Silicon Chemistry

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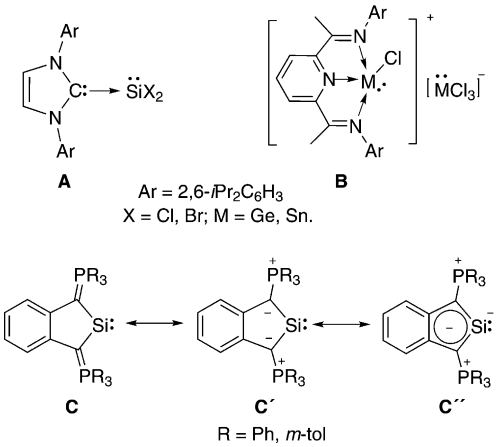
The Elusive Silyliumylidene $[ClSi:]^+$ and Silathionium $[ClSi{=}S]^+$ Cations Stabilized by Bis(Iminophosphorane) Chelate Ligand**

*Yun Xiong, Shenglai Yao, Shigeyoshi Inoue, Elisabeth Irran, and Matthias Driess**

In memory of Dr. Detlef Schröder

Silylenes, the silicon analogues of singlet carbenes, are highly reactive compounds with dicoordinate divalent silicon atoms. Parent silylene and its derivatives $R_2Si:$ with small organic groups R represent reactive intermediates, which have been investigated in the gas-phase, in diluted solutions, and in frozen rare-gas matrices at low temperatures.[1] Likewise, dichlorosilylene ($:SiCl_2$) is an elusive divalent silicon species, which plays a particular role in the Siemens process, in the chemical vapor deposition of thin silicon films, and in dry etching of silicon wafers by elemental chlorine, as well as in the plasma etching of silicon and silicon dioxide interfaces. Although synthesis and reactivity of gaseous $:SiCl_2$ has been investigated since 1964,[2] studies on its reactivity have been limited to the gas phase and matrix-isolation systems at low temperatures (77 K), because it polymerizes readily to $(SiCl_2)_n$ at higher temperatures.[3] Since 1994, the concept of donor–acceptor stabilization has been very successfully applied to the synthesis of several types of isolable cyclic[4,5] and acyclic silylenes.[6a,b] Recent progress includes the striking synthesis of stable $H_2Si:$ complexes, reported by Rivard, Robinson, and their respective co-workers.[6c,d] In 2009, the research groups of Roesky[7a] and Filippou[7b] showed that dihalosilylenes $:SiX_2$ (X = Cl, Br) can be stabilized by N-heterocyclic carbenes (NHCs) to form isolable NHC→SiX_2 complexes **A** (Scheme 1). The latter represent long-sought convenient dihalosilicon(II) precursors. Another challenge is the synthesis of isolable divalent silicon cations, that is, silyliumylidene cations ($[RSi:]^+$; R = H, halogen, organo groups). Remarkably, by utilizing suitable thermodynamic and/or kinetic stabilization, the first isolable silyliumylidene cations RSi^+ (R = pentaalkylcyclopentadienyl, β-diketiminate), which bear bulky monovalent substituents R with additional donor sites, could be synthesized.[8] Other types of silyliumylidenes would be very attractive for employment as versatile building blocks and Lewis acid catalysts. Accordingly, monochlorosilyliumylidene $[ClSi:]^+$ appears to be a very promising silyliumylidene precursor, because the chlorine atom could be replaced by suitable nucleophiles R to pave the way to other types of silyliumylidene derivatives $[RSi:]^+$. However, $[ClSi:]^+$ can only be generated by gas-phase synthesis, for example, by hollow cathode discharge of $SiCl_4$ diluted in a helium atmosphere, and can only be detected by infrared spectroscopy and mass spectrometry in the gas phase under unusual experimental conditions.[9]



Scheme 1. NHC-stabilized dihalosilylenes **A**, chlorogermyliumylidenes and their tin analogues **B**, and the bis(phosphorus ylide)-stabilized silylenes **C**.

Very recently, Reid, Roesky, Stalke, and their respective co-workers synthesized the cationic chlorogermyliumylidene[10a] and chlorostannyliumylidene[10b] complexes **B** through a Lewis base mediated autoionization of $GeCl_2$ and $SnCl_2$ in the presence of a neutral tridentate donor ligand (Scheme 1). In 1996, Cooks and co-workers reported a mass spectrometry study of bis(pyridine)-supported $[ClSi:]^+$.[9e] However, an isolable complex that bears the chlorosilyliumylidene cation is still unknown. The formation of **B** prompted us to develop a Lewis base stabilized chlorosilyliumylidene $[ClSi:]^+$ by employing a bis(ylide) donor ligand. Recently, we have shown that a bis(phosphorus ylide) can serve as an effective donor to stabilize highly Lewis acidic Si^{II} sites (see carbocyclic silylene **C** in Scheme 1).[11] Herein, we report the synthesis of the first isolable chlorosilyliumylidene species **2** stabilized by the bis(iminophosphorane) chelate ligand **1**. Moreover, the reactivity of **2** toward elemental sulfur, which leads to the unprecedented chlorosilathionium complex **3** (Scheme 2), is presented.

Because of the two N=P*n*Bu_3 ylide moieties, which are bonded at positions 1 and 8 of the naphthalene ring, the neutral ligand **1** behaves both as a very strong Brönsted and Lewis base (Scheme 2). Thus, treatment of trichlorosilane

[*] Dr. Y. Xiong, Dr. S. Yao, Prof. Dr. S. Inoue, Dr. E. Irran, Prof. Dr. M. Driess
Technische Universität Berlin, Department of Chemistry: Metalorganics and Inorganic Materials, Sekr. C2
Strasse des 17. Juni 135, 10623 Berlin (Germany)
E-mail: matthias.driess@tu-berlin.de
Homepage: http://www.driess.tu-berlin.de

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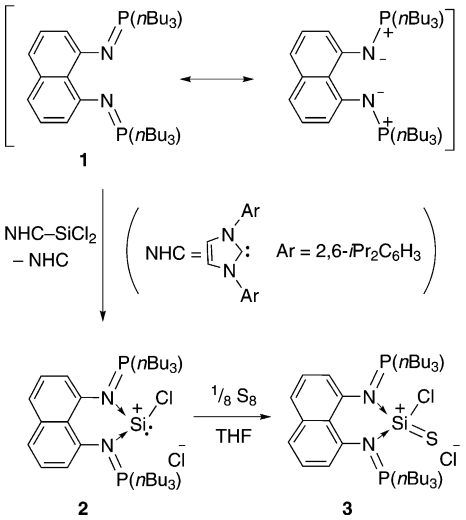


Scheme 2. Synthesis of the chlorosilyliumylidene chloride complex **2** and its oxidation to chlorosilathionium salt **3**.

with two molar equivalents of **1** leads to its dehydrochlorination and subsequent trapping of [Cl_2Si:] by **1** to give **2**. However, the yield of the desired product **2** was very low (≈5% according to ^{31}P NMR spectroscopy), thus preventing isolation. Fortunately, the reaction of **1** with equimolar amounts of NHC→$SiCl_2$ **A** in toluene at room temperature furnished **2** in 46% yield of isolated product. Complex **2** is insoluble in toluene and sparingly soluble in THF, thus indicating that the compound is a salt. This assumption has been confirmed by X-ray diffraction analysis. Colorless crystals of **2** suitable for X-ray diffraction analysis were obtained from mixtures of THF and dichloromethane at −20 °C. The complex crystallized in the monoclinic space group $P2_1/n$. As expected, the silicon center is threefold coordinated by one chlorine atom and two nitrogen atoms from the bis(iminophosphorane) chelate ligand (Figure 1),

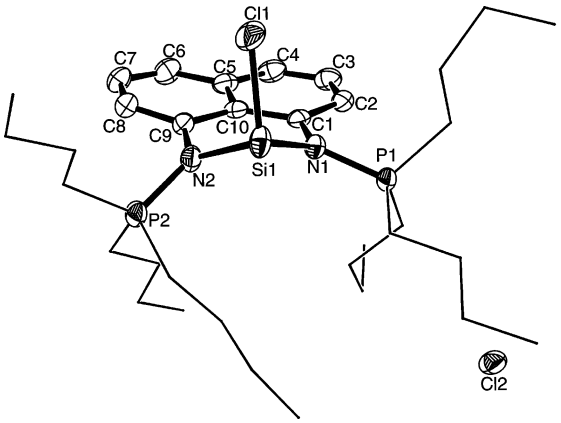
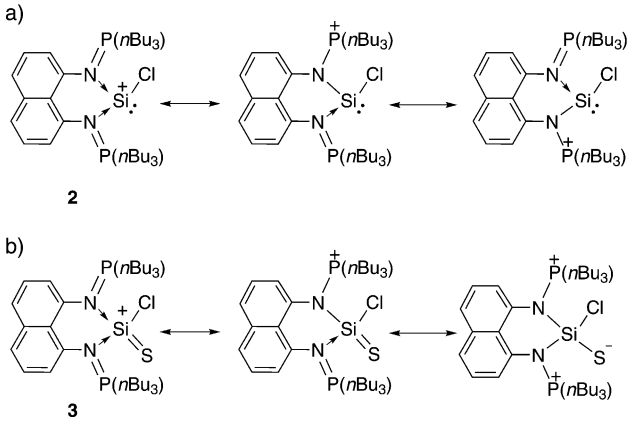


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms and one THF molecule are omitted for clarity. Selected bond distances [Å] and angles [°]: Si1–N1 1.847(3), Si1–N2 1.835(3), Si1–Cl1 2.172(2), P1–N1 1.666(3), P2–N2 1.659(3); N1-Si1-N2 92.4(1), N1-Si1-Cl1 97.0(1), N2-Si1-Cl1 97.2(1), P1-N1-Si1 120.0(2), P2-N2-Si1 121.6(2), P1-N1-C1 118.5(2), P2-N2-C8 118.5(2), P2-N2-C8 118.5(2), P1-N1-C1 118.5(2).

which is significantly different from fourfold coordinated cations $[ClGe]^+$ and $[ClSn]^+$ (Scheme 1, **B**). The second chlorine atom, which acts as a counter ion, locates far away from the silicon center (the smallest distance is 6.704 Å). Notably, the degree of pyramidalization at the silicon atom in **2** (286.6°) is close to that in **A** (289.7°).[7a] The six-membered C_3N_2Si ring in **2** is puckered with the silicon atom out of the plane that is defined by the C_3N_2 atoms. The dihedral angle between the plane defined by the C_3N_2 and the plane defined by the N_2Si is 38°.

The Si1−Cl1 distance of 2.172(2) Å is in good agreement with the mean Si−Cl distance observed in the structure of NHC→$SiCl_2$ **A** (2.166(2) Å)[7a] and with that in [PhC(N*t*Bu)$_2$SiCl] (2.156(1) Å).[7c] Both Si−N bond distances in **2** are almost identical (1.847(3) and 1.835(3) Å) and marginally shorter than those in [PhC(N*t*Bu)$_2$SiCl] (1.870(2) Å).[7c] The P1−N1 (1.666(3) Å) and P2−N2 bond lengths (1.659(3) Å) are also similar and range between those of P−N single bonds (1.75–1.80 Å)[12a] and P=N double bonds (1.51–1.57 Å),[12b] thus suggesting that the positive charge in the cation of **2** should be delocalized on both P=N ylide moieties (Scheme 3). In comparison with the ^{31}P NMR spectra of its precursors



Scheme 3. Resonance structures of the cation in a) **2** and b) **3**.

[**1**·HBr] ($\delta = 41$ ppm) and **1** ($\delta = 11$ ppm), compound **2** shows a downfield-shifted signal at $\delta = 57.7$ ppm in the ^{31}P NMR spectrum recorded in [D_2]dichloromethane. The ^{29}Si{^{1}H} NMR spectrum of **2** exhibits a triplet at $\delta = -3.3$ ppm (^2J(Si,P) = 22.3 Hz), a shift that is close to those of the donor-supported three-coordinate neutral silicon(II) chlorides LSi(Ar)Cl (L = 1,3,4,5-tetramethyl-imidazol-2-ylidene, Ar = 2,6-$Mes_2C_6H_3$, $\delta = 2.34$ ppm; Ar = 2,6-$Trip_2C_6H_3$ (Trip = 2,4,6-*i*$Pr_3C_6H_2$), $\delta = 0.77$ ppm),[7d] and comparable to those of the N-donor-stabilized chlorosilylene [PhC(N*t*Bu)$_2$SiCl] ($\delta = 14.6$ ppm)[7c] and NHC→$SiCl_2$ **A** ($\delta = 19.1$ ppm).[7a] Owing to the threefold coordination of the Si^{II} atom and distinct nature of the donor ligand, the ^{29}Si chemical shift of **2** is very different from those of the β-diketiminate-substituted silyliumylidene cation with a two-coordinate silicon atom ($\delta = 69.3$ ppm)[8b] and the pentamethylcyclopentadienyl-substituted cation with a penta-coordinate silicon atom ($\delta = -400.2$ ppm).[8a]

In order to gain a better understanding of the structural and electronic properties of the cation in **2**, DFT calculations of **2** without counteranion were performed at the B3LYP level using 6-31G(d) basis set (see the Supporting Information). The calculated structural parameters of the cation closely matched those found in the crystal structure of **2** (Figures 1 and 2a). The LUMO of **2** is mainly represented by the π system of naphthalene (Figure 2b). The HOMO of the cation is a π-bonding orbital comprised of the ten π-electron

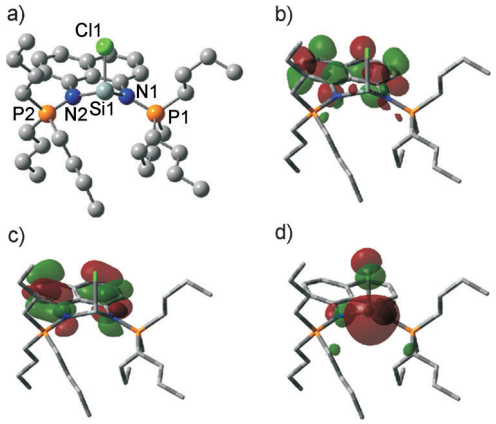


Figure 2. a) Calculated structure of the cation in **2** (B3LYP/6-31G(d) level). Calculated molecular orbitals of the cation in **2**: b) LUMO (−0.1295 eV), c) HOMO (−0.2867 eV), d) HOMO-1 (−0.2917 eV). Hydrogen atoms are omitted for clarity.

naphthalene moiety and the lone pairs at the nitrogen atoms of the P–N ylide groups (Figure 2c). The lone pair orbital at the silicon atom is clearly observed in the HOMO-1 (Figure 2d). It should be noted that the energy difference between HOMO and HOMO-1 is very small with ca. 0.005 eV. This fact may lead to interesting reactivity, both on the naphthalene system and at the silicon(II) center. According to the Natural Population Analysis (NPA) charges, each P atom in the P–N ylide moieties bears a large positive net charge (+1.902 and +1.906), while the N atoms have negative charges (−1.185 and −1.184) as expected. Furthermore, the silicon atom has a positive charge (+0.957). Additionally, the Wiberg Bond Index (WBI) values of the P–N (0.898 and 0.899) and the Si–N bonds (0.451 and 0.448) indicate ylide and dative bond character, respectively. Owing to the aforementioned ylide resonance stabilization, the cation in **2** possesses the resonance structure shown in Scheme 3a.

Compound **2** is very sensitive toward air and moisture, yet stable in the solid state under dry inert atmosphere and dissolved in absolute THF. Although crystals of **2** could be obtained in solutions of THF and dichloromethane at low temperature, slow decomposition occurs in dichloromethane at ambient temperature, thus leading to protonated ligand **1**·HCl and unidentified products. Interestingly, complex **2** reacts with elemental sulfur in THF at ambient temperature to furnish new compound **3** as sole product (Scheme 2). The latter species shows a singlet at $\delta = 66$ ppm in the ^{31}P NMR spectrum with a down-field shift compared to precursor **2**. The ^{29}Si NMR spectrum of **3** shows a triplet at $\delta = -26.7$ ppm with a coupling constant of $^{2}J(\mathrm{Si,P}) = 9.4$ Hz, thus showing a significant up-field shift compared to the resonance signal of **2** (−3.3 ppm, $^{2}J(\mathrm{Si,P}) = 22.3$ Hz). The latter up-field shift results from the higher oxidation state of the Si atom of **3**. In addition, the smaller ^{2}J(Si,P) coupling constant in **3** reflects the decrease of the 3s orbital electron density of the Si atom, owing to the formation of a Si=S bond. However, the chemical shift of **3** is close to those values that were reported recently for Si=S containing complexes with four-coordinate silicon atoms, ranging from $\delta = -40.7$ to 1.57 ppm.[13a–e] Compound **3** could be isolated as colorless crystals in 81% yield and its molecular structure was elucidated by single-crystal X-ray diffraction analysis (Figure 3).

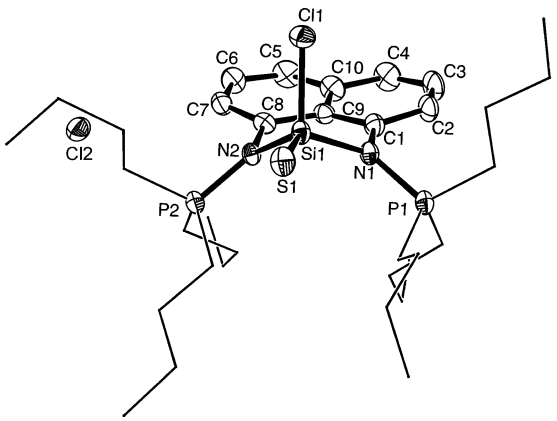


Figure 3. Molecular structure of **3**. Thermal ellipsoids are drawn at 50% probability level. Two independent molecules are present in the asymmetric unit; only molecule 1 is shown here. Hydrogen atoms and one THF molecule are omitted for clarity. Selected bond distances [Å] and angles [°]: *Mol. 1*: Si1–N1 1.776(3), Si1–N2 1.786(3), Si1–Cl1 2.087(2), Si1–S1 1.984(2), P1–N1 1.677(3), P2–N2 1.663(3); N1-Si1-N2 97.0(1), N1-Si1-S1 120.6(1), N2-Si1-S1 119.2(1), N1-Si1-Cl1 102.0(1), N2-Si1-Cl1 102.5(1), S1-Si1-Cl1 112.5(1), P1-N1-C1 117.8(2), Si1-N1-C1 113.0(2), P1-N1-Si1 129.1(2), P2-N2-Si1 128.5(2), P2-N2-C8 118.7(2), Si1-N2-C8 112.8(2); *Mol. 2*: Si2–N3 1.794(3), Si2–N4 1.784(3), Si2–S2 1.977(2), Si2–Cl3 2.082(2), P3–N3 1.667(4), P4–N4 1.667(3); P3-N3-Si2 128.1(2), P4-N4-Si2 122.3(2), N4-Si2-N3 96.4(2), N4-Si2-S2 116.5(1), N3-Si2-S2 121.6(1), N4-Si2-Cl3 102.5(1), N3-Si2-Cl3 102.7(1), S2-Si2-Cl3 114.2(1).

Complex **3** crystallizes in the triclinic space group $P\bar{1}$ as a separate ion pair with a noncoordinating chloride anion. Two independent molecules are found in the asymmetric unit. In both structures, the silicon centers are tetrahedrally coordinated by two nitrogen atoms from the chelate ligand, one chlorine atom, and one sulfur atom. In comparison with the structure of the cation in **2**, the six-membered C_3N_2Si ring in **3**, owing to the tetrahedral coordination of the Si atom, is more puckered, and the dihedral angles between the planes that are defined by the C_3N_2 and N_2Si atoms increase significantly (49.6° and 49.3° vs. 38° in **2**). Despite the increase of the coordination number of the silicon atom in **3** compared with that of **2**, oxidation of the silicon atom from +II to +IV leads to a shortening of the Si–Cl distances (2.087(2) Å,

2.082(2) Å vs. 2.171(2) Å in **2**). The same trend can be found for the mean Si–N distance (1.785 Å) in **3** compared with that in **2** (1.840(3) Å). The Si–S bond distances (1.984(2) Å and 1.977(2) Å) in **3** are very close to those reported recently for related donor-supported Si=S complexes, which range from 1.984(8) to 2.079(6) Å.[13] The latter Si–S distances are significantly longer than the calculated value (1.917 Å) for $S{=}SiCl_2$ described by Schnöckel et al. in 1989.[14] As a result of the ylide (betain-like) nature of the P=N and the Si=S moieties, several resonance structures play an important role in the stabilization of the elusive chlorosilathionium cation in **3** (Scheme 3b). Because of the presence of four-coordinate silicon center, the Si=S bonding situation in the cation in **3** is similar to that already discussed for related Si=X systems.[14b]

In summary, employment of the neutral bidentate bis(ylide) ligand **1** enabled the formation and structural characterization of the first chlorosilylliumylidene complex **2**. Facile oxidation of the silicon(II) atom in **2** by elemental sulfur led to the formation and structural characterization of the unprecedented chlorosilathionium complex, which bears a betain-like Si=S subunit. Compound **2** and **3** could be valuable building blocks for new silicon species, as they both feature a Cl–Si subunit. In addition, the cations in **2** and **3** represent potentially strong Lewis acid catalysts for organic transformations.[15] Respective studies are currently in progress.

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