Silicon Chemistry

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Synthesis and Characterization of [PhC(N*t*Bu)$_2$]SiCl: A Stable Monomeric Chlorosilylene**

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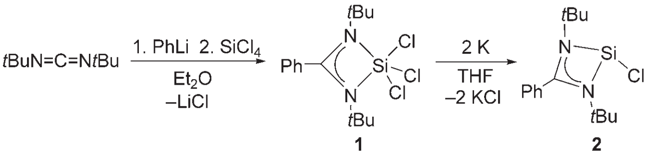
Dedicated to Professor Karl Otto Christe
on the occasion of this 70th birthday

The chemistry of gaseous silicon dichloride has attracted much attention over recent decades owing to its carbene-like properties.[1] Gaseous silicon dichloride can be prepared by the reaction of silicon with silicon tetrachloride at high temperatures; however, it is unstable at room temperature and polymerizes to insoluble perchloropolysilene $(SiCl_2)_n$.[2] Therefore, gaseous silicon dichloride is not suitable for the preparation of chlorosilylene of composition RSiCl. Until now no such compounds have been synthesized and structurally characterized. In contrast, heavier Group 14 metal chlorocarbene analogues are well known and their reactivities have been extensively investigated.[3] Nevertheless, stable silylene complexes $(Me_5C_5)_2Si$[4] and $[(SiMe_3)C(PMe_2)_2]_2Si$,[5] as well as N-heterocyclic silylene compounds,[6] have been isolated and structurally characterized. Herein, we describe the preparation and characterization of a donor-stabilized chlorosilylene complex [PhC(N*t*Bu)$_2$]SiCl.

The reaction of *tert*-butylcarbodiimide (*t*BuN=C=N*t*Bu) with one equivalent of PhLi in Et$_2$O followed by treatment with SiCl$_4$ afforded [PhC(N*t*Bu)$_2$]SiCl$_3$ (**1**; Scheme 1). Compound **1** was obtained as colorless crystalline solid in 47% yield and its structure confirmed by NMR spectroscopic, EI mass-spectrometric, and elemental analysis. A similar amidinato silicon trichloride $[PhC(NSiMe_3)_2]SiCl_3$ was synthesized by the reaction of $LiN(SiMe_3)_2$ with PhCN and SiCl$_4$.[7]



Scheme 1. Synthesis of **2**.

Treatment of **1** with two equivalents of potassium in THF for 17 h afforded the novel monomeric chlorosilylene [PhC(N*t*Bu)$_2$]SiCl (**2**) in 10% yield. Compound **2** is the first example of a system stable at room temperature that contains a Si^{II}–Cl bond. The coordination number of the silicon atom in **2** is comparable to that in $(Me_5C_5)_2Si$[4] and $[(SiMe_3)C(PMe_2)_2]_2Si$.[5] It is suggested that **2** is stabilized kinetically by the sterically hindered amidinate ligand. Similar amidinato complexes of heavier Group 14 metal carbene analogues, such as $[MeC(NC_6H_{11})_2][N(SiMe_3)_2]Ge$,[8] $[p\text{-}PhC_6H_4C(NSiMe_3)_2]_2Sn$,[9] and $[MeC(NSiMe_3)_2]_2Pb$[9] have been reported.

Compound **2** was isolated as a colorless crystalline solid with good solubility in solvents such as diethyl ether, toluene, and THF; furthermore, it is stable in solution or the solid state at room temperature in an inert atmosphere. It has been characterized by elemental analysis, spectroscopic methods, and X-ray studies. The ^{1}H and ^{13}C NMR spectra of **2** displayed one set of resonances that result from the amidinate ligand. The resonances show an upfield shift relative to those of **1**. The shift is probably due to the lower oxidation state of the silicon center in **2**. The ^{29}Si NMR spectrum of **2** exhibits one singlet ($\delta = 14.6$ ppm), which lies between two-coordinate silicon in Si[N(*t*Bu)CHCHN(*t*Bu)] ($\delta = 78.3$ ppm) and four-coordinate silicon in Si[N(*t*Bu)CHCHN(*t*Bu)]Cl$_2$ ($\delta = -40.7$ ppm).[6a] Moreover, it shows a downfield shift relative to that of five-coordinate silicon in **1** ($\delta = -98.6$ ppm).

The molecular structure of **2** with an atom-numbering scheme is shown in Figure 1. Compound **2** is the first example of a monomeric heteroleptic silylene.[10] The amidinate ligand is bonded in a *N*,*N′*-chelate fashion to the silicon center and

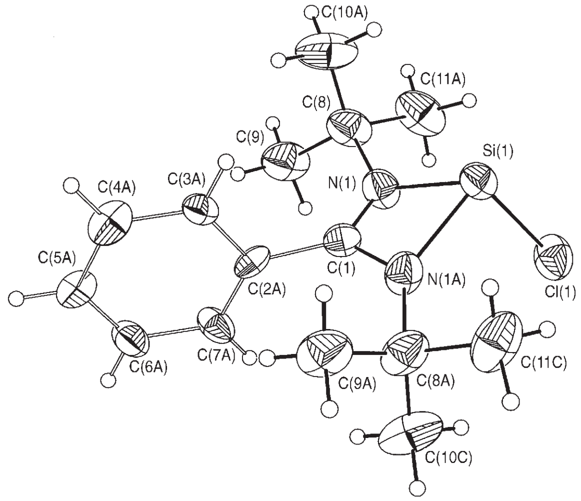


Figure 1. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: N(1)-Si(1) 1.870(2), N(1A)-Si(1) 1.917(2), Si(1)-Cl(1) 2.156(1), N(1)-C(1) 1.333(2), N(1A)-C(1) 1.333(2); N(1)-Si(1)-N(1A) 68.35(8), N(1)-Si(1)-Cl(1) 95.82(6), N(1A)-Si(1)-Cl(1) 96.56(6), C(1)-N(1)-Si(1) 91.86(10), N(1)-C(1)-N(1A) 105.94(18).

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displays a trigonal pyramidal geometry. The sum of the bond angles at the silicon center is 260.73°, which is significantly smaller than that of 330.0° in the tetra-coordinated silylene $[(SiMe_3)C(PMe_2)_2]_2Si$.[5] This geometry is consistent with a stereoactive lone pair at the silicon center. The four-membered Si(1)-N(1)-C(1)-N(1A) ring is planar, and the phenyl group is orthogonally arranged to this plane. The Si(1)−Cl(1) bond length (2.156(1) Å) is in good agreement with the electron-diffraction data of gaseous silicon dichloride (2.083 Å).[11] The Si^{II}−Cl bond length in **2** is also similar to that in $(SiCl_2)_n$ (2.120(9) and 2.088(9) Å).[12] The C−N bond lengths in **2** (C(1)−N(1): 1.333(2) Å; C(1)−N(1A): 1.333(2) Å) are the same and are approximately intermediate between the C−N double and C−N(sp^2) single bond lengths. This geometry shows considerable delocalization throughout the NCN backbone of the ligand. The N(1)-Si(1)-N(1A) angle (68.35(8)°) in **2** is comparable to that in $[MeC(N\textit{i}Pr)_2]_2SiCl_2$ (68.8(1) and 69.0(1)°).[13] The Si(1)−N(1) bond length (1.870(2) Å) is slightly longer than the $Si{-}N_{amide}$ bond length in a silicon(IV) complex $(C_5H_3N\text{-}6\text{-}Me\text{-}2\text{-}NSiMe_3)SiCl_3$ (1.753(5) Å).[14]

According to the crystallographic data, there is a complicated binding situation among the four-membered Si(1)-N(1)-C(1)-N(1A) ring, silicon center, and the chlorine atom. Compound **2** was investigated by means of quantum chemical calculations. The molecule was first fully optimized with the DFT-variant B3L YP[15] as implemented in the Gaussian G03[16] program suite employing a basis set including diffuse and polarization functions termed 6-31+G(2pd,3df).[17] The calculated structural parameters (C(1)-N(1A): 1.339 Å; C(1)-N(1): 1.339 Å; N(1A)-Si(1): 1.893 Å; N(1)-Si(1): 1.893 Å; C(1)-N(1A)-Si(1): 91.59°; N(1A)-Si(1)-N(1): 68.95°; C(8 A)-N(1A)-Si(1): 134.22°; N(1A)-Si(1)-Cl(1): 100.09°) are in good agreement with the crystallographic data. The natural-bond-orbital (NBO)[18] analysis shows that the C(1)−N(1) bond is formed by $sp^{1.59}$ hybrids on the nitrogen centers and $sp^{3.89}$ hybrids on the carbon atom, with the nitrogen atoms contributing 63% of the electronic density. The situation for the Si−N bonds is completely different because the nitrogen atom contributes 85% to the bond, with an orbital having s character, and the silicon atom contributes to this bond with a pure p orbital. The highly acute bond angle is a direct result of this s–p-orbital overlapping. The Si−Cl bond is made up of a nearly pure p orbital on the silicon atom and a p-rich hybrid on the chlorine atom. The dominant p character of the orbitals involved in these bonds gives the possibility for a strongly delocalized situation as shown in Figure 2.

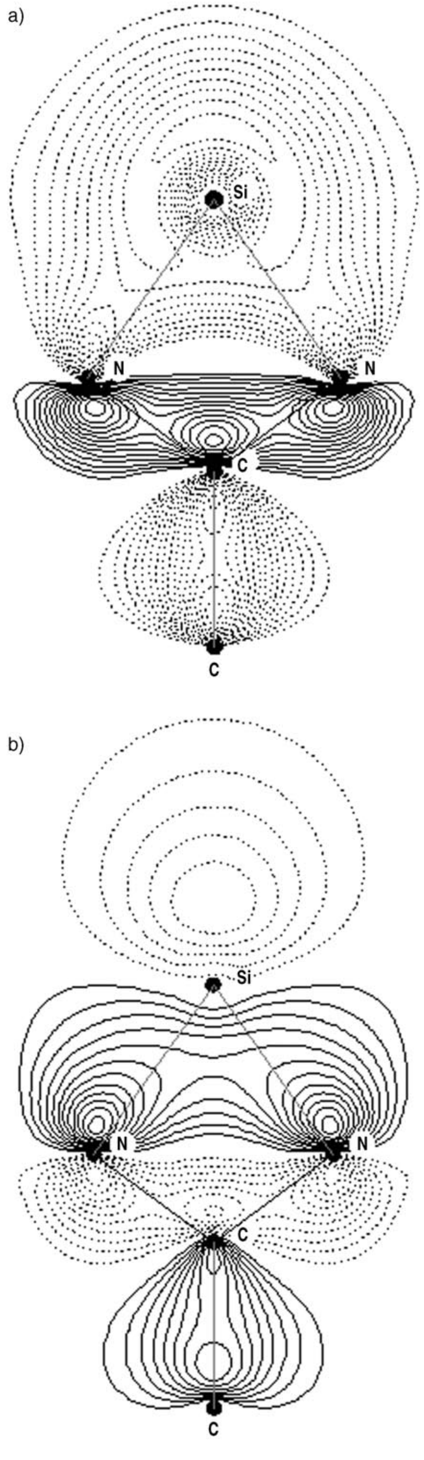

Figure 2. Contour level plots of two binding molecular orbitals (a, b) with different line styles that represent the phase of wave function. For clarity, the remaining atoms have been omitted.

In summary, a novel monomeric chlorosilylene complex has been prepared and fully characterized. Compound **2** can serve as functionalized silylene in metathesis reactions, thus possibly leading to a new era in silicon(II) chemistry. Moreover, the corresponding RCCl compound is not known so far.

Experimental Section

All manipulations were carried out in an inert atmosphere of dinitrogen using standard Schlenk techniques and in a dinitrogen filled glove box.

1: PhLi (7.2 mL, 13.0 mmol, 1.8 M in cyclohexane/Et_2O (7:3)) was added to a solution of $\textit{t}BuN{=}C{=}N\textit{t}Bu$ (2.5 mL, 13.0 mmol) in Et_2O (80 mL) at −78 °C. The solution was raised to ambient temperature and stirred for 1 h. $SiCl_4$ (1.6 mL, 14.0 mmol) was added to this solution at −78 °C. The resulting yellow suspension was stirred overnight at ambient temperature. The precipitate was filtered, and the filtrate was concentrated under reduced pressure until colorless crystals of **1** (2.23 g, 47.0%) were obtained. M.p. 178 °C; elemental analysis (%) calcd for $C_{15}H_{23}Cl_3N_2Si$: C 49.24, H 6.34, N 7.66; found: C 49.07, H 6.14, N 7.61; ^1H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 1.17$ (s, 18H, *t*Bu), 6.68–6.85 ppm (m, 5H, Ph); $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 25 °C): $\delta = 31.7$ (CMe_3), 56.5 (CMe_3), 127.9, 128.1, 128.2, 128.5, 130.2, 131.9 (Ph), 171.9 ppm (NCN); $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6, 25 °C): $\delta = -98.6$ ppm; EI MS: *m*/*z*: 366 [M^+], 329 [M^+-Cl].

2: THF (80 mL) was added to a mixture of **1** (1.98 g, 5.41 mmol) and finely divided potassium (0.43 g, 11.0 mmol) at ambient temperature. The resulting red mixture was stirred for 17 h. The solvent was then removed in vacuo, and the residue was extracted with toluene (50 mL). The insoluble precipitate was filtered off, and the red filtrate was concentrated to yield colorless crystals of **2** (0.16 g, 10.0%). M.p. 159 °C; elemental analysis (%) calcd for $C_{15}H_{23}ClN_2Si$: C 61.10, H 7.87, N 9.51; C 60.95, H 7.64, N 9.35; ^1H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 1.08$ (s, 18H, *t*Bu), 6.78–7.05 ppm (m, 5H, Ph); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): $\delta = 31.4$ (CMe_3), 53.7 (CMe_3), 127.4, 127.9, 128.4, 129.8, 133.0 (Ph), 166.7 ppm (NCN); $^{29}Si\{^1H\}$ NMR (60 MHz, C_6D_6, 25 °C): $\delta = 14.6$; EI-MS: *m*/*z*: 295 [M^+], 231 [$M^+-Si-Cl$].

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[10] Crystal data for **2** ($C_{15}H_{23}ClN_2Si$): $M_r = 294.89$; $a = 14.2675(11)$, $b = 10.8409(11)$, $c = 11.9518(9)$ Å; $\alpha = 90$, $\beta = 114.926(5)$, $\gamma = 90°$; $V = 1676.4(2)$ Å^3; $Z = 4$; space group $C2/c$ (monoclinic); $T = 133(2)$ K; $\lambda = 0.71073$ Å; $\mu = 0.290$ mm^{-1}; $\rho_{calc} = 1.168$ g cm^{-3}; $2\theta_{max} = 24.74°$; $F(000) = 632$; 8610 measured reflections, 1416 independent and 1253 observed reflections ($I > 2\sigma(I)$); $R1 = 0.0382$, $wR2 = 0.1020$; largest diff. peak and hole 0.242/−0.158 e Å^{-3}. The crystal data were collected on a Stoe Image Plate IPDS II System. The structure was solved by direct phase determination (SHELXS-97)[19] and refined for all data by full-matrix least squares methods on F^2. All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations. CCDC-297194 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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