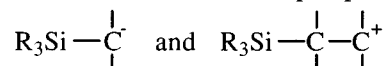


## An Organosilicon Chemistry Primer

**Organosilanes** are compounds containing a silicon to carbon bond. The chemistry of these compounds is generally similar to the chemistry of organic compounds. The silicon atom is more electropositive than carbon, leading to four primary distinctions.

1. Nucleophilic substitution at silicon is more facile than at carbon.
2. Bond energies with the electronegative elements oxygen, fluorine and chlorine are greater than with a carbon.
3. A silicon-carbon bond stabilizes a carbanion in the alpha position, and a carbocation in the beta position.

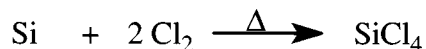


4. The Si-H bond is polarized with Si<sup>+</sup> and H<sup>-</sup>, generally resulting in an anti-Markovnikov addition to olefins under catalytic conditions and the ability under limited conditions to transfer hydride.

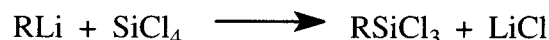
Organosilanes are derived from elemental silicon. Silicon in turn is produced from silica or quartz.



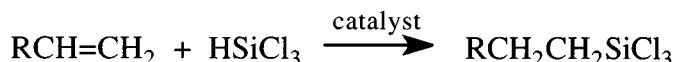
**Chlorosilanes** are often intermediates in production of organosilanes.



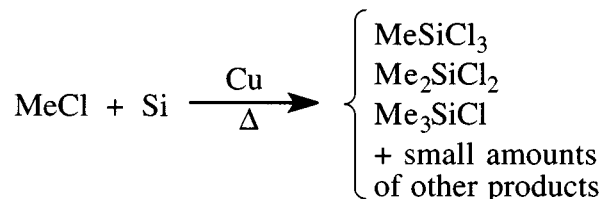
The chlorosilanes can be reacted either with Grignard reagents or alkali metal organics to give organic substitution. For example:



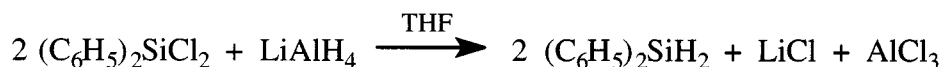
A more efficient route is through hydrosilylation of an olefin, which is catalyzed by such materials as chloroplatinic acid, di-*t*-butyl peroxide, and in limited instances amine complexes and aluminum chloride.



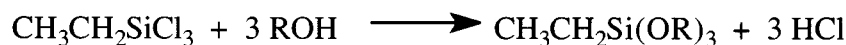
The greatest quantities of organosilanes are methyl substituted. They are produced by a direct process.



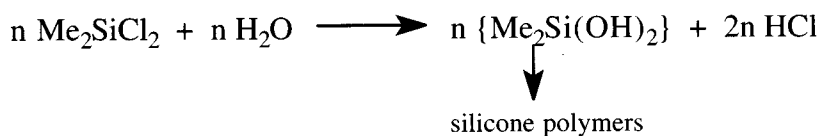
Chlorosilanes undergo several important reactions. Chlorine may be replaced with hydrogen either by treatment with hydride reducing agents or transfer of a hydride from other silyl hydrides.



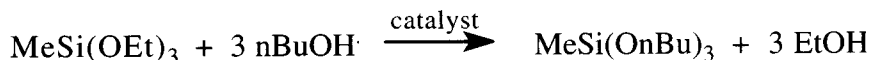
Chlorosilanes react with protic materials, forming alkoxy silanes with alcohols, aminosilanes with primary and secondary amines, and silanols with water.



The reaction with water is particularly important in that it provides a basis for silicone manufacture. Dimethyldichlorosilane is difunctional. It reacts with water to form cyclic or straight chain polymers.



**Alkoxysilanes** (silane esters) undergo most of the reactions of chlorosilanes and are generally more convenient reagents. They are more resistant to hydrolysis. Increasing the size or steric bulk of the alkoxy group decreases reactivity. Like chlorosilanes, they yield siloxanes on hydrolysis, but the byproduct is alcohol rather than hydrogen chloride. They undergo exchange with hydroxyl containing materials under conditions similar to those for transesterification of carboxylic acid esters.



Alkoxysilanes undergo displacement of -OR on reaction with Grignard reagents, and reduction on treatment with metal hydrides.

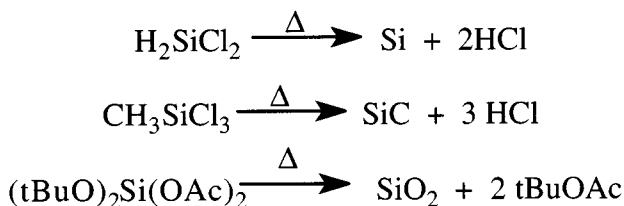
**Hydrogen bound to silicon** can behave as a reducing agent. Triethylsilane and diphenylsilane are employed in the reduction of ketones and esters. Polymethylhydrosiloxane has similar properties.



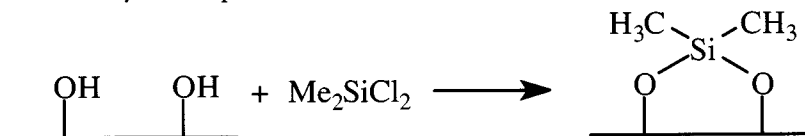
Halogenoid substituted silanes exhibit unique properties. The halogenoids include isocyanate, isothiocyanate, azide and nitrile groups. The last two are of particular synthetic importance since they replace hydrazoic acid and hydrogen cyanide in many synthetic reactions.

**Silylation** is the replacement of the active hydrogen in a compound with a substituted silane group. The conspicuous applications are the preparation of blocked intermediates and derivatization for chromatography.

**Surface synthesis** and modification of a wide range of substrates may be accomplished with silanes. Deposition techniques include the preparation of silicon for semiconductors with silane, dichlorosilane, and trichlorosilane. Silicon carbide deposition is carried out at high temperature with methyltrichlorosilane. Silicon dioxide may be deposited from acyloxysilanes by a thermal process or by a hydrolytic process from esters.



Utilization of organosilanes has been directed toward surface modification rather than synthesis. Dimethyldichlorosilane, dimethyldiethoxysilane, trimethylchlorosilane and hexamethyldisilazane are employed to reduce surface interaction of siliceous materials and aluminas. Fluorinated alkylsilanes provide surfaces with even lower surface energy.



Treatment of surfaces can be used to tailor surfaces with particular properties for chromatography, extraction, and exchange resin applications. Self-assembled monolayers of these materials have been employed in microcontact printing.

Silanes with reactive organic substitution are employed in thermoset and thermoplastic composites as coupling agents. Amine, olefin, methacrylate, mercaptan, epoxy and cationic functionalities are usually employed. Bonding may be directly through covalent bonds or by modification of filler affinity through introduction of hydrogen bonding or ionic interaction sites.