

Facile Synthesis of a Rare Chlorosilylene–BH₃ Adduct

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Dedication to Professor Hansgeorg Schnöckel on the occasion of his 70th birthday

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The first stable chlorosilylene–BH₃ adduct was synthesized in the reaction of N-heterocyclic carbene (NHC) stabilized dichlorosilylene either with equivalent amounts of LiBH₄ or with equivalent amounts of a BH₃·THF solution. The chloro-

silylene–BH₃ adduct was characterized by single-crystal X-ray structural analysis, NMR and IR spectroscopy, EI mass spectrometry, and elemental analysis.

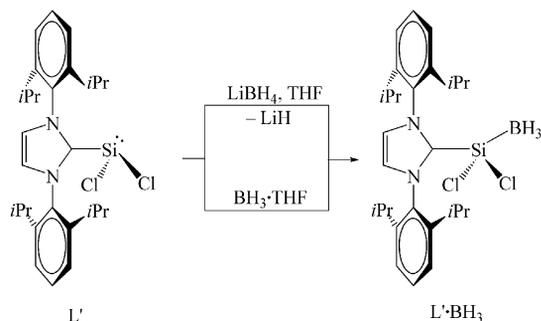
Introduction

Silylenes are considered as silicon analogues of carbenes, existing as a neutral bivalent silicon atom^[1] with two non-bonding electrons as the HOMO, which possesses nucleophilic character, and an empty p-orbital as the LUMO, which exhibits electrophilic character. Having both the nucleophilic and electrophilic reactive sites at the silicon atom, silylenes are considered to have an ambiphilic character and behave as Lewis acids as well as Lewis bases.^[2] Due to the availability of both nucleophilic and electrophilic reaction center, the chemistry of silylenes is of intense interests to scientists.^[1–5] After the report of the first stable N-heterocyclic silylene (NHSi) by West et al.,^[6] the chemistry of stable N-heterocyclic silylenes (NHSis) has attracted much attention, whereas the NHCs (N-heterocyclic carbenes) have led to burgeoning research activities and to many applications in chemistry.^[7,8] Recently, we reported on the high-yield synthesis of NHC-stabilized dichlorosilylene LSiCl₂ [L = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] by employing a new synthetic procedure comprising the reductive elimination of HCl from trichlorosilane in the presence of NHC under mild reaction conditions.^[9a] Furthermore, we synthesized PhC(N*t*Bu)₂SiCl in high yield using lithium bis(trimethylsilyl)amide as dehydrochlorinating agent.^[9b] These routes are completely different from the other conventional synthetic procedures reported so far by using strong reducing agents, such as potassium or potassium graphite, for the synthesis of silylene or other compounds with low-valent silicon. We have also reported on the reac-

tivity of LSiCl₂ with the Lewis acid B(C₆F₅)₃^[10] and investigated the reactivity with transition metal complexes.^[11] Inspired by exploring the chemistry further towards reducing agents, we treated LSiCl₂ with the strong reducing agent LiBH₄. In the present report, we describe LSiCl₂ that forms LSiCl₂·BH₃ either with equivalent amounts of LiBH₄ or with equivalent amounts of a BH₃·THF solution, which is the first stable chlorosilylene–BH₃ adduct.

Results and Discussion

The reaction of equimolar amounts of LSiCl₂ (L') with LiBH₄ afforded the colorless crystalline solid LSiCl₂·BH₃ (L'·BH₃) in quantitative yield with good solubility in THF. (Scheme 1). We surmised that there should be an elimination of LiH. It is interesting to mention that stable carbene reacts with LiMH₄ (M = Al, Ga, In) to form carbene–MH₃ complexes.^[12] Further, catalytic amounts of SnCl₄,^[13] TiCl₄^[14] and CoCl₂^[15] are known to react with LiBH₄ or NaBH₄ to give stoichiometric amounts of BH₃. The same adduct L'·BH₃ was also synthesized by direct reaction of



Scheme 1. Synthesis of L'·BH₃.

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equivalent amounts of L' with BH₃·THF solution. Moreover, L'·BH₃ is stable in solution as well as in the solid state at room temperature under an inert gas. It has been characterized by elemental analysis, spectroscopic methods and single-crystal X-ray structural studies.

The coordination of the boron atom to the silicon atom can be readily noticed in the ²⁹Si NMR spectrum. The adduct resonates at $\delta = 30.72$ ppm. Moreover, it shows a quartet resonance, which indicates the coupling of the silicon nucleus with the quadrupolar ¹¹B ($I = 3/2$) nucleus. The coupling constant J_{SiB} is 60 Hz. The ¹¹B NMR spectrum of L'·BH₃ exhibits a resonance at $\delta = -38.75$ ppm and displays a quartet resonance with an intensity of 1:3:3:1 indicating the coupling of the hydrogen atoms to the boron atom in the BH₃ unit ($J_{\text{BH}} = 95$ Hz). The ¹H NMR spectrum of L'·BH₃ exhibits a quartet resonance in the range $\delta = -1.02$ to $+0.40$ ppm for the B–H environment with an intensity of 1:1:1:1, which indicates the coupling of the hydrogen nuclei with the quadrupolar ¹¹B nucleus ($J_{\text{HB}} = 94$ Hz). In the IR spectrum we were able to observe the band for the $\nu_{\text{B-H}}$ vibrations at 2356 and 2320 cm⁻¹. Compound L'·BH₃ shows the molecular ion peak in the EI mass spectrum at $m/z = 500.1$. In addition to that the structure was confirmed by single-crystal X-ray structural analysis.

The molecular structure of L'·BH₃ is shown in Figure 1. The adduct crystallizes in the monoclinic space group $P2_1/n$. Both the silicon and boron atoms are four-coordinate and display a distorted tetrahedral geometry. The silicon coordination environment is derived from one carbon atom of the carbene, two chlorine atoms and one boron atom, whereas the boron atom features three hydrogen atoms and one silicon atom. The silicon–boron bond length in L'·BH₃ is 1.965(2) Å, which is shorter than that in L'·B(C₆F₅)₃ [2.106(6) Å], and the angle $\angle \text{C-Si-B}$ in L'·BH₃ [119.61(9)°]

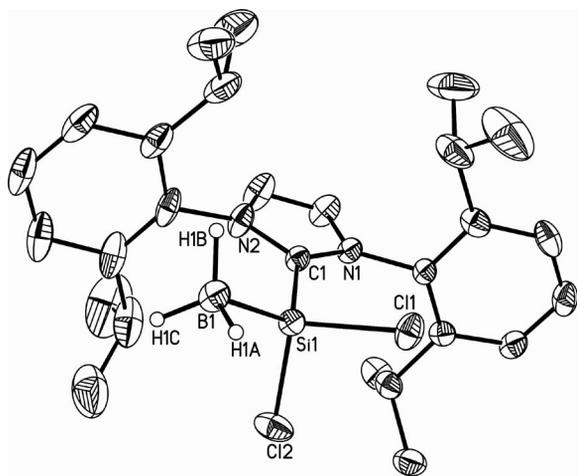


Figure 1. Molecular structure of L'·BH₃. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity except for the BH₃ moiety. Selected bond lengths [Å] and angles [°]: B(1)–Si(1) 1.965(2), C(1)–Si(1) 1.937(2), Si(1)–Cl(1) 2.0787(7), Si(1)–Cl(2) 2.0892(8); C(1)–Si(1)–B(1) 119.61(9), Cl(1)–Si(1)–Cl(2) 101.91(3), C(1)–Si(1)–Cl(1) 101.95(6), C(1)–Si(1)–Cl(2) 99.44(6), B(1)–Si(1)–Cl(1) 116.34(8), B(1)–Si(1)–Cl(2) 114.76(8).

is smaller when compared with that of L'·B(C₆F₅)₃ [132.3(2)°]. The average Si–Cl distance in L'·BH₃ is 2.0839(7) Å [Si–Cl_{av} of L' 2.1664(17) Å]. L'·BH₃ exhibits an Si–C bond length of 1.937(2) Å, which is shorter when compared to that of L' [Si–C 1.985(4) Å].

Conclusions

In this study, we report on the first stable chlorosilylene–BH₃ adduct from the reaction of N-heterocyclic carbene stabilized dichlorosilylene either with equivalent amounts of LiBH₄ or with equivalent amounts of a BH₃·THF solution.

Experimental Section

General: All manipulations were carried out under dinitrogen by using standard Schlenk techniques and in a dinitrogen-filled glove box. Solvents were purified by a solvent purification system MBRAUN MB SPS-800. All chemicals were purchased from Aldrich and used without further purification. L' was prepared as reported in the literature.^[9] ¹H, ¹³C, ¹¹B and ²⁹Si NMR spectra were recorded with a Bruker Avance DPX 200 or a Bruker Avance DRX 500 spectrometer by using [D₈]THF as solvent. Chemical shifts δ are given relative to SiMe₄. The EI mass spectrum was obtained by using a Finnigan MAT 8230 instrument. The IR spectrum was recorded with a Bio-Rad Digilab FTS7 spectrometer in the range of 4000–350 cm⁻¹ as nujol mulls. Elemental analysis was performed by the Institut für Anorganische Chemie, Universität Göttingen. The melting point was measured in a sealed glass tube with a Büchi B-540 melting point apparatus.

Synthesis of L'·BH₃

Method A: THF (60 mL) was added to a 100 mL Schlenk flask containing L' (2.31 g, 4.73 mmol) and LiBH₄ (0.11 g, 5.05 mmol), and the reaction mixture was stirred at room temperature overnight. The solution was filtered, and the solvent was removed in vacuo. Finally, the compound was washed with toluene (20 mL), and the solvents were evaporated to dryness to obtain a pure colorless crystalline solid (1.95 g, 81.93%).

Method B: To a solution of L' (2.00 g, 4.10 mmol) in THF (60 mL) a BH₃·THF solution (1.0 M, 4.2 mL, 4.20 mmol) was added at -78 °C, and then the flask was allowed to come to room temperature and the mixture stirred overnight. Then the solution was filtered, and the solvent was removed in vacuo. Finally, the compound was washed with toluene (20 mL), and the solvents were evaporated to dryness to obtain a pure colorless crystalline solid (1.55 g, 75.60%).

M.p. 210 °C (dec.). C₂₇H₃₉BCl₂N₂Si (501): calcd. C 64.67, H 7.84, N 5.59; found C 64.42, H 7.84, N 5.46. ¹H NMR (200 MHz, [D₈]THF, 25 °C): $\delta = -1.02$ to 0.40 (q, $J_{\text{HB}} = 94$ Hz, 3 H, BH₃), 1.15 [d, $J = 6.84$ Hz, 12 H, CH(CH₃)₂], 1.38 [d, $J = 6.72$ Hz, 12 H, CH(CH₃)₂], 2.59 [m, 4 H, CH(CH₃)₂], 7.34 (m, 4 H, ArH), 7.51 (m, 2 H, ArH), 7.89 (s, 2 H, CH) ppm. ¹³C{¹H} NMR (125.75 MHz, [D₈]THF, 25 °C): $\delta = 22.87$, 26.06 [CH(CH₃)₂], 30.08 [CH(CH₃)₂], 124.83, 125.43, 128.35, 131.95, 134.32, 146.44, 156.48 (NCH and C₆H₃) ppm. ¹¹B{¹H} NMR (160.46 MHz, [D₈]THF, 25 °C): $\delta = -38.75$ (q, $J_{\text{BH}} = 95$ Hz, 1 B, BH₃) ppm. ²⁹Si{¹H} NMR (99.36 MHz, [D₈]THF, 25 °C): $\delta = 30.72$ (q, $J_{\text{SiB}} = 60$ Hz) ppm. EI-MS: m/z : 500.1 [M⁺]. FT-IR (Nujol): $\tilde{\nu} = 2356$ (w), 2320 (shoulder) [$\nu(\text{B-H})$] cm⁻¹.

Crystallography: Colorless crystals suitable for single-crystal X-ray analysis were obtained by keeping L'·BH₃ in THF solution at –32 °C for 3 d. A single crystal was mounted at low temperature in inert oil under argon by applying the X-Temp2 device.^[16] The data of L'·BH₃ was collected with a Bruker D8 three-circle diffractometer equipped with a SMART APEX II CCD detector and an INCOATEC Mo microsource with INCOATEC Quazar mirror optics.^[17] The data were integrated with SAINT,^[18] and an empirical absorption correction with SADABS^[19] was applied. The structure was solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods on F² (SHELXL-97).^[20] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically in calculated positions by using a riding model with their U_{iso} values constrained to 1.5 × U_{eq} of their pivot atoms for terminal sp³ carbon atoms and 1.2 × U_{eq} for all other carbon atoms. CCDC-791729 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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