

## Module 3 : Organometallic chemistry of p-block elements

### Lecture 5 : Organosilicon and organogermanium compounds

#### Objectives

#### In this lecture you will learn the following

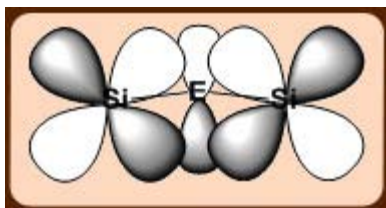
- Organosilicon and organogermanium compounds.
- Compounds with Si=Si and Ge=Ge bonds.

#### Organosilicon and organogermanium 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.  $(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3$  which is resistant to moisture and air.

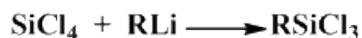


The lone pairs on O are partially delocalized into vacant  $\sigma^*$ - orbitals of Si, as a result the directionality of the Si-O bond is reduced making the structure more flexible.

This flexibility permits silicone elastomers to remain rubber-like down to very low temperature.

Delocalization also accounts for low basicity of an O atom attached to silicon as the electrons needed for the O atom to act as a base are partially removed.

The planarity of  $\text{N}(\text{SiH}_3)_3$  is also explained by the delocalization of the lone pair on N which makes it very weakly basic.



Si—C bonds are relatively strong (bond enthalpy is  $318 \text{ kJ mol}^{-1}$ ) and  $\text{R}_4\text{Si}$  derivatives possess high thermal stabilities.

$\text{Et}_4\text{Si}$  on chlorination gives  $(\text{ClCH}_2\text{CH}_2)_4\text{Si}$ , in contrast to the chlorination of  $\text{R}_4\text{Ge}$  or  $\text{R}_4\text{Sn}$  which yields  $\text{R}_n\text{GeCl}_{4-n}$  or  $\text{R}_n\text{SnCl}_{4-n}$ .

$\text{Me}_2\text{SiCl}_2$  on hydrolysis produce silicones.



$(\eta^1\text{-C}_5\text{Me}_5)_2\text{SiBr}_2$  on treatment with anthracene/potassium gives  $\text{Cp}^*_2\text{Si}$

Solid state structure of  $\text{Cp}^*_2\text{Si}$  consists of two independent molecules which differ in the relative orientations of the Cp rings.

In one molecule, they are parallel and staggered whereas in the other, they are tilted with an angle of  $167^\circ$  at Si.

The reaction between  $\text{R}_2\text{SiCl}_2$  and alkali metal or alkali naphthalides give cyclo- $(\text{R}_2\text{Si})_n$  by loss of  $\text{Cl}^-$  and Si—Si bond formation.

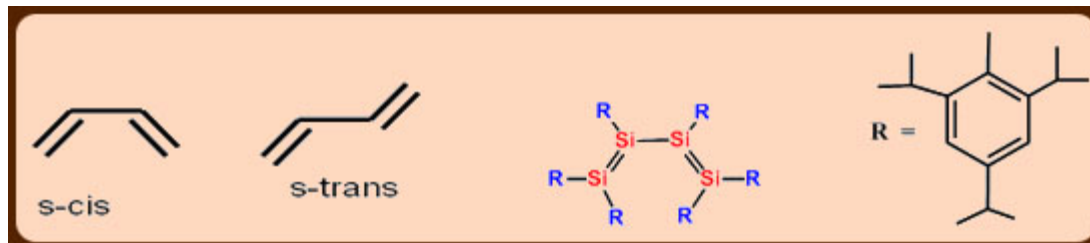
Bulky R groups favour small rings [e.g. (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>6</sub>Si<sub>3</sub> and Bu<sub>6</sub>Si<sub>3</sub>] while smaller R groups encourage the formation of large rings [Me<sub>12</sub>Si<sub>6</sub>, Me<sub>14</sub>Si<sub>7</sub> and Me<sub>32</sub>Si<sub>16</sub>]



Bulky substituents stabilize R<sub>2</sub>Si=SiR<sub>2</sub> compounds. The sterically demanding 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub> 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.

