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Facile Synthesis of a Rare Chlorosilylene–BH_3 Adduct

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

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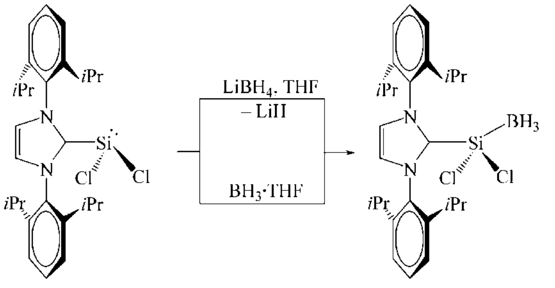
The first stable chlorosilylene–BH_3 adduct was synthesized in the reaction of N-heterocyclic carbene (NHC) stabilized dichlorosilylene either with equivalent amounts of $LiBH_4$ or with equivalent amounts of a BH_3·THF solution. The chlorosilylene–BH_3 adduct was characterized by single-crystal X-ray 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 nonbonding 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 $LSiCl_2$ [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 $PhC(NtBu)_2SiCl$ 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 reactivity of $LSiCl_2$ with the Lewis acid $B(C_6F_5)_3$[10] and investigated the reactivity with transition metal complexes.[11] Inspired by exploring the chemistry further towards reducing agents, we treated $LSiCl_2$ with the strong reducing agent $LiBH_4$. In the present report, we describe $LSiCl_2$ that forms $LSiCl_2·BH_3$ either with equivalent amounts of $LiBH_4$ or with equivalent amouts of a BH_3·THF solution, which is the first stable chlorosilylene–BH_3 adduct.

Results and Discussion

The reaction of equimolar amounts of $LSiCl_2$ (L′) with $LiBH_4$ afforded the colorless crystalline solid $LSiCl_2·BH_3$ (L′·BH_3) 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 $LiMH_4$ (M = Al, Ga, In) to form carbene–MH_3 complexes.[12] Further, catalytic amounts of $SnCl_4$,[13] $TiCl_4$[14] and $CoCl_2$[15] are known to react with $LiBH_4$ or $NaBH_4$ to give stoichiometric amounts of BH_3. The same adduct L′·BH_3 was also synthesized by direct reaction of



L′

L′·BH_3

Scheme 1. Synthesis of L′·BH_3.

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equivalent amounts of L′ with BH_3·THF solution. Moreover, L′·BH_3 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 ^{29}Si 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 ^{11}B ($I = 3/2$) nucleus. The coupling constant J_{SiB} is 60 Hz. The ^{11}B NMR spectrum of L′·BH_3 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 BH_3 unit ($J_{\mathrm{BH}} = 95$ Hz). The ^{1}H NMR spectrum of L′·BH_3 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 ^{11}B nucleus ($J_{\mathrm{HB}} = 94$ Hz). In the IR spectrum we were able to observe the band for the $\nu_{\mathrm{B-H}}$ vibrations at 2356 and 2320 $\mathrm{cm^{-1}}$. Compound L′·BH_3 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′·BH_3 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′·BH_3 is 1.965(2) Å, which is shorter than that in L′·$B(C_6F_5)_3$ [2.106(6) Å], and the angle ∠C–Si–B in L′·BH_3 [119.61(9)°] is smaller when compared with that of L′·$B(C_6F_5)_3$ [132.3(2)°]. The average Si–Cl distance in L′·BH_3 is 2.0839(7) Å [Si–$\mathrm{Cl_{av}}$ of L′ 2.1664(17) Å]. L′·BH_3 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].

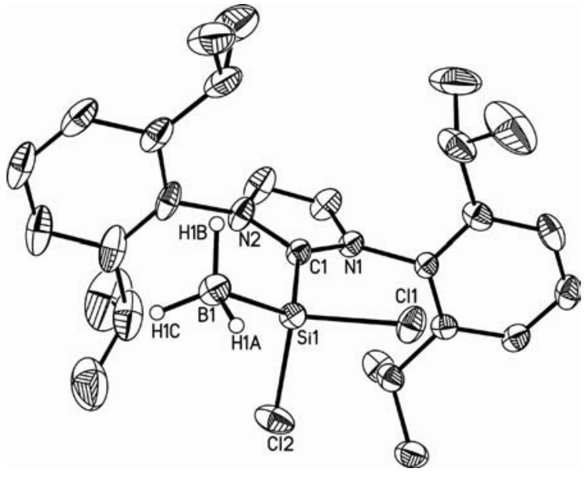

Figure 1. Molecular structure of L′·BH_3. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity except for the BH_3 moiety. Selected bond lengths [Å] and angles [°]: B(1)–Si(1) 1.965(2), C(1)–Si(1) 1.937(2), Si(1)–Cl(1) 2.0787(7), Si(1)–Cl(2) 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).

Conclusions

In this study, we report on the first stable chlorosilylene–BH_3 adduct from the reaction of N-heterocyclic carbene stabilized dichlorosilylene either with equivalent amounts of $LiBH_4$ or with equivalent amounts of a BH_3·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] ^{1}H, ^{13}C, ^{11}B and ^{29}Si NMR spectra were recorded with a Bruker Avance DPX 200 or a Bruker Avance DRX 500 spectrometer by using [D$_8$]THF as solvent. Chemical shifts δ are given relative to $SiMe_4$. 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 $\mathrm{cm^{-1}}$ 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′·BH_3

Method A: THF (60 mL) was added to a 100 mL Schlenk flask containing L′ (2.31 g, 4.73 mmol) and $LiBH_4$ (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 BH_3·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.). $C_{27}H_{39}BCl_2N_2Si$ (501): calcd. C 64.67, H 7.84, N 5.59; found C 64.42, H 7.84, N 5.46. ^{1}H NMR (200 MHz, [D$_8$]THF, 25 °C): $\delta = -1.02$ to 0.40 (q, $J_{\mathrm{HB}} = 94$ Hz, 3 H, BH_3), 1.15 [d, $J = 6.84$ Hz, 12 H, CH(CH_3)$_2$], 1.38 [d, $J = 6.72$ Hz, 12 H, CH(CH_3)$_2$], 2.59 [m, 4 H, CH(CH$_3$)$_2$], 7.34 (m, 4 H, ArH), 7.51 (m, 2 H, ArH), 7.89 (s, 2 H, CH) ppm. ^{13}C{^{1}H} NMR (125.75 MHz, [D$_8$]THF, 25 °C): $\delta = 22.87$, 26.06 [CH(CH$_3$)$_2$], 30.08 [CH(CH$_3$)$_2$], 124.83, 125.43, 128.35, 131.95, 134.32, 146.44, 156.48 (NCH and C_6H$_3$) ppm. ^{11}B{^{1}H} NMR(160.46 MHz, [D$_8$]THF, 25 °C): $\delta = -38.75$ (q, $J_{\mathrm{BH}} = 95$ Hz, 1 B, BH$_3$) ppm. ^{29}Si{^{1}H} NMR (99.36 MHz, [D$_8$]THF, 25 °C): $\delta = 30.72$ (q, $J_{\mathrm{SiB}} = 60$ Hz) ppm. EI-MS: m/z: 500.1 [M$^+$]. FT-IR (Nujol): $\tilde{\nu}$ = 2356 (w), 2320 (shoulder) [ν(B–H)] $\mathrm{cm^{-1}}$.

Crystallography: Colorless crystals suitable for single-crystal X-ray analysis were obtained by keeping $L'{\cdot}BH_3$ 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 $L'{\cdot}BH_3$ 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 F^2 (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 $1.5 \times U_{eq}$ of their pivot atoms for terminal sp^3 carbon atoms and $1.2 \times U_{eq}$ 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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