Notes

High-Yield Synthesis of the First *arachno*-Silaborane

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*Summary: arachno-$B_9H_{13}(SMe_2)$ was transformed into arachno-$MeSiB_9H_{12}(NHMe_2)$ (**1**) by reaction with $MeHSi(NMe_2)_2$. The new silaborane was characterized by ^1H, ^{29}Si, and ^{11}B NMR techniques. The {SiB_9} cluster geometry is related to the $B_{10}H_{14}^{2-}$ framework, with the Si atom occupying position 6.*

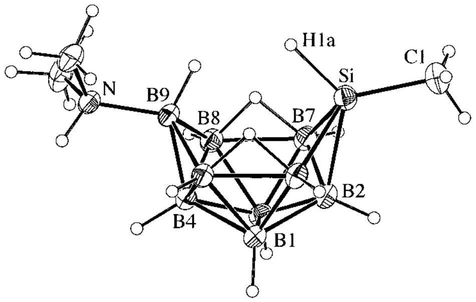
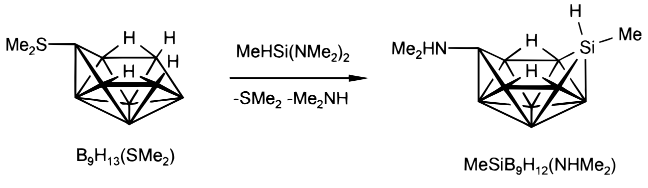


Figure 1. Molecular structure of *arachno*-$MeSiB_9H_{12}$-$(NHMe_2)$ (**1**).

Scheme 1



1

The incorporation of heteroatoms into the skeleton of boranes has been of special interest in borane cluster chemistry for quite some time. In 1963 the remarkable reaction of acetylene with $B_{10}H_{12}(SMe_2)_2$ was developed, the beginning of the well-known 1,2-dicarba-*closo*-dodecaborane(12) chemistry.[1] Carboranes are by far the best investigated family of main group heteroboranes. In the last years there has been also increasing interest in the syntheses of other main group heteroboranes especially azaboranes[2] and thiaboranes.[3] Two examples of silacarboranes [*commo*-3,3′-$Si(3,1,2\text{-}SiC_2B_9H_{11})_2$, $\{(Me_3Si)_2C_2B_4H_4\}_2Si$] are known from the reaction of $SiCl_4$ with the respective carborane.[4,5] We are investigating the less developed family of silaboranes. Recently we studied the nucleophilic degradation of *o*-silaborane[6] leading to the first *nido*-silaborane.[7] In this paper we present the high-yield synthesis of the first *arachno*-silaborane. Reaction between $B_9H_{13}(SMe_2)$[8] and excess $MeHSi(NMe_2)_2$ at 80 °C overnight leads to the title compound **1** in quantitative yield (on the basis of ^{11}B NMR) (Scheme 1). Recrystallization of **1** from benzene/hexane gave analytically pure crystalline *arachno*-silaborane in 85% yield. The constitution of **1** can be deduced unambiguiously from the NMR data. Six ^{11}B NMR signals with a ratio of 1:1:2:1:2:2 can be assigned to the silaborane skeleton on the basis of a 2D COSY $^{11}B/^{11}B$ NMR experiment. In solution the molecule exhibits C_s symmetry with a mirror plane through Si, B2, B4, and B9. No cross peaks are observed between the resonances of B atoms which are connected by hydrogen bridges;[9] however, cross peaks for the bonds B2−B5/B7 which are opposite to the Si atom are visible.[10] The ^1H NMR resonances for the boron-bonded H atoms can be assigned to the B atoms on the basis of a 2D HMQC $^1H/^{11}B$ NMR experiment, with the bridging H atoms located at −5.03 ppm. A doublet ($^3J = 3$Hz) for the methyl group at 0.40 ppm and a quartet ($^3J = 3$Hz) for SiH at 1.50 ppm clearly indicate the MeSiH group. The ^{29}Si NMR shows a doublet ($^1J = 238$ Hz) at −80.6 ppm. The molecular structure of **1** has been established by an X-ray diffraction study and is shown in Figure 1. Selected bond lengths and angles of **1** appear in Table 2. The geometry of the silaborane derivative is related to that of the isoelectronic $B_{10}H_{14}^{2-}$[11] borate. The B−B bond lengths in the open face (B5, B7, B8, B9, B10) of **1** are slightly shorter than in $B_{10}H_{14}^{2-}$ (average 1.883 Å). The other B−B bond lengths in **1** [1.730(5)−1.813(6) Å] correspond to the values in $B_{10}H_{14}^{2-}$ (1.729−1.807 Å). Two of the three Si−B bond lengths [Si−B5 2.134(4), Si−B7 2.152(4) Å] belong to the open face of the cluster and therefore are ~0.1 Å longer than the Si−B2 bond length [2.037(4) Å], which is in the range of known Si−B distances.[6,7] The B−N [1.591(4) Å] bond length is typical for amine−

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Table 1. Crystallographic Data for 1

formula	$C_3H_{22}B_9NSi$
fw	197.6
space group	$P\bar{1}$ (No. 2)
a, Å	8.666(3)
b, Å	11.184(2)
c, Å	6.917(1)
α, deg	93.89(1)
β, deg	105.02(2)
γ, deg	87.44(2)
V, Å^3	645.7(5)
ρ_{calc}, g/cm^3	1.016
Z	2
F(000)	212
λ, Å	1.5418
μ(Cu Kα), cm^{-1}	11.85
cryst dimens, mm	0.4 × 0.4 × 0.15
T, K	233
scan mode	ω
scan range, deg	$5 < \theta < 70$
tot. data	2553
unique obs data ($I > 1\sigma(I)$)	2020
no. of variables	212
R, R_w [$w^{-1} = \sigma^2(F_o)$]	7.2, 8.6
max resid dens, e Å^{-3}	0.3

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 1

Si−C1	1.850(4)	B2−B7	1.800(6)
Si−B2	2.037(4)	B3−B4	1.769(5)
Si−B5	2.134(4)	B3−B7	1.757(6)
Si−B7	2.152(4)	B3−B8	1.780(5)
Si−H1a	1.53(3)	B4−B8	1.748(6)
B1−B2	1.744(5)	B4−B9	1.733(5)
B1−B3	1.813(6)	B4−B10	1.730(5)
B1−B4	1.753(5)	B5−B10	1.858(6)
B1−B5	1.756(6)	B7−B8	1.869(5)
B1−B10	1.773(5)	B8−B9	1.851(5)
B2−B3	1.745(6)	B9−B10	1.881(6)
B2−B5	1.788(6)	N−B9	1.591(4)
C1−Si−B2	112.5(2)	B5−Si−H1a	99(1)
C1−Si−B5	117.6(1)	B7−Si−H1a	94(1)
C1−Si−B7	124.7(2)	Si−B5−B10	114.4(3)
C1−Si−H1a	123.(1)	B5−B10−B9	114.1(3)
B2−Si−B5	50.7(2)	N−B9−B10	120.2(3)
B2−Si−B7	50.8(1)	N−B9−B8	116.4(2)
B2−Si−H1a	125(1)	B7−B8−B9	115.6(3)
B5−Si−B7	91.3(2)	Si−B7−B8	112.7(2)

boranes $R'_3N{-}BR_3$.[12] Isoelectronic analogues of **1** are 9-[$(C_6H_{11})NC$]-6-NHB_9H_{11},[13] 9-$N(C_2H_5)_3$-6-SB_9H_{11},[14] and [6-CB_9H_{14}]$^-$.[15] With the straightforward high-yield syntheses (85% yield) of **1**, we found the second example for the incorporation of a Si atom into the framework of a boron cluster by reaction with $MeHSi(NMe_2)_2$. The $MeHSi(NMe_2)_2$ silane used has been proven to act as a source of a silicon vertex in the remarkable syntheses of *o*-silaborane.[6]

Experimental Section

General Procedure. All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere using standard Schlenk or vacuum line techniques.

Syntheses of 9-(Dimethylamine)-6-methyl-6-sila-*arachno*-decaborane(12) (1). $B_9H_{13}(SMe_2)$ (1.16 g, 6.72 mmol) and $MeHSi(NMe_2)_2$ (5.00 g, 37.80 mmol) are stirred at 80 °C over night. After all volatiles are removed the remaining white solid is dissolved in benzene and recrystallized from a mixture of benzene and hexane. **1** is a colorless crystalline material which melts at 82 °C. Yield: 1.13 g, 5.72 mmol, 85%. $^1H\{^{11}B\}$ NMR (499.66 MHz, acetone-d_6): δ −5.03 (s, br, 2H, μ-H7/8, 5/10), −0.39 (s, 1H, H9), 0.40 (d, $^3J = 3$ Hz, 3H, SiMe), 0.61 (s, 2H, H1/3), 1.46 (s, 2H, H5/7), 1.50 (q, $^3J = 3$ Hz, 1H, SiH), 2.04 (obscured by acetone signal) (s, H8/10), 2.17 (s, 2H, H2, H4), 2.75 (d, $^3J = 5$ Hz, 9H, NMe), 5.72 (s, br, 1H, NH). ^{11}B NMR (160.31 MHz, acetone-d_6): δ −40.0 (d, $^1J = 147$ Hz, 2B, B1/3), −26.9 (d, $^1J = 153$ Hz, 2B, B5/7), −18.1 (d, $^1J = 122$ Hz, 1B, B9), −11.5 (d, $^1J = 140$ Hz, 2B, B8/10), −5.8 (d, $^1J = 136$ Hz, 1B, B4), −2.8 (d, $^1J = 140$ Hz, 1B, B2). ^{13}C NMR (125.64 MHz, acetone-d_6): δ −6.7 (SiMe), 45.4 (NMe). ^{29}Si NMR (99.27 MHz, acetone-d_6): δ −80.6 (d, $^1J = 238$ Hz, SiH). MS (MAT 95, Finnigan MAT): m/z 198, M$^+$. Anal. Calcd for $C_3H_{22}NB_9Si$: C, 18.24; H, 11.22; N, 7.09. Found: C, 17.92; H, 11.26; N, 7.12.

X-ray Structure Determination of 1. Geometry and intensity data were collected on an Enraf-Nonius CAD4 diffractometer with Cu Kα radiation (1.5418 Å, graphite monochromator). A summary of crystallographic data, data collection parameters, and refinement parameters is given in Table 1. The structure was solved by direct methods using SHELXS-86[16] and refined with MolEN.[17] The F_c values were corrected for secondary extinction[18] (7.49×10^{-6}). All hydrogen atoms were located in difference Fourier syntheses. In the final full-matrix refinement, non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were refined with isotropic displacement parameters. The hydrogen atom bonded to nitrogen was treated as riding.

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Supporting Information Available: Complete tables of unit cell parameters, H atom parameters, thermal parameters, bond distances, bond angles, and positional and anisotropic thermal parameters for **1** (7 pages). Ordering information is given on any current masthead page.

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