Main Group Chemistry

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Lecture – 59

Organometallic compounds of Main Group Elements

Welcome to MSP lecture series on main group chemistry this is the last, but one lecture in the series of 60 lectures on main group elements. Of course, this is going to be the last lecture on organometallic chemistry of main group elements as well, after that I will be concluding the entire chemistry I spoke in the last 59 lectures. So, let me continue with the organosilicon compounds of course, while discussing group 14 chemistry, I did mention about organosilicon compounds and also I discussed about those polymers and all those things, let me just revisit again.

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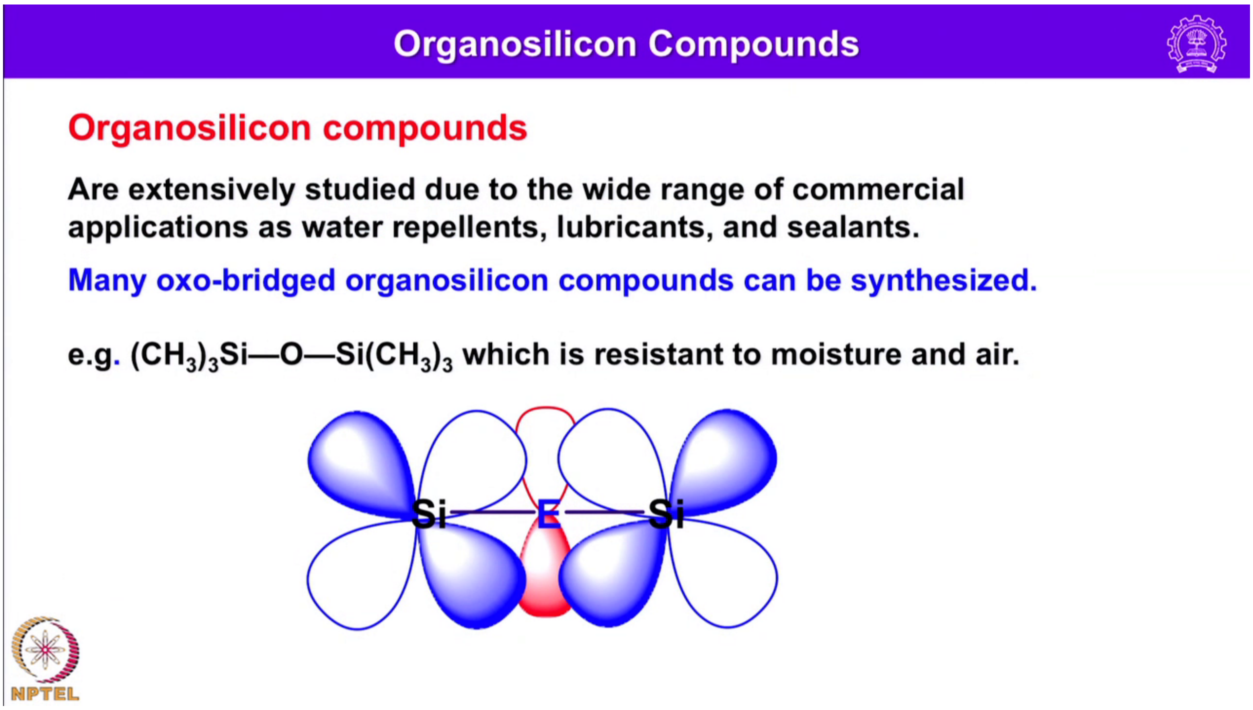

Organosilicon Compounds

Organosilicon compounds

Are extensively studied due to the wide range of commercial applications as water repellents, lubricants, and sealants.

Many oxo-bridged organosilicon compounds can be synthesized.

e.g. $(CH_3)_3Si—O—Si(CH_3)_3$ which is resistant to moisture and air.

This organosiliocn compounds are extensively studied due to the wide range of commercial applications as water repellents lubricants and sealants.

Many oxo-bridged organosiliocn compounds can be synthesized. So, one such example is shown here, you can see between this trialkyl trimethyls silicon; there is a oxygen bridge, which is resistant to moisture and air because here there is an extensive delocalization of oxygen lone pair over silicon empty orbitals, as result what happens the bond is resistant to moisture and air and also it has elasticity in it. So, the lone face on auction or partially localized into the vacant sigma star orbitals of silicon as a result the directionality of the SiO bond is reduced making the structure more flexible. So, if you go back you know I showed here it is not essentially the silicon 3 d orbital which overlap with 2 p orbitals of oxygen, it is essentially sigma star of m e 3 S i that interacts with pi electrons present on oxygen this is called negative hyper conjugation, and in some books if they referred as d pi p pi interaction it is not correct because the 3 d orbitals are too high in energy and they are not really used in any bonding in case of silicon.

Although we come across sodium hexaflorosilicate Na 2 Si of 6 where silicon has coordination number 6, it is a again a hypervalent molecule 2 fluorine atoms whatever they are giving 4 electrons, they essentially remain nonbonding that I showed when I was discussing molecular orbital theory of polyatomic molecules, especially in case of Sulphur hexafluoride. So, the flexibility permits silicon elastomer to remain rubber like down to very low temperature, d localization also accounts for low basicity of an oxygen atom attached to silicon, as the electrons needed for the oxygen atom to act as base or partially removed. As a result the Lewis basicity is also reduced the planarity of trimethylsilane plar nsi h 3 three times is also explained by the delocalization of the lone pair on nitrogen, is also very weak basic in nature.

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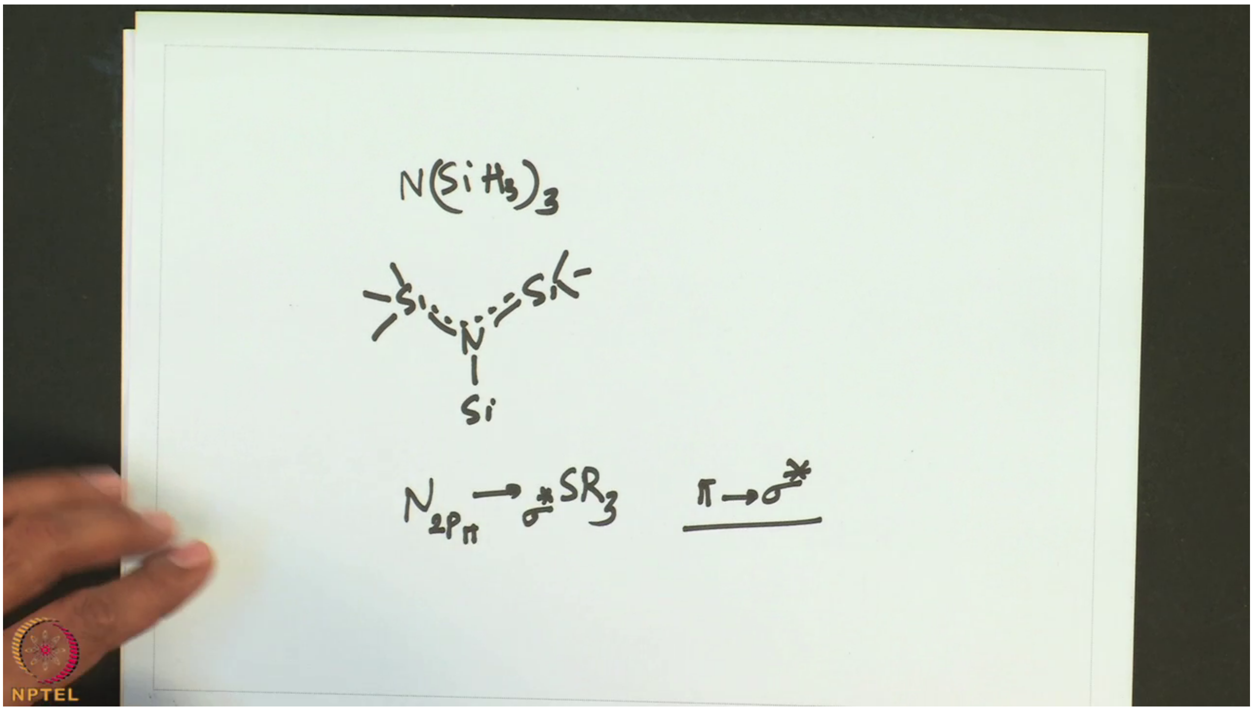

For example, if you are considering N SiH 3 times one can write here n.

So, here the delocalization is there as a result this loan pair is delocalized into I can call essentially 2 P pi to SR 3 sigma star. So, we can call it as pi to sigma star. So, this is called negative hyper conjugation because of this one what happens electron are delocalized, as a result this nitrogen is no longer Lewis basic in nature or it is very very weak base compare to triethylamine or tri methylamine. So, let us look into the preparation of some of organosiliocn compounds, I did mention that I had discussed earlier, but let me come and write some of these reactions here.

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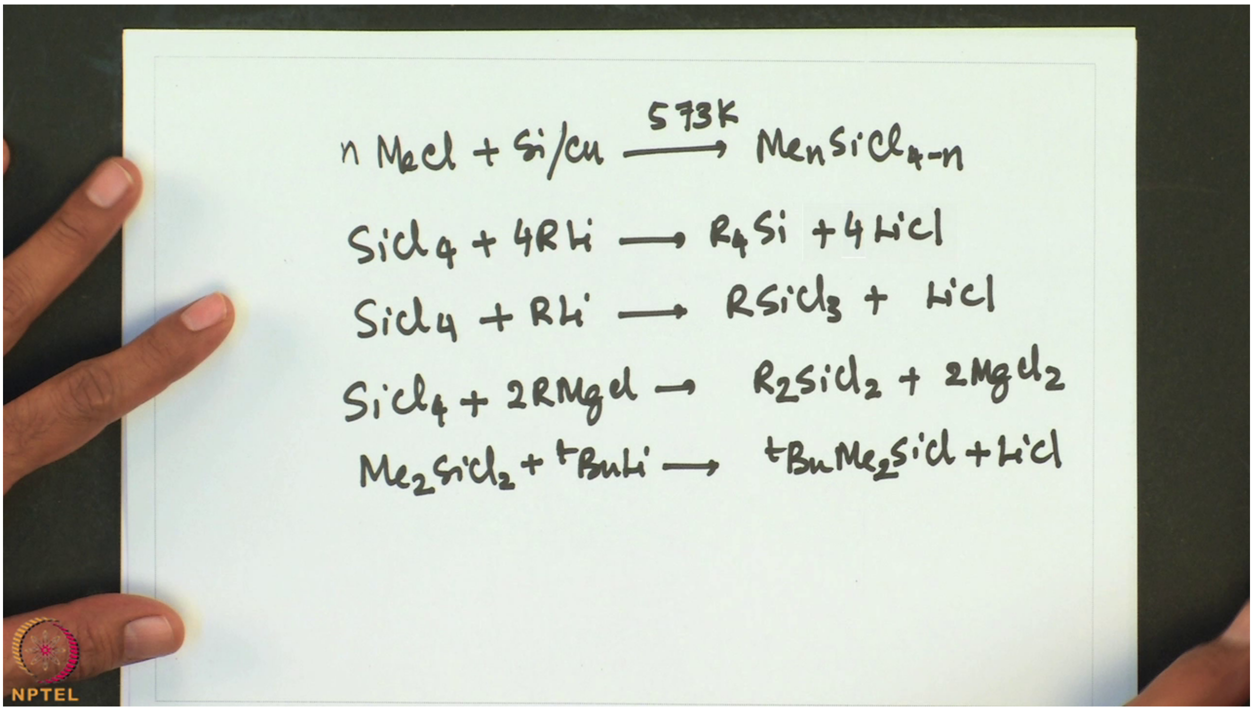

$n\,MeCl + Si/Cu \xrightarrow{573K} Me_nSiCl_{4-n}$

$SiCl_4 + 4RLi \longrightarrow R_4Si + 4LiCl$

$SiCl_4 + RLi \longrightarrow RSiCl_3 + LiCl$

$SiCl_4 + 2RMgCl \longrightarrow R_2SiCl_2 + 2MgCl_2$

$Me_2SiCl_2 + {}^tBuLi \longrightarrow {}^tBuMe_2SiCl + LiCl$

Methyl chloride is treated with silicon over heated copper at 573 kelvin to form Men Si C l 4 minus n. If I take SiCl 4 and treat with 4 equivalents of Rli it gives r 4 Si for example, SiCl 4 3 can tetra chloride is treated with 4 equivalents of methyl lithium.

If forms tetramethylsilane or treatment with one equivalent of Rli gives RSiCl 3 plus LiCl one can also react silicon tetrachloride with Grignard reagent 2 RMgcl it gives or dimethyl dichlorosilane on treatment with tertiary butyl lithium gives tertiary butyl dimethyl chloro silane like this one can do a series of reactions to get desired compounds made. So, silicon carbon bonds are actively strong here, the bond enthalpy is about 380 kilo joules per mole and R 4 Si tetra alkyl silane is posses very high thermal stabilities tetraethylsilane on chlorination gives Cl CH 2 to CH 2 Si 4 times.

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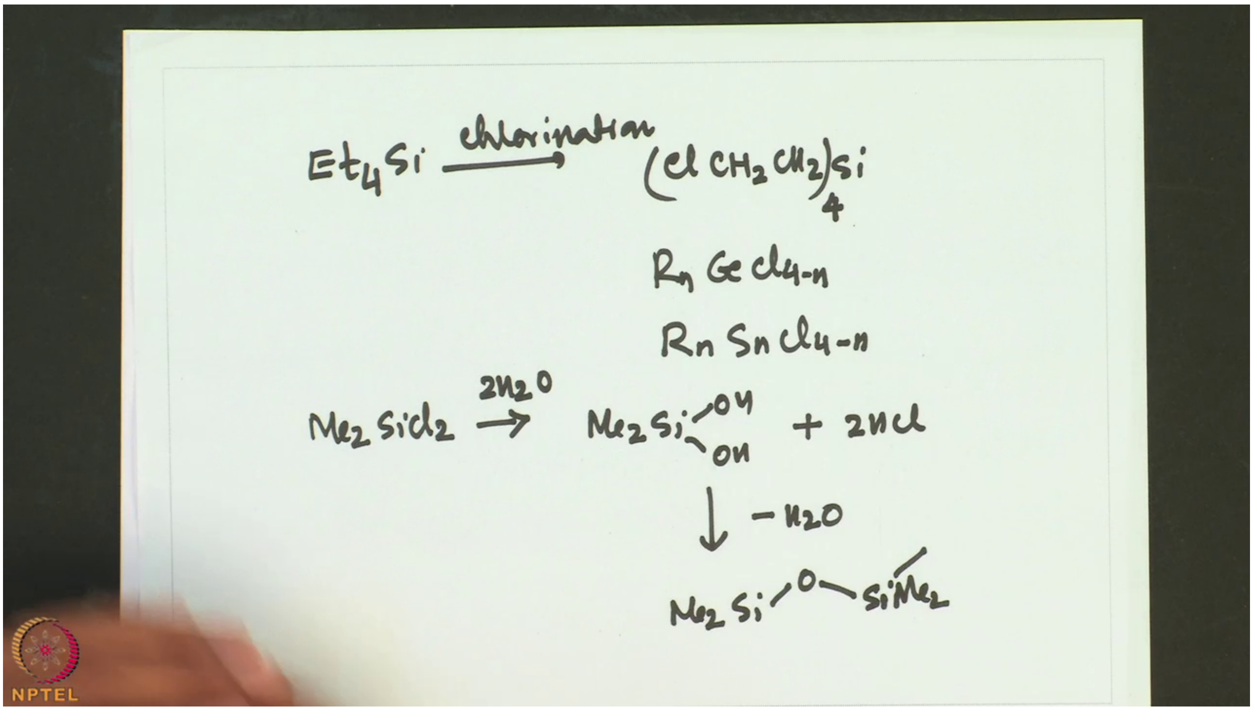

So, in contrast to the chlorination of R 4 tetra alkyl germanium or tetra alkyl tin, which essentially yield similar reactions yield RnGcl 4 minus n or Rn Sncl 4 minus n. So, this is the difference between the reactivity of silicon to carbon bond and rest of the group 14 members. Me 2 Sicl to dimethyl dichlorosilane on hydrolysis produces silicons, initially it can give Me 2 Si OH plus 2 Hcl and this can undergo. So, it can continue like this. If it is more it just it can undergo hydrolysis to form hi or a cyclic structure. Me 3 Sicl can react with sodium Cp to give cyclopentadienyl compound as well.

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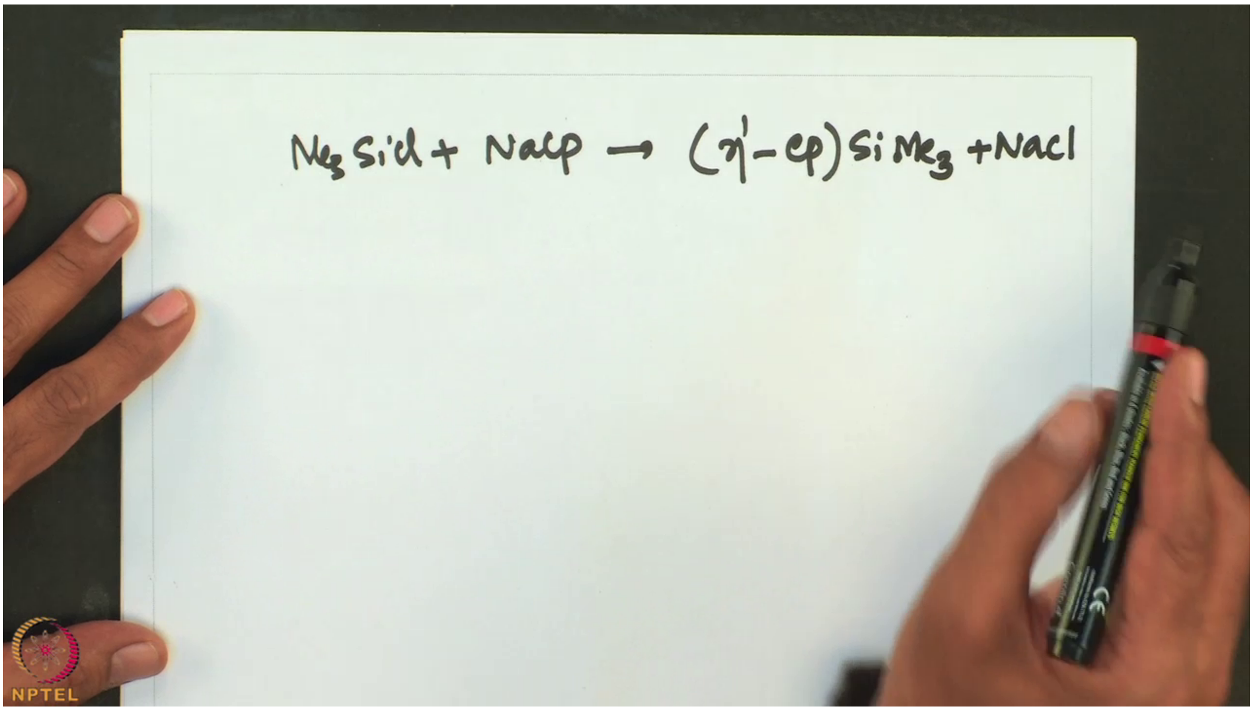

$Me_3SiCl + NaCp \rightarrow (\eta^1\text{-}cp)SiMe_3 + NaCl$

For example Me 3 Sicl when its reacted with NaCp it gives of course, here hepatocyty is 1.

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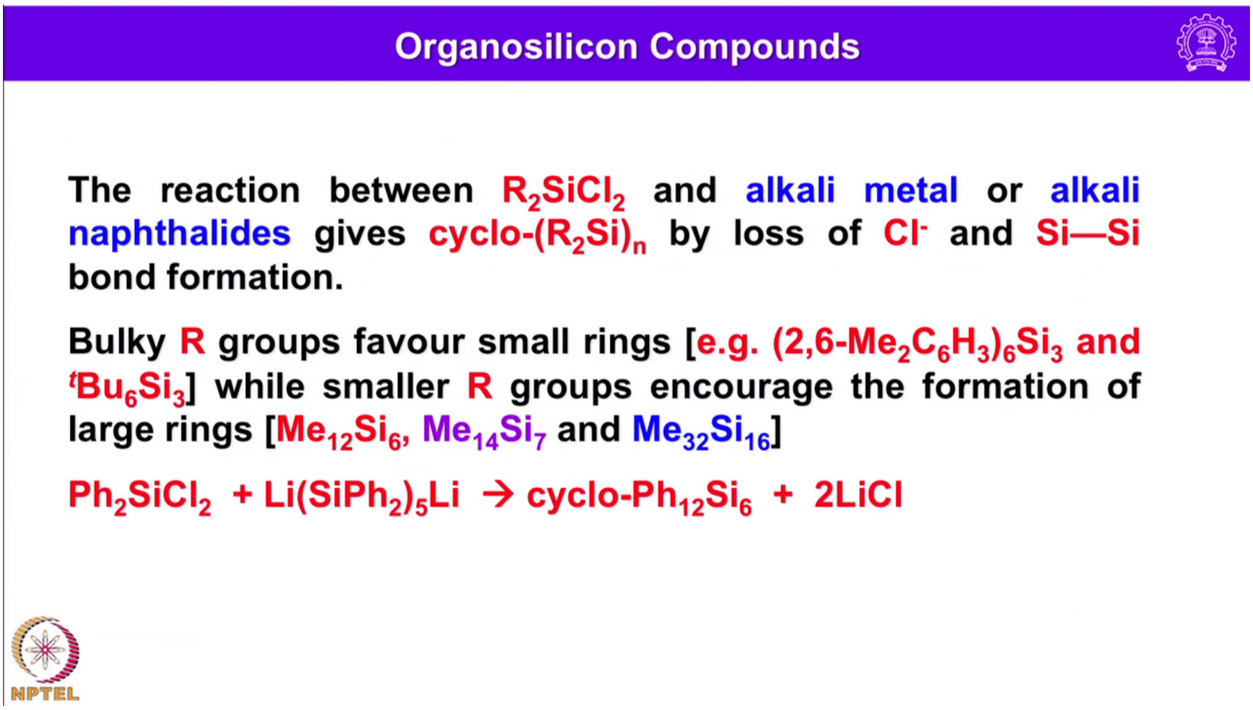

Organosilicon Compounds

The reaction between R_2SiCl_2 and alkali metal or alkali naphthalides gives cyclo-$(R_2Si)_n$ by loss of Cl^- and Si—Si bond formation.

Bulky R groups favour small rings [e.g. $(2,6\text{-}Me_2C_6H_3)_6Si_3$ and ${}^tBu_6Si_3$] while smaller R groups encourage the formation of large rings [$Me_{12}Si_6$, $Me_{14}Si_7$ and $Me_{32}Si_{16}$]

$Ph_2SiCl_2 + Li(SiPh_2)_5Li \rightarrow \text{cyclo-}Ph_{12}Si_6 + 2LiCl$

The reaction between dialkyl dichlorosilane and alkali metal or alkali naphthalides gives a cyclic compound of this type by loss of chloride, and Si-Si bond formation takes place here. So, bulky R groups favour smaller rings, and if you use sufficiently bulky group even a Si-Si double bonder component can also be made for example, here diphenyl dichlorosilane when its treated with here SiPh 2 5 times having Si-Si 5 leakages with di lithiated one it can give, a hexamer of this type having Si-Si bond and each silicon having 2 phenyl groups. So, bulky substituent stabilizes diffuse sufficiently bulky substituents it can stabilize Si-Si double bond.

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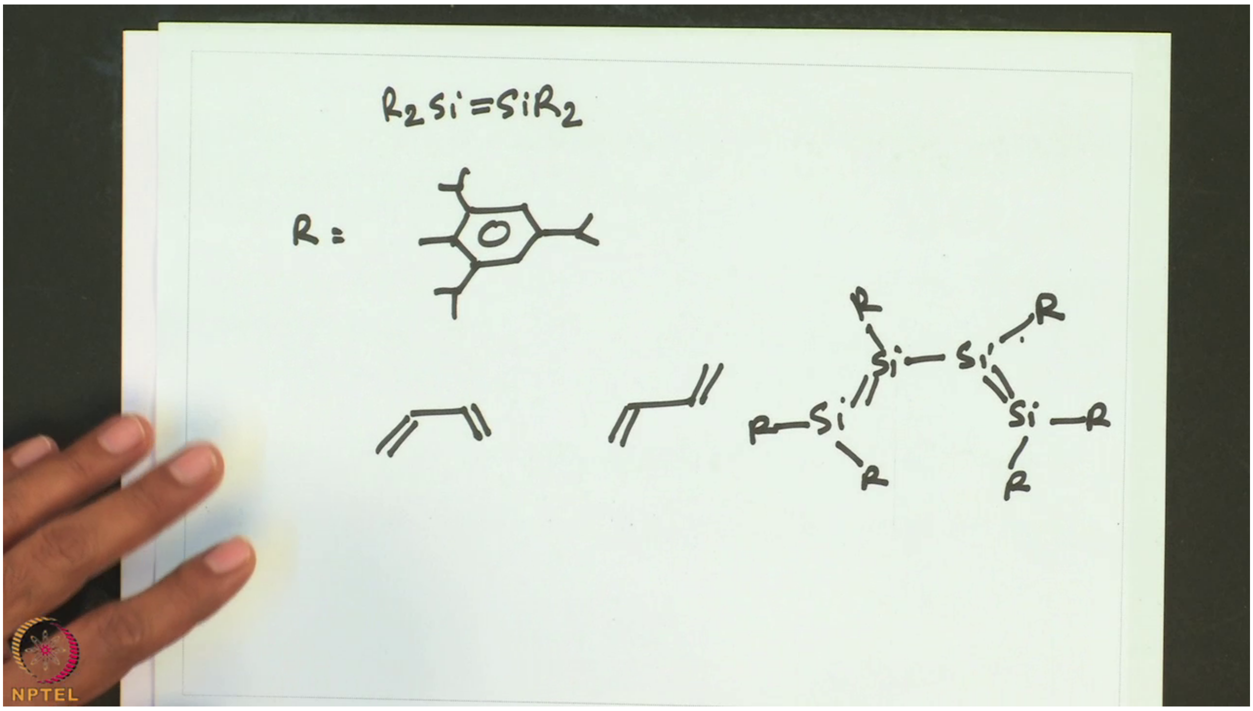

For example R 2 Si something like thing, they sterically demanding 2 4 6 for example, in these cases R can be one can you something like this. 2, 4, 6 diisopropyl phenyl group, ok.

So, this is essentially a first example of a compound having silicon see coming double bond, this type of compounds are also known.

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One can also make a compound of this type as well. Of course, similar compounds unknown for germanium as well and here also again bulky groups are used 2 force diisopropyl phenyl group.

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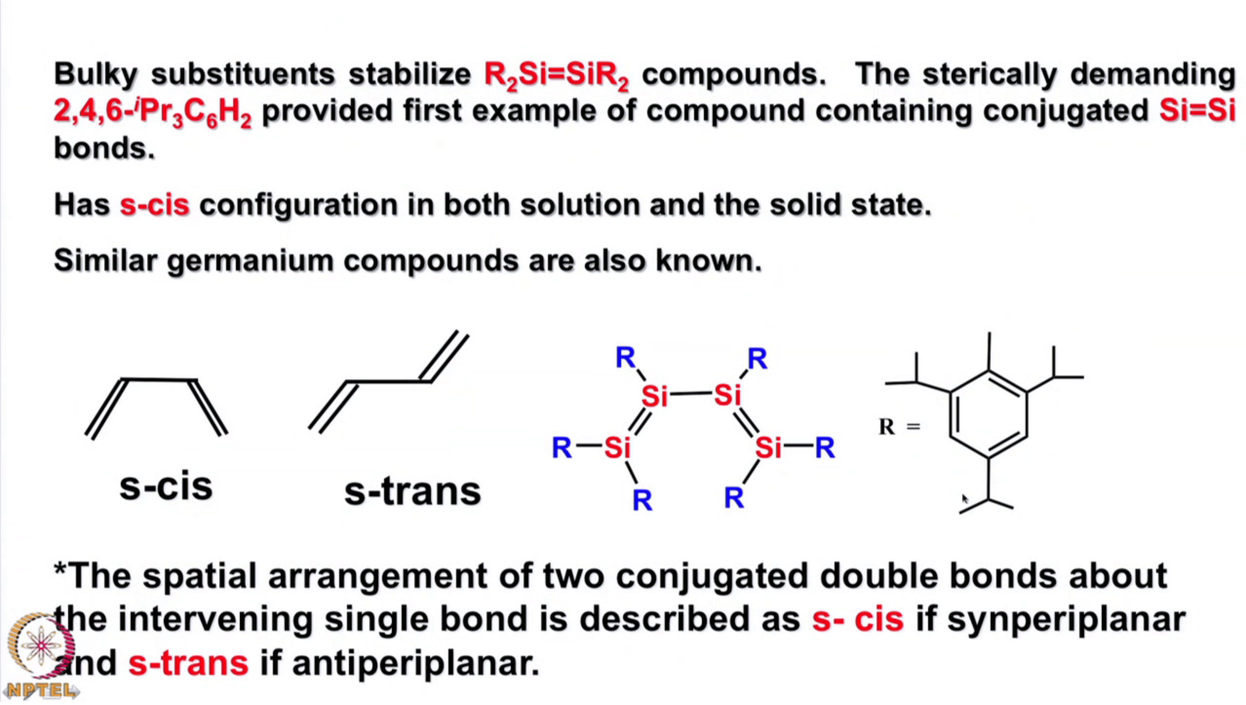

Bulky substituents stabilize $R_2Si{=}SiR_2$ compounds. The sterically demanding 2,4,6-^{i}$Pr_3C_6H_2$ provided first example of compound containing conjugated Si=Si bonds.

Has s-cis configuration in both solution and the solid state.

Similar germanium compounds are also known.

*The spatial arrangement of two conjugated double bonds about the intervening single bond is described as s- cis if synperiplanar and s-trans if antiperiplanar.

And the spatial arrangement of 2 conjugated double bonds about the intervening single bond is described as s-cis if synperiplanar and s-trans if antiperiplanar. So, this is how the naming of these 2 different confirmations.

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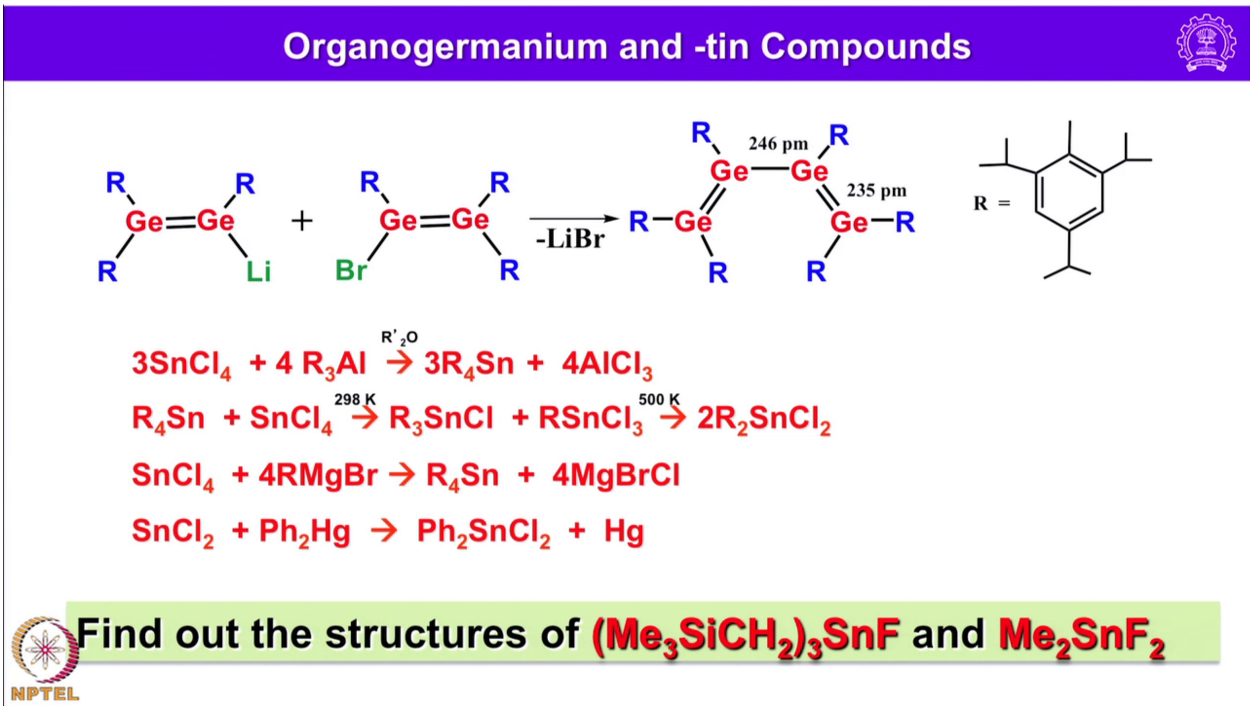

Organogermanium and -tin Compounds

$3SnCl_4 + 4\,R_3Al \xrightarrow{R'_2O} 3R_4Sn + 4AlCl_3$

$R_4Sn + SnCl_4 \xrightarrow{298\ K} R_3SnCl + RSnCl_3 \xrightarrow{500\ K} 2R_2SnCl_2$

$SnCl_4 + 4RMgBr \rightarrow R_4Sn + 4MgBrCl$

$SnCl_2 + Ph_2Hg \rightarrow Ph_2SnCl_2 + Hg$

Find out the structures of $(Me_3SiCH_2)_3SnF$ and Me_2SnF_2

Organo germanium compounds as I mentioned similar organo germanium compounds can also be made you can see here of course, here one can take this a lithium reagent, and one can have halide reagent and then when you combine lithium bromide is liberated that leads to the formation of this butadiene type compounds here. You can also see with the tin one can make organo tin compounds using one of these methods here ok.

Or depending upon the compounds we need to prepare you can choose the right kind of organometallic reagent. Of course, if you are can find out the structures of Me 3 SiCH 2 whole trice SnF as well as dimethyl difluoro tin compound; of course, one can use valence bond theory conveniently to arrive at the structures of this 2 compounds.

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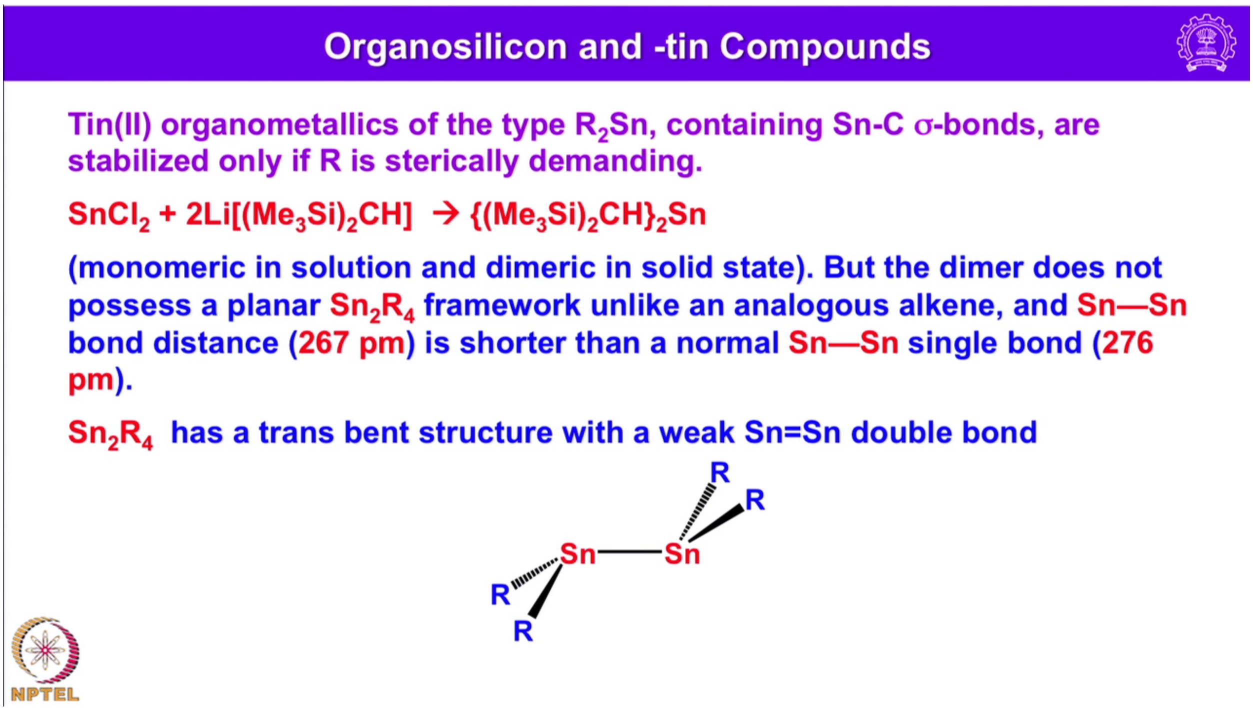

Organosilicon and -tin Compounds

Tin(II) organometallics of the type R_2Sn, containing Sn-C σ-bonds, are stabilized only if R is sterically demanding.

$SnCl_2 + 2Li[(Me_3Si)_2CH] \rightarrow \{(Me_3Si)_2CH\}_2Sn$

(monomeric in solution and dimeric in solid state). But the dimer does not possess a planar Sn_2R_4 framework unlike an analogous alkene, and Sn—Sn bond distance (267 pm) is shorter than a normal Sn—Sn single bond (276 pm).

Sn_2R_4 has a trans bent structure with a weak Sn=Sn double bond

Tin 2 organometallic compounds of the type R 2 Sn containing Sn carbons sigma bonds are stabilized only if R is sterically demanding; that means, with very bulky group R 2 Sn can undergo dimerization for example, Sn C l 2 I have shown one reaction, here SnCl 2 treated with this very bulky lithium salt, leads to the formation of a R 2 Sn type compound, and it is monomeric in solution and dimeric in solid state and, but the dimer does not possess a planar Sn 2 R 4 similar to ethylene slightly different and here Sn's Sn bond distance is 267 which is shorter than a normal Sn-Sn bond distance of 276 picometer. So, this indicates some multiple bond character in this compound that mean the Sn 2 R 4 has a trans bend structure with a weak Sn-Sn double bond. It appears something like this.

So, it is in contrast to the carbon analogue Sn C 2 R 4 ethylene derivative, it has a planar structure whereas; this one is a bend structure then how to explain the bonding in this one. So, one can explain bonding using a different hybration concept here.

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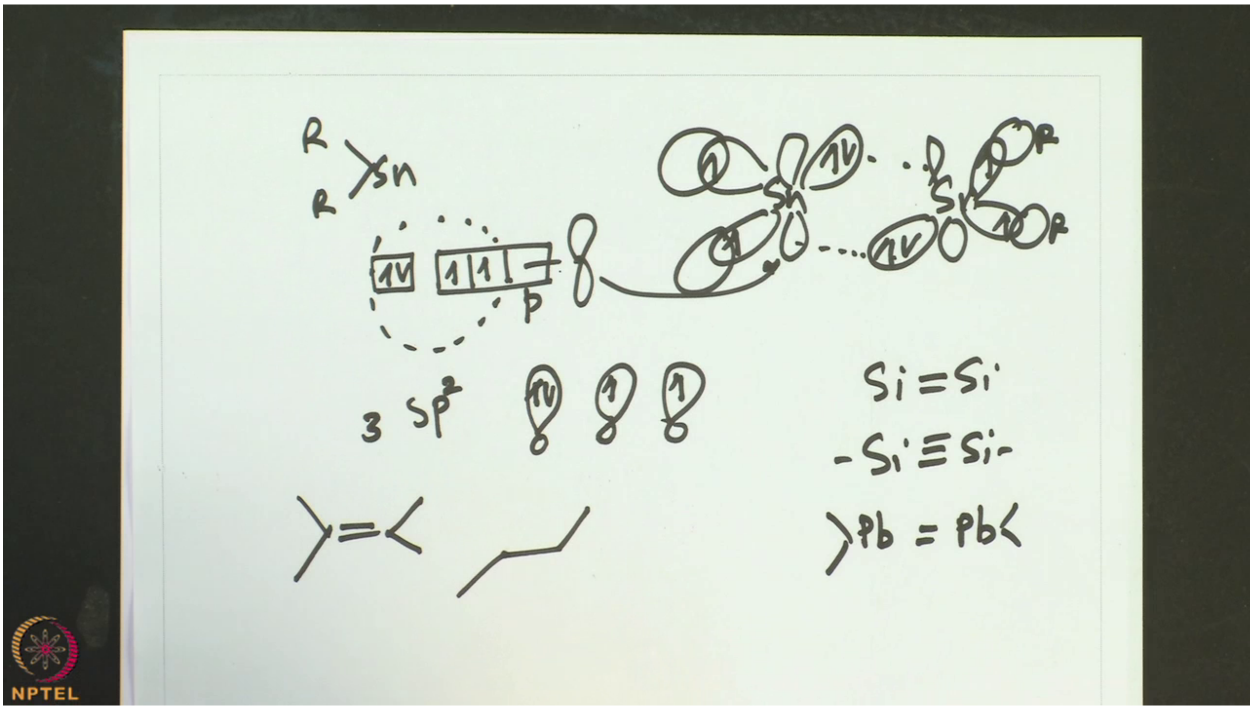

So, here let us consider R R Sn in the; for this one of course, Sn has ns 2 np 2 electronic configuration, we have something like this. So, initially we have something like this. So, now, prior to the reaction what happens it undergoes hybridization Sp 2 hybridization. In this Sp 2 hybridization basically what happens electron is not promoted here to the one of the p. One of the p remains empty and now these undergo hybridization to form 3 SP 2 hybrid orbital.

So, 3 SP 2 hybrid will be having a situation like this now, 2 electrons one electron one electron. So, now, with Sn one electron, one electron and 2 electron are there. So, now, here we have this p orbital is here. So, this is coming here it is perpendicular to that one. So, of course, here R is there. So, this is completed this is completed. So, one more such species will come here this is your P orbital. So, this is with R completed SP a covalent bond, now these 2 will interact. So, in order to facilitate this interaction they cannot be it cannot be something like this, it has to be something like this. So, in this case appropriate orientation of this mtp orbital can come and it in interact with this one ok.

So; that means, here this is very interesting of course, here if you overall consider 4 bonds are there 4 electrons are there, 2 covalent bonds are there, but on the other hand this is little different and also this is week; however, it add some multiple bond character here yes.

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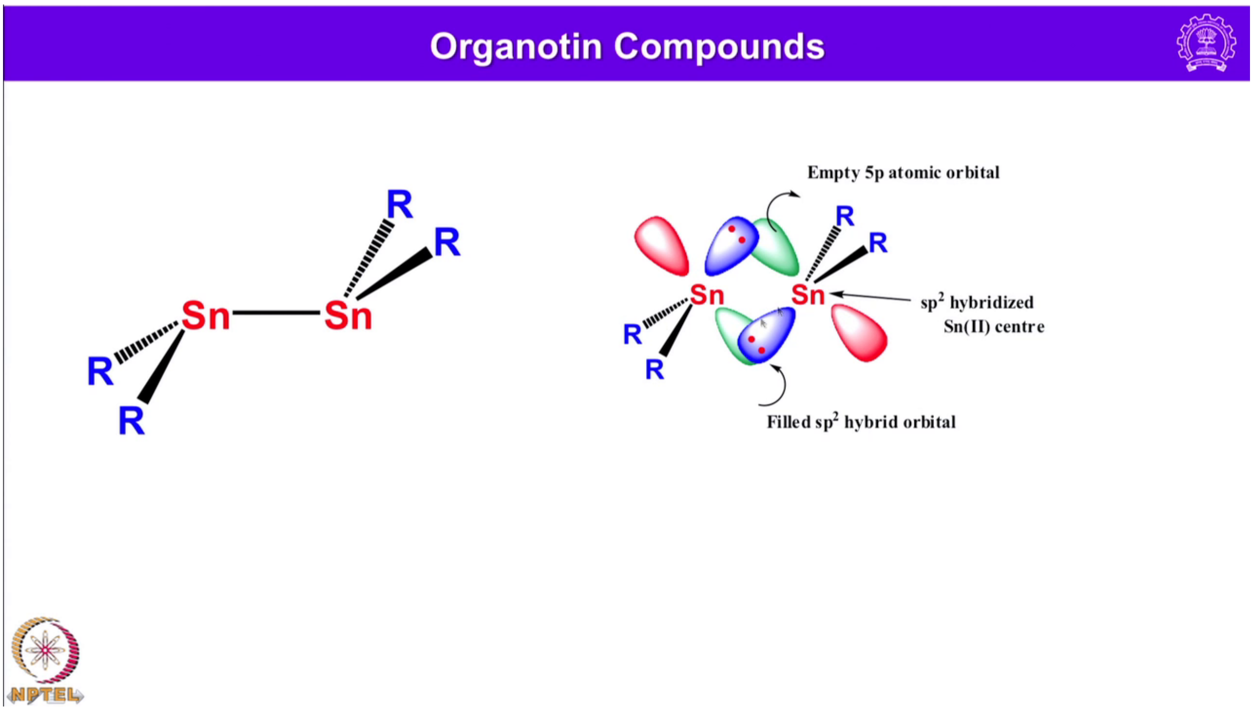

Organotin Compounds

We can see here this is a sp 2; having 2 electrons and this sp 2 having one electron each are completed the bonding here covalent bonds and here this is a P orbital orientation and this the P orbital orientation in order to facilitate the interaction between this lone pairs and one of the mtp orbital, a they have to be bent in this fashion as a result the overlapping happens that results in the organotin compound having this kind of structure. And similar kind of bonding concept can be utilized in explaining the silicon silicon double bond as well as tin tin double bond and lead lead double bond as well.

So, silicon silicon double bond one can use even silicon silicon triple bond also one can use this method, and also pb pb double bond also one can explain using this kind of sp 2 hybridization having 2 sp orbital having one electron and one sp 2 having 2 electron, and having a m t p orbital they interact in this fashion to form this kind of bonding.

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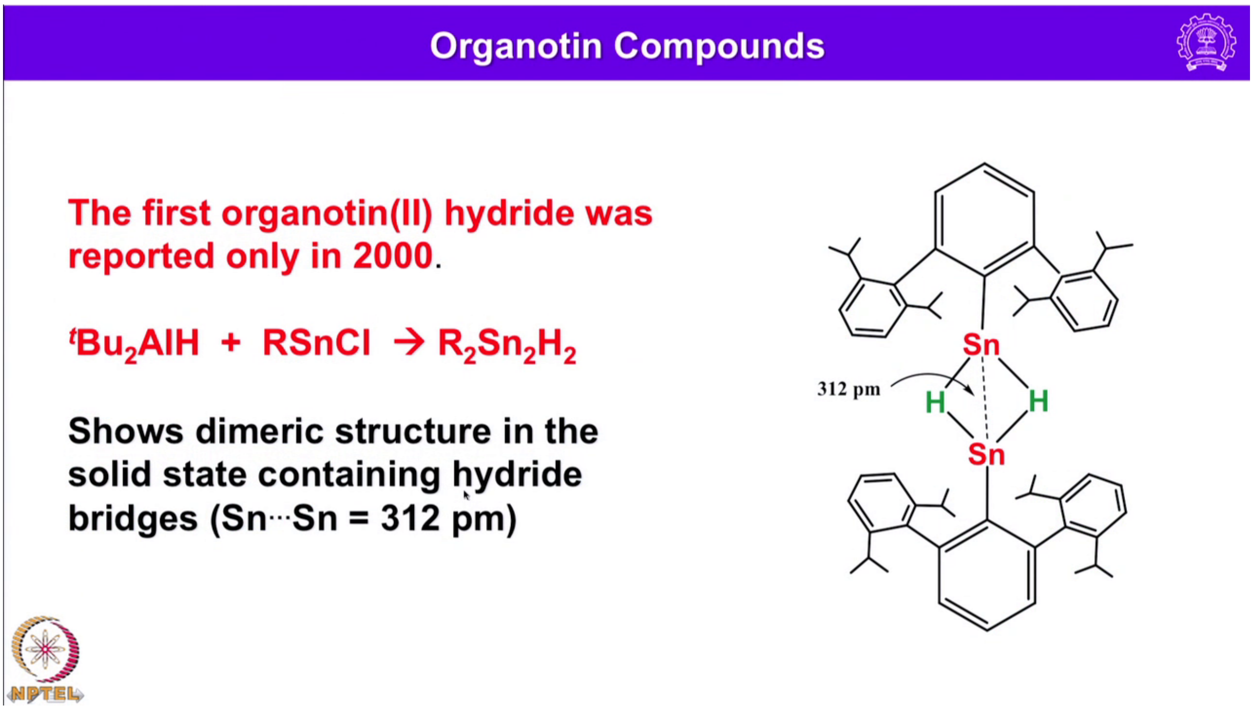

Organotin Compounds

The first organotin(II) hydride was reported only in 2000.

$^t\mathrm{Bu}_2\mathrm{AlH} + \mathrm{RSnCl} \rightarrow \mathrm{R}_2\mathrm{Sn}_2\mathrm{H}_2$

Shows dimeric structure in the solid state containing hydride bridges (Sn···Sn = 312 pm)

The first organotin hydride was reported only recently in 2000. So, this was prepared in this fashion, di butyl aluminum hydride was treated with RSnCl to form R 2 Sn 2 H 2 here, and this shows dimeric structure in the solid state containing hydrate bridges like this and this Sn-Sn distance is to 312 picometer and of course, here also very bulky groups are employed to stabilize this SNH bond.

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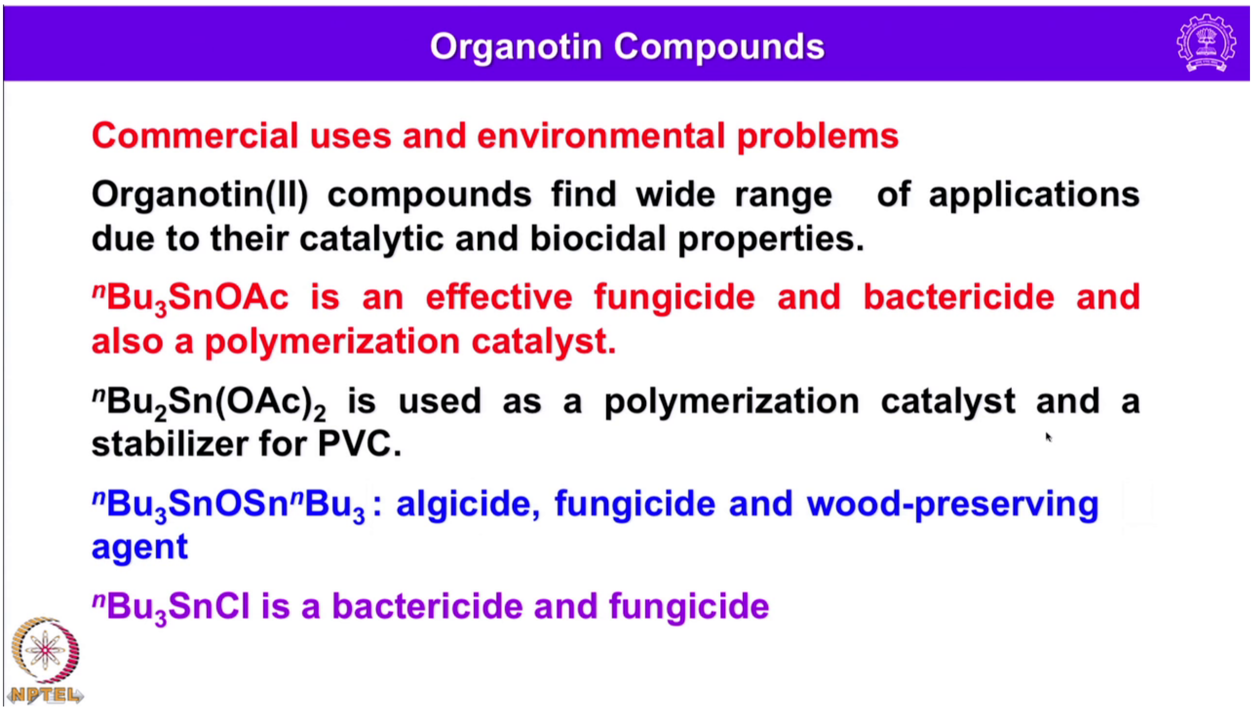

Organotin Compounds

Commercial uses and environmental problems

Organotin(II) compounds find wide range of applications due to their catalytic and biocidal properties.

$^{n}Bu_3SnOAc$ is an effective fungicide and bactericide and also a polymerization catalyst.

$^{n}Bu_2Sn(OAc)_2$ is used as a polymerization catalyst and a stabilizer for PVC.

$^{n}Bu_3SnOSn^{n}Bu_3$: algicide, fungicide and wood-preserving agent

$^{n}Bu_3SnCl$ is a bactericide and fungicide

So, commercial uses and environmental problems let us look into it. So, organotin compounds find wide range of applications due to their catalytic and biocidal properties, this compound Bu 3 Sn OAc acetate compound of tin is an effective fungicide and bactericide and also a polymerization catalyst, and also this one is also use as a polymerization catalyst and a stabilizer for polyvinyl chloride, and this compound is also used an algicide fungicide and also wood preserving agent and tributyltin chloride is a bactericide, and fungicide and this one triphenyl tin hydroxide used as an agricultural fungicide for crops such as potato sugar beet and peanuts.

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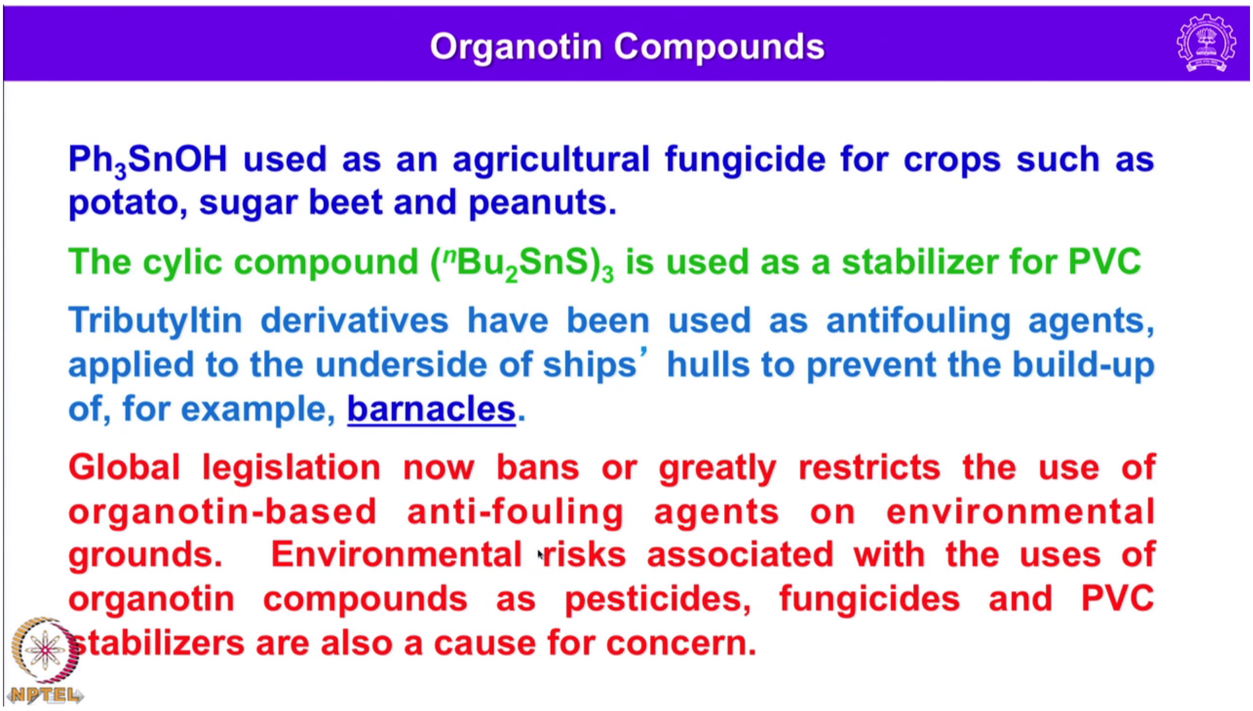

Organotin Compounds

Ph_3SnOH used as an agricultural fungicide for crops such as potato, sugar beet and peanuts.

The cylic compound $(^{n}Bu_2SnS)_3$ is used as a stabilizer for PVC

Tributyltin derivatives have been used as antifouling agents, applied to the underside of ships' hulls to prevent the build-up of, for example, barnacles.

Global legislation now bans or greatly restricts the use of organotin-based anti-fouling agents on environmental grounds. Environmental risks associated with the uses of organotin compounds as pesticides, fungicides and PVC stabilizers are also a cause for concern.

And this sulphur a cyclic compound is used as a stabilizer for polyvinyl chloride, tributyltin derivative have been used as antifouling agents, applied to the underside of shapes hulls to prevent the buildup for example, barnacles, I will tell you what are barnacles.

Global legislation now bans or greatly restricts the use of organotin based anti-fouling agents, on environmental grounds. So, environmental risks associated with the uses of organotin compounds as pesticides, fungicides, and PVC stabilizer also a cause for concern. So, a barnacle is a type of arthropod belonging to infra class siri pedia in the sub phylum crustacea and is hence related to crabs and lobsters ok.

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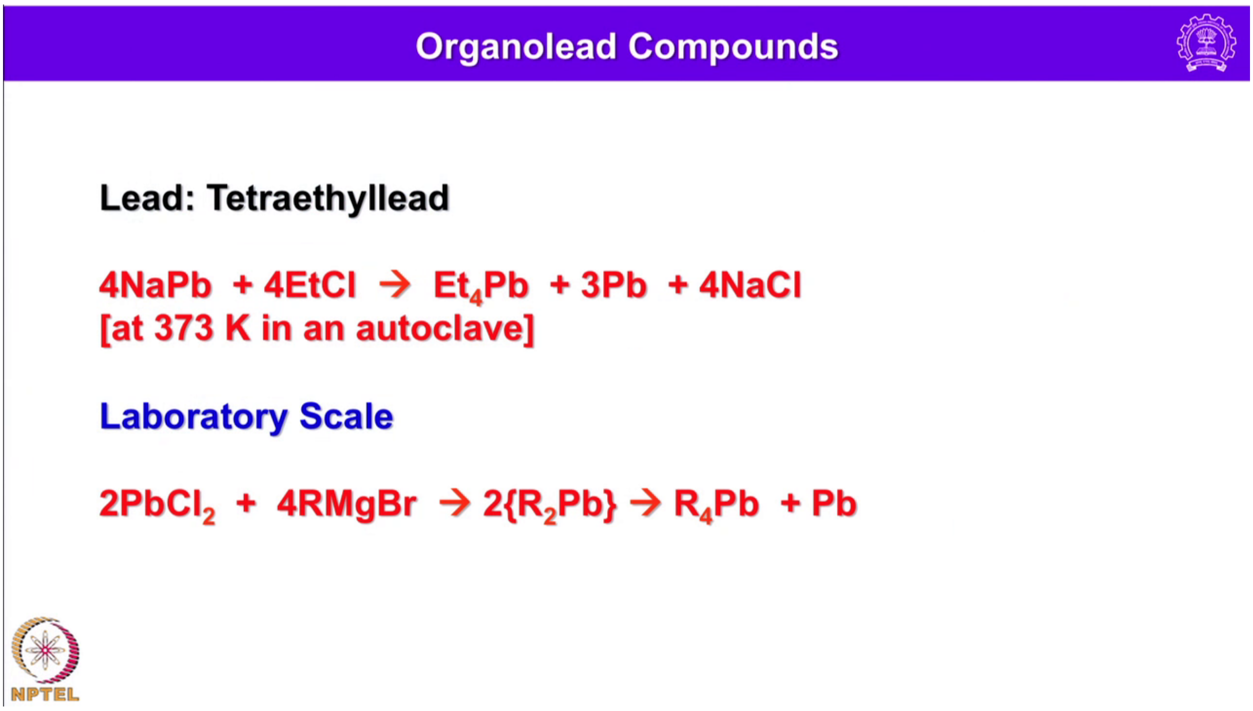

Organolead Compounds

Lead: Tetraethyllead

$4NaPb + 4EtCl \rightarrow Et_4Pb + 3Pb + 4NaCl$
[at 373 K in an autoclave]

Laboratory Scale

$2PbCl_2 + 4RMgBr \rightarrow 2\{R_2Pb\} \rightarrow R_4Pb + Pb$

And tetraethyl lead is another important compound, used to be an additive for the petrol that is prepared starting from sodium Pb treated with 4 equivalents of ethyl chloride to form tetraethyl lead and of course, this reaction is performed in an autoclave 373 kelvin. So, laboratory scale involves the treatment of lead chloride PbCl 2 with 4 equivalents of Grignard reagent RMgBR.

This gives R 2 Pb and it further undergoes this proportional into R 4 Pb plus Pb comes ok.

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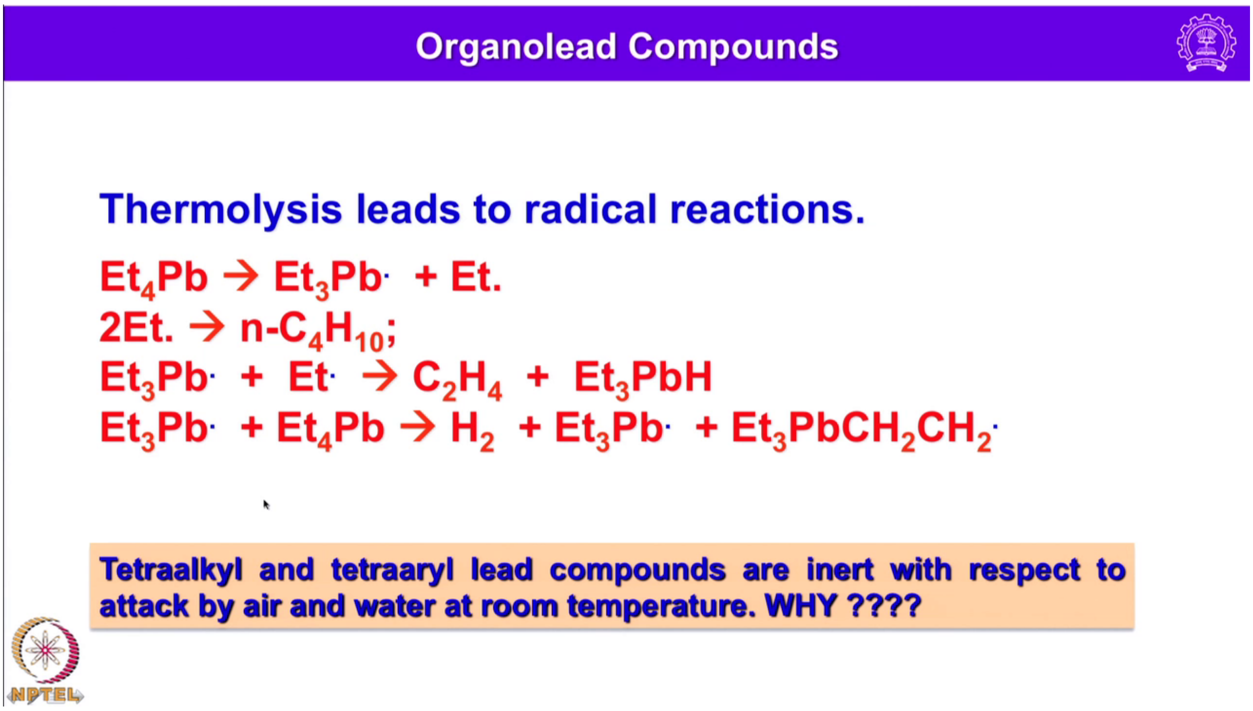

Organolead Compounds

Thermolysis leads to radical reactions.

$Et_4Pb \rightarrow Et_3Pb\cdot + Et.$

$2Et. \rightarrow n\text{-}C_4H_{10};$

$Et_3Pb\cdot + Et\cdot \rightarrow C_2H_4 + Et_3PbH$

$Et_3Pb\cdot + Et_4Pb \rightarrow H_2 + Et_3Pb\cdot + Et_3PbCH_2CH_2\cdot$

Tetraalkyl and tetraaryl lead compounds are inert with respect to attack by air and water at room temperature. WHY ????

So, thermolysis leads to radical reactions here, these radical reactions are responsible for its utility in an additive agent in petrol of course, because of its toxic environmental issues, now no longer this is added that is a reason people use unleaded petrol for their automobiles. Tetraalkyl and tetraaryl lead compounds are inert with respect to attack by air and water at room temperature, the reason is very simple therefore, coordinated and they are stabilized and they do not have empty orbital, and the next empty orbitals are quite high in energy. As a result they are quite stable towards hydrolysis under normal circumstances at room temperature if you heat it of course, they undergo hydrolysis.

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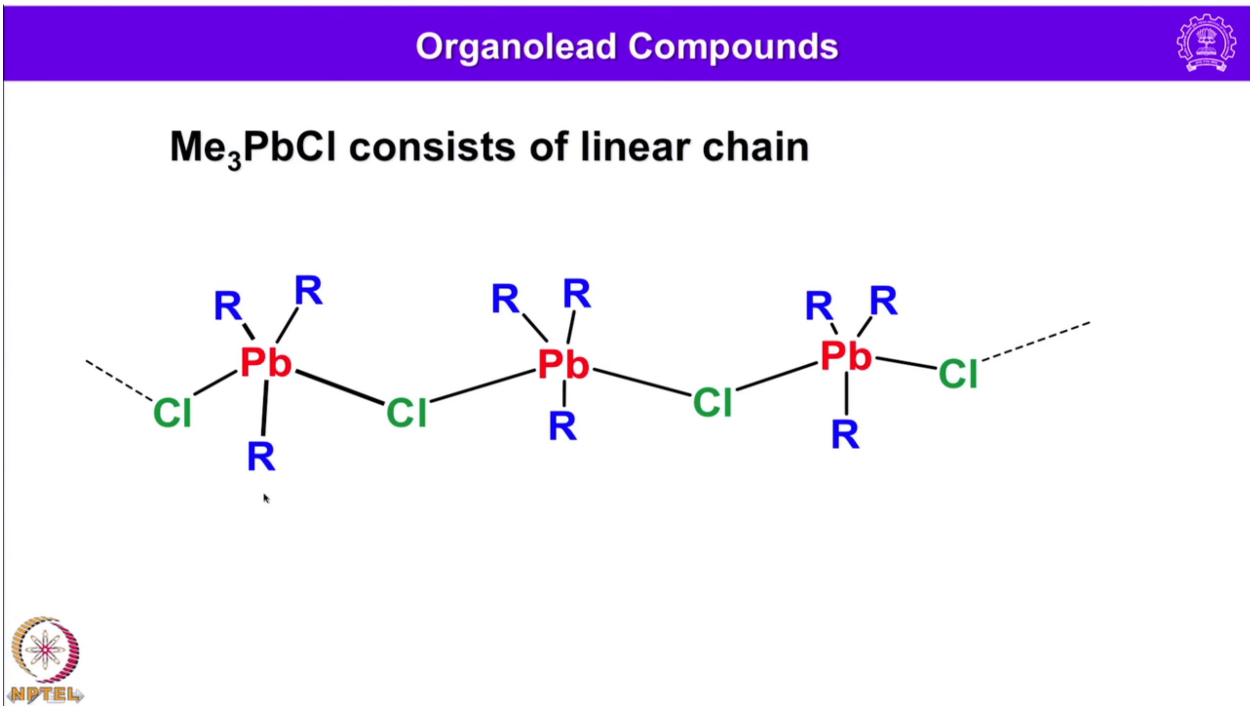

Organolead Compounds

Me_3PbCl consists of linear chain

So, this trimethyllead chloride consist of linear chains, this cyclopentadienyl lead compound solid state structure is shown here.

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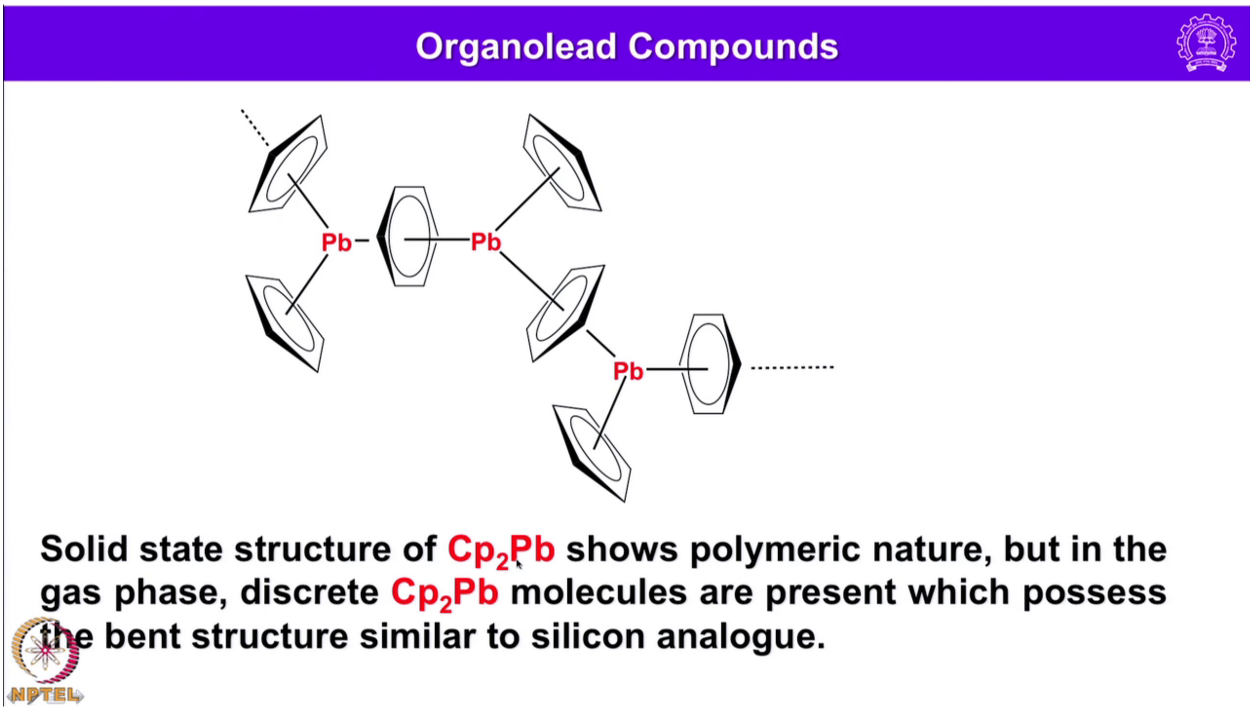

Organolead Compounds

Solid state structure of Cp_2Pb shows polymeric nature, but in the gas phase, discrete Cp_2Pb molecules are present which possess the bent structure similar to silicon analogue.

It shows polymeric structure, but in the gas phase discrete ferrozine type molecules are present which possess the bend structure similar to silicon analogue.

Of course as I mentioned R 2 Pb double bond Pb r 2 double bonded dimmer of R 2 Pb the structure of this one is very similar to the tin compound.

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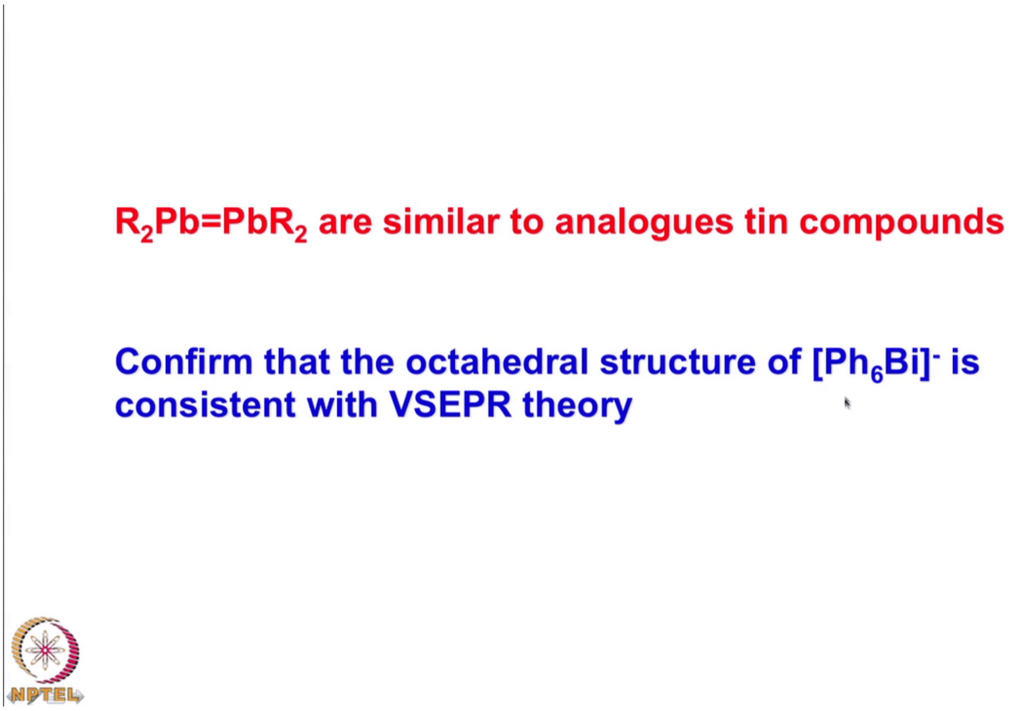

$R_2Pb{=}PbR_2$ are similar to analogues tin compounds

Confirm that the octahedral structure of $[Ph_6Bi]^-$ is consistent with VSEPR theory

And of course, one can also look into the structure of hexa phenyl bismuth, using vsepr theory this is a problem for you can work out.

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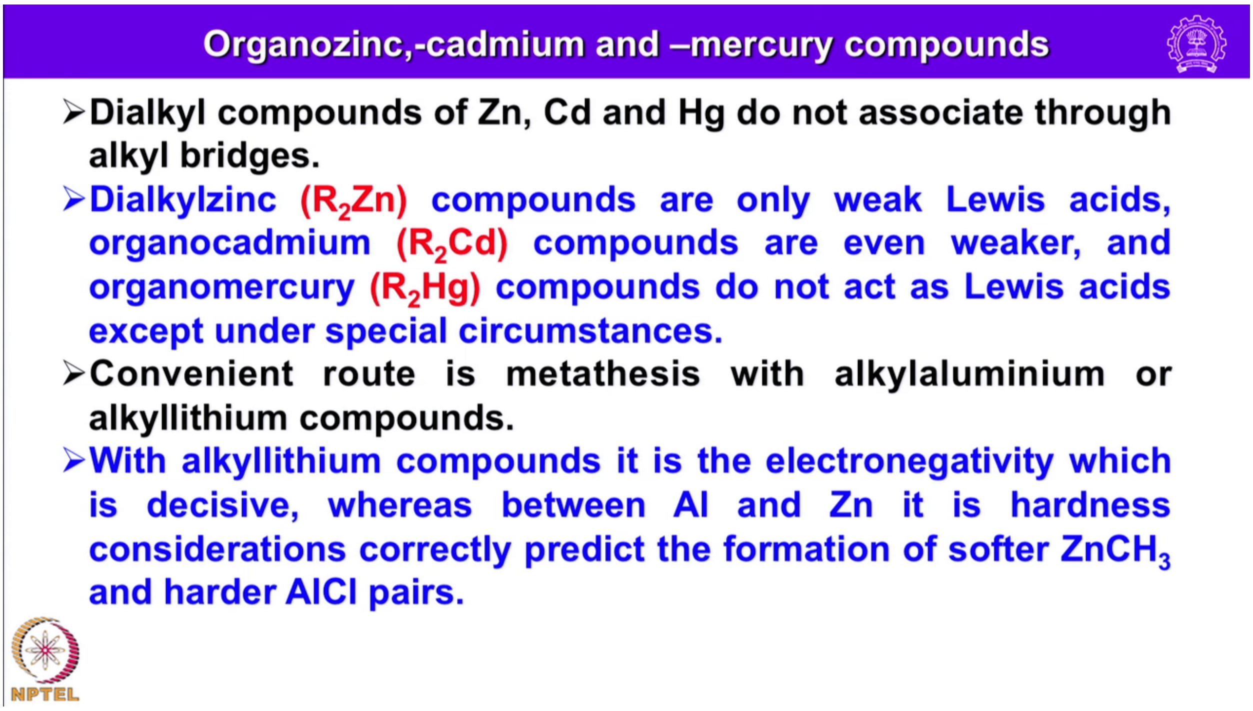

Organozinc,-cadmium and –mercury compounds

- Dialkyl compounds of Zn, Cd and Hg do not associate through alkyl bridges.
- Dialkylzinc (R_2Zn) compounds are only weak Lewis acids, organocadmium (R_2Cd) compounds are even weaker, and organomercury (R_2Hg) compounds do not act as Lewis acids except under special circumstances.
- Convenient route is metathesis with alkylaluminium or alkyllithium compounds.
- With alkyllithium compounds it is the electronegativity which is decisive, whereas between Al and Zn it is hardness considerations correctly predict the formation of softer $ZnCH_3$ and harder AlCl pairs.

Let us look into organo zinc cadmium and mercury compounds, this dialkyl compounds of zinc cadmium and mercury do not associate through alkyl bridges, and this compounds are only weak Lewis acids orgaocadmium compounds are even weaker and organomercury compounds do not act as Lewis acids, except under special circumstances. Convenient route is metathesis and with alkyl aluminum or alkyl lithium compounds with alkyl lithium compounds, it is the electronegativity which is decisive whereas, between aluminum and zinc it is hardness consideration correctly predictive formation of softer methyl, zinc or harder aluminum chloride pairs ok.

So, whether zinc has an affinity towards methyl and aluminum has an affinity towards a chloride is what the deciding factor in such reactions.

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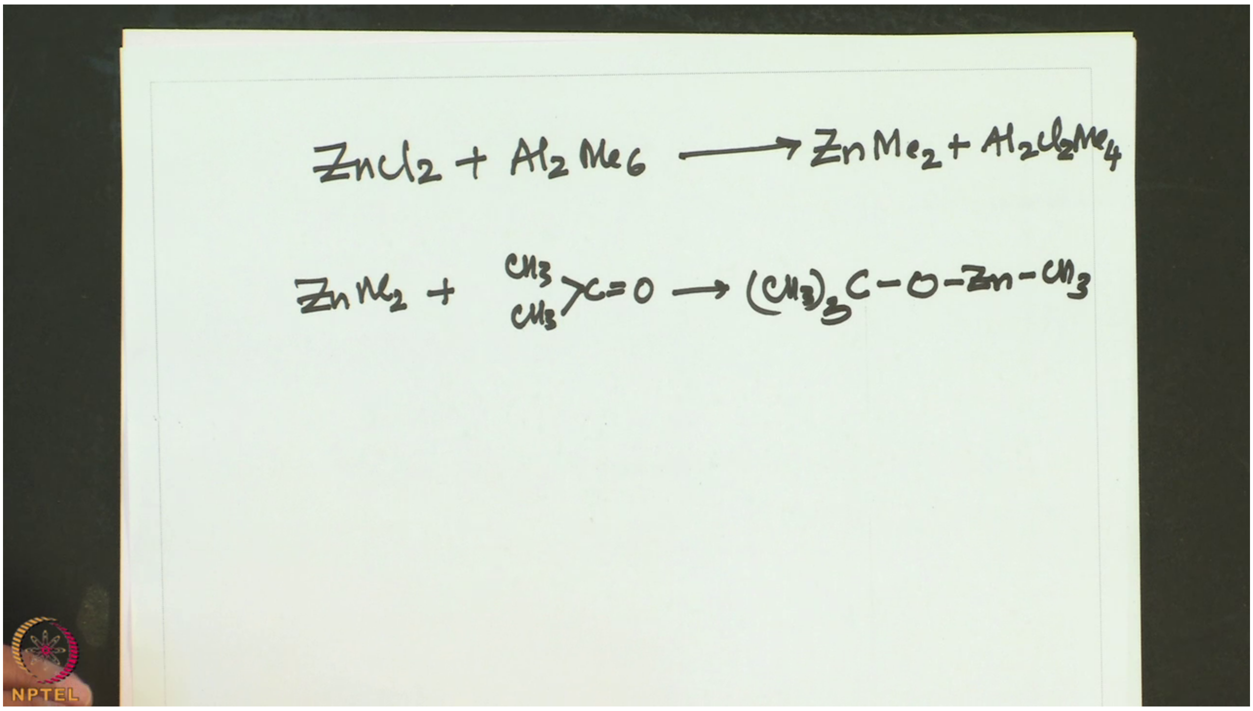

$$ZnCl_2 + Al_2Me_6 \longrightarrow ZnMe_2 + Al_2Cl_2Me_4$$

$$ZnMe_2 + (CH_3)_2C{=}O \longrightarrow (CH_3)_3C{-}O{-}Zn{-}CH_3$$

For example, let us look into this reaction here Zncl 2 plus A l 2 Me 6. If you see here of course, it readily a happens to form dimethylzinc plus Al 2 cl 2 Me 4. Here if you see zinc has an affinity towards methyl group as aluminum has a field towards chloride because its more Lewis acidic in nature alkyl zinc compounds are highly pyrophoric and are really hydrolyzed, where as alkyl cadmium compounds at more slowly with air due to mild Lewis acidity dialkylzinc and dialkyl cadmium compounds form stable complexes with amines especially with cladding amines, and zinc to carbon has greater carbon ionic character than the cadmium to carbon bond.

For example addition of alkyl zinc compounds across the carbonyl group of ketone, and let us take dimethylzinc and consider a ketone here. So, it forms. So, it is something like this it forms this reaction do not proceed with the less polar alkyl cadmium, or alkyl mercury compounds, but organo lithium, organo magnesium and organo aluminum compounds can promote this reaction readily since all of which contain metals with lower electro negativity than zinc.

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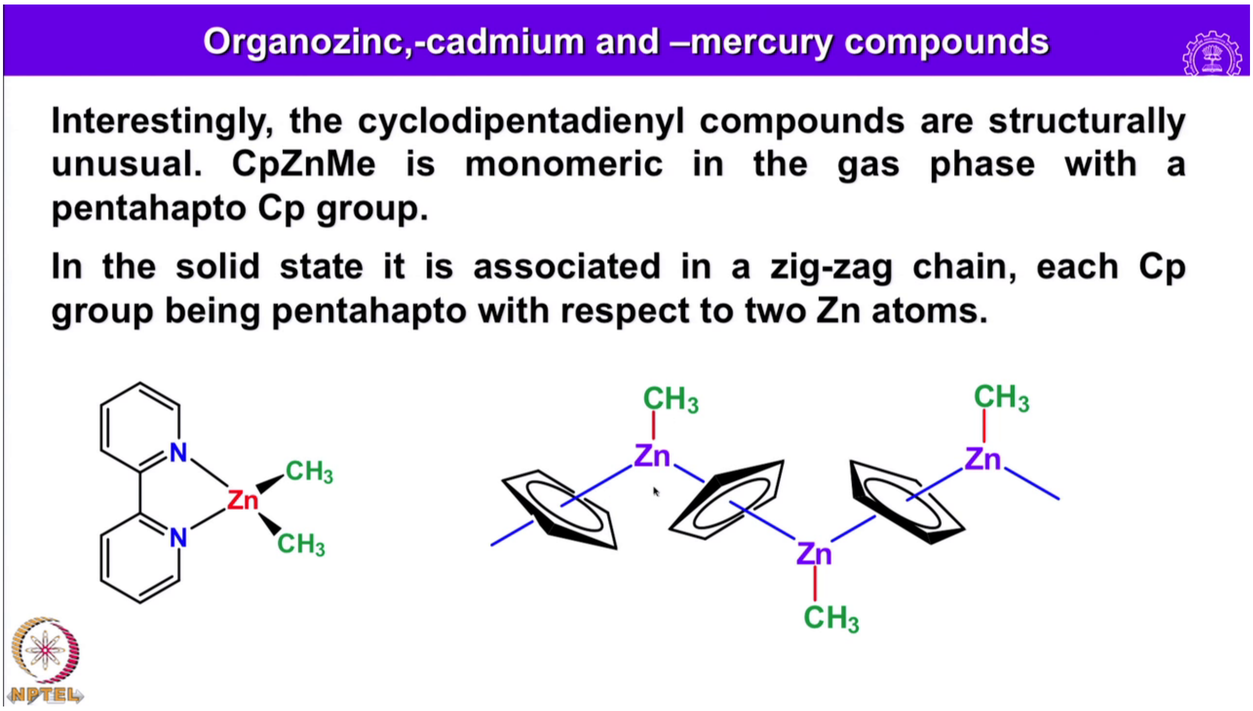

Organozinc,-cadmium and –mercury compounds

Interestingly, the cyclodipentadienyl compounds are structurally unusual. CpZnMe is monomeric in the gas phase with a pentahapto Cp group.

In the solid state it is associated in a zig-zag chain, each Cp group being pentahapto with respect to two Zn atoms.

So, interestingly the cyclodipentadienyl compounds are structurally unusual CpZnMe is monomeric in the gas phase with a pentahapto Cp group, in the solid state it is associated in a zigzag chain, each Cp group being pentahapto with respect to 2 zinc atoms. So, this is the complex with 2 to dash bipyridine and of course, this is how a methyl cyclodipentadienyl zinc compound forms one dimensional zigzag chain.

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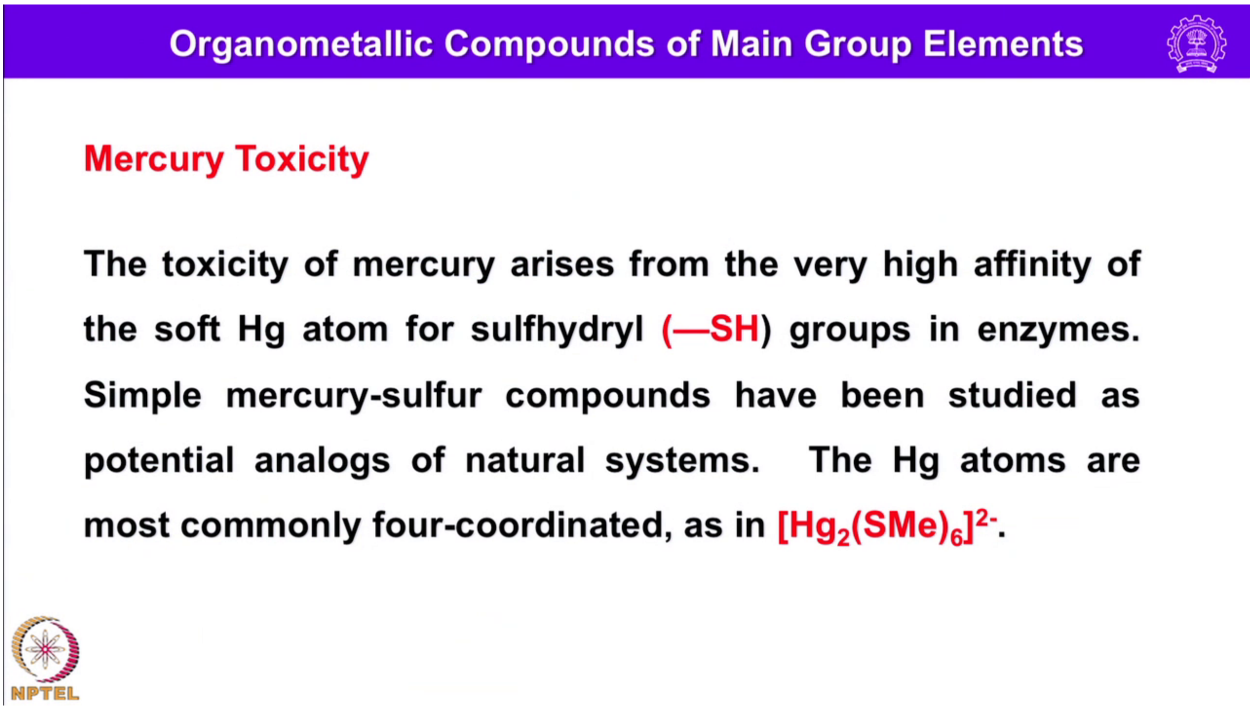

Organometallic Compounds of Main Group Elements

Mercury Toxicity

The toxicity of mercury arises from the very high affinity of the soft Hg atom for sulfhydryl (—SH) groups in enzymes. Simple mercury-sulfur compounds have been studied as potential analogs of natural systems. The Hg atoms are most commonly four-coordinated, as in $[Hg_2(SMe)_6]^{2-}$.

Talk little bit about mercury toxicity, the toxicity of mercury arise from the very high affinity of the soft mercury atom from sulfhydryl groups in the enzymes. Simple mercury sulphur compounds have been studied as potential analogs of natural system, the mercury atoms are most commonly 4 coordinated something like this ok.

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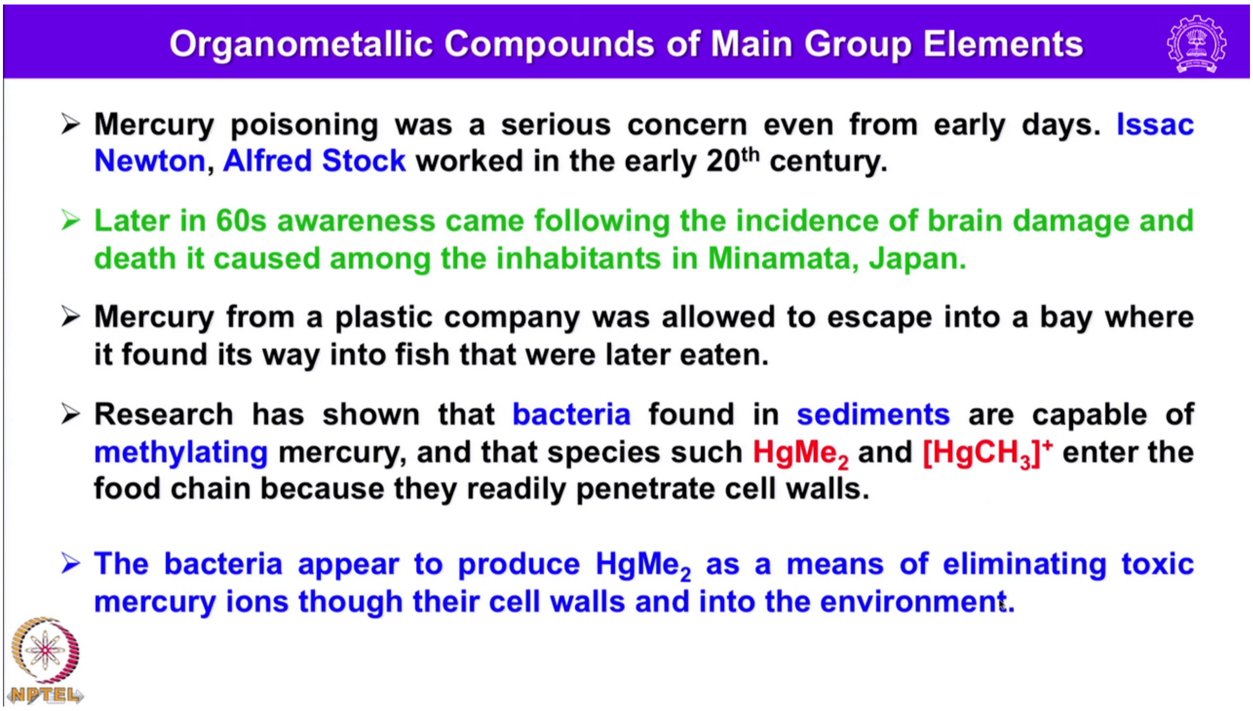

Organometallic Compounds of Main Group Elements

- Mercury poisoning was a serious concern even from early days. Issac Newton, Alfred Stock worked in the early 20th century.
- Later in 60s awareness came following the incidence of brain damage and death it caused among the inhabitants in Minamata, Japan.
- Mercury from a plastic company was allowed to escape into a bay where it found its way into fish that were later eaten.
- Research has shown that bacteria found in sediments are capable of methylating mercury, and that species such $HgMe_2$ and $[HgCH_3]^+$ enter the food chain because they readily penetrate cell walls.
- The bacteria appear to produce $HgMe_2$ as a means of eliminating toxic mercury ions though their cell walls and into the environment.

So, mercury poisoning versus serious concern even from early days Issac Newton Alfred stock worked in the early 20th century, he experienced this mercury poisoning. Later in sixties awareness came following the incidence of brain damage and death it caused among the inhabitants in Minamata Japan, mercury from a plastic company was allowed to escape into a bay, where it found its way into fish that were later eaten. Research has shown that bacteria found in sediments are capable of methylating mercury, and that species such as dimethylmercury or methylmercury cations enter the food chain because they readily penetrate cell walls.

So, the bacteria appears to produce dimethylmercury as a means of eliminating toxic mercury ions through their cell walls and into the environment before I conclude let me give one reaction here. So, just following reaction here, look into this reaction I already showed zinc chloride with trimethylaluminum gives dimethylzinc, plus dichloro tetramethyl aluminum dimmer. Yes this reaction occurs here and if you just look into it aluminum has 2 methyl bridges, and it forms 3 centered 2 electron bonds when it is reacted with zinc chloride, there is a possibility to abstract chlorides from zinc. So, that can be utilized for making lcl al bridging.

So, that now it become say a 4 electron bond; that means, it forms 3 centered 4 electron bond, as a result this compound is more stabilized. So, yes this reaction occurs. So, one can analyze in this fashion and whether you can considered Lewis acidity, whether you can consider hard and soft interaction or you can consider electro negativity one of this entity is will come very handy, in looking to the reaction and analyzing them whether this reaction happens or not. So, with this I complete the organometallic chemistry not in depth, but briefly and in my next lecture I will conclude overall whatever I discuss so for in the last 59 lectures.

Thank you very much.