OrganoSilicon Compounds

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Silicon is just like carbon, **but:**

- Larger
  - five- and six-coordinate structures positive

- More electropositive
  - easier attack by nucleophiles

- Does not want to form multiple bonds
  - SiO$_2$ vs CO$_2$

Organo Ge etc ... compounds: slow transition to more typical metal chemistry; M$^{II}$ becomes more stable for Pb
Bonds to silicon

- Si-C: bond covalent, unreactive
- Si-O, Si-F: very ("abnormally") strong
- Si-Cl, Si-Br, Si-I: reactive
- Si-Si: weak (!)
- Si=Si and Si=C: weak, very reactive
Silicones!

\[
\text{Cl-Si-Cl} \xrightarrow{\text{H}_2\text{O}} \left[\text{HO-Si-OH}\right] \xrightarrow{-\text{H}_2\text{O}} \left[\text{Si-O}\right]_n
\]

OrganoSilicon Compounds
Silicones

- Based on strong -Si-O- backbone
  - a pure -Si-Si- backbone would be weak
- "Slick"
- Viscosity change little with temperature
  - silicone oil
- Easy chemical modification and/or attachment to a surface
  - Silan
  - Silylation of GC column surfaces
The Si-O-Si bond

- Si-O-Si flexible
  - Is also seen in structures of SiO₂
- No dπ-pπ bond !!!!
Chain folding - silicones vs alkanes

At low temperatures, both alkanes and silicones prefer to form extended chains.

At higher temperature:

- For alkanes, the main change is formation of "gauche defects", i.e. partially folded chains.
  - Reduces contacts between chains, lowers viscosity

- For silicones, a wider range of Si-O-Si angles will occur, mainly around 180°, resulting in more extended chains.
  - Increases contacts between chains
  - Counteracts the "normal" viscosity decrease, so viscosity stays nearly constant
  - Very useful for high-temperature synthetic lubricants
Synthesis

- **Direct synthesis**
  - Si is not electropositive enough for unassisted direct synthesis
  - An Si/Cu alloy works better:
    \[
    \text{RCI} + \text{Si/Cu} \xrightarrow{\Delta} \text{R}_2\text{SiCl}_2 + \text{RSiCl}_3 + \text{R}_3\text{SiCl} + \ldots
    \]

- **Metathesis**
  \[
  \text{SiCl}_4 \xrightarrow{\text{RLi}} \text{R}_4\text{Si}
  \]

- **Hydrosilylation**
  \[
  \text{HSiCl}_3 + \text{R} \rightarrow \text{R} - \text{SiCl}_3
  \]
  Catalyzed/initiated by light, free radicals, many transition metal compounds.
Reactivity

- Nucleophilic attack
  \[ \text{Me}_3\text{SiPh} + \text{F}^\ominus \rightleftharpoons \text{Me}_3\text{SiF} + "\text{Ph}^\ominus" \]

- Electrophilic attack (on C!)
  \[ \text{Me}_3\text{SiPh} + \text{H}^\oplus \rightleftharpoons \text{SiMe}_3 \text{H} \quad \text{H}_2\text{O} \rightarrow \]

- With halogens
  \[ \text{Si} - \text{C} \xrightarrow{X_2} \text{Si} - \text{X} + \text{X} - \text{C} \]

- \( \text{R}_3\text{Si} \) often behaves like a "large hydrogen"
Sterics down group IV

Ph₄C  Ph₄Si  Ph₄Ge  Ph₄Sn  Ph₄Pb
Higher coordination numbers

- **Ph₄Si**
  - 4-coordinate
- **Ph₃SiF₂⁻**
  - 5-coordinate
- **Ph₂Si(tropolonate)₂**
  - 6-coordinate
Maybe not useful, but certainly beautiful

$C_6(SiMe_2OMe)_6$