1-Boraadamantane: Reactivity Towards Di(1-alkynyl)silicon and -tin Compounds: First Access to 7-Metalla-2,5-diboranorbornane Derivatives

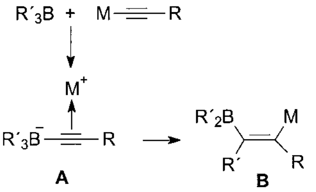
Bernd Wrackmeyer,*[a] Wolfgang Milius,[a] Elena V. Klimkina,[b] and Yuri N. Bubnov[b, c]

Abstract: 1-Boraadamantane (**1**) reacts with di(1-alkynyl)silicon and -tin compounds **2** ($Me_2M(C{\equiv}CR)_2$: M = Si; R = Me (**a**), *t*Bu (**b**), $SiMe_3$ (**c**); M = Sn, R = $SiMe_3$ (**e**)) in a 1:1 ratio by intermolecular 1,1-alkylboration, followed by intramolecular 1,1-vinylboration, to give siloles **5a–c** and the stannole **5e**, respectively, in which the tricyclic 1-boraadamantane system is enlarged by two carbon atoms. Owing to the high reactivity of **1**, a second fast intermolecular 1,1-alkylboration competes with the intramolecular 1,1-vinylboration as the second major step in the reaction if the substituent R at the C≡C bond is small (**2a**) and/or if the M−C≡ bond is also highly reactive, as in **2d** (M = Sn, R = Me) and **2e** (M = Sn, R = $SiMe_3$). This leads finally to the novel octacyclic 7-metalla-2,5-diboranorbornane derivatives **8a**, **8d**, and **8e**, of which **8e** was characterized by X-ray analysis in the solid state. 1,1,2,2-Tetramethyldi(1-propynyl)disilane, $MeC{\equiv}C{-}SiMe_2SiMe_2{-}C{\equiv}CMe$ (**3**), reacts with **1** to give mainly a 1,2-dihydro-1,2,5-disilaborepine derivative **9** and the octacyclic compound **11**, which is analogous to **8a** but with an Me_4Si_2 bridge. All new products were characterized in solution by ^{1}H, ^{11}B, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectroscopy. For **8** and **11**, highly resolved ^{29}Si and ^{119}Sn NMR spectra revealed the first two-bond isotope-induced chemical shifts, $^{2}\Delta^{10/11}B(^{29}Si)$ and $^{2}\Delta^{10/11}B(^{119}Sn)$ respectively, to be reported.

Keywords: alkynes · boron · boraadamantanes · organoboration · silicon · tin

Introduction

1-Boraadamantane (**1**),[1] which is isoelectronic with the 1-adamantyl cation,[2] is a peculiar trialkylborane, since the three-coordinate boron atom, which normally prefers a trigonal planar environment, occupies a position fitting much better in tetrahedral surroundings. This explains the markedly increased Lewis acidic character of **1** when compared with other trialkylboranes. Trialkylboranes R'_3B are known to react with many 1-alkynylmetal compounds [Eq. (1)]: after cleavage of the M−C≡ bond and formation of a borate-like zwitterionic intermediate (**A**), in which the fragment M is coordinated sideways-on to the C≡C bond, an R′ group is then transferred from boron to the neighboring alkynyl carbon atom, leading to an organometallic-substituted alkene (**B**), in which the boryl group and the fragment M occupy *cis* positions (with a few exceptions) at the C=C bond. Since the R'_2B group and R′ end up at the same carbon atom, this type of reaction has been called 1,1-organoboration.[3]



(1)

Recently we have reported on reactions of **1** with mono-1-alkynyltin, -germanium, and -silicon compounds.[4] It was found that 1,1-organoboration occurs readily, even with the fairly unreactive 1-alkynylsilanes, by enlargement of the tricyclic system to give 4-methylene-3-borahomoadamantanes. Apparently there is sufficient strain in these heterocycles for 1,1-deorganoboration also to take place readily, and the thermodynamically controlled products are formed under much milder conditions than in the case of noncyclic trialkylboranes, such as triethylborane (Et_3B). The properties of the highly reactive **1** make it an attractive candidate for 1,1-organoboration reactions of more complex systems. Here we disclose the results of a study of the reactivity of **1** towards some di(1-alkynyl)silicon (**2a–c**) and di(1-alkynyl)tin com

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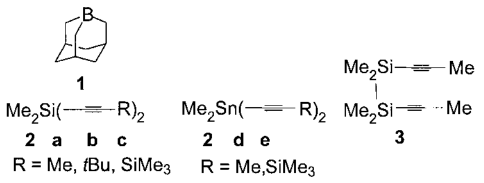
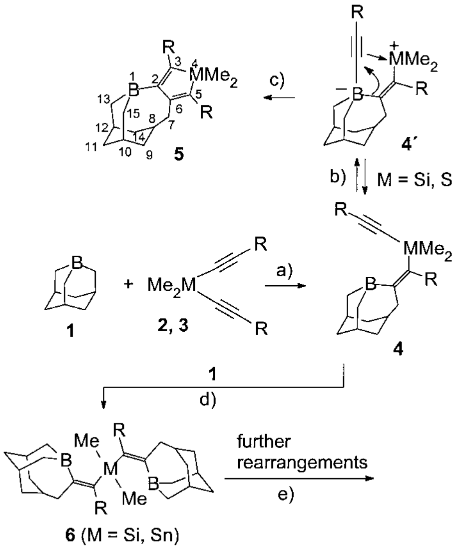


pounds(**2d**, **2e**), and 1,1,2,2,-tetramethyldi(1-propynyl)disilane (**3**), all of which had already been studied extensively in 1,1-organoboration reactions with Et_3B.[3]

Results and Discussion

General considerations: The reaction of 1-boraadamantane (**1**) with di-1-alkynylsilicon and -tin compounds is expected to follow the pathways outlined in Equation (2). The reactions



(2)

should start analogously to those described for mono-1-alkynyl compounds to give the 4-methylene-3-borahomoadamantanes **4** [Eq. (2), route a], which, however, could not be isolated in the present study. ^{29}Si NMR signals from reaction mixtures indicated the presence of compounds of the **4** type. The intramolecular reaction [Eq. (2), route b] first gives zwitterionic intermediates of the **4′** type (in analogy to **A**), which finally rearrange to the tetracyclic metallole derivatives **5** [Eq. (2), route c]. Compounds analogous to **4′** have already been isolated and characterized by X-ray structural analysis.[5] So far, the route to siloles analogous to **5** has always been observed for the reactions of di(1-alkynyl)dimethylsilanes with various trialkylboranes,[6] whereas it has been shown that the formation of stannoles depends on both the R group and the trialkylborane. Thus, the 1:1 reaction of **2d** with Et_3B has led mainly to a peralkylated 1,4-stannabora-2,5-cyclohexadiene derivative,[7] and in the presence of an excess of Et_3B a 2,5-diborylated 1-stanna-3-cyclopentene was obtained.[7] On the other hand, the reactions of **2e** or related di(1-trimethylsilylethynyl)tin compounds with Et_3B selectively and quantitatively afford stannole derivatives analogous to **5**.[8, 9]

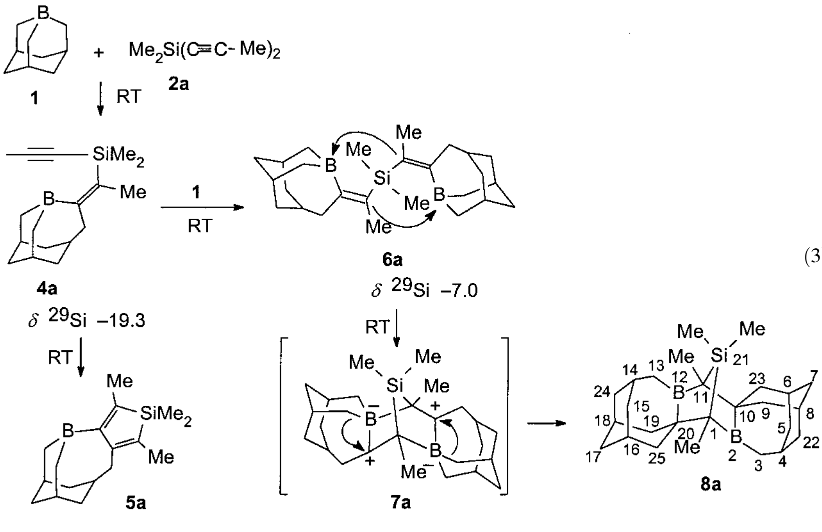
Owing to the enormous reactivity of **1**, a further intermolecular 1,1-alkylboration may well compete with the intramolecular reaction in Equation (2), route b. The second intermolecular 1,1-alkylboration [Eq. (2), route d] leads to the bis(alkenyl)silicon and -tin compounds of the **6** type. It has been shown previously that such compounds are rather unstable with respect to various rearrangements [Eq. (2), route e];[10] these were therefore of interest, since strain in the 4-methylene-3-borahomoadamantane framework and the thereby increased Lewis acidity of the boron atoms may cause different behavior from that of 1,1-organoboration products of Et_3B.

Reactions of 1-boraadamantane (1) with the di-1-alkynylsilanes 2a–c: The reactions of **1** with the di-1-alkynylsilane **2a** are summarized in Equation (3). There is indeed competition between the 1:1 and the 2:1 reactions, and, depending on the reaction conditions (see Table 1), a considerable amount of the novel octacyclic compound **8a** is formed together with the silole derivative **5a**. The intermediate **7a** is proposed, considering the highly Lewis acidic character of the boron atoms in **6a**. The conversion of **7a** into **8a** by a 1,2-shift of a CH_2 group from the boron to the neighboring carbon atom in each half of the molecule, as indicated, should be straightforward. According to semiempirical AM1 calculations,[11, 12] **8a** is more stable than **6a** by 18.9 kcal mol^{-1} and **7a** is higher in energy than **6a** by 28 kcal mol^{-1}. The progress of this reaction

Table 1. Dependence on R of the product ratio **5**:**8** from the reaction of **1** with **2a**–**c**, and the reaction conditions.

R	Conditions of reaction	**5**:**8** Ratio [%][a]
Me	**1** added to **2a**, RT, pentane, 1 d	**5a**:**8a** = 90:10
Me	**2a** added to **1**, RT, pentane, 1 d	**5a**:**8a** = 40:60
*t*Bu	**1** added to **2b**, RT, pentane, 2 h	**5b**:**8b** = 100:0
*t*Bu	**2b** added to **1**, RT, pentane, 2 h	**5b**:**8b** = 100:0
$SiMe_3$	**1** added to **2c**, −50 °C to RT or RT, pentane, 10 h	**5c**:**8c** = 100:0
$SiMe_3$	**2c** added to **1**, RT, pentane, 10 h	**5c**:**8c** = 100:0

[a] Determined from ^{13}C and ^{29}Si NMR spectra of the crude mixture.



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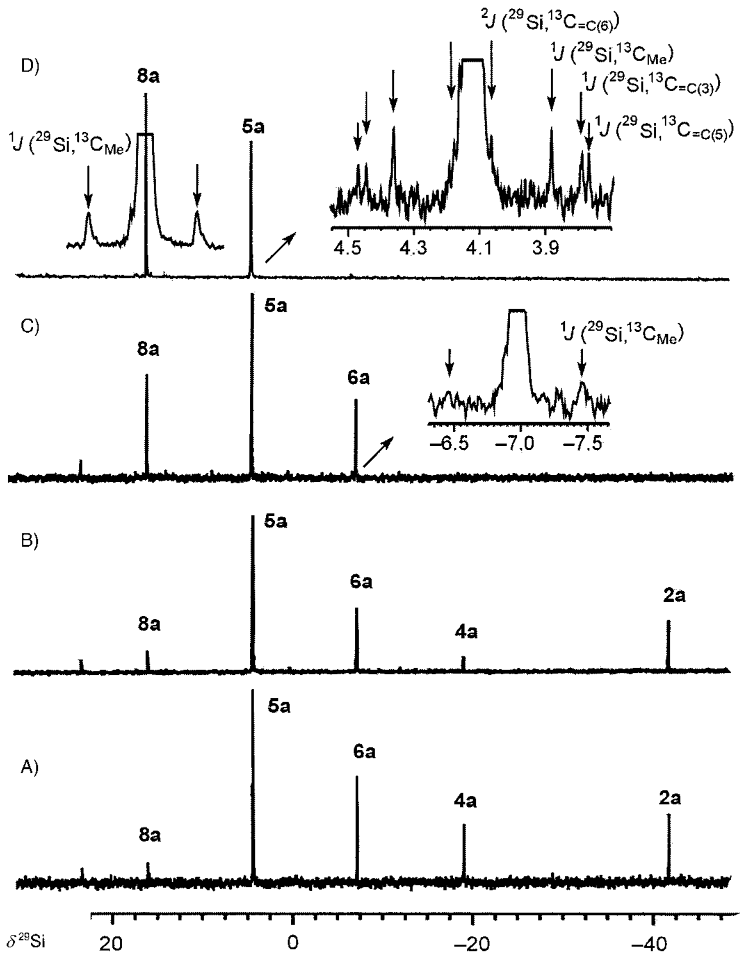
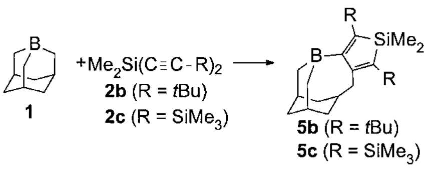


Figure 1. Progress of the 1,1-organoboration of **2a** with **1**, monitored by 49.7 MHz ^{29}Si NMR spectroscopy (refocused INEPT, ^{1}H-decoupled). Compounds **1** and **2a** were mixed (ratio 1:1.2), and kept at 25 °C. ^{13}C satellites are marked by arrows; the assignment of the ^{29}Si resonances is based on their change in intensity as a function of time and corresponding changes in the ^{1}H and ^{13}C NMR spectra. A) 40 min after mixing; B) as A), but 1 h later; C) 30 min after adding a further 0.2 equiv. of **1** to the reaction mixture of B); D) as C), 36 h later.

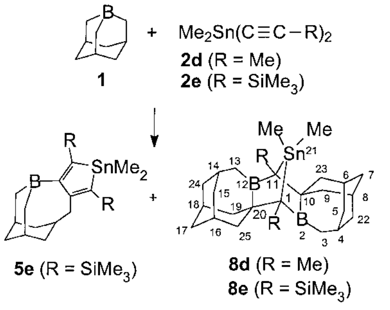
can be monitored conveniently by ^{29}Si NMR spectroscopy (Figure 1); the signals at $\delta = -19.3$ and -7.0 are tentatively assigned to **4a** and **6a**, respectively, present in the reaction mixture.

As a result of the presence of bulky groups such as *t*Bu or SiMe$_3$ at the C≡C bonds in **2b** and **2c**, the second intermolecular 1,1-organoboration becomes slower than the intramolecular reaction. Therefore, the reactions of **2b** and **2c** with **1** give the siloles **5b** or **5c** exclusively [Eq. (4)], independently of the reaction conditions (Table 1). Again,[6] 1,1-organoboration offers interesting alternatives to other much more cumbersome silole syntheses.[13]



(4)

Reactions of 1-boraadamantane (1) with the di-1-alkynyltin compounds 2d and 2e: It is well known that 1-alkynyltin compounds are much more reactive towards trialkylboranes than their silicon analogues.[3] Taking into account the highly electrophilic nature of **1**,[1] one would expect a second intermolecular 1,1-organoboration to compete efficiently with any intramolecular reaction (see Equations (2) and (3)), even if a bulky substituent (such as R = SiMe$_3$ in **2e**) is linked to the C≡C bond. In the reactions of **2d** and **2e** with **1** [Eq. (5) and Table 2], **8d** is formed selectively from **2d**, and from **2e** there is always a significant amount of **8e** formed along with the stannole derivative **5e**.



(5)

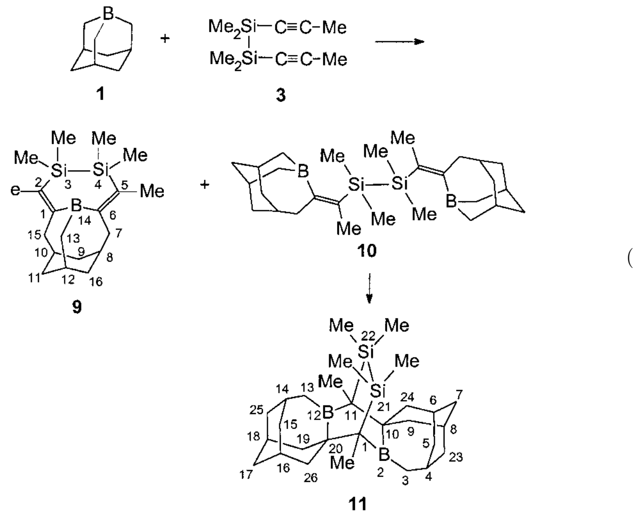
Reactions of 1-boraadamantane (1) with 1,1,2,2-tetramethyl-di(1-propynyl)disilane (3): The disilane derivative **3** behaves differently from di(1-alkynyl)silanes towards triorganoboranes. Its 1,1-organoboration leads selectively to 1,2-dihydro-1,2,5-disilaborepine derivatives,[14, 15] of which the molecular structure was recently determined by X-ray analysis of the product obtained from the reaction of **3** with triphenylborane.[15] In agreement with the previous results,[14, 15] the 1,2-dihydro-1,2,5-disilaborepine derivative **9** is the main product of the reaction of **1** with **3**, regardless of the reaction conditions [Eq. (6) and Table 3]. However, the second intermolecular 1,1-organoboration cannot be suppressed completely, leading first to **10** and finally to **11**, which is analogous to **8**. Again, ^{29}Si NMR serves as an extremely valuable tool to monitor the reaction of **1** with **3** (Figure 2).

The silole and stannole derivatives **5** are colorless, air-sensitive, waxy solids. In contrast, the compounds **8** and **11** are

Table 2. Dependence on R of the product ratio **5**:**8** from the reaction of **1** with **2d** and **2e**, and the reaction conditions.

R	Conditions of reaction	**5**:**8** Ratio [%][a]
Me	**1** added to **2d** (1:1), –50 °C to RT, pentane, 1 h	**5d**:**8d** 0:100
Me	**2d** added to **1** (1:2), RT, pentane, 1 h	**5d**:**8d** 0:100
SiMe$_3$	**1** added to **2e** (1:1), –50 °C to RT, pentane, 2 h	**5e**:**8e** 80:20
SiMe$_3$	**2e** added to **1** (1:2), RT, pentane or CDCl$_3$	**5e**:**8e** 60:40

[a] Determined from ^{13}C and ^{119}Sn NMR spectra of the crude mixture.



(6)

Table 3. Dependence of the product ratio **9**:**10**:**11** of the reaction of **1** with **3** on the reaction conditions.

Conditions of reaction	**9**:**10**:**11** Ratio [%][a]
1 added to **3**, RT, pentane, 1 h at 25 °C	95:5:0
1 added to **3**, RT, pentane, 2 d at 25 °C, or $CDCl_3$, 2 h at 60 °C	95:0:5
3 added to **1**, RT, pentane, 1 h at 25 °C	80:20:0
3 added to **1**, RT, pentane, 5 d at 25 °C	80:0:20

[a] Determined from ^{29}Si and ^{13}C NMR spectra of the crude mixture.

colorless, air-sensitive, crystalline solids which are rather insoluble in pentane and can therefore be readily separated and purified by recrystallization. The best single crystals were obtained for **8e** and these were studied by X-ray analysis.

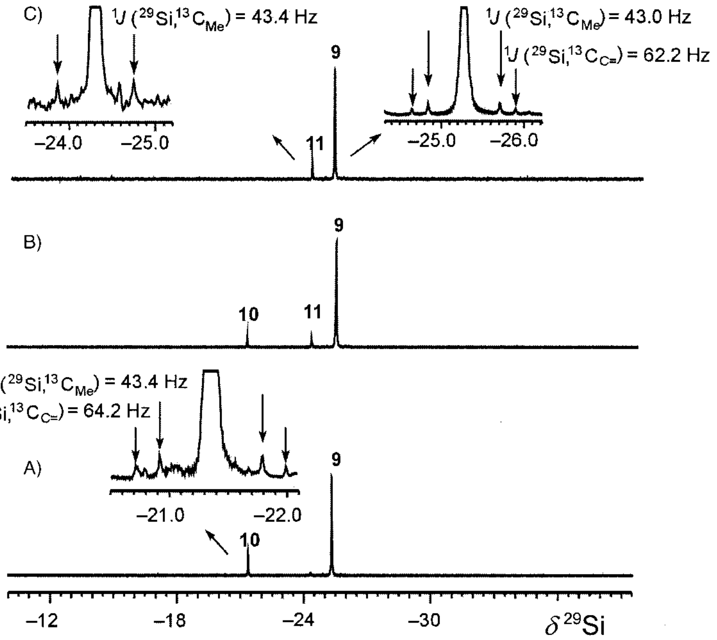


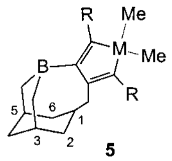
Figure 2. 49.7 MHz ^{29}Si NMR spectra (refocused INEPT) of the mixture obtained from the reaction of **1** with **3**. Compounds **1** and **3** were mixed (ratio 2:1) and kept at 25 °C. ^{13}C satellites are marked by arrows. A) 1 h after mixing; B) as A), but after one day, when the signal for **11** becomes visible; C) as B), but after five days, when the signal for **10** is no longer observed, and the reaction is finished.

NMR spectra: The proposed structures in solution are supported by extensive NMR data (Tables 4 and 5, and Experimental Section). In cases of ambiguity, the assignment of ^{1}H and ^{13}C NMR signals was always confirmed by two-dimensional ^{1}H/^{1}H COSY, ^{1}H/^{1}H NOE difference spectroscopy, and two-dimensional ^{1}H/^{13}C HETCOR experiments based on $^1J(^{13}C,^1H)$ or on $^nJ(^{13}C,^1H)$ ($n = 2, 3$). The refocused INEPT pulse sequence[16] with ^{1}H decoupling was used to record ^{29}Si and ^{119}Sn NMR spectra. In most cases it was possible to detect ^{13}C satellites in the ^{29}Si or ^{119}Sn NMR spectra in order to obtain information complementing that from ^{29}Si or $^{117/119}$Sn satellites in the ^{13}C NMR spectra.

The silole and stannole derivatives **5** are readily identified by their typical pattern in the ^{13}C NMR spectra in the range of the olefinic carbon atoms. There are three sharp signals (two of which have satellites indicating one-bond scalar ^{29}Si–^{13}C or $^{117/119}$Sn–^{13}C coupling) and one broad signal[17] for the boron-bonded ^{13}C nuclei. The seven-membered ring in **9** also shows a typical pattern in the range for the olefinic carbon atoms (one sharp and one broad signal) and there are two $^{13}C(SiMe_2)$ signals, since the ring is nonplanar.[15] The puzzling feature of the ^{13}C NMR spectra of **8** or **11** was the presence of nine (eight sharp and one broad) readily detected ^{13}C NMR signals for the carbon atoms which previously belonged to the 1-bora-adamantane molecule. These signals indicate a completely asymmetric structure, although the R groups and the $SiMe_2$ or $SnMe_2$ units are represented only by single signals. The absence of any signals in the range for olefinic or alkynyl carbon atoms prompted us to take a closer look within the range of quaternary aliphatic carbon atoms in order to detect weak, broad signals of boron-bonded ^{13}C nuclei. The presence of such signals finally enabled us to propose the molecular structure of **8** and **11**, which was then confirmed by X-ray structural analysis for the solid state of **8e**. The ^{13}C NMR spectrum of **8e** (Figure 3) is typical of **8a**–**d** and also of **11**.

All δ^{11}B values are in the range 83–90, which is typical of ^{11}B nuclei linked to three carbon atoms in the absence of BC(pp)π interactions.[18] This is in agreement with molecular models, based on AM1 calculations,[11, 12a] of the siloles or stannoles **5**, indicating that the most stable structure has the formally empty boron p_z orbital oriented perpendicular to the π orbitals of the diene system. The possibility that the boron atoms in **8** or **11** gain electron density by hyperconjugation is reflected to some extent by δ^{11}B values if one considers the increase in ^{11}B nuclear shielding by approximately 7 ppm in **8d** and **8e** when compared with **8a**. Any hyperconjugative interac-

Table 4. ^{13}C, ^{119}Sn, ^{29}Si, and ^{11}B NMR data[a] of the tetracyclic compounds **5**[b], **9**[b] and the bistricyclic compound **10**.[b]



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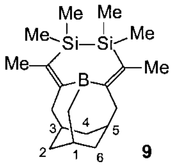

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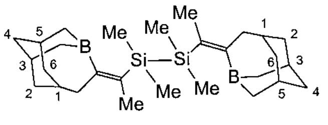
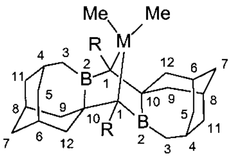


10

		M = Si			M = Sn	
	R = Me **5a**[c]	R = *t*Bu **5b**[d]	R = SiMe$_3$ **5c**[e]	R = SiMe$_3$ **5e**[f]	**9**[g]	**10**[h]
δ^{13}C MMe$_2$	– 5.1 (47.6)	0.2 (47.2)	– 2.5 (47.9)	– 6.3 [232.7]	– 2.8 (43.4) – 1.7 (42.9)	– 3.0 (43.4)
δ^{13}C B–C=	169.0 (br)	168.6 (br)	186.8 (br)	185.7 (br)	166.1 (br)	162.8 (br)
δ^{13}C BC=*C*M	133.3 (65.3)	146.3 (64.9)	142.4 (62.5) (SiMe$_3$) (46.7) (SiMe$_2$)	141. 7 [217.0] (64.5)	129.5 (62.0) (Si) (5.8) (Si–*Si*)	125.1 (64.6)
δ^{13}C CH$_2$C=*C*M	131.3 (70.1)	147.3 (67.8)	141.3 (61.7) (SiMe$_3$) (50.8) (SiMe$_2$)	142.7 [276.6] (63.2)	–	–
δ^{13}C CH$_2$–*C*=	151.5 (11.4)	151.4 (11.9)	168.8 (11.9) (9.0)	165.6 [100.6] (11.4)	–	–
δ^{13}C *C*H$_2$–C=	39.6	40.1 (6.67)	45.6 (9.5) (5.2)	46.3 [94.9]	39.6 (8.6)	33.6 (14.3)
δ^{13}C B–CH$_2$	35.7 (br)	35.0 (br)	35.5 (br)	36.0 (br)	37.5 (br)	36.2 (br)
δ^{13}C C (1)	26.2	26.6	27.0	27.3	25.7	30.3
δ^{13}C C(2), C(6)	36.4	36.6	36.7	36.5	36.3	37.2
δ^{13}C C(3), C(5)	35.7	34.3	35.1	35.1	27.6	33.9
δ^{13}C C(4)	36.2	37.5	39.1	37.1	32.2	37.4
δ^{29}Si	4.1 (69.9) (65.0) (47.7) (11.6)	5.8 (67.9) (65.2) (46.7) (11.6)	Me$_2$Si: 24.1 {11.8} (47.3)[i] Me$_3$Si: – 9.6 {12.0} (50.5) Me$_3$Si: – 11.0 {11.2} (51.6)	– 8.2 ⟨99.5⟩ (64.1) (51.3) (11.6) – 7.9 ⟨104.7⟩ (63.4) (51.3)	– 25.4 [j] (62.2) (43.0)	– 21.4 [k] (64.2) (43.4)
δ^{119}Sn	–	–	–	112.8	–	–
δ^{11}B	88.4	86.3	89.3	89.7	82.8	82.5

[a] In CDCl$_3$; coupling constants (±0.5 Hz) $^nJ(^{119}$Sn,^{13}C) are given in square brackets, $^nJ(^{29}$Si,^{13}C) in round brackets, $^nJ(^{29}$Si,^{29}Si) in brace brackets, and $^nJ(^{119}$Sn,^{29}Si) are given in angle brackets; (br) denotes broad ^{13}C resonances of boron-bonded carbon atoms. [b] The numbering of the cycles has been changed for better comparison of data for **5**, **9** and **10**. [c] Other δ^{13}C data: 12.6 (8.1), 16.4 (8.0) (*C*H$_3$–C=). [d] Other δ^{13}C data: 31.9, 32.5 ((*C*H$_3$)$_3$C); 34.4, 35.3 (Me$_3$*C*). [e] Other δ^{13}C data: 0.9 (51.5) (Me$_3$Si), 1.0 (50.5) (Me$_3$Si). [f] Other δ^{13}C data: 1.4 (50.9) [9.6] (Me$_3$Si), 1.5 (51.4) [9.4] (Me$_3$Si). [g] Other δ^{13}C data: 15.3 (*C*H$_3$–C=). [h] Other δ^{13}C data: 16.2 (*C*H$_3$–C=). [i] At 243 K: δ^{29}Si = 24.1 (50.6) (47.0) (Me$_2$Si); – 9.2 {11.3} (62.3) (51.0) (Me$_3$Si); – 10.8 {11.2} (61.6) (51.0) (Me$_3$Si). [j] At 243 K: δ^{29}Si = – 25.6 (61.8) (43.2). [k] At 243 K: δ^{29}Si = – 21. 4.

Table 5. ^{13}C, ^{119}Sn, ^{29}Si, and ^{11}B NMR data[a] of the octacyclic compounds **8**[b] and **11**.[b]



8, 11

δ^{13}C	M = Si R = Me **8a**[c]	R = Me **8d**[c]	M = Sn R = SiMe$_3$ **8e**[c]	M = Si – Si R = Me **11**[d]
δ^{13}C MMe$_2$	1.3 (44.1)	– 1.1 [201.6]	2.4 [225.5][e]	– 2.2 (43.9)[f] – 1.4 (43.4)[g]
δ^{13}C B–C(10)	38.3 (br)	39.1 (br)	44.1 [20.0] (br)	38.6 (br)
δ^{13}C R-*C*-M	42.9 (br)	55.8 [178.2] (br)	51.4 [80.0] (br)	39.6 (br)
δ^{13}C B–CH$_2$	38.6 (br)	37.6 (br)	40.8 [32.0] (br)	40.5 (br)
δ^{13}C C(6) (CH)	29.9	29.9 [9.6]	30.4	29.5
δ^{13}C C(8) (CH)	29.1	29.3 [7.9]	30.1 [8.4]	29.7
δ^{13}C C(4) (CH)	30.4	30.3	29.4	29.6
δ^{13}C C(9) (CH$_2$)	34.7	40.0 [98.9]	46.2 [103.4]	38.8
δ^{13}C C(12) (CH$_2$)	36.3	39.5	39.9 [24.0]	34.8
δ^{13}C C(7) (CH$_2$)	36.5	35.4	35.9	35.4
δ^{13}C C(5) (CH$_2$)	39.1	35.9	38.8 (32.4)	35.8
δ^{13}C C(11) (CH$_2$)	39.5	37.1	37.3	37.9
δ^{13}C R	7.6	12.1 [3.3]	SiMe$_3$: 5.2 [27.6] (49.2)[h]	11.2
δ^{29}Si	15.8[i] (43.9) (8.9)	–	– 3.5 (49.0) ⟨4.8⟩	– 24.3[j,k] (43.4)
δ^{119}Sn	–	68.8[l] [201.5] [178.7] [98.7]	84.7	–
δ^{11}B	90.8	83.2	84.9	86.0

[a] In CDCl$_3$; coupling constants (±0.5 Hz) $^nJ(^{119}$Sn,^{13}C) are given in square brackets, $^nJ(^{29}$Si,^{13}C) in round brackets, $^nJ(^{119}$Sn,^{29}Si) in angle brackets; (br) denotes broad ^{13}C resonances of boron-bonded carbon atoms. A positive sign of isotope induced chemical shifts $^2\Delta^{10/11}$B(^{29}Si or ^{119}Sn) indicates that the resonance of the heavy isotopomer lies at higher frequency. [b] The numbering of the cycles has been changed for better comparison of **8** with **11**. [c] δ^{13}C (125.8 MHz, 300 K). [d] δ^{13}C (62.89 MHz, 298 K). [e] ^1J(CH) = 129.5 Hz; ^5J(CH) = 1.9 Hz. [f] ^1J(CH) = 120.0 Hz; ^3J(CH) = 44.9 Hz. [g] ^1J(CH) = 121.5 Hz. [h] ^1J(CH) = 118.3 Hz; ^5J(CH) = 2.6 Hz. [i] $^2\Delta^{10/11}$B(^{29}Si) = 6.5 ± 0.5 ppb; measured at B_0 = 11.5 T and 5.75 T. [j] At 243 K: δ^{29}Si = 24.5. [k] $^2\Delta^{10/11}$B(^{29}Si) = 5.0 ± 0.5 ppb; measured at B_0 = 11.5 T and 5.75 T. [l] $^2\Delta^{10/11}$B(^{119}Sn) = 21.9 ± 0.5 ppb; measured at B_0 = 11.5 T and 5.75 T.

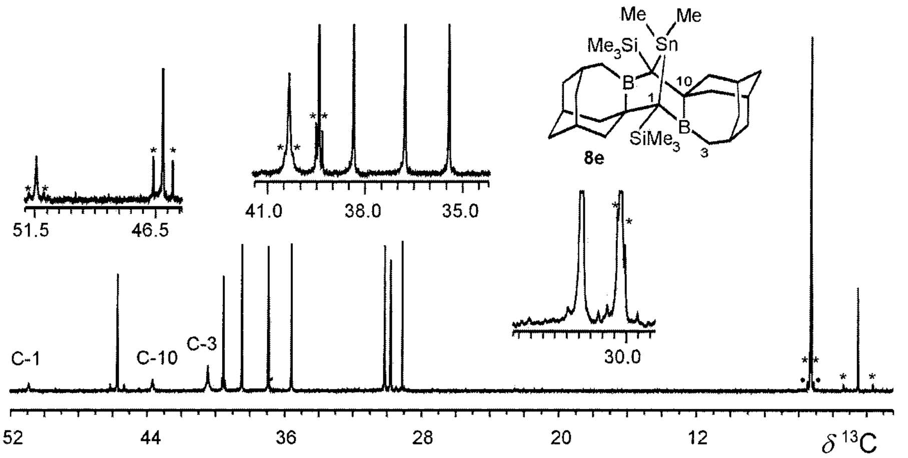


Figure 3. 125.8 MHz ^{13}C{^{1}H} NMR spectrum of 1,11-bis(trimethylsilyl)-21,21-dimethyl-21-stanna-2,12-diboraoctacyclo[9.9.1.1^{4,8}.1^{6,10}.1^{14,18}.1^{16,20}.0^{2,10}.0^{12,20}]pentacosane **8e** (in CDCl$_3$, 25 ± 1 °C). The assignments are based on the $^{117/119}$Sn (*) and ^{29}Si satellites (●), and the broad ^{13}C(1,3,10) NMR signals.

tion within a B–C–Si fragment should become stronger if silicon is replaced by tin.[19] The ^{119}Sn and ^{29}Si NMR spectra of all the compounds studied showed the expected simple patterns in agreement with the proposed structures, and δ^{29}Si[20] and δ^{119}Sn values[21] were found in the expected ranges. Typically, the nuclei in the 7 position in **8** are deshielded, since they belong to strained five-membered rings. Hyperconjugative effects may contribute to this deshielding. Such effects are not reflected by δ^{29}Si values of **11**, in which the two silicon atoms are part of six-membered rings. The shielding of these ^{29}Si nuclei appears to be unaffected, since it is even larger than in **10**, the precursor of **11**. The geometry of a 1,2,4,5,7,7-hexamethyl-7-sila-2,5-diboranorbornane has been optimized by ab initio MO calculations (RHF/6-311G[12a]) (Figure 4), and the chemical shifts have been calculated[12a] (GIAO NMR shielding tensors by RHF/6-311++G[12b]). The calculated δ^{11}B value (+86.1) agrees reasonably well with the experimental data for **8a** (+90.8). The difference between the calculated (+44.2) and the experimental δ^{29}Si value (+15.4) may be due to lack of a reliable reference: the SiH$_4$, with experimental δ^{29}Si = −93.1, which was used gave calculated δ^{29}Si values which differed by up to 30, depending on the basis sets.

The magnitude of vicinal coupling constants $|^3J(^{119}\mathrm{Sn},^{13}\mathrm{C})|$ in **8d** and **8e** shows the typical dihedral dependence:[22] the larger values are found for a dihedral angle of 161.7° and the values that are small or close to zero correspond to a dihedral angle of 80.3° (dihedral angles are taken from the solid-state molecular structure of **8e** (vide infra)).

The attempts to produce highly resolved ^{29}Si or ^{119}Sn NMR spectra for **8** and **11** were rewarded, since isotope-induced chemical shifts $^2\Delta^{10/11}$B(^{29}Si) and $^2\Delta^{10/11}$B(^{119}Sn) could be observed for the first time for organic frameworks[23] (Figure 5). This effect was not observed for the ^{29}Si resonance of **8e** (R = SiMe$_3$). The prediction of sign and magnitude of two-bond isotope effects in A–X–Y fragments (in which A is the resonant nucleus) is far from straightforward.[24] However, it is agreed that mass-induced changes in the X–Y bond (in **8** or **11** the respective C–B bond) are mainly responsible. The first observation of these

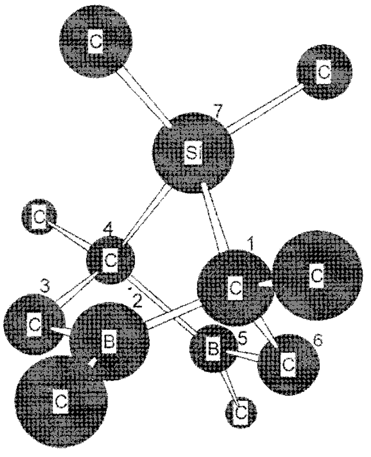


Figure 4. Optimized (RHF/6-311G) geometry of 1,2,4,5,7,7-hexamethyl-7-sila-2,5-diboranorbornane. Selected bond lengths [pm] and angles [°]: C(1)–B(2) 157.3, C(3)–B(2) 159.7, C(3)–C(4) 157.7, B–C(Me) 157.6, C(1)-S-i(7) 194.3, Si(7)–C(Me) 190.6; C(Me)-Si-C(Me) 108.2, C(1)-Si-C(4) 87.0.

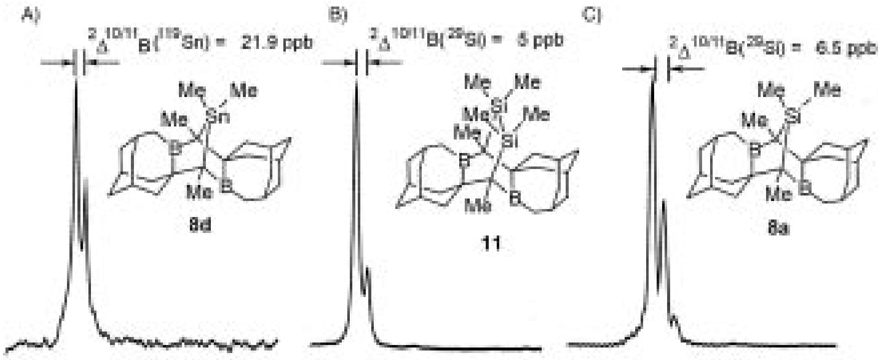


Figure 5. The isotope-induced chemical shift $^2\Delta^{10/11}$B(^{119}Sn) observed for **8d**, and $^2\Delta^{10/11}$B(^{29}Si) for **11** and **8a**. The line width of the signals for the ^{10}B–^{29}Si or ^{10}B–^{119}Sn isotopomers is always somewhat smaller than for the corresponding ^{11}B–^{29}Si or ^{11}B–^{119}Sn isotopomers. In A) and C) there are weak signals as shoulders (**8d**) or partly resolved (**8a**) which can be ascribed to isotopomers containing two ^{10}B nuclei. A) 186.5 MHz ^{119}Sn{^{1}H} NMR spectrum of **8d** (refocused INEPT). B) 99.4 MHz ^{29}Si{^{1}H} NMR spectrum of **11** (refocused INEPT spectrum); note that the intensity of the signal for the ^{29}Si(^{10}B) isotopomer is only half of that in **8a** (see spectrum C), since there is only one boron atom in the neighborhood (two bonds) of a particular silicon atom. C) 99.4 MHz ^{29}Si{^{1}H} NMR spectrum of **8a** (refocused INEPT).

effects in the present work should stimulate a search for such effects in related molecules containing boron and silicon and/or tin.

X-ray structural analysis of 8e:[25] The molecules of the octacyclic compound **8e** (Figure 6) are found in layers which are separated by CH_2Cl_2 molecules (disordered). There are no evident intermolecular interactions. The endocyclic Sn–C bonds are slightly longer than the exocyclic Sn–C bonds, as would be expected by considering the small endocyclic C(11)-Sn-C(11′) bond angle (79.55(19)°). The surroundings of the boron atoms are trigonal planar, within experimental error. The B–C(8) (157.2(7) pm) and B–C(11) (157.4(7) pm) bond lengths are within the normal range, when compared with Et_3B ($d_{B\text{-}C}$ = 157.2–157.5 pm[26]) or *B*-hexamethylhexabora-adamantane ($d_{B\text{-}C}$ = 157 pm[27]), whereas the bonds B–C(1) (160.4(8) pm) and B′–C(1′) (161.2(8) pm) are somewhat extended. All C–C bonds next to the boron atoms are elongated (for example, C(1)–C(11′) = 160.7(6) pm) relative to other C–C bonds in **8e**, and also in comparison with Et_3B ($d_{C\text{-}C}$ = 152.5–153.3 pm[26]). One of the arguments for hyperconjugation in Et_3B is the wide B-C-C bond angle (118.9°)[26]. This argument cannot be used here, since the strain of the octacyclic structure enforces a wide range of B-C-C bond angles (B-C(11)-C(1′) = 102.7° to C(7)-C(8)-B = 120.5°).

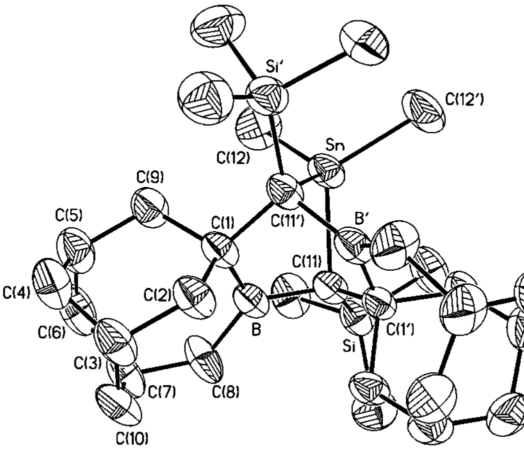


Figure 6. Molecular structure of the octacyclic compound **8e**. Selected bond lengths [pm] and angles [°]: Sn–C(12) 216.5(6), Sn–C(12′) 217.1(7), Sn–C(11) 220.6(5), Sn–C(11′) 221.6(5), Si–C(11) 188.7(5), B–C(1) 160.4(8), B–C(8) 157.2(7), B–C(11) 157.4(7), C(1)–C(2) 156.0(6), C(1)–C(9) 156.2(7), C(2)–C(3) 153.9(7), C(3)–C(4) 151.8(10), C(3)–C(10) 152.5(10), C(5)–C(9) 155.2(8), C(7)–C(8) 153.1(8); C(12)-Sn-C(12′) 104.7(3), C(11)-Sn-C(11′) 79.55(19), C(8)-B-C(11) 122.0(5), C(8)-B-C(1) 121.3, C(11)-B-C(1) 116.6(4), Si-C(11)-Sn 110.7(2); dihedral angles: C(2)-C(1)-C(11′)-Sn 161.7, C(8′)-B′-C(11′)-Sn 140.4, C(9′)-C(1)′-C(11)-Sn 80.3, B-C(1)-C(11′)-B′ 58.4.

Experimental Section

Starting materials and general techniques: The synthesis and handling of all compounds were carried out in an atmosphere of dry argon, and carefully dried solvents were used throughout. Starting materials **1**,[1] **2**,[28] and **3**[15] were prepared as described.

Electron impact mass spectra (EI-MS (70 eV)) were recorded on a Finnigan MAT 8500 instrument with a direct inlet, and NMR measurements on a Bruker ARX 250 or DRX 500 spectrometer; ^1H, ^{11}B, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra were obtained by direct measurement or refocused INEPT[16] based on $^2J(^{29}Si,^1H) \approx 7$ Hz and $^2J(^{119}Sn,^1H) \approx 50$ Hz). Chemical shifts are given with respect to Me_4Si (δ^1H ($CHCl_3/CDCl_3$) = 7.24; $\delta^{13}C$ ($CDCl_3$) = 77.0; $\delta^{29}Si = 0$ for $\Xi(^{29}Si)$ = 19.867184 MHz); external Me_4Sn ($\delta^{119}Sn = 0$ for $\Xi(^{119}Sn)$ = 37.290665 MHz); external $BF_3 \cdot OEt_2$ ($\delta^{11}B = 0$ for $\Xi(^{11}B)$ = 32.083971 MHz). Assignments are based on two-dimensional $^1H/^1H$ COSY, $^1H/^1H$ NOE difference, and two-dimensional $^1H/^{13}C$ HETCOR experiments.

General procedure for synthesis of the tetracyclic compounds 5a, 5b, 5c, 5e, and 9: A solution of **1** (about 1–2 mmol) in pentane (2–4 mL) was added to an equimolar amount of **2a–c**, **2e** or **3** in pentane or CH_2Cl_2 solution (5 mL) at room temperature, or at −50 °C (for **2e**). After the solution had been stirred for 2 h (for **2b**, **2e**, **3**), 10 h (for **2c**), or one day (for **2a**) at room temperature, the solvent was removed in vacuo (8–9 Torr). Mixtures containing **5a/8a**, **5e/8e**, and **9/10** were obtained, and all the NMR spectra indicated that there were no further impurities. According to the NMR data, the siloles **5b** and **5c** were formed selectively in a state of high purity and could be used for further transformations without further purification.

3,4,4,5-Tetramethyl-4-sila-1-boratetracyclo[8.3.1.1^{8,12}.0^{2,6}]pentadeca-2,5-diene (5a): ^1H NMR (250.1 MHz, $CDCl_3$, 298 K): $\delta = 0.11$ (s, $^nJ(^{29}Si,^1H)$ = 6.8 Hz, 6H; Me_2Si), 1.45–1.65 (m), 1.71 (s, 6H; Me–C=), 1.85–2.05 (m), 2.25–2.45 (m, 1H; H(8)), 2.53 (m, 2H), 2.59 (d, 2H; H(7)).

3,5-Bis(*tert*-butyl)-4,4-dimethyl-4-sila-1-boratetracyclo[8.3.1.1^{8,12}.0^{2,6}]pentadeca-2,5-diene (5b): ^1H NMR (250.1 MHz, $CDCl_3$, 298 K): $\delta = 0.31$ (s, $^nJ(^{29}Si,^1H)$ = 6.4 Hz, 6H; Me_2Si), 0.97 (s, 9H; CMe_3), 1.15 (s, 9H; CMe_3), 1.45–1.6 (m, 7H), 1.7–1.9 (m, 3H), 2.3 (m, 1H; H(8)), 2.4 (m, 2H), 2.74 (d, 2H; H(7)).

4,4-Dimethyl-3,5-bis(trimethylsilyl)-4-sila-1-boratetracyclo[8.3.1.1^{8,12}.0^{2,6}]-pentadeca-2,5-diene (5c): ^1H NMR (250.1 MHz, $CDCl_3$, 298 K): $\delta = 0.03$ () (s, $^nJ(^{29}Si,^1H)$ = 6.4, 9H; Me_3Si), 0.15 (s, $^nJ(^{29}Si,^1H)$ = 6.4, 9H; Me_3Si), 0.22 (s, $^nJ(^{29}Si,^1H)$ = 6.4, 6H; Me_2Si), 1.45–1.65 (m, 7H), 1.85–2.0 (m, 3H), 2.37 (m, 1H; H(8)), 2.5 (m, 2H), 2.93 (d, 2H; H(7)).

4,4-Dimethyl-3,5-bis(trimethylsilyl)-4-stanna-1-boratetracyclo-[8.3.1.1^{8,12}.0^{2,6}]pentadeca-2,5-diene (5e): ^1H NMR (250.1 MHz, $CDCl_3$, 298 K): $\delta = 0.03$ (s, $^nJ(^{29}Si,^1H)$ = 6.4 Hz, 9H; Me_3Si), 0.14 (s, $^nJ(^{29}Si,^1H)$ = 6.4 Hz, 9H; Me_3Si), 0.35 (s, $^nJ(^{119}Sn,^1H)$ = 51.2 Hz, 6H; Me_2Sn), 1.4–1.7 (m), 1.8–2.1 (m), 2.4 (m, 1H), 2.47 (m, 2H), 2.94 (d, 2H; H(7)).

2,3,3,4,4,5-Hexamethyl-3,4-disila-14-boratetracyclo[8.4.1.1^{8,12}.0^{6,14}]hexadeca-1,5-diene (9): ^1H NMR (250.1 MHz, $CDCl_3$, 298 K): $\delta = 0.04$ (s, $^nJ(^{29}Si,^1H)$ = 6.6 Hz, 6H; MeSi), 0.14 (s, $^nJ(^{29}Si,^1H)$ = 6.4 Hz, 6H; MeSi), 1.47 (m, 2H; H(11a), H(16a)), 1.52 (m, 2H; H(11b), H(16b)), 1.55 (d, 2H; B–CH_2, 5.5), 1.66 (s, 6H; CH_3–C=), 2.0–2.55 (m, 9H).

General procedure for diboraoctacyclic compounds 8a, 8d, 8e, and bis(boratricyclo)undecane (10): A solution of **2d** or **2e** (1 mmol), or **2a** or **3** (1.5 mmol) in pentane or CH_2Cl_2 (5 mL), was added dropwise to a solution of **1** (2 mmol) in pentane (2 mL) at room temperature. After the solution had been stirred for 1–2 h, or one day (for **2a**), at room temperature, the solvent was removed in vacuo (8–9 Torr). The mixtures contained **5a/8a**, **5d/8d**, **5e/8e**, or **9/10**, and all the NMR spectra indicated that there were no further impurities.

1,11,21,21-Tetramethyl-21-sila-2,12-diboraoctacyclo-[9.9.1.1^{4,8}.1^{6,10}.1^{14,18}.1^{16,20}.0^{2,10}.0^{12,20}]pentacosane (8a). ^1H NMR (250.1 MHz, $CDCl_3$, 298 K): $\delta = -0.05$ (s, $^nJ(^{29}Si,^1H)$ = 6.1 Hz, 6H; Me_2Si), 0.85–1.1 (m), 1.1 (s, 6H; CH_3–CSi), 1.15–1.4 (m), 1.7–1.9 (m), 2.0–2.25 (m).

1,11,21,21-Tetramethyl-21-stanna-2,12-diboraoctacyclo-[9.9.1.1^{4,8}.1^{6,10}.1^{14,18}.1^{16,20}.0^{2,10}.0^{12,20}]pentacosane (8d): Compound **8d** was purified by recrystallization from pentane/CH_2Cl_2. M.p. 134–136 °C; EI-MS: *m/z* (%): 496 (27) $[M]^+$, 346 (100) $[M - Me_2SnH]^+$; ^1H NMR (250.1 MHz, $CDCl_3$, 298 K): $\delta = 0.24$ (s, $^nJ(^{119}Sn,^1H)$ = 47.9 Hz, 6H; Me_2Sn), 0.95–1.05 (m), 1.2–1.3 (m), 1.34 (s, $^nJ(^{119}Sn,^1H)$ = 67.6 Hz, 6H; CH_3–C), 1.4–1.5 (m), 1.7–1.8 (m), 1.85–1.9 (m), 2.0 (m), 2.11 (m).

21,21-Dimethyl-1,11-bis(trimethylsilyl)-21-stanna-2,12-diboraoctacyclo-[9.9.1.1^{4,8}.1^{6,10}.1^{14,18}.1^{16,20}.0^{2,10}.0^{20}]-pentacosane (8e): Compound **8e** was purified by recrystallization from pentane/CH_2Cl_2. Single crystals[25] of **8e** (m.p. 233–237 °C) were obtained by crystallization from CH_2Cl_2. EI-MS: *m/z* (%): 612 (17) $[M]^+$, 597 (36) $[M - CH_3]^+$, 539 (5) $[M - SiMe_3]^+$, 462 (100) $[M - Me_2SnH]^+$; ^1H NMR (500.1 MHz, $CDCl_3$, 298 K): $\delta = 0.19$ (s,

^1J(CH) = 118.1 Hz, $^nJ(^{29}$Si,^{1}H) = 6.2 Hz, 18H; 2SiMe$_3$), 0.40 (s, ^1J(CH) = 129.2 Hz, $^nJ(^{119}$Sn,^{1}H) = 46.6 Hz, 6H; SnMe$_2$), 1.3–1.4 (m, 6H; H(22a), H(24a), H(9a), H(19a), H(5a), H(15a)), 1.49 (m, 2H; H(7a), H(17a)), 1.55–1.65 (m, 4H; H(3a), H(13a), H(7b), H(17b)), 1.68 (dm, 2H; H(23a), H(25a)), 1.77–1.9 (m, 6H; H(22b), H(24b), H(5b), H(15b), H(8), H(18)), 1.92–2.1 (m, 10H; H(3b), H(13b), H(6), H(16), H(9b), H(19b), H(23b), H(25b), H(4), H(14).

1,2-{Bis[(*E*)-*1*-(3-boratricyclo[4.3.1.1^{3,8}]undeca-4-yliden)]ethyl}-1,1,2,2-tetramethyldisilane (10): ^{1}H NMR (250.1 MHz, CDCl$_3$, 298 K): $\delta = 0.02$ (s, 12H; Me$_2$Si), 1.25–1.7 (m), 1.6 (s, 6H; Me−C=), 1.7–1.9 (m), 2.0–2.4 (m).

1,11,21,21,22,22-Hexamethyl-21,22-disila-2,12-diboraoctacyclo-[9.9.2.1^{4,8}.1^{6,10}.1^{14,18}.1^{16,20}.0^{2,10}.0^{12,20}]hexacosane (11): A solution of **3** (3 mmol) in pentane (5 mL) was added dropwise to a solution of **1** (6 mmol) in pentane (5 mL) at room temperature. The reaction mixture was stirred for five days at room temperature. After removal of all volatile material in vacuo (9 Torr) and by distillation (70–90 °C/0.01 Torr), the residue containing **9/11** was purified by crystallization from pentane/CHCl$_3$ to give the pure product **11** (0.155 g; 11%). M.p. 220–223 °C; EI-MS: *m/z* (%): 462 (100) $[M]^+$, 447 (5) $[M-\text{CH}_3]^+$, 389 (24) $[M-\text{SiMe}_3]^+$; ^{1}H NMR (500.1 MHz, CDCl$_3$, 300 K): $\delta = 0.03$ (s, 6H; ^1J(CH) = 119.8 Hz, 2Me$_2$Si), 0.06 (s, 6H; ^1J(CH) = 121.2 Hz, 2Me$_2$Si), 0.94 (dm, 2H; H(24a), H(26a)), 1.17 (s, 6H; CH$_3$−C), 1.29 (dm, 2H; H(9a), H(19a)), 1.40–1.52 (m, 12H; H(5a), H(15a), H(23a), H(25a), 2H(7), 2H(17), 2H(3), 2H(13)), 1.72–1.83 (m, 6H; H(5b), H(15b), H(9b), H-(9b), H(23b), H(25b)), 1.85 (m, 2H; H(4), H(14)), 1.89 (dm, 2H; H(24b), H(26b), 14.2), 1.97 (m, 2H; H(6), H(16)), 2.06 (m, 2H; H(8), H(18)).

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[25] X-ray crystallographic investigation of **8e**. The reflection intensities were collected on a Siemens P4 diffractometer (Mo$_{K\alpha}$ radiation, $\lambda = 71.073$ pm, graphite monochromated). Structure solution and refinement were carried out with the program package SHELXTL-PLUS V. 5.1. Measuring temperature for the structure determination was 296 K. All non-hydrogen atoms were refined with anisotropic temperature factors. The positions of the hydrogen atoms were calculated. All hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors. C$_{30}$H$_{50}$B$_2$Si$_2$Sn · 0.8CH$_2$Cl$_2$ crystallized as a light yellow plate, 0.45 × 0.19 × 0.15 mm, in the monoclinic space group $P2_1/c$ with the lattice parameters $a = 999.06(13)$, $b = 3318.2(5)$, $c = 1114.3(3)$ pm, $\beta = 108.980(11)°$, $V = 3493.2(10) \times 10^6$ pm^3, $Z = 4$, $\mu = 1.049$ mm^{-1}; 7369 reflections were collected in the range $3° \leq 2\theta \leq 50°$, 6074 independent reflections, 4912 assigned to be observed $[I > 2\sigma(I)]$, full-matrix least-squares refinement against F^2 with 361 parameters converged at $R1/wR2$ values of 0.071/0.174. Empirical absorption correction (Ψ-scans) resulted in min./max. transmission factors of 0.0663/0.2536; the max./min. residual electron density was $2.44/-1.60 \times 10^{-6}$ e pm^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-148281 (**8e**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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