Organo-Substituted 1,2-Dihydro-1,2,5-disilaborepines

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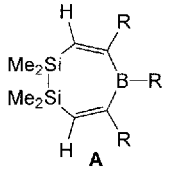
1,2-Di-1-propynyl-tetramethyldisilane (**1**) reacts with triorganoboranes R_3B [R = Et (**2a**), CH_2Ph (**2b**), Ph (**2c**), 2-thienyl (**2d**)], 9-ethyl-9-borabicyclo[3.3.1]nonane (**3**), and diethyl(*N*-pyrrolyl)borane (**4**) by twofold 1,1-organoboration to give selectively the respective organo-substituted 1,2-dihydro-1,2,5-disilaborepines **5a–d**, **6**, and **7** in high yields. The compounds **5–7** were characterized by ^1H-, ^{11}B-, ^{13}C-, and ^{29}Si-NMR spectroscopy in solution. The molecular structures of the disilane **1** and of the heterocycle **5c** were determined by X-ray structure analysis.

Introduction

1,1-Organoboration of 1-alkynylsilanes[1] has considerable potential in heterocyclic synthesis, as has been shown for siloles[2], spiro-bisiloles[3], and other heterocycles[4,5]. 1,2-Diethynyltetramethyldisilane was the first example of a 1-alkynylsilane to react with trialkylboranes such as trimethyl- and triethylborane[6] by 1,1-organoboration. The 1,1-dihydro-1,2,5-disilaborepines **A** were obtained, and their molecular structure in solution was proposed mainly on the basis of NMR-spectroscopic data[6]. Low-temperature ^1H- and ^{13}C-NMR spectra of these compounds[7] indicate that the seven-membered ring is non-planar. The ^{11}B nuclear shielding ($\delta^{11}B$ ca. +80) is significantly reduced with respect to comparable 1-bora-2,5-cyclohexadienes ($\delta^{11}B$ ca. +53 to +73[8]). This suggests that the boron atom is shifted out of the plane.



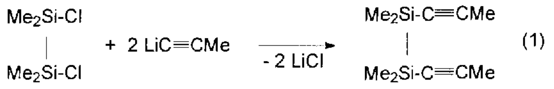
A

In the present work we describe the synthesis and molecular structure of 1,1,2,2-tetramethyl-1,2-di-1-propynyldisilane **1**, and the reaction of **1** with triorganoboranes such as **2** and 9-ethyl-9-borabicyclo[3.3.1]nonane (**3**), and also with diethyl(*N*-pyrrolyl)borane **4**. The intention was to discover whether triorganoboranes other than Me_3B or Et_3B, or even diethyl (*N*-pyrrolyl)borane, could be used for 1,1-organoboration of 1-alkynylsilanes. A first successful attempt using **3** in the reaction with tetrakis(3,3-dimethyl-1-butynyl)silane has been reported[9]. It was shown recently that **4** reacts with 1-alkynyltin compounds by 1,1-ethyloboration almost as fast as triethylborane[10]. Furthermore, it was hoped to obtain crystalline material in order to determine the molecular structure of 1,2-dihydro-1,2,5-disilaborepines for the first time.

Results and Discussion

Synthesis and Molecular Structure of Tetramethyl-1,2-di-(1-propynyl)disilane (1)

The disilane **1** was prepared in a straightforward way[11] according to eq. 1. It is a colorless solid which can be handled in air, it is insensitive to moisture and readily soluble in hydrocarbons and chlorinated hydrocarbons. It solidifies after distillation to give single crystals suitable for X-ray structure analysis.



1

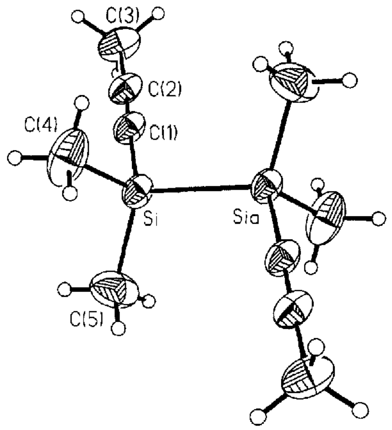
The molecular structure of **1** is shown in Figure 1 and experimental data relevant to the X-ray structure analysis[12] are given in Table 1. All bond lengths and angles are found in the expected range, and the centrosymmetric molecular structure of **1** exhibits no unusual features.

1,1-Organoboration of Tetramethyl-1,2-di(1-propynyl)disilane (1)

In general, 1,1-organoboration reactions of 1-alkynylsilanes proceed slowly (several hours or days) and require temperatures ≥100°C[1–6,9]. This is also true for the reaction of **1** with triethylborane **2a**, carried out either in boiling **2a** or in boiling toluene (eq. 2) to give the organo-substituted 1,2-dihydro-1,2,5-disilaborepines **5a**. Under these conditions, many other organoboranes undergo dehydroboration[6,13], and therefore, numerous side-reactions usually lead to complex mixtures of compounds. Dehydroboration cannot occur in boranes such as tribenzylborane **2b**, triphenylborane **2c**, and tri(2-thienyl)borane **2d**. The reaction of these boranes with **1** in boiling toluene affords the heterocycles **5b–d** in essentially quantitative yield.

The compounds **5** are sensitive to oxygen and to moisture. Compound **5a** is a liquid which partly decomposes upon distillation under reduced pressure into the starting

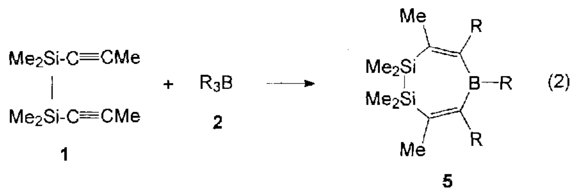
Figure 1. Molecular structure of 1 including thermal ellipsoids for non-hydrogen atoms with 50% probabilities[a]



[a] Selected bond lengths [pm] an bond angles [°]: Si–SiA 232.7(1), Si–C1 183.0(1), Si–C4 187.1(3), Si–C(5) 187.1(2), C1–C2 120.1(2), C2–C3 145.9(2); C1–Si–C4 108.4(1), C4–Si–C5 112.0(1), C1–Si–C5 108.6(1), Si–C1–C2 179.2(2), C1–C2–C3 178.8(2).

Table 1. Data for the X-ray analyses of the disilane **1** and the 1,2-dihydro-1,2,5-disilaborepine **5c**

	1	5c
Formula	$C_{10}H_{18}Si_2$	$C_{28}H_{33}BSi_2$
Molecular mass	194.4	436.5
Crystal system	Monoclinic	Monoclinic
Space group; Z	$P2_1/c$; 2	$P2_1/n$; 4
Crystal size [mm³]	0.75 × 0.25 × 0.20	0.40 × 0.25 × 0.20
Lattice parameters [Å] [°]	a = 7.975(2), b = 12.866(2), c = 6.651(2); β = 105.93(3)	a = 9.700(2), b = 30.502(6), c = 9.915(3); β = 117.23(3)
Volume [Å³]	656.3	2608.4(9)
ρ(calcd.) [g/cm³]	0.984	1.112
Diffractometer	Siemens P4; graphite monochromator	
Radiation [Å]	Mo-K_α, λ = 0.710 73	
Temperature [K]	173	296
2 Θ Range	2.0 – 60°	2.0 – 60°
Reflections collected	2647	16103
Unique/obs. reflections	1910 (no refl. omitted)	7608; 5307 [$F > 2.0\sigma(F)$]
System used	SHELXTL - PLUS	
Solution	Direct methods	
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0001F^2$	$w^{-1} = \sigma^2(F) + 0.0000F^2$
R; R_w (refined against F)	6.06% / 5.60%	7.51% / 3.12%
Number of param. refined	56	281
Max./min. resid. elec. dens.	0.98 / –0.28 [e / Å³]	0.55 / –0.36 [e / Å³]

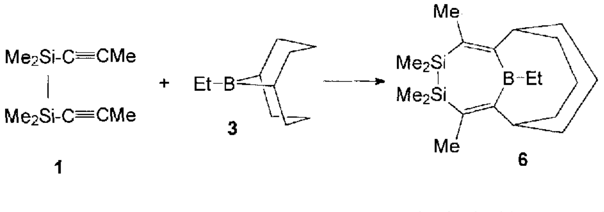


(2)

	a	b	c	d
R	Et	Bz	Ph	2-thienyl

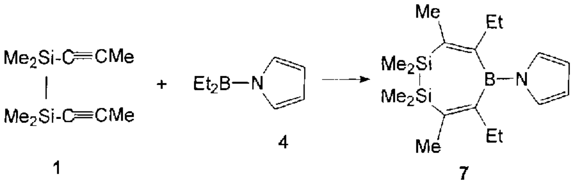
materials; **5b** is a waxy solid, whereas **5c**, **d** are solids which can be recrystallized from hexane or pentane. In the case of **5c** and **5d**, single crystals suitable for X-ray analysis were obtained. The result of the X-ray analysis was straightforward in the case of **5c** (vide infra), whereas strong disorder of the thienyl groups[14] in single crystals of **5d** prevented a meaningful structural solution.

The result of the reaction of **3** with **1** is shown in eq. 3. Although the reaction is slow, it proceeds selectively to **6** by twofold expansion of the 9-borabicyclo[3.3.1]nonane ring. The product is a crystalline solid, although to date it has not been possible for it to be converted into single crystals.



(3)

The reaction of **1** with an excess of diethyl(*N*-pyrrolyl)borane **4** is complete after three weeks in boiling toluene. Again the 1,2-dihydro-1,2,5-disilaborepine **7** is formed selectively (eq. 4). The pyrrolyl group remains at the boron atom, inviting further transformations by taking advantage of the reactive B–N bond.



(4)

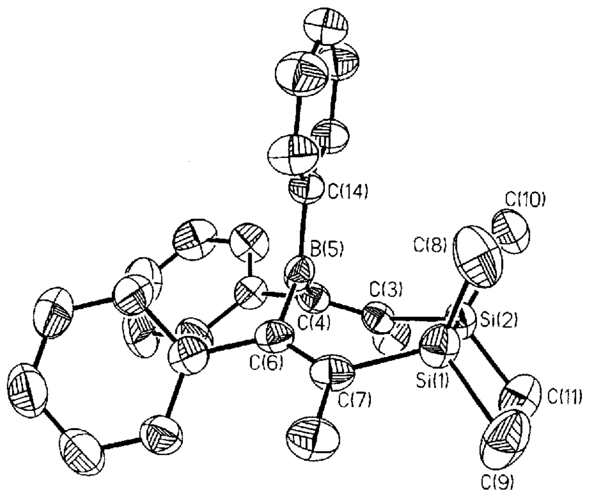
Molecular Structure of 1,2-Dihydro-1,1,2,2,3,7-hexamethyl-4,5,6-triphenyl-1,2,5-disilaborepine (5c)

The molecular structure of **5c** is shown in Figure 2, and experimental data relevant to the X-ray structure analysis[12] are given in Table 1. The seven-membered ring is non-planar, in agreement with the NMR data in solution. The boron atom is shifted by 66 pm out of the best plane of the seven ring atoms (mean deviation 28.4 pm). The SiMe groups in 1- and 2-positions are almost exactly in eclipsed positions [torsion angles C(8)Si(1)Si(2)C(10) 3.6°, C(9)Si(1)Si(2)C(11) 5.5°], and there are only small torsion angles (≤3°) between the substituents at the C=C bonds. However, the torsion angles C(3)C(4)B(5)C(14) and C(7)C(6)B(5)C(14) are close to 90°, and therefore, any CB(pp)π interactions involving the olefinic carbon atoms must be insignificant. In contrast, the phenyl group at the boron atom is hardly twisted against the C(4)C(6)B(5)C(14) plane (<4°). These peculiar structural features lead to a distinct packing effect in the crystal as shown in Figure 3. The *B*-phenyl groups of alternating molecules of **5c** are placed on top of each other (distance between the planes of the phenyl rings 390 pm) in order to achieve the best space-filling arrangement.

NMR Spectroscopic Results

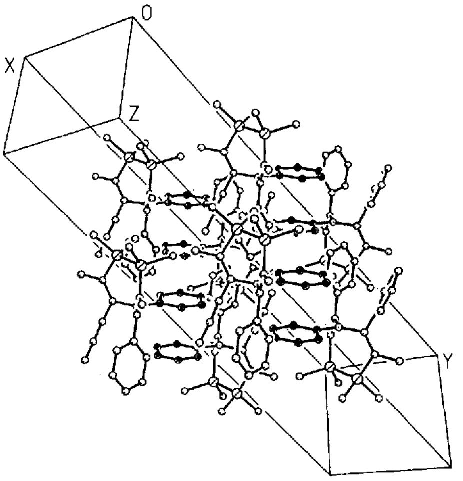
The ^{11}B-, ^{13}C- and ^{29}Si-NMR data are given in Table 2. This data and the ^{1}H-NMR spectra (see Experimental Section) are fully in accord with the proposed structures. In the case of **5d** and **6**, the non-planar seven-membered ring

Figure 2. Molecular structure of **5c** (without hydrogen atoms) including thermal ellipsoids with 50% probabilities[a]



[a]Selected bond lengths [pm] and bond angles [°]: Si1−Si2 237.3(1), Si−C(Me) (average) 187.7, Si1−C7 186.6(2), Si2−C3 188.7(2), C3−C4 134.2(3), C6−C7 137.1(3); B5−C4 157.2(3), B5−C6 158.8(4), B5−C14 154.8(3); C8−Si1−C9 106.1(1), C10−Si2−C11 108.1(1), Si1−Si2−C3 116.0(1), Si2−Si1−C7 114.7(1), Si2−C3−C4 119.8(2), Si1−C7−C6 119.9(2), C3−C4−B5 121.5(2), B5−C6−C7 119.3(2), C4−B5−C6 120.8(2), C4−B5−C14 120.0(2), C6−B5−C14 119.2(2)

Figure 3. View of the unit cell of **5c**; the *B*-phenyl carbon atoms are indicated by full circles



is evident from the room temperature ^{1}H- and ^{13}C-NMR spectra, by the non-equivalence of the SiMe groups. In the case of the other compounds, **5a**−**c** and **7**, the SiMe NMR signals are broad at room temperature and split into two ^{1}H- and two ^{13}C- resonance signals between 0 to −10°. The barrier to ring inversion can be evaluated[15] as $\Delta G^{\neq} = 55 \pm 1$ kJ/mol for **5a**−**c** and 58 ± 1 kJ/mol for **5d**. The δ^{11}B values are in accord with the molecular structure as determined for **5c**, where π interactions between the boron atoms and the olefinic ring carbon atoms are unlikely. The δ^{29}Si values are in the expected range for disilanes[16,17]. Coupling constants $^1J(^{29}\text{Si},^{13}\text{C})$ for methyl groups and olefinic carbon atoms are also found in the typical range[17].

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Experimental Section

All reactions were performed in an atmosphere of dry nitrogen, using carefully dried solvents and oven-dried glass ware. Starting materials such as $Me_4Si_2Cl_2$, propyne, *n*BuLi in hexane (1.6 M) were obtained and used as commercial products; the boranes Et_3B[18], 9-Et-9-BBN[19], $(PhCH_2)_3B$[20], Ph_3B[21], tri(2-thienyl)borane[22], and diethyl(*N*-pyrrolyl)borane[23] were prepared following the literature procedures. – Elemental analyses (C, H) were carried out by Fa. Pascher (Remagen). – EI-MS (70 eV): VARIAN MAT CH7 with direct inlet. – NMR spectra: ^{1}H, ^{11}B, ^{13}C, and ^{29}Si NMR by using Bruker ARX 250, AC 300, or DRX 500 instruments, all equipped with multinuclear units and variable temperature control; chemical shifts are given with respect to Me_4Si [$\delta^1\text{H}(C_6D_5H) = 7.15$, $(CHCl_3/CDCl_3) = 7.24$, $(C_6D_5CD_2H) = 2.03$: $\delta^{13}\text{C}(C_6D_6) = 128.0$, $(CDCl_3) = 77.0$, $(C_6D_5CD_3) = 20.4$: $\delta^{29}\text{Si} = 0$ for $\Xi(^{29}\text{Si}) = 19.867184$ MHz], Et_2O-BF_3[$\delta^{11}\text{B} = 0$ for $\Xi(^{11}\text{B}) = 32.083971$ MHz].

1,1,2,2-Tetramethyl-1,2-di(1-propynyl)disilane (**1**): A solution of 8.5 g of propyne (237 mmol) of 300 ml of hexane was cooled to −78°C in a 1-l two-necked flask equipped with a magnetic stirring bar, a dropping funnel, a dry-ice condenser, and a gas outlet connected to the N_2-line. After adding of 148 ml of *n*-butyl lithium in hexane (1.6 M, 237 mmol) within 3 h, the mixture was allowed to reach ambient temperature. Then 22.5 g of $Me_4Si_2Cl_2$ (119 mmol) was added within 15 min, followed by heating at reflux for 12 h. All insoluble material was removed by filtration, the solvent was removed in vacuo (11 Torr), and fractional distillation of the residue gave first 12.5 g (80%) of **1** as a colorless liquid (b.p. 82°C/11 Torr) which then solidified to colorless crystals (m.p. 36°C) suitable for X-ray structural analysis. – ^{1}H NMR (250 MHz, C_6D_6): $\delta^1\text{H} = 0.20$ (s, 12H, MeSi); 1.58 (s, 6H, Me-C≡). – ^{13}C NMR (62.9 MHz, C_6D_6): $\delta^{13}\text{C}$ [$J(^{29}\text{Si},^{13}\text{C})$] = −2.6 [59.4, 5.8] (MeSi); 4.8 (Me); 81.6 [79.0, 7.4] (≡CSi); 105.3 [15.2] (≡C). – ^{29}Si NMR (49.7 MHz, C_6D_6): $\delta^{29}\text{Si} = -38.4$.

1,1-Organoboration of the Disilane **1**. – *General Procedure:* To a solution of 0.73 g (3.7 mmol) of the disilane **1** in 20 ml of toluene an equimolar amount of the respective borane is added in one portion. This mixture is heated for 3 d at reflux, and then the solvent is removed in vacuo. In the case of **5a**, **b**, and **7** the pure products were left as colorless oils or waxy solids, whereas in the case of **5c**, **d**, and **6** further purification by recrystallization from hexane was straightforward.

5a: Decomposes in part into the starting materials at the attempted distillation at ca. 100°C/10^{-3} Torr. – ^{1}H NMR (500 MHz, [D$_8$]toluene, 25°C): $\delta^1\text{H} = 0.08$ (s, 12H, MeSi); 1.31 (q, 2H), 0.91 (t, 4H), (EtB); 1.74 (s, 6H, Me-C=); 2.15 (q), 0.94 (t) (10H, Et-C=).

5b: ^{1}H NMR (500 MHz, C_6D_6, 25°C): $\delta^1\text{H} = 0.21$ (broad s, 12H, MeSi); 1.72 (s, 6H, Me-C=); 2.66 (s, 2H, CH_2B); 3.06 (s, 4H, CH_2C=); 6.75−7.15 (m, 15H, Ph).

5c: M.p. 125°C. – ^{1}H NMR (500 MHz, [D$_8$]toluene, 25°C): $\delta^1\text{H} = 0.08$ (broad s, 12H, MeSi), 1.98 (s, 6H, Me-C=); 6.80−7.05 (m, 15H, Ph). – $C_{28}H_{33}BSi_2$ (436.5) calcd. C 77.04, H 7.62, found C 76.75, H 7.73.

5d: M.p. 103°C. – ^{1}H NMR (500 MHz, [D$_8$]toluene, 25°C): $\delta^1\text{H}$ = 0.02 (s), 0.26 (s) (12H, MeSi); 2.20 (s, 6H, Me-C=); 6.15 (m), 6.56 (m), 6.90 (m) (6H, 2-thienyl-C=); 7.10 (m), 7.42 (m), 7.86 (m)

Table 2. ^{11}B-, ^{13}C-, and ^{29}Si-NMR data[a] of the 1,2-dihydro-1,2,5-disilaborepines **5**, **6**, and **7**

Comp. No.	δ^{13}C(3,7)	δ^{13}C(4,6)	δ^{13}C(RB)	δ^{13}C(MeSi)	δ^{11}B	δ^{29}Si
5a	132.0 [62.3, 6.0] 15.5	165.1 [br] 23.7, 13.7	22.3, 9.1 [br]	–2.8 [43.2]	+80.0	–24.6
5b	136.6 [60.4, 6.0] 17.3	160.9 [br] 35.8 [c]	40.3 [b] [br]	–2.1 [43.5]	+78.0	–23.8
5c	135.3 [60.2, 6.0] 18.3	163.7 [br] 141.1 [e]	142.2 [d] [br]	–2.5 [43.5]	+72.0	–24.3
5d	139.6 [59.6, 6.0] 19.0	153.4 [br] 142.4 [g]	147.4[f] [br]	–2.1, –3.0 [43.5, 43.0]	+68.0	–23.8
6	124.0 [61.0, 6.0] 15.2	169.0 [br] 37.2 [h]	22.0,9.7 [br]	–1.3, –1.4 [42.6, 43.6]		–26.3
7	136.8 [61.6, 6.0] 15.7	158.6 [br] 25.0, 13.8	128.9 [i]	–2.6, –3.3 [43.5, 43.5]	+54.0	–24.1

[a] Samples in [D$_8$]toluene (ca. 10–15%, at 25°C); coupling constants J(^{29}Si, ^{13}C) are given in square brackets in Hz; [br] denotes the broad ^{13}C-NMR signal of a carbon atom linked to boron. – [b] Other δ^{13}C values: 140.7 (*i*), 128.4 (m), 126.2 (*p*). – [c] Other δ^{13}C values: 140.1 (*i*), 129.1 (*o*), 128.6 (m), 126.1 (*p*). – [d] Other δ^{13}C values: 141.4 (*o*), 128.1 (m), 133.8 (*p*). – [e] Other δ^{13}C values: 129.5 (*o*), 128.3 (m), 126.2 (*p*). – [f] Other δ^{13}C values: 145.3 (3), 129.3 (4), 140.7 (5). – [g] Other δ^{13}C values: 127.0 (3), 127.9 (4), 125.7 (5). – [h] Other δ^{13}C values: 33.3, 30.2, 23.5, 21.8 (–CH$_2$–). – [i] Other δ^{13}C value: 114.6 (pyrrole-C3,4).

(3H, 2-thienyl-B). – $C_{22}H_{27}BS_3Si_2$ (454.6) calcd. C 58.13, H 5.94, found C 58.59, H 6.09.

6: M.p. 96–100°C (decomposes at attempted distillation at 110°C/10^{-3} Torr). – ^{1}H NMR (250 MHz, [D$_8$]toluene, 25°C): δ^1H = 0.18 (s), 0.26 (s) (12H, MeSi); 1.73 (s, 6H, Me-C=); 1.55 (q), 1.07 (t) (5H, EtB); 3.37 (t) (2H, CH-C=); 1.45–2.05 (m, 12H, six CH$_2$).

7: ^{1}H NMR (250 MHz, [D$_8$]toluene, 25°C): δ^1H = –0.18 (s), 0.16 (s) (12H, MeSi); 1.31 (q), 0.97 (t), (5H, EtB); 1.83 (s) (6H, Me-C=); 2.39 (m), 0.97 (t) (10H, Et-C=); 6.26 (m), 6.83 (m) (4H, pyrrole). – $C_{18}H_{32}BNSi_2$ (329.4) calcd. C 65.63, H 9.79, N 4.25, found C 64.87, H 9.93, N 4.35.

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[12] Further details of the crystal structure analyses are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-406696 (**1**) and CSD-406697 (**5c**), the names of the authors and the journal citation.

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