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Silicon Chemistry

Lewis Base Stabilized Dichlorosilylene**

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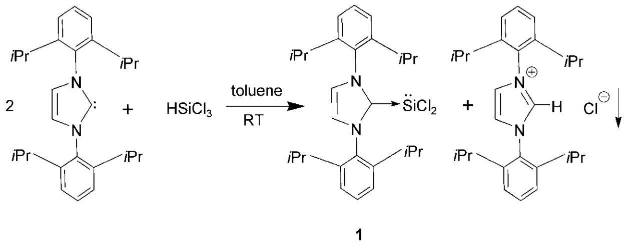
Dedicated to Professor Yitzhak Apeloig

The chemistry of silicon is mainly based on silicon(IV), whereas that of silicon(II) is still in its infancy. Silylene (R_2Si:) is a molecule with a divalent neutral silicon atom having a lone pair of electrons. Silylenes are key intermediates in various photochemical, thermal, and metal reduction reactions of organosilicon compounds.[1] Therefore, silylenes play a vital role in the field of silicon chemistry.[2] Until 1994, silylenes were generally considered to be very reactive unstable species that decompose or polymerize readily at temperatures above 77 K.[3] This situation changed when West et al. reported the first N-heterocyclic silylene that is stable at room temperature.[4a] Since then, a fair number of cyclic silylenes and a dialkyl silylene have been reported.[4–6] Only one example of a monochlorosilylene[6] that is stable at room temperature has been published, and it was characterized by X-ray diffraction; no dihalosilylenes that are stable at room temperature have been reported to date. Gaseous dichlorosilylene has been known for many years; at room temperature, it condenses to polymeric $(SiCl_2)_n$. Its properties were already studied by Schmeisser[7] and Schenk[8] in 1964. Some reactions of condensed $SiCl_2$ with acetylene and with benzene were carried out by Timms[9] in 1968, and resulted in brown polymeric products of unknown composition. A literature survey reveals that there have been few reports[10–12] on the synthesis and properties of cyclic and linear polydichlorosilanes. A polymeric perchloropolysilane $(SiCl_2)_n$ was reported by West et al. in 1998[13] and was studied by single crystal X-ray diffraction. However, access to dichlorosilylenes that are stable at room temperature and with electronic structure and properties are quite similar or close to those of unstable examples, such as $SiCl_2$, is still a challenge. Of course, efforts of making a stable version of a very reactive species may cause a change of its behavior. How an unstable species can be stabilized is a matter of keen interest for the scientific and industrial community.

Addition reactions of $HSiCl_3$ with different organic compounds in the presence of various tertiary amine bases were reviewed by Benkeser,[14] and the existence of the trichlorosilyl anion as an intermediate was postulated. Moreover, Jung et al. reported[15] the trapping of dichlorosilylene, which was generated by the reaction of $HSiCl_3$ in the presence of phosphonium chloride in a stainless steel cylinder at 150 or 180 °C, by conjugated dienes and by an alkyne. In their proposed mechanism, species of dichlorosilylene or the trichlorosilyl anion as intermediates were discussed but not isolated.

In 1995, Kuhn et al.[16a] prepared N-heterocyclic carbene (NHC) adducts of $SiCl_4$. We have used N-heterocyclic carbenes as dehydrochlorinating agents for the preparation of germylene[16b] and metal hydroxides.[16c-e] Very recently, Robinson and co-workers reported a Lewis base stabilized low-valent silicon compound[17] in which the silicon atom is present in the formal oxidation states +1 or zero, but no dichlorosilylene was isolated.

Almost all silylenes or low-valent silicon compounds reported to date were prepared by reductions of their parent compounds using strong reducing agents, such as potassium metal or KC_8. Herein, we report the synthesis of the first base-stabilized dichlorosilylene that is stable at room temperature, L^1SiCl_2 (**1**; L^1 = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). This compound is formed under mild reaction conditions by reductive elimination of HCl from trichlorosilane in the presence of the NHC (L^1; Scheme 1), and was isolated in 79 % yield from the toluene-soluble reaction components and purified by washing with *n*-hexane. The insoluble NHC·HCl salt was recovered by filtration and can be recycled to NHC using KO*t*Bu.



Scheme 1. Synthesis of base-stabilized dichlorosilylene **1**.

A multistep procedure was also developed to prepare **1** using L^1SiCl_4 (**2**)[17] and two equivalents of potassium graphite in toluene (Scheme 2).Similarly, reduction of L^2SiCl_4 (**3**; L^2 = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) with KC_8 afforded the dichlorosilylene L^2SiCl_2 (**4**). Colorless crystals of **1** were obtained from a toluene solution at −35 °C in 48 % yield, whereas **4** was crystallized in 28 % yield as a pale yellow solid from a mixture of toluene and *n*-hexane (2:1) solution. Compounds **1** and **4** are stable at room temperature under inert atmosphere, and are soluble in toluene and THF.

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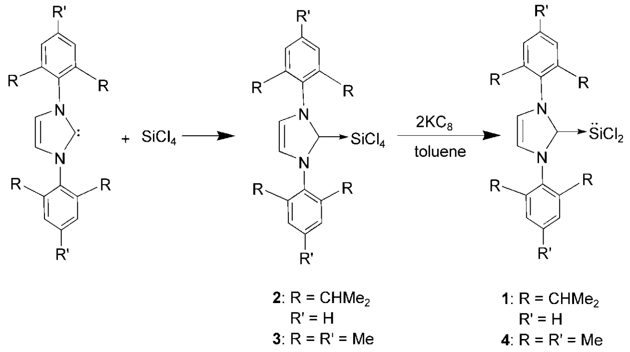
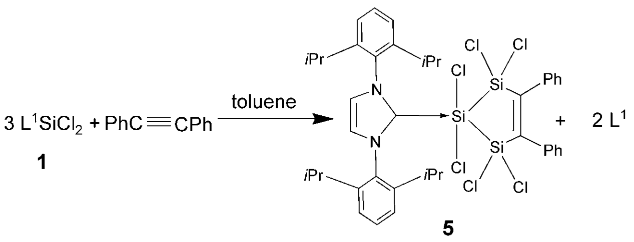


Scheme 2. Synthesis of silanes $LSiCl_4$ (**2**, **3**) and silylenes $LSiCl_2$ (**1**, **4**).

Base-stabilized dichlorosilylene **1** also reacts with diphenylacetylene at room temperature (Scheme 3) to form 1,1,2,2,3,3-hexachloro-4,5-diphenyl-1,2,3-trisilacyclopent-4-ene **5** as a colorless solid in 68% yield.



Scheme 3. Reaction of **1** with diphenylacetylene to form **5**.

The NHC attached to the silicon atom is the key factor in stabilizing the dichlorosilylenes **1** and **4**. However, the reaction of **1** with excess diphenylacetylene reveals that the NHC is labile enough to liberate the NHC and $SiCl_2$ species during the course of the reaction for generating derivative **5**. Therefore, base-stabilized dichlorosilylenes **1** and **4** may be considered as structural motifs more closely related to the free $SiCl_2$ than the previously reported silylenes.[4–6] For this reason, the facile availability of the $LSiCl_2$ system offers a precursor to explore silicon(II) chemistry.

The dichlorosilylenes **1** and **4** and trisilacyclopentene derivative **5** were characterized by elemental analysis and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. ^{1}H and ^{13}C NMR spectra of **1** and **4** show resonances for NHC moieties, which are significantly different and appear somewhat upfield in comparison to those observed for **2** and **3**, respectively. The ^{29}Si NMR of **1** and **4** have signals at $\delta = 19.06$ and 17.84 ppm, respectively, which are in the range of those for $(LSiCl)_2$[17] ($\delta = 38.4$ ppm) and $[PhC(tBuN)_2]SiCl$[6] ($\delta = 14.6$ ppm). Compound **5** has ^{29}Si NMR signals at $\delta = -2.84$ and -142.47 ppm; these values are consistent with cyclic silicon compounds.[18]

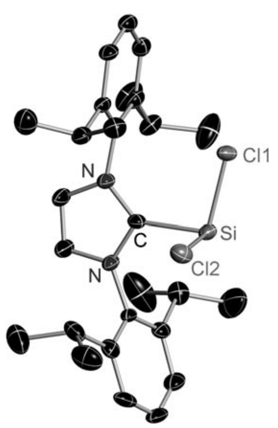


Figure 1. Molecular structure of **1**. Ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°] (as averages of two independent molecules): Si–C 1.985(4), Si–Cl1 2.1585(16), Si–Cl2 2.1743(18); Cl1-Si-Cl2 97.25(6), C-Si-Cl2 94.66(13), C-Si-Cl1 98.80(12).

The molecular structure of **1** was also determined by single-crystal X-ray diffraction studies. Dichlorosilylene **1** (Figure 1) crystallizes in the monoclinic space group $P2_1/c$. Compound **1** features trigonal pyramidal geometry at the threefold-coordinated silicon atom, with the stereochemically active lone pair at the apex. The sum of the bond angles at the silicon atom in **1** (289.74°; compare with 291.08° in the gas-phase optimized structure) is significantly smaller than that in $(L^1SiCl)_2$ (308.0°)[17] but larger than in $[PhC(tBuN)_2]SiCl$ (260.73°).[6] The Si–C bond length (1.985(4) Å) in **1** is slightly longer than that reported for **2** (1.928(2) Å) and $(L^1SiCl)_2$ (1.934(6) Å).[17] The mean Si–Cl bond distance (2.1664(16) Å) is comparable to the sum of the Si and Cl covalent radii (2.16 Å)[19] and is in good agreement with that observed in $[PhC(tBuN)_2]SiCl$ (2.156(1) Å).[6]

To analyze the electronic structure of silylene **1**, DFT computations employing Turbomole[20] at the BP/TZVP[21,22] level were performed. After a geometry optimization starting from the crystal coordinates, a topological analysis of the resulting electron density according to Bader's QTAM (quantum theory of atoms in molecules)[23] followed. In the Laplacian of $\rho(\mathbf{r})$, four valence-shell charge concentrations (VSCCs) near silicon were found; one of them in the non-bonding region can be interpreted within QTAM as marking lone-pair density (LP_{Si}). The angles between LP_{Si}-Si-C-(carbene), LP_{Si}-Si-Cl(in-plane) and LP_{Si}-Si-Cl(orthogonal) are 114.40°, 121.93° and 123.37°, respectively. We presume that the non-coordinated $SiCl_2$ moiety (Cl-Si-Cl angle only 97.25(6)° in the solid state, and 99.47° in the gas-phase optimized structure) is weakly sp^2-hybridized. In the solid state, **1** adopts an almost trigonal planar arrangement, which is only slightly distorted toward a pyramidal geometry in the contact Lewis acid–base pair. The electrostatic interaction of the Lewis base carbene ligand and the electronically depleted silicon atom (Figure 2) results in a side-on coordination of the carbene ligand. The sum of bond angles at the silicon atom and the lone pair LP_{Si} at the apex of a trigonal pyramid is 289.74° from the crystal structure, and 291.08° after optimization in the gas phase.

Although a few trisilacyclopentenes have been reported,[24] none of them has been characterized by single-crystal X-ray diffraction until now. Compound **5** crystallizes in the triclinic space group $P\bar{1}$ (Figure 3) with toluene as lattice solvent. It contains three $SiCl_2$ moieties in a five-membered Si_3C_2 ring. One silicon atom (Si2) in **5** is five-coordinate, and

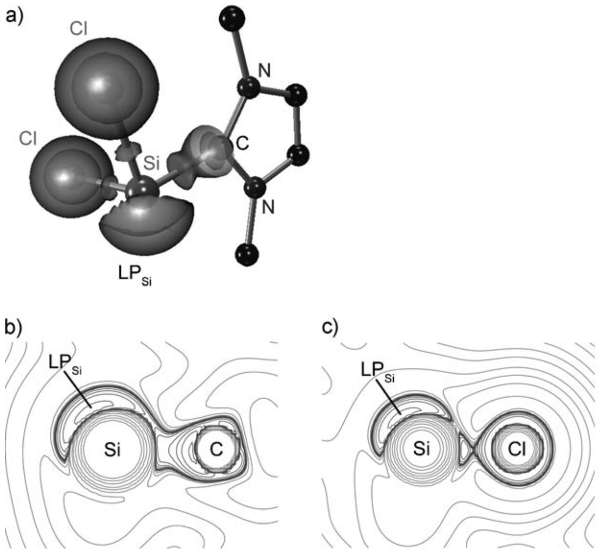


Figure 2. a) Isosurface plot of $\nabla^2\rho(\mathbf{r})$ of **1** at the -0.53 eÅ^5 level around silicon. LP = electron lone pair. b,c) Contour plots of $-\nabla^2\rho(\mathbf{r})$ in the C-Si-VSCC plane (b) and in the Cl(in-plane)-Si-VSCC (c). Local charge concentrations: dark gray; charge depletions: light gray. The contour values are at 0.2×10^n, 0.4×10^n, and 0.8×10^n, with $n = -3, \pm2, \pm1$.

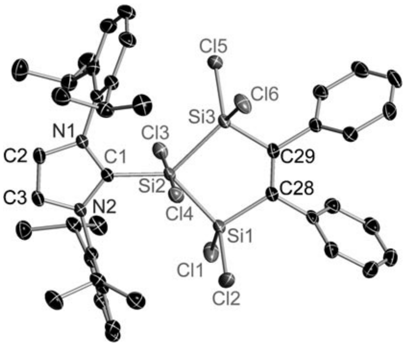


Figure 3. Molecular structure of **5**. Ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: Si2–C1 1.9110(17), Si2–Si1 2.3233(7), Si2–Si3 2.3234(7), Si2–Cl3 2.2588(7), Si2–Cl4 2.2491(7), Si1–Cl1/Cl2(av.) 2.0432(8), Si3–Cl5/Cl6(av.) 2.0508(7), C28–C29 1.354(2); Cl3-Si2-Cl4 177.07(3), C1-Si2-Si1 132.64(6), C1-Si2-Si3 135.08(6), Si1-Si2-Si3 92.23(2).

both chlorine atoms occupy the axial positions of a distorted trigonal bipyramidal polyhedron. The equatorial positions are occupied by the two adjacent silicon atoms Si1 and Si3, and the third position is held by C1 of the NHC. The Si2–C1 bond in **5** (1.911(17) Å) is in the range of those observed for **2** and $(L^1SiCl)_2$.[17] The other two silicon atoms are four-coordinate in a distorted tetrahedral environment. The Si–Si bonds (2.323 Å, mean value) are comparable to the Si–Si bond in α-silicon (2.36 Å)[25] and close to the sum of silicon covalent radii (2.34 Å).[19] The mean values of the Si–Cl bond lengths for the $SiCl_2$ moiety coordinated to the NHC (2.254(7) Å) are slightly longer than in **1** because of the higher coordination. The Si–Cl bonds in the NHC-free $SiCl_2$ residues (2.047(7) Å) in **5** are slightly shorter than those in **2** (2.189(5) Å, axial),[17] **1** (2.1700(17) Å, and $(SiCl_2)_n$ (2.120(9) and 2.088(9) Å).[13]

In summary, dichlorides of germanium, tin, and lead are commercially available, but no dichloride of silicon that is stable at room temperature had been isolated. Now, the availability of base-stabilized dichlorosilylene precursors, such as **1** and **4**, offer the potential to explore their reactivity. Trisilacyclopentenes are known;[24] however none containing two chlorine atoms bound to the silicon atoms had been isolated and characterized. Therefore, compound **5** is primed for further substitution and reduction reactions.

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