APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2007; **21**: 676–681
Published online 11 April 2007 in Wiley InterScience
(www.interscience.wiley.com) DOI:10.1002/aoc.1223

Ionic 1,2,5-oxonia- and zwitterionic 1,2,5-oxasilaboratole derivatives. Synthesis and molecular structures

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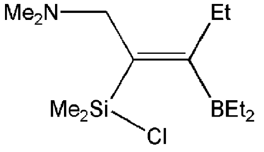
Alkenes bearing a chlorosilyl and a diethylboryl group in *cis*-positions at the C=C bond together with a dimethylaminomethyl group in geminal position to the silyl group were subjected to hydrolysis (a) and alcoholysis [ROH: R = Me (b), Et (c), ^{i}Pr (d)]. In the case of the alkene 1 containing a chloro(dimethyl)silyl group, novel ammonium salts 3a–d were isolated as 2,5-dihydro-1,2,5-oxoniaboratole derivatives. In contrast, the alkene 2, containing a chloro(methyl)silyl group, did not give defined products under the same reaction conditions. In the presence of traces of water in diethylamine, 2 reacted at the Si–H and Si–Cl bonds to give a zwitterionic disiloxane 4, a 2,5-dihydro-1,2,5-oxasilaboratole derivative. The new compounds were characterized in solution by ^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR spectroscopy, and for two examples (3a and 4) by X-ray structure analysis in the solid state. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: heterocycles; ammonium salts; silanes; boranes; NMR; X-ray

INTRODUCTION

Alkenylsilanes bearing an additional organometallic substituent at the C=C bond, such as a boryl group, are attractive synthons for further transformations.[1–11] Their synthetic potential may be further enhanced if there are functional groups present at silicon and/or in other substituents at the C=C bond.[8–11] Recently we have succeeded in the synthesis of the alkenes **1** and **2** by 1,1-ethylboration[12] of the corresponding alkyn-1-yl(chloro)silanes.[13] NMR data indicate a weak intramolecular N–Si coordination in both **1** and **2**.[13]



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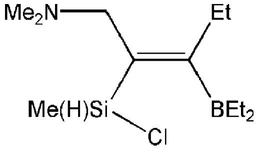

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Both alkenes **1** and **2** offer numerous reactive sites, and we have started now to study their reactivity towards protic reagents such as water and alcohols. These reagents should preferably attack the Si–Cl bond, and the HCl thus formed can be trapped immediately by the amino function in the molecules to give ammonium salts with novel functionalities. In analogy to similar systems without the CH_2NMe_2 substituent, which were prepared by a completely different route,[14,15] intramolecular O–B coordination should lead to 1,2-dihydro-1,2,5-oxoniasilaboratole derivatives.

RESULTS AND DISCUSSION

We have reproduced the synthesis of **1** and **2**. The alkene **2** has been reported to be thermally unstable and to decompose upon attempted distillation.[13] However, after optimizing the reaction conditions and carrying out the synthesis on a somewhat larger scale, **2** could be obtained after distillation in 30–40% yield in repeated experiments along with an impurity and a small amount of the (*E*)-isomer.

The reactions of **1** with water and alcohols proceed to give **3** (Scheme 1) in essentially quantitative yield. The compounds **3** are colourless solids, fairly stable towards moisture and air, almost insoluble in non-polar solvents and slightly soluble in $CHCl_3$ (**3b–d**) and THF (**3a–d**). The solution-state structures of **3a–d** follow from a consistent set of ^{1}H, ^{11}B, ^{13}C and

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Contract/grant sponsor: Deutsche Forschungsgemeinschaft.
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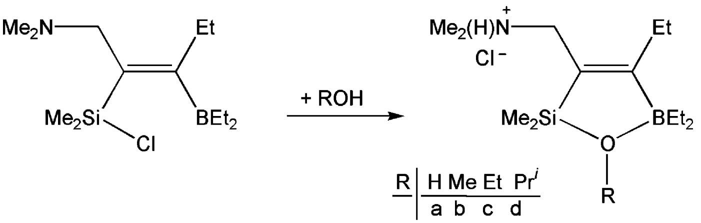


1

3

Scheme 1. Hydrolysis and alcoholysis of the chlorodimethylsilyl(diethylboryl)alkene **1**.

Table 1. ^{13}C, ^{29}Si and ^{11}B NMR data[a] of the compounds **3a, 3b, 3c, 3d, 4**

	δ^{13}C, Si–C=	=C–B	SiMe	CH_2	NMe_2	BEt_2	Et	R	δ^{29}Si	δ^{11}B
3a R = H[b]	124.4	191.0 (br)	3.5 (57.1)	56.6	42.9	12.0	15.3	—	25.7	12.5
						17.5 (br)	25.1			
3b R = Me	119.6 (83.7)	190.3 (br)	−1.1 (57.7)	54.7	41.8	9.6	13.1	48.7	32.7	17.5
						12.1 (br)	23.3			
3c R = Et	119.9 (83.3)	189.2 (br)	0.5 (58.3)	54.5	41.9	9.7	13.5	60.6	30.5	19.4
						13.1 (br)	23.1	15.9		
3d R = ^{i}Pr	119.5 (84.1)	187.4 (br)	2.6 (56.4)	53.3	41.4	9.5	12.5	71.6	25.2 (84.1)	20.6
						13.5 (br)	22.6	23.2	(56.4)	
4	119.8	190.6 (br)	−2.7	54.3	42.0	10.4	13.9	—	5.5	5.3
						17.1 (br)	23.9			

[a] In $CDCl_3$ at 23 °C; coupling constants $^1J(^{29}Si,^{13}C)$ (±0.3 Hz) are given in parentheses; (br) indicates broad ^{13}CNMR signals owing to partially relaxed $^{13}C-^{11}B$ spin–spin coupling.
[b] In THF-d_8.

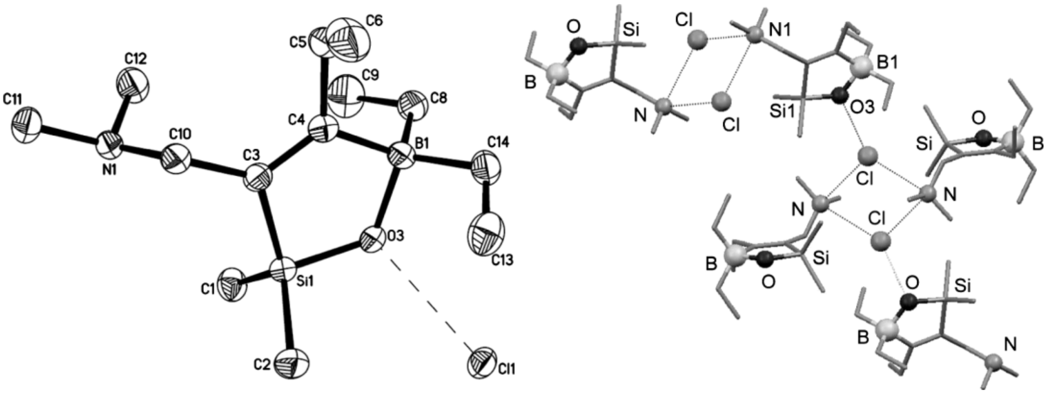


Figure 1. Structure of the ammonium salt **3a**. Left: ORTEP plot (50% probability ellipsoids; hydrogen atoms are omitted for clarity; structural parameters are given in Table 2). Right: linkage of cations and anions in the crystal lattice by hydrogen bridges.

^{29}Si NMR data (Table 1). The ^{11}B nuclear shielding in the compounds **3** decreases with increasing bulkiness of the group R, indicating considerable changes in the strength of the coordinative B–O bond.

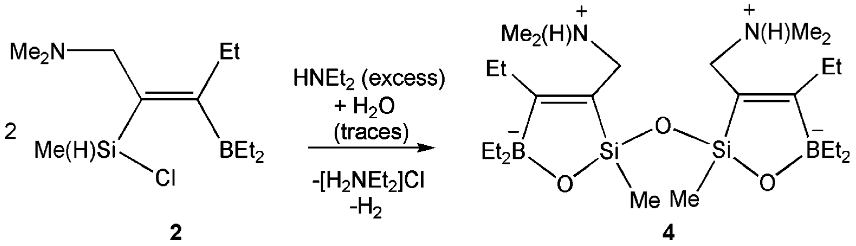
The salt **3a** was crystallized from acetone to give single crystals suitable for X-ray structural analysis. The molecular structure of **3a** itself and its association in the lattice is shown in Fig. 1. In the lattice, the ions are linked by O–H···Cl (e.g. Cl1–O3 2.95 Å) and weaker N–H···Cl contacts (e.g. Cl1–N 3.22 and 3.25 Å). Other intermolecular interactions are negligible. The five-membered ring is almost planar (maximum deviation from plane 0.02 Å). This is the first direct structural evidence for such types of ions. All bond distances fall into the expected ranges. The rather small endocyclic bond angle O3–Si1–C3 = 94.1(1)° is expected for a five-membered ring. The tetrahedral surroundings of the boron atom are also distorted, as indicated by the small endocyclic bond angle C4–B1–O3 = 100.0(1)°.

The analogous chemistry of **2** turned out to be much more complex. Apparently, the Si–H function disturbs straightforward reactions, when compared with the behaviour of **1**. Under comparable experimental conditions uncontrolled decomposition takes place, either of the alkene **2** itself or of the product(s) initially formed, when **2** reacts with water or alcohols. Therefore, it was decided to use a milder protic reagent such as diethylamine, which can also serve as a base in competition with the CH_2NMe_2 group. A related potential product, a 1,2-dihydro-1,2,5-azoniasilaboratole derivative has already been described, containing the $SiMe_2$ fragment instead of Si(H)Me and a Bu group instead of CH_2NMe_2.[16] After adding an excess of commercial diethylamine to a solution of **2** in benzene, again uncontrolled decomposition was observed. However, a small amount of crystalline materials could be isolated and identified by NMR spectroscopy in solution and by X-ray structure analysis in the solid state as the zwitterionic 2,5-dihydro-1,2,5-oxasilaboratole derivative **4** (Scheme 2).

Starting from **2**, both the Si–Cl and the Si–H functions were hydrolysed by water present in unpurified diethylamine, condensation took place, and the HCl was trapped by diethylamine instead of the CH_2NMe_2 group.

The molecular structure of **4** (Fig. 2) shows the disiloxane arrangement, where the substituents are oriented in a way to minimize steric interactions. As in the case of **3a** and related examples,[16] the B-ethyl groups are tilted towards the ring. This appears to be a solid-state effect since *ab initio* calculations of optimized gas phase structures of model compounds (see above) always show one B-ethyl group pointing away from the ring. The molecules **4** are linked in the crystal lattice via intermolecular hydrogen bridges (e.g. N1–H101–O2: N1–O2 2.62 Å) to give dimers (Fig. 2). In addition, there are intramolecular bridges (e.g. N2–H102–O1: N2–O1 2.63 Å) between each half of the disiloxane units.

The structural parameters of the rings of **4** differ from those of **3a**. The deviation from planarity in the rings in **4** is somewhat greater (0.035 and 0.062 Å), the B–O and Si–O(endocyclic) bond lengths are slightly shorter by 0.07–0.08 Å, and the distortion of the tetrahedral surroundings of both boron and silicon atoms is less severe. One of the most interesting features in siloxanes is the bond



Scheme 2. Hydrolysis of the chloromethylsilyl(diethylboryl)alkene **2**.

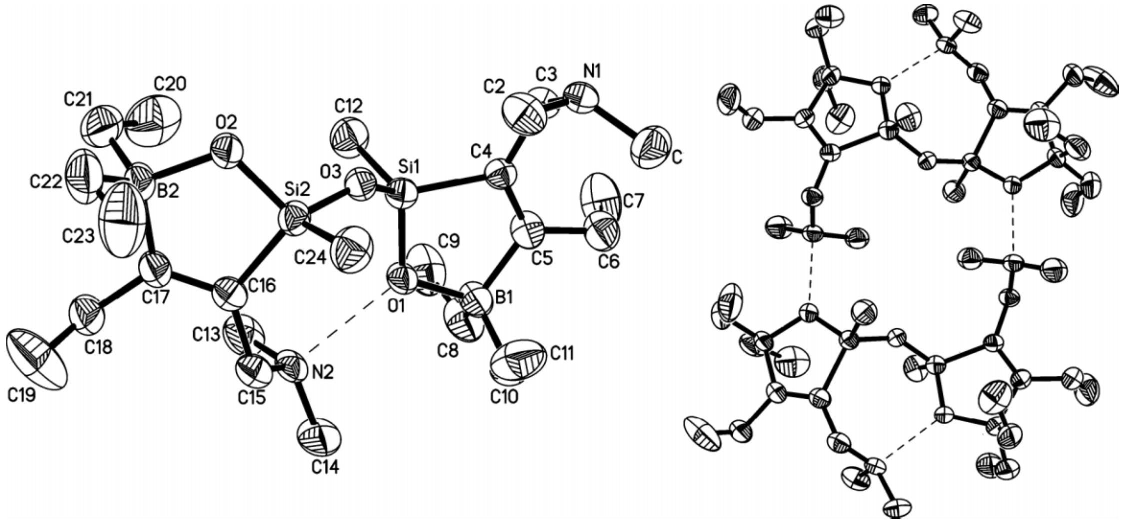


Figure 2. Molecular structure of the zwitterionic compound **4** (ORTEP plots; 50% probability; hydrogen atoms are omitted for clarity; the positions of bridging hydrogen atoms are between the N and O atoms connected by dashed lines). Left: single molecule with intramolecular hydrogen bridging. Right: dimer formed by intermolecular hydrogen bridging. Structural parameters are given in Table 2.

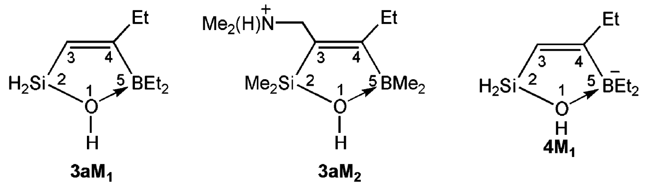
angle Si–O–Si, which in the case of **4** is 147.6(1)°, within the typical range.[17–24] Considering the fairly bulky groups at the silicon atoms, one might have expected an even wider angle. However, this would disfavour the intramolecular hydrogen bridge. Since Si–O–Si bond angles are flexible over a wide range,[17–24] the gain in energy by intramolecular hydrogen bridging in **4** may enforce the degree by which the Si–O–Si unit is bent.

The comparison between calculated [B3LYP/6- 311 + G(d,p)][25] gas phase structures of model compounds **3aM$_1$**, **3aM$_2$** and the corresponding experimental (solid state) parameters for **3a** as well as for **4M** and **4** is shown in Scheme 3. Apparently, the coordinative O–B bond in compounds of type **3**, clearly evident from the X-ray structural analysis and also from the ^{11}B chemical shift,[14,15,26] is not well reproduced by the calculations. The weakening of Si–O and B–O bonds in the Si–O–B units, found experimentally for **3a** in comparison with **4**, is overestimated in the calculations. In contrast to **3aM$_1$**, **3aM$_2$** and **3a**, all relevant data for the pair **4M** and **4** agree reasonably well. The calculated δ^{11}B values (GIAO method,[27] using the respective optimized geometry) of **3aM$_1$**, **3aM$_2$** (δ^{11}B +28.9 and +25.1) differ expectedly from the experimental data, considering the failure of the method in describing correctly the coordinative O–B bond. However, the calculated δ^{11}B value of **4M** (δ^{11}B +2.3) is close to the experimental data given for the different substitution pattern in the model compound.

EXPERIMENTAL SECTION

All preparative work was carried out by observing necessary precautions to exclude traces of oxygen and moisture, when appropriate. Dichloro(dimethyl)silane, chloro(methyl)silane, *N,N*-dimethyl-propargyl-amine (97%), triethylborane and butyllithium in hexane (1.6 M) were used as commercial products without further purification. The alkyn-1-ylsilanes required for the synthesis of **1** and **2** were prepared as described.[28] Alkene **1** was obtained as reported,[13] whereas the procedure for **2** was optimized as above. NMR spectra were recorded at 23 °C on Varian Inova 300 and Varian Inova 400 spectrometers, both equipped with multinuclear units, using C_6D_6, $CDCl_3$ or THF-d_8 solutions (<5%) in 5 mm tubes. Chemical shifts are given with respect to Me_4Si [δ^1H (C_6D_5H) = 7.15, δ^1H($CHCl_3/CDCl_3$) = 7.25 (±0.02); δ^{13}C (C_6D_6) = 128.0, δ^{13}C($CDCl_3$) = 77.0 (±0.1); δ^{29}Si = 0(±0.1) for Me_4Si with $\Xi(^{29}Si) = 19.867184$ MHz], and δ^{11}B = 0 (±0.3) for BF_3–OEt_2 with $\Xi(^{11}B) = 32.083971$ MHz. ^{29}Si NMR spectra were recorded using the refocused INEPT pulse sequence with ^{1}H decoupling.[29,30] The melting points (uncorrected) were determined using a Büchi 510 or a Stuart Scientific smp 3 melting point apparatus.

Bond angles [°] calcd. (exp.)		3a	4
O-Si-C3	95.4	93.9 (94.1)	99.1 (99.2)
Si-O-B	111.8	113.8 (115.6)	113.0 (112.0)
O-B-C4	99.4	98.1 (100.0)	104.5 (104.2)



Bond lengths [Å] calcd. (exp.)		3a	4
O-Si	1.729	1.720 (1.697)	1.636 (1.620)
O-B	1.802	1.777 (1.620)	1.546 (1.551)
Si-C3	1.830	1.871 (1.856)	1.857 (1.839)
B-C4	1.616	1.612 (1.612)	1.659 (1.636)

Scheme 3. Comparison between some calculated [B3LYP/6–311+G(d,p)] structural parameters of model compounds (**M**) and the experimental data.

[(Z)-2-chloro(methyl)silyl-3-diethylboryl-pent-2-enyl]-dimethyl-amine, 2

A mixture of [3-chloro(methyl)silyl-prop-2-ynyl]-dimethyl-amine (3.54 g, 21.9 mmol) with triethylborane (9.5 ml, 65.7 mmol) was heated in a closed Schlenk tube under Ar at 105 °C for 36 h. Then, the excess BEt_3 was removed in a vacuum at room temperature, and the oily colourless residue was purified by fractional distillation to give 2.27 g (40%) of a colourless, extremely air- and moisture-sensitive liquid (b.p. 94–96 °C/0.5 Torr). The product was identified as the alkene **2** by comparison with known[13] ^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR data. The (*E*)-isomer (δ^{29}Si −9.4; δ^{11}B 5.8 indicates the coordinative N–B bond) and an unidentified impurity (δ^{29}Si 20.2, δ^{11}B 6.8) were present in small amounts (<10%).

[(Z)-3-Diethylboryl-2-hydroxy(dimethyl)silyl-pent-2-enyl]-dimethyl-ammonium chloride, the 2,5-dihydro-1,2,5-oxoniasilaboratole derivative, 3a

A solution of **1** (1.5 g, 5.5 mmol) in THF (25 ml) was cooled to −78 °C. The same amount of aqueous THF (0.5 ml H_2O in 25 ml of THF) was added under nitrogen gas, and the mixture was allowed to reach room temperature. All volatiles were removed in a vacuum, and the residue was taken up in pentane. Filtration and washing with pentane gave **3a** as a white powder. Crystalline samples of **3a** were obtained from a solution in acetone at room temperature (m. p. = 81 °C). ^{1}H NMR (400 MHz; THF-d_8): δ = 0.72 (s, 6H, $SiMe_2$), 2.23, 1.01 [q, t, 2H, 3H, =C–Et, $^3J(^1H,^1H) = 7.6$ Hz], 0.43, 0.74 [q, t, 4H, 6H, BEt_2, $^3J(^1H,^1H) = 7.2$ Hz], 2.74 (s, 6H, NMe_2), 3.81 (s, 2H, NCH_2), 9.14 (s, broad, 1H, NH), 12.65 (s, broad 1H, OH).

The compounds **3b, 3c, 3d** were prepared in the same way, except that the respective alcohol was added as a mixture with THF. The 2,5-dihydro-1,2,5-oxoniasilaboratoles **3b, 3c** and **3d** were isolated as white powders. **3b**: m. p. = 131 °C. ^{1}H NMR (300 MHz; C_6D_6): δ = 0.34 (s, 6H, $SiMe_2$), 1.86, 0.67 [q, t, 2H, 3H, =C–Et, $^3J(^1H,^1H) = 7.4$ Hz], 0.14, 0.28 [m, t, 4H, 6H, BEt_2, $^3J(^1H,^1H) = 7.48$ Hz], 2.53 [d, 6H,

DOI: 10.1002/aoc

NMe$_2$, $^3J(^1\mathrm{H},^1\mathrm{H}) = 5.2$ Hz], 3.56 [d, 2H, NCH$_2$, $^3J(^1\mathrm{H},^1\mathrm{H}) = 6.4$ Hz], 3.18 (s, 3H, OMe), 10.13 (s, 1H, NH). **3c**: ^{1}H NMR (400 MHz; CDCl$_3$): $\delta = 0.39$ (s, 6H, SiMe$_2$), 1.83, 1.07 [q, t, 2H, 3H, =C–Et; $^3J(^1\mathrm{H},^1\mathrm{H}) = 7.6$ Hz], 0.30, 0.15 [t, m, 6H, 4H, BEt$_2$, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7.5$ Hz], 2.52 [d, 6H, NMe$_2$, $^3J(^1\mathrm{H},^1\mathrm{H}) = 5.4$ Hz], 3.53 [d, 2H, NCH$_2$, $^3J(^1\mathrm{H},^1\mathrm{H}) = 6.5$ Hz], 3.66, 0.66 [q, t, 2H, 3H, OEt, $^3J(^1\mathrm{H},^1\mathrm{H}) = 6.9$ Hz], 10.40 (s, 1H, NH). **3d**: ^{1}H NMR (300 MHz; CDCl$_3$): $\delta = 0.34$ (s, 6H, SiMe$_2$), 1.78, 0.56 [q, t, 2H, 3H, =C–Et, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7.4$ Hz], 0.26, 1.02 [q, t, 4H, 6H, BEt$_2$, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7.4$ Hz], 2.48 (s, 6H, NMe$_2$), 3.47 (s, 2H, NCH$_2$), 4.18, 1.02 [sp, d, 1H, 6H, O^{i}Pr, $^3J(^1\mathrm{H},^1\mathrm{H}) = 7.2$ Hz], 9.42 (s, 1H, NH).

Table 2. Selected bond lengths (Å) and angles (deg) of the compounds **3a** and **4**

3a		4	
		Si1–O3; Si2–O3	1.618(3); 1.644(3)
Si1–O3	1.697(1)	Si1–O1	1.629(2)
Si1–C1	1.854(2)	Si1–C12	1.851(4)
Si1–C2	1.843(2)		
Si1–C3	1.856(2)	Si1–C4	1.839(4)
B1–C4	1.612(2)	B1–C5	1.636(6)
B1–C14	1.613(2)	B1–C10	1.654(7)
B1–C8	1.616(3)	B1–C8	1.605(6)
B1–O3	1.629(2)	B1–O1	1.552(5)
C3–C4	1.348(2)	C4–C5	1.359(5)
C3–C10	1.504(2)	C3–C4	1.511(5)
C4–C5	1.520(2)	C5–C6	1.523(5)
C5–C6	1.519(3)	C6–C7	1.500(6)
C2–Si1–C1	111.27(10)		
C4–C3–Si1	110.22(11)	C5–C4–Si1	105.8(3)
C3–C4–B1	119.83(14)	C4–C5–B1	116.6(3)
C4–C3–C10	123.81(14)	C5–C4–C3	125.1(3)
O3–Si1–C3	94.07(7)	O1–Si1–C4	99.21(15)
O3–Si1–C1	107.62(8)	O1–Si1–C12	113.00(18)
O3–Si1–C2	108.91(8)		
C1–Si1–C3	117.20(8)	C4–Si1–C12	111.86(19)
C2–Si1–C3	115.78(9)		
C3–C4–C5	122.78(15)	C4–C5–C6	124.3(4)
C5–C4–B1	117.39(14)	C6–C5–B1	119.0(3)
C10–C3–Si1	125.63(12)	C3–C4–Si1	128.2(3)
C8–B1–O3	107.02(13)	C8–B1–O1	109.6(4)
C4–B1–O3	100.01(12)	C5–B1–O1	104.2(3)
C4–B1–C8	113.01(14)	C5–B1–C8	115.3(4)
C14–B1–O3	107.07(13)	C10–B1–O1	107.8(4)
C14–B1–C8	113.35(14)	C10–B1–C8	111.3(4)
C4–B1–C14	114.97(14)	C5–B1–C10	108.1(4)
B1–O3–Si1	115.63(10)	B1–O1–Si1	112.0(2)
		Si1–O3–Si2	147.54(16)
		O3–Si1–O1	109.67(14)
		O3–Si1–C4	117.43(15)
		O3–Si1–C12	105.83(18)

Table 3. Crystal data and structure refinement for **3a** and **4**

	3a	4
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions	$a = 10.561(2)$ Å	$a = 7.9660(16)$ Å
	$b = 12.257(3)$ Å	$b = 13.181(2)$ Å
	$c = 13.557(3)$ Å	$c = 29.487(5)$ Å
	$\beta = 90.20(3)°$	$\beta = 96.430(14)°$
Volume	1755.0(6) Å^3	3076.7(10) Å^3
Z	4	4
Absorption coefficient	0.277 mm^{-1}	0.157 mm^{-1}
F(000)	640	1278
Crystal size	$0.3 \times 0.3 \times 0.4$ mm^3	$0.3 \times 0.4 \times 0.5$ mm^3
Theta range for data collection	1.9–25.7°	1.4–25.7°
Reflections collected	23152	40813
Independent reflections	3318 [$R_{\mathrm{int}} = 0.040$]	5814 [$R_{\mathrm{int}} = 0.141$]
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3318/0/287	5814/0/310
Goodness-of-fit on F^2	1.01	0.89
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.035$,	$R1 = 0.067$,
	$wR2 = 0.077$	$wR2 = 0.152$
R indices (all data)	$R1 = 0.048$,	$R1 = 0.135$,
	$wR2 = 0.081$	$wR2 = 0.173$
Largest difference peak and hole	0.37 and −0.13 eÅ^{-3}	0.89 and −0.21 eÅ^{-3}

Zwitterionic disiloxane, the 2,5-dihydro-1,2,5-oxasilaboratole derivative 4

To a cooled (−78 °C) solution of **2** (1.0 g, 3.85 mmol) in toluene (15 ml), diethylamine (1.5 g, 20 mmol) was added in a Schlenk tube, and the stirred reaction mixture was allowed to reach room temperature. A colourless precipitate was formed, and at the wall of the tube, close to the upper level of the solution, a small amount of crystalline materials was observed, of which 12 mg could be separated. The ^{1}H NMR spectra of the crystals thus obtained showed numerous signals which could not be assigned unambiguously, whereas the ^{11}B, ^{13}C and ^{29}Si NMR data (Table 1) of the main product in solution were in accord with the proposed structure of **4**, confirmed by the subsequent X-ray structure analysis.

X-ray structure analyses of the heterocycles 3a and 4

The X-ray structure analyses of **3a** and **4** were carried out for single crystals selected in perfluorinated oil[31] at room temperature at 191(2) K, using a STOE IPDS II system equipped with an Oxford Cryostream low-temperature unit (Table 3). Structure solution and refinement were accomplished using SIR97,[32] SHELXL-97[33] and WinGX.[34] The data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publications nos CCDC 632722 (**3a**) and 632723 (**4**).

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft and by the DAAD (K.S.).

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DOI: 10.1002/aoc