Transition Metal Organometallic Chemistry : Principles to Applications
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Week – 03
Lecture – 14
TM σ – alkyl complexes and its applications

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. We have been discussing an important topic which is transition metal sigma alkyl complexes over the last few lectures and have been looking at it from the methods that are available for the preparations. We have also looked at the reactivity the stability of this compounds.

In particular, in the last lecture we have looked at different strategies that are available to stabilize this transition metal sigma alkyl complexes which otherwise are very reactive compounds and all of these strategies that we have encountered are focus towards one particular decomposition reaction which is beta elimination. And what we had seen that all of these strategies are put in place to suppress beta eliminations in transition metal sigma alkyl complexes and if done successfully they impart reasonable stability to do this organometallic compounds.

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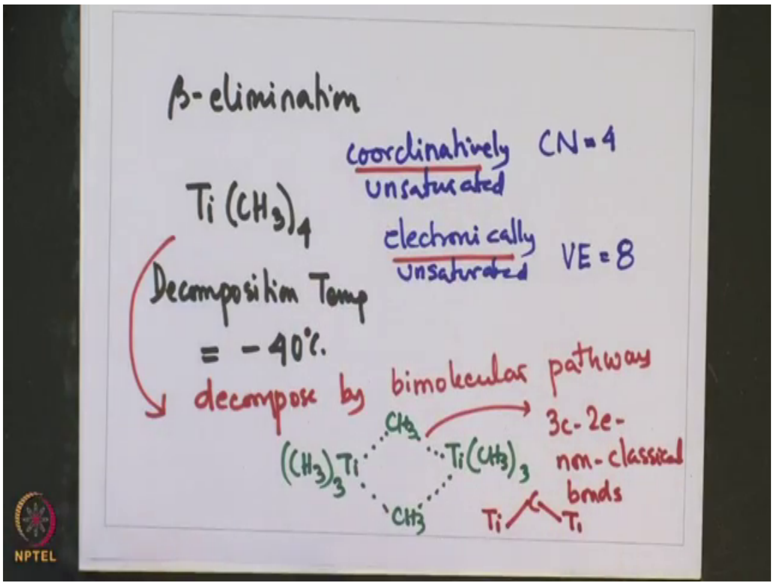
β-elimination

$Ti(CH_3)_4$

coordinatively unsaturated CN = 4

electronically unsaturated VE = 8

Decomposition Temp = −40°C.

decompose by bimolecular pathway

3c-2e- non-classical bonds

So, in the pretext of beta elimination we had seen that there are primarily 3 approaches towards inhibiting it. The first one is sort of the application of Bret's rule the second one applies towards ligands which does not have beta hydrogen. So, that beta hydrogen elimination does not undergo and last one is the one that focuses on the metal center by making the metal center coordinatively saturated as a result beta hydrogen elimination is inhibited.

Now, with that in mind we were in the last class we were looking at the reasons for decomposition of titanium tetra methyl.

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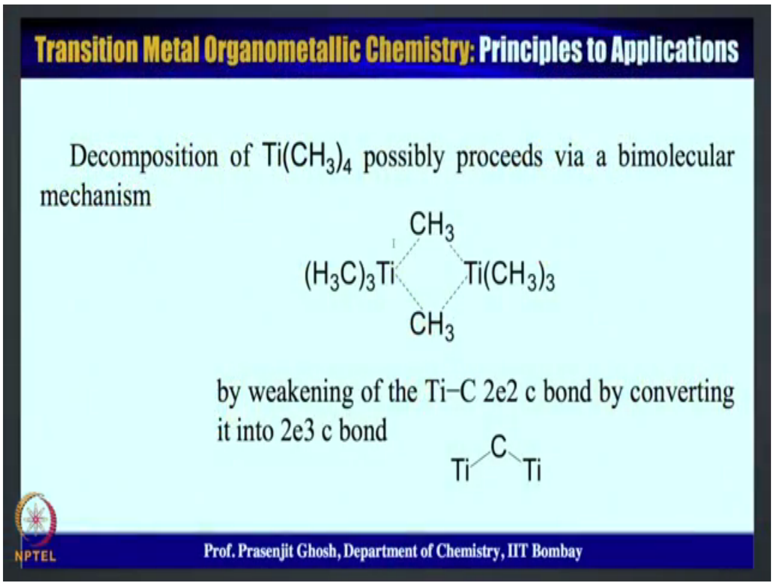

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Decomposition of $Ti(CH_3)_4$ possibly proceeds via a bimolecular mechanism

by weakening of the Ti–C 2e2 c bond by converting it into 2e3 c bond

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Titanium tetra methyl is a highly reactive compound that has a decomposition temperature of around minus 40 degree centigrade and these compound is both coordinatively unsaturated as well as electronically unsaturated, as well as electronically unsaturated coordinatively unsaturated means that it has a coordination number of 4. So, still most of the transition metal exhibit coordination number as high up to 6. So, in that from that pretext is still coordinatively unsaturated and it also is electronically unsaturated as it has total valence electrons of 8. So, this is highly electronically unsaturated as it has 8 valence electron as opposed to the inner transition meta complexes which obey 18 valence electron rule.

And because of this extensive unsaturation both coordinative as well as electronic this titanium tetra methyl decompose by a bimolecular pathway, that involves the interaction of titanium with the titanium methyl bond of enabling molecule. These weekends, the titanium methyl bond as these are 3 centered two electron non classical bonds resulting in decomposition of this titanium tetra methyl moiety.

Now, while analyzing this one can concede that if somehow the coordinative saturation along titanium if it is increased either by coordination increase coordination or through sterics then one should be able to attend more stable titanium complex.

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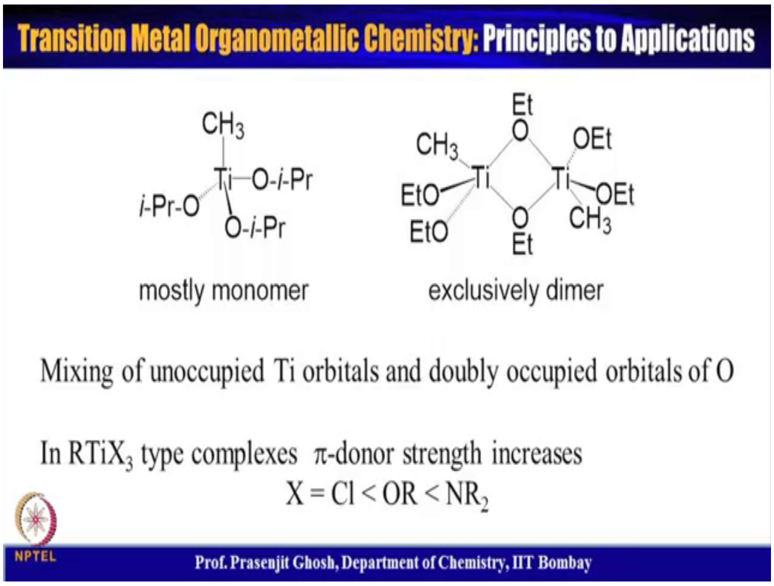

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mostly monomer

exclusively dimer

Mixing of unoccupied Ti orbitals and doubly occupied orbitals of O

In $RTiX_3$ type complexes π-donor strength increases

$X = Cl < OR < NR_2$

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For example, if one goes to titanium methyl tri ethoxide where you have one alkyl attached to titanium for example.

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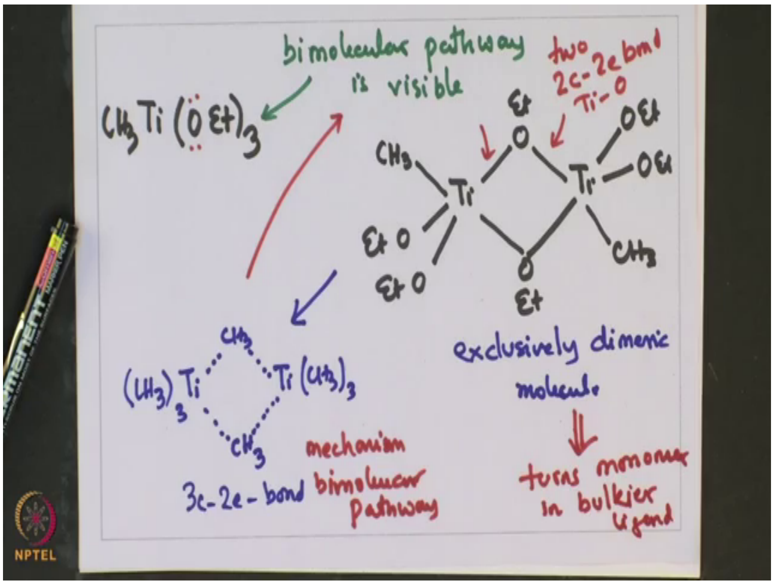

Then one sees that because of this oethoxy which is slightly more bigger than the methyl moiety and also the oxygen has lone pair in it which are stereo genic in nature. Then this bimolecular pathway can sort of more conspicuous is more conspicuous or is visible in this complex as this complex exclusively exist as a dimer of the type shown. So, this is exclusively dimeric molecule and this fully supports or gives evidence to the bimolecular pathway as observed in the titanium tetra methyl complex.

The difference been this is a 3c 2e bond whereas, in this case the there are two 2 classical 2c 2e bonds between titanium and oxygen otherwise this bears that to testimony to the fact that titanium is both electronically as well as coordinatively unsaturated in this titanium tetra methyl complex and that it undergoes the decomposition pathway using this bimolecular mechanism.

Now, if one improves or increases the steric bond of this ethoxide in titanium to something which is more bulkier for example, say isopropoxide even this dimmer becomes a monomer. So, that brings us to a very important compound which is titanium methyl tri isopropoxide.

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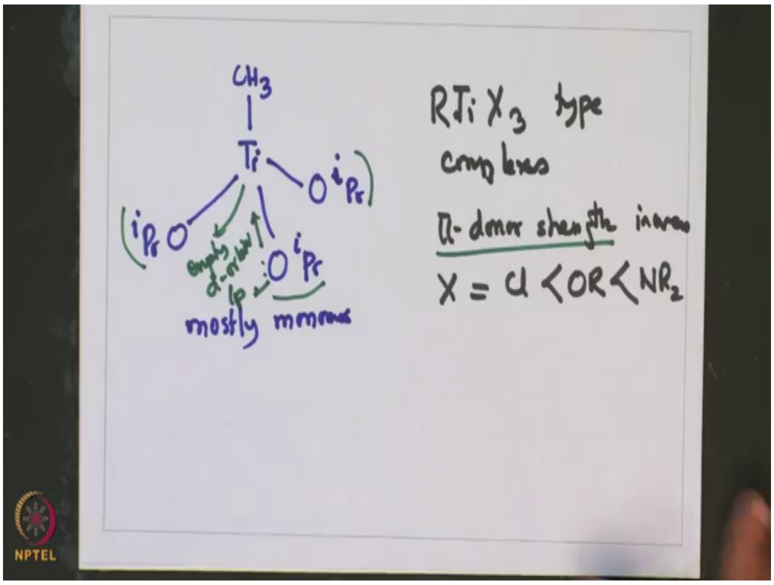

RTiX$_3$ type complexes

π-donor strength increase

X = Cl < OR < NR$_2$

This is mostly monomer.

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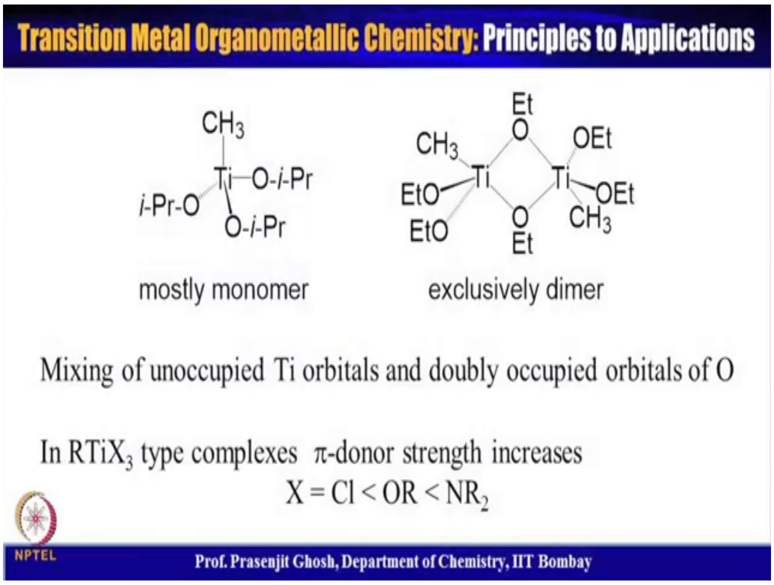
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mostly monomer

exclusively dimer

Mixing of unoccupied Ti orbitals and doubly occupied orbitals of O

In RTiX$_3$ type complexes π-donor strength increases

X = Cl < OR < NR$_2$

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now for this kind of complexes RTiX 3 type complexes the pi donor strength increases along X in chloride less that OR less than NR 2.

Another interesting observation to be made over here that apart from the bulk of the isopropyl moieties that make this complex monomer there is also some kind of pi interaction occurring between the oxygen lone pair and the empty d orbital of titanium and oxygen lone pair. And hence the importance of pi donors strength increases and it turns out that the pi donors strength increases from X being a halide to alcooxide to dialkyli I mean moiety.

Now, we come to this important observation of the fact then that when all the criterias for suppressing beta elimination are realized. The 3 criterias being that formation of the olefin is inhibited from beta elimination going to the olefin being energetically unfavorable, the second criteria is that the ligand would not have any beta hydrogens on the beta carbon so that the beta elimination anyway will be inhibited and lastly if the metal central metal atom in the organometallic compound is coordinatively saturated then it will not participate in any kind of beta elimination process.

Now, if one were to design a molecule where all of the 3 criterias are fulfilled then that molecule is expected to be very stable.

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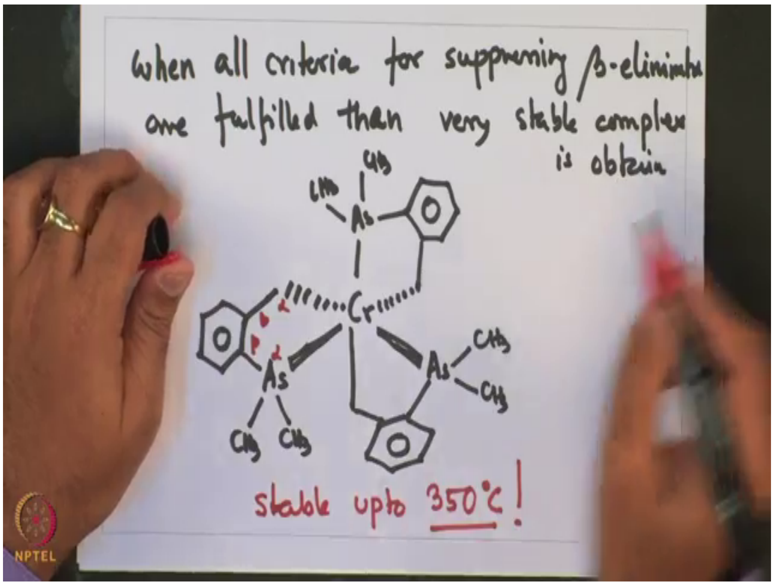

when all criteria for suppressing β-eliminatn are fulfilled than very stable complex is obtain

stable upto 350°C!

When all criteria that we have discussed for suppressing beta elimination are fulfilled then very stable complex is obtained. For example, this particular chromium complex which has a dimethyl arsine and a aryl group with CH 2, 3 of this ligand bound to the metal center of this type what results is as very extremely stable compound that is stable up to 350 degree centigrade.

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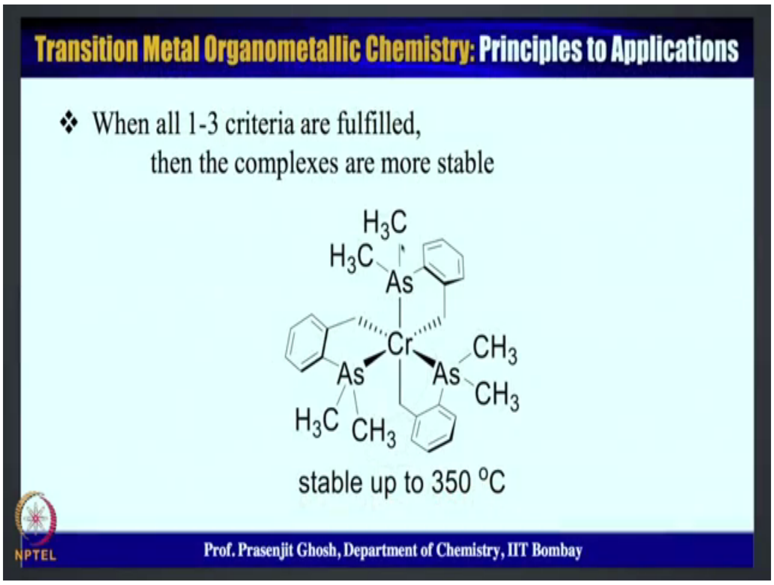

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- When all 1-3 criteria are fulfilled,
  then the complexes are more stable

stable up to 350 °C

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So, this is extremely stable compound and what we see that all the criterias of beta elimination have been inhibited. For example, there is no beta hydrogens that the both the beta positions are blocked. Secondly, that these will not give a olefin that would be energetically favorable and lastly the metal being 6 coordinated with arsine and 3 dimethyl, 2 of the dimethyl moieties and phenyl reign is extremely coordinatively saturated. So, no way can the metal center chromium participate in any kind of beta hydrogen elimination.

So, the formation of this compounds testifies that the approaches which have been undertaken towards inhibiting beta elimination is a successful one as a result one can obtain organometallic compound that is extremely stable. Also this example negates the fact or belief that organometallic compounds are thermodynamically unstable what it turns out that the thermodynamic stability is not much an issue for organometallic compound whereas, kinetic reactivity resulting to its so called observed instability is what is the primary reason for their extremely high reactive nature and that if be suppressed by obtaining a proper understanding of their decomposition pathway.

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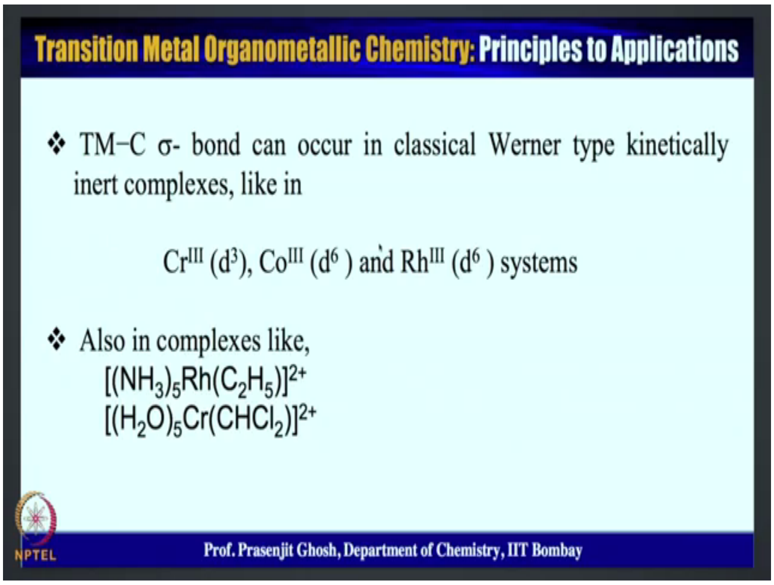

- TM−C σ- bond can occur in classical Werner type kinetically inert complexes, like in

  Cr^{III} (d^3), Co^{III} (d^6) and Rh^{III} (d^6) systems

- Also in complexes like,
  $[(NH_3)_5Rh(C_2H_5)]^{2+}$
  $[(H_2O)_5Cr(CHCl_2)]^{2+}$

For example transition metal sigma bonds can occur in classical Werner type kinetically inert complexes.

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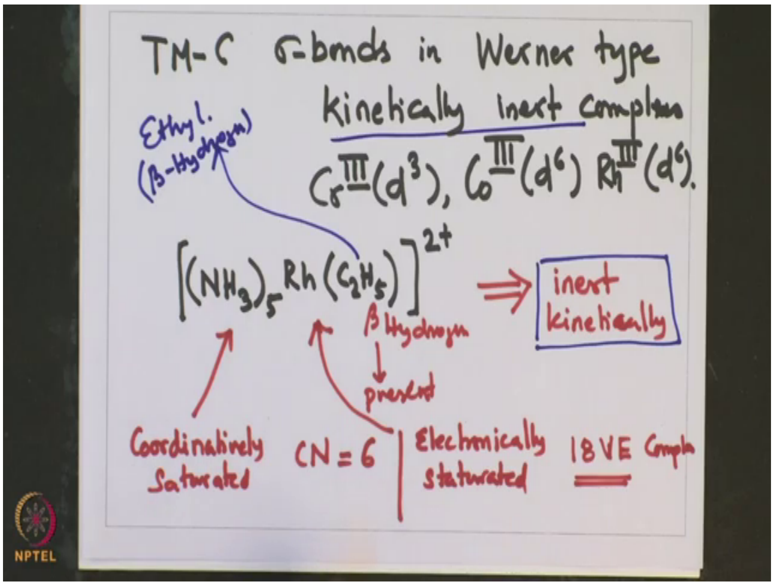
TM-C σ-bonds in Werner type kinetically inert complexes

$Cr^{III}(d^3)$, $Co^{III}(d^6)$ $Rh^{III}(d^6)$.

Ethyl. (β-Hydrogen)

$[(NH_3)_5Rh(C_2H_5)]^{2+} \Rightarrow$ inert kinetically

β Hydrogen ↓ present

Coordinatively Saturated CN = 6

Electronically staturated 18VE Complex

So, these are being kinetically inert as they are both kinetically as well as coordinatively saturated. For example, these are mainly seen for chromium 3, d 3 systems cobalt 3 d 6 systems rhodium 3, d 6 systems. For example, rhodium pinta amine 2 plus where 5 ammonia and 1 ethyl group is bound to the rhodium.

So, rhodium has 5 ammonia and ethyl group ethyl group has the beta hydrogen; however, this compound is kinetically inert as the metal center is both coordinatively and electronically saturated. So, coordinatively saturated means it has a coordination number of 6 and electronically saturated meaning that it is 18 valence electron complex. The 18 comes from 10 plus 10 from the amine plus 1, 11 and rhodium in neutral method is 9, 11 plus 9, 20 and there is two chart. So, this is the 18 valence electron complex.

So, this complex as we saw being both electronically and coordinatively saturate is because of this saturation this complex is overall kinetically inert despite having ethyl moiety which has beta hydrogen. So, what we saw that if the third criteria for elimination is satisfied properly then the ethyl moiety despite having a beta hydrogen cannot eliminate and the compound becomes kinetically inert that this is a very interesting example.

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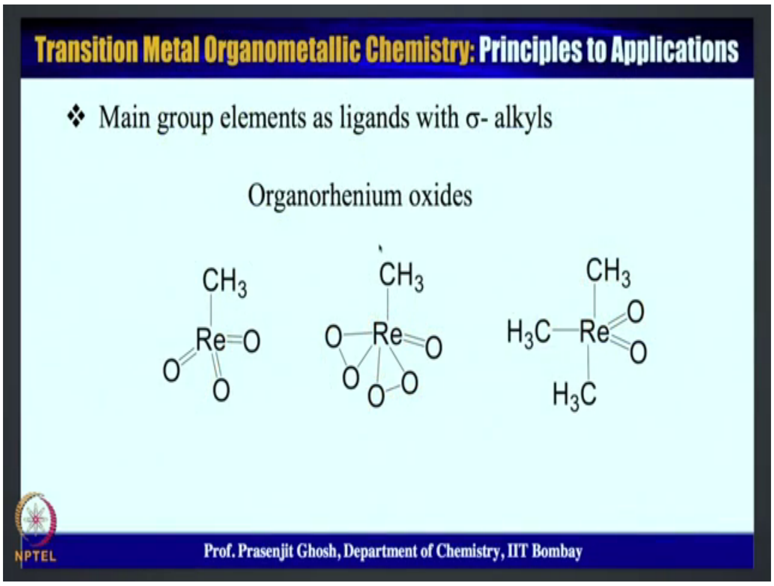

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- Main group elements as ligands with σ- alkyls

Organorhenium oxides

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Another example is transition metal alkyl bond when bound to main group elements as ligands sometimes are also stable and the example is this class of compounds call organo rhenium oxides.

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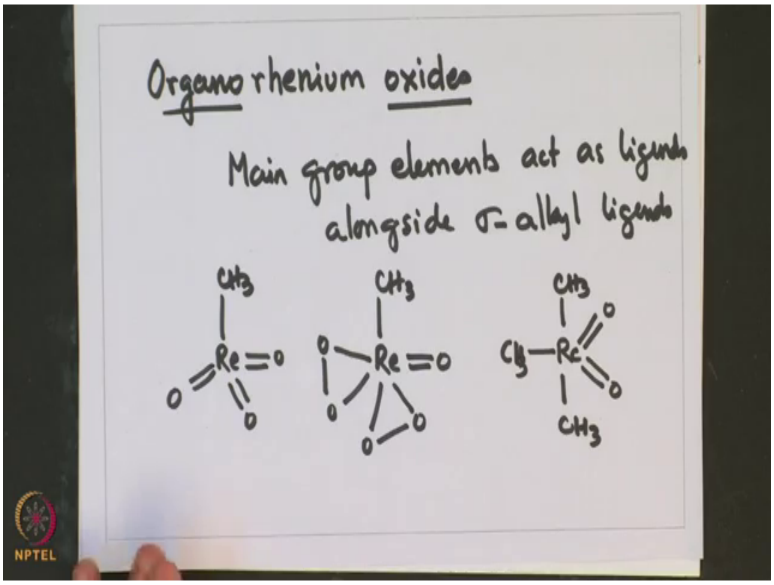

Organo rhenium oxides

Main group elements act as ligands alongside σ-alkyl ligands

So, in organo rhenium oxides main group elements act as ligand in addition to or alongside sigma alkyl ligands to illustrate this like to give the following examples methyl rhenium trioxide or methyl rhenium oxo this peroxide or dioxo rhenium trimethyl. These are a class of compounds where there is a rhenium alkyl moiety bound to heavier atoms.

This compounds has tremendous applications is various in various catalytic reactions which we will take up in the following class. In this class I summarize that we have looked into the kinetically inert nature of transition metal sigma alkyl complexes. The reason behind that and also how to make extremely stable transition metal sigma alkyl complexes by suppression of various beta hydrogen elimination pathways and if all of that strategies are put in place in a single molecule if all of them is realized all together then extremely stable transition metal sigma alkyl complexes may be synthesized. And also we have seen that if a metal center is coordinatively as well as electronically saturated then metal sigma alkyl groups despite having beta hydrogens they would not eliminate and the compound would be more stable.

With these we look forward to this important class of compounds in the next lecture called organo rhenium oxides which has very good applications in chemical catalysis and oxidation reactions and that will be the subject of topic for the next lecture.

Thank you.