metal so that metal is a reluctant pi donor and hence stretching frequency increases.

(Refer Slide Time: 20:09)



Oxidative addition reactions of Vaska's complex

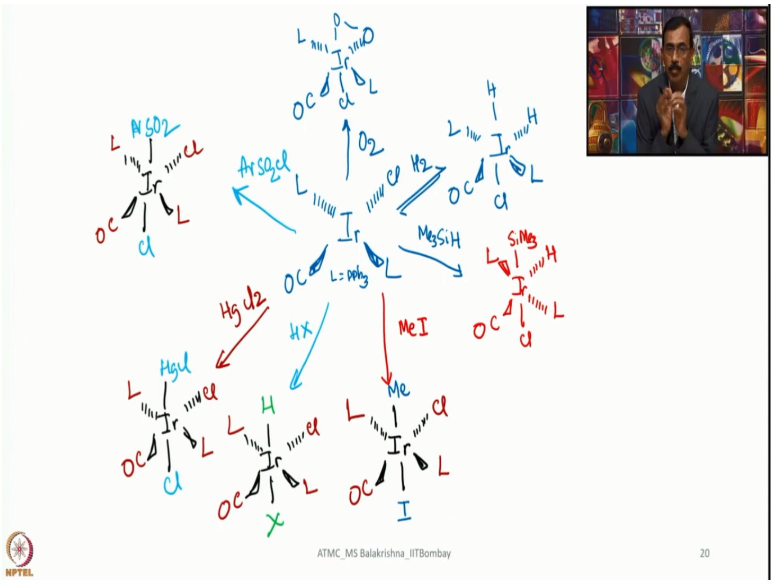
Lauri Vaska

L. Vaska, *J. Am. Chem. Soc.*, **1961**, 83, 2784

ATMC_MS Balakrishna_IITBombay

And of course, in the next couple of slides I am going to show you different type of oxidative addition that one can perform on this Vaska's compound and I have taken all these from Lauri Vaska paper published in 1961 in Journal of American Chemical Society (20:27), this is the famous Vaska's compound this is Lauri Vaska.

(Refer Slide Time: 20:31)



ATMC_MS Balakrishna_IITBombay

Let me write a few reactions to begin with to make you familiar with oxidative addition and thereby I can also allow you to distinguish between the type of reactions and how they are added and why they are added and how that can be explained. Simply I write L here you should remember L = triphenylphosphine. Now let me start with oxygen, next let me consider important reaction addition of H_2 here.

Next let me consider another important reaction in terms of its utility in organic synthesis, tri methyl silane. Then we consider methyl iodide and one more reaction I would write here HX. So, now I have written about seven reactions in all seven cases, seven different type of substrate molecules are performing or undergoing oxidative addition on iridium(I) and in all these cases you can see iridium end up with plus 3 state and having 18 electrons and having 6 coordination number.

Let me discuss all these reactions in my next lecture until then have an excellent time reading chemistry and understanding oxidation reaction. And thank you for your kind attention and see you in my next lecture to discuss these things in a more elaborated manner, thank you.