3.6: Organotin and Organolead Compounds

Learning Objectives

In this section you will learn the following

- *Organotin and organolead compounds and their preparation.*
- *Bonding in tin compounds with Sn=Sn double bonds.*
- *Uses and environmental issues with tin compounds.*
- Reactivity of tetraethyl lead.
- Structural features of organolead compounds.

Organotin and organolead compounds

Preparation of Sn(IV) derivatives

$$3\,SnCl_3 + 4\,R_3Al \xrightarrow{R'2O} 3\,R_4Sn + 4\,AlCl_3$$

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

$$SnCl_4 + 4\,RMgBr \longrightarrow R_4Sn + 4\,MgBrCl$$

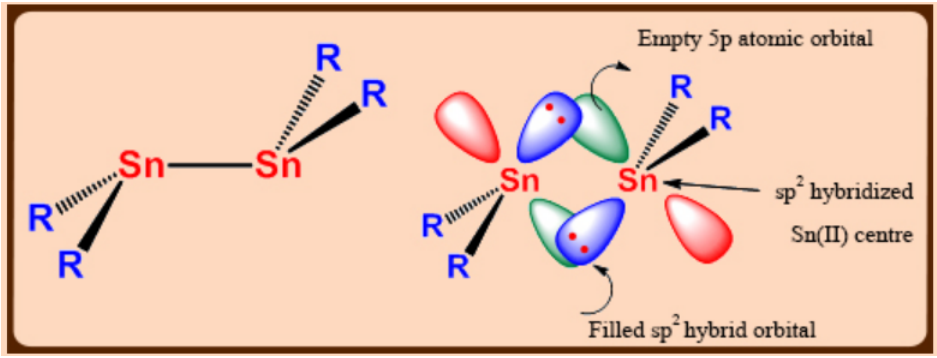
$$SnCl_2 + Ph_2Hg \longrightarrow Ph_2SnCl_2 + Hg$$

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

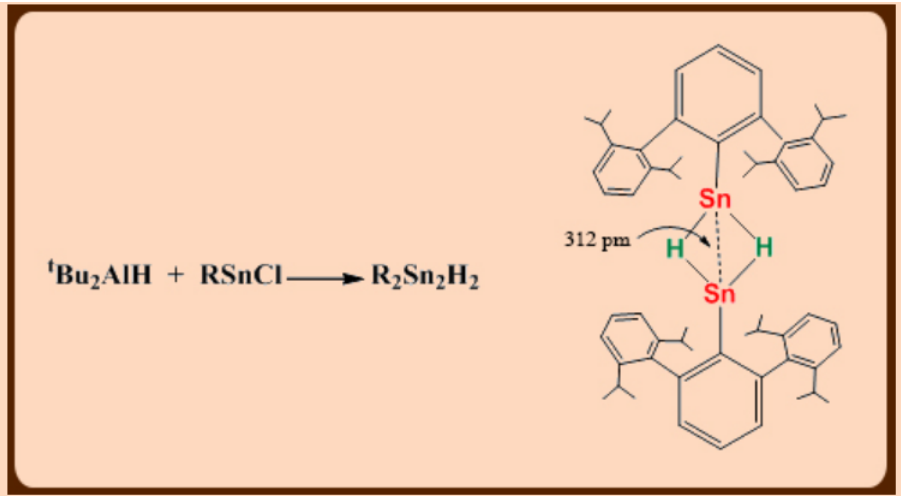
$$SnCl_2 + 2\,Li[(Me_3Si)_2CH] \longrightarrow [(Me_3Si)_2CH]_2Sn$$

(monomeric in solution and dimeric in solid state). But the dimer does not possess a planar Sn_2R_4framework 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



Look into the reactions of R_3SnCl with various reagents to form useful tin containing starting materials
The first organotin(II) hydride was reported only in 2000.



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

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.
- $^{n}Bu_3SnOSn^{n}Bu_3$ is algicide, fungicide and wood-preserving agent.
- $^{n}Bu_3SnCl$ is a bactericide and fungicide.
- 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.

*A barnacle is a type of arthropod belonging to infraclass Cirripedia in the sub-phylum Crustacea, and is hence related to crabs and lobsters.

Organolead compounds

Tetraethyllead

$$4\,\mathrm{NaPb} + 4\,\mathrm{EtCl} \longrightarrow \mathrm{Et_4Pb} + 3\,\mathrm{Pb} + 4\,\mathrm{NaCl}[at\ 373K\ in\ an\ autoclave]$$

Laboratory Scale,

$$2\,\mathrm{PbCl_3} + 4\,\mathrm{RMgBr} \xrightarrow[-4MgBrCl]{Et2O} 2\,(\mathrm{R_2Pb}) \longrightarrow \mathrm{R_4Pb} + \mathrm{Pb}$$

Thermolysis leads to radical reactions.

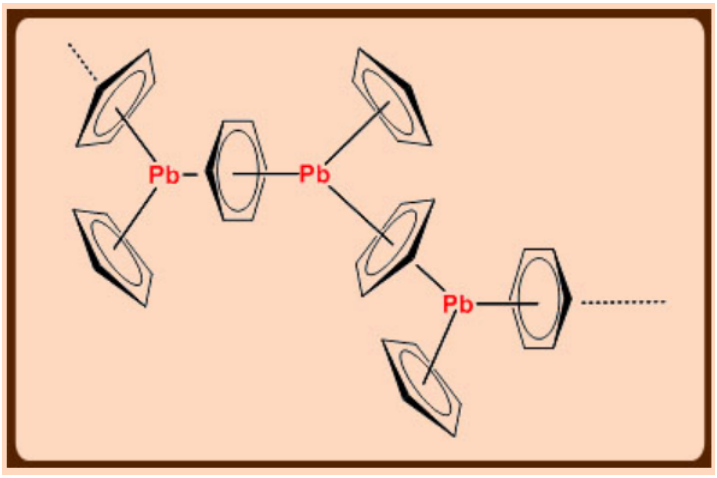
$$\mathrm{Et_4Pb} \longrightarrow \mathrm{Et_3Pb} + \mathrm{Et}$$

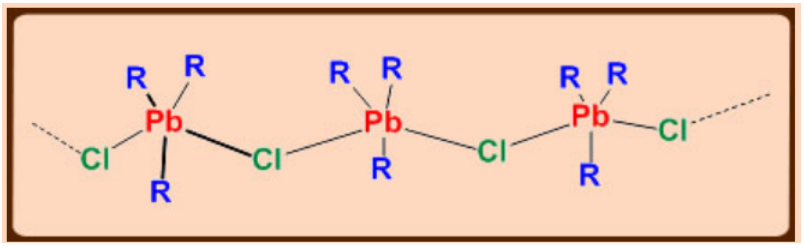
$$2\,\mathrm{Et} \longrightarrow \mathrm{n{-}C_4H_{10}}$$

$$\mathrm{Et_3Pb} + \mathrm{Et} \longrightarrow \mathrm{C_2H_4} + \mathrm{Et_3PbH}$$

$$\mathrm{Et_3Pb} + \mathrm{Et_4Pb} \longrightarrow \mathrm{H_2} + \mathrm{Et_3Pb} + \mathrm{Et_3PbCH_2CH_2}$$

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





Me_3PbCl consists of linear chain

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.

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

Problems

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

Solution: use VSEPR theory