Reactivity of 1,6-Bis(trimethylsilyl)-hexa-3-ene-1,5-diynes towards Triethylborane, Triallylborane, and 1-Boraadamantane: First Molecular Structure of a 4-Methylene-3-borahomoadamantane Derivative, and the First 6,8-Diborabicyclo[2.2.2]oct-2-ene Derivative

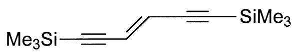
Bernd Wrackmeyer,*[a] Wolfgang Milius,[a] Oleg L. Tok,[b] and Yuri N. Bubnov[b]

Abstract: Compounds (*E*)- (**1**) and (*Z*)-1,6-bis(trimethylsilyl)-hexa-3-ene-1,5-diyne (**2**) react with triethylborane (**3**) by 1,1-ethylboration in a 1:1 or 1:2 molar ratio (in the case of **1**), whereas in the case of **2** only the 1:1 product is formed. The analogous reactions of **1** or **2** with triallylborane (**4**) are more complex because of competition between 1,1-allyl- and 1,2-allylboration. Again, compound **2** reacts only with one equivalent of **4**. In the case of 1-boraadamantane (**5**), 1,1-organoboration of **1** and **2** takes place either at one or at both C≡C bonds leading to compounds containing the 4-methylene-3-borahomoadamantane unit(s). The product of the reaction of **1** with two equivalents of **5** was characterized by X-ray structure analysis. The primary products of the reaction of **2** with **5** rearrange upon heating by deorganoboration and organoboration to give finally a tetracyclic compound **24** that contains an exocyclic allenylidene group. The product of the 1:2 reaction of **2** with **5** rearranges to give the 6,8-dibora-bicyclo[2.2.2]oct-2-ene derivative **25**. All reactions were monitored by ^1H, ^{11}B, ^{13}C, and ^{29}Si NMR spectroscopy.

Keywords: alkynes · allylboration · boron · boraadamantane · organoboration

Introduction

Reactions of alkynes containing organometallic substituents with triorganoboranes have afforded a large variety of novel alkenes, allenes, and heterocycles.[1] When there are several C≡C bonds present, it is often difficult to predict the structure of the products, and, depending on the nature of the borane, rather unusual products, difficult to prepare by other methods, can be formed. In this context the reactivity of the trimethylsilyl-substituted enediynes **1** and **2** towards triorganoboranes is of interest. In this work we report on the results of the reactions of **1** and **2** with triethyl- (**3**), triallylborane (**4**), and 1-boraadamantane (**5**). Triethylborane (**3**) is representative of the family of "normal" trialkylboranes, and numerous results of 1,1-organoboration reactions using this borane are already available.[1] Triallylborane (**4**) is a special case owing to permanent allylic rearrangement,[2] and its chemistry has been studied in great detail,[3] including the competition reactions between 1,1-allyl- and 1,2-allylboration of alkynes containing organometallic substituents.[4, 5] Another special triorganoborane is 1-boraadamantane (**5**),[6] isoelectronic with the 1-adamantyl cation,[7] which contains a highly Lewis-acidic center. This arises in **5** because the three-coordinate boron atom, which usually prefers a trigonal-planar geometry, is forced into pyramidal surroundings to reduce some of the strain in the tricylic system. It has already been found that **5** reacts readily even with 1-alkynylsilanes, which proved to be inert towards boiling Et_3B.[8, 9]



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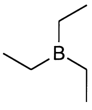

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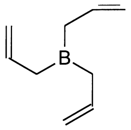

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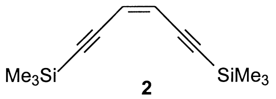

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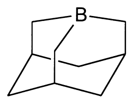

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Results and Discussion

Reactions of triethylborane (3) with the 1-alkynylsilanes 1 and 2: The results of the reaction of Et_3B (**3**) with the

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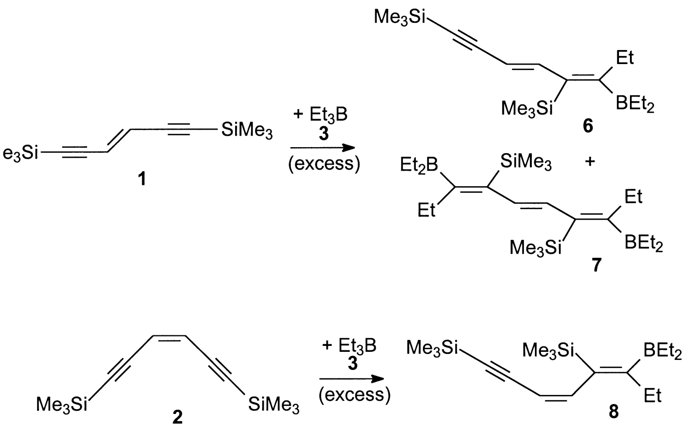
alkynylsilanes **1** and **2** are summarized in Scheme 1. In the case of **2**, only one of the Si–C≡ bonds is attacked to give the 1,1-ethylboration product **8**, whereas **1** reacts either to give the 1:1 product **6** or to the 1:2 product **7**. The structures of **6**–**8** can be deduced from the consistent set of NMR data (Table 1). The compounds **6**–**8** are formed quantitatively as colorless, air-sensitive oils.



Scheme 1. Reactions of **1** and **2** with **3**.

Reactions of triallylborane 4 with the 1-alkynylsilanes 1 and 2: Both compounds **1** and **2** react with triallylborane **4** by 1,1- and 1,2 allylboration, where, in the latter case, the boron atom ends up at the olefinic carbon atom next to the silicon atom. In the 1,1-allylboration, the *E* configuration is preferred in the products. These complex mixtures are best analyzed by ^{29}Si NMR spectroscopy as shown in Figure 1. The products **9**, **10**, and **14**–**18**, observed in the reaction mixtures are shown in Scheme 2 and Scheme 3, respectively. Apparently, the enediyne **1** reacts with **4** in a 1:1 and a 1:2 molar ratio (Figure 1 A), whereas the enediyne **2** reacts only at one of the C≡C bonds, and potential products such as **11**–**13** are not formed to an appreciable amount (Figure 1 B; Scheme 2).

Reactions of 1-boraadamantane 5 with the 1-alkynylsilicon compounds 1 and 2: 1-Boraadamantane (**5**) reacts readily with **1** or **2**, either in a 1:1 or in a 2:1 molar ratio (Scheme 4 and Scheme 5, respectively). In the case of the reaction of two equivalents of **5** with **1**, the product is the colorless solid **20**, which could be recrystallized from benzene to give single crystals suitable for X-ray structure analysis (vide infra). The 1:1 reaction of **5** with **2** first gave a mixture containing three compounds, the starting alkyne **2**, the 1:1 product **21** and the 2:1 product **22**, all of which were readily identified by their NMR data. Heating of this reaction mixture led to the formation of a new compound **24**, and neither the alkyne **2** nor the products **20** and **21** remained in the mixture. The 1,1-organoboration is reversible,[1] and it was shown previously that 1,1-deorganoboration is particularly facile in the case of 4-methylene-3-borahomoadamantane derivatives.[8] Eventually the alkene **23** (not detected) is formed with *Z* configuration instead of **21** with *E* configuration. In contrast to **21**, the Lewis-acidic boron atom in the *Z* isomer **23** can intramolecularly approach the remaining Si–C≡ bond. This attack is then followed by a shift of one hydrogen atom to the terminal alkynyl carbon atom, and the formation of new C–C and B–C bonds, to give **24**. The new product **24** could be isolated as a colorless solid, and the IR and NMR data (see Figure 2 for the ^{13}C NMR spectrum) were conclusive with respect to a tetracyclic structure with an exocyclic allenylidene group.

When **2** reacts with two equivalents of **5**, the triene **22** is formed selectively (Scheme 5). Heating of **22** (2 h, 90 °C) induces rearrangements, most likely through compounds which possess the *Z* configurations at the C=C bonds bearing the organometallic substituents. Finally, the 6,8-dibora-

Table 1. ^{13}C and ^{29}Si NMR data[a] of the 1,1-organoboration products **6**–**10**, and **19**–**22**.

Compd	$\delta(^{13}C)(1)$ (br)	$\delta(^{13}C)(2)$	$\delta(^{13}C)(3)$	$\delta(^{13}C)(4)$	$\delta(^{13}C)(5)$	$\delta(^{13}C)(6)$	$\delta(^{29}Si)(1)$	$\delta(^{29}Si)(2)$
6[b]	171.3	134.2	144.3	109.7	106.9	95.8	– 5.5	– 18.5
7[c]	165.4	136.0 (68.9)	131.3	–	–	–	– 6.1	–
8[d]	164.8	136.5 (66.7)	146.5	121.4	105.3 (16.6)	98.3 (86.1)	– 6.1	– 18.8
9[e]	158.6	139.4 (65.5)	145.8	110.2	105.0 (16.5)	98.8 (88.3)	– 5.5	– 18.6
10[f]	161.7	144.0	142.6	107.3	105.1 (16.3)	102.5 (84.2)	– 15.6	– 18.2
19[g]	172.0	130.7 (67.6)	144.2	108.8	107.4 (16.3)	95.7 (85.5)	– 4.8	– 17.5
20[h]	166.4	132.7 (68.6)	130.9 [4.8]	–	–	–	– 5.2	–
21[i]	167.0	133.5 (67.3)	145.9	109.2	105.5 (16.6)	98.1 (86.4)	– 4.5	– 18.9
22[j]	167.0	135.6 (68.8)	130.1	–	–	–	– 5.2	–

[a] In C_6D_6; coupling constants $J(^{29}Si,^{13}C)$ are given in parentheses ± 0.3 Hz; br denotes a ^{13}C NMR signal broadened by partially relaxed $^{13}C-^{11}B$ spin-spin coupling. [b] Other ^{13}C NMR data: $\delta = 0.7$ (Me_3Si, 54.4); 1.0 (Me_3Si, 52.0); 10.0 (Et); 14.2 (Et); 21.0 (br, Et_2B); 23.2 (Et, 7.0). [c] Other ^{13}C NMR data: $\delta = 1.5$ (Me_3Si, 51.1); 10.2 (Et_2B); 14.4 (Et); 21.3 (br, Et_2B); 23.5 (Et, 7.2). [d] Other ^{13}C NMR data: $\delta = 0.4$ (Me_3Si, 51.3); 0.6 (Me_3Si, 56.1); 10.2 (Me); 13.7 (Me); 22.3 (br, CH_2B); 25.7 (CH_2). [e] Other ^{13}C NMR data: $\delta = 0.3$ (Me_3Si, 56.4); 0.6 (Me_3Si, 51.6); 37.5 (br, CH_2B); 38.4 (CH_2, 7.2). [f] Other ^{13}C NMR data: $\delta = 0.3$ (Me_3Si, 56.1); 1.1 (Me_3Si, 51.8); 36.9 (br, CH_2B); 43.8 (CH_2, 7.2). [g] Other ^{13}C NMR data: $\delta = 0.7$ (Me_3Si, 56.4); 1.2 (Me_3Si, 50.6); 30.8 (CH); 34.3 (CH_2); 34.6 (CH); 36.2 (br, CH_2B); 37.5 (CH_2, [6.2]); 37.7 (CH_2). [h] Other ^{13}C NMR data: $\delta = 1.9$ (Me_3Si, [50.9]); 31.1 (CH); 34.6 (CH); 35.1 (CH_2); 36.7 (br, CH_2B); 37.8 (CH_2, [5.6]); 37.9 (CH_2). [i] Other ^{13}C NMR data: $\delta = 0.7$ (Me_3Si, 51.1); 0.8 (Me_3Si, 56.1); 30.9 (CH); 35.1 (CH); 36.8 (br, CH_2B); 37.7 (CH_2); 37.9 (CH_2). [j] Other ^{13}C NMR data: $\delta = 1.4$ (Me_3Si, 50.6); 31.2 (CH); 35.0 (CH); 36.5 (br, CH_2B); 38.0 (CH_2); 38.1 (CH_2).

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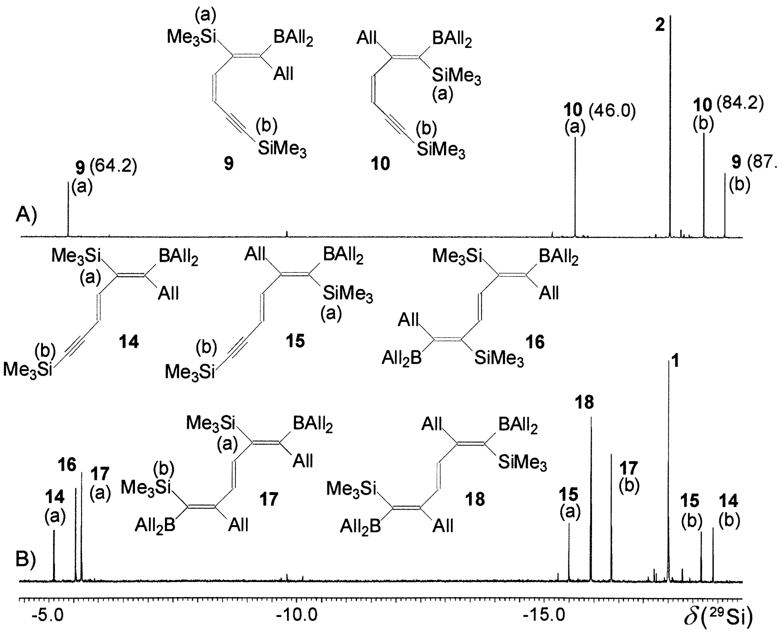
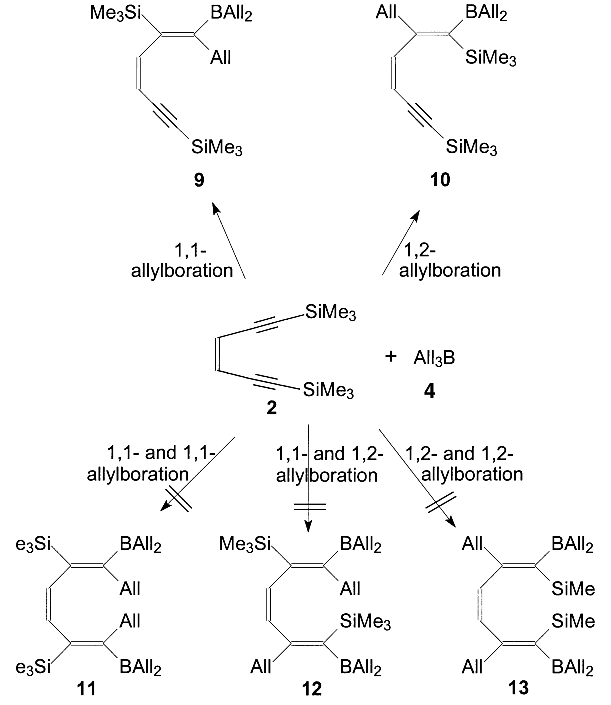


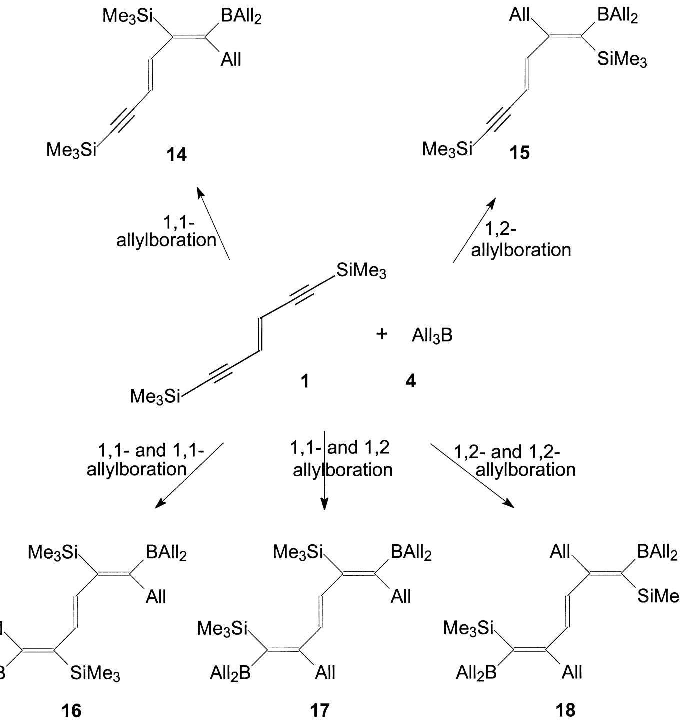
Figure 1. 99.4 MHz ^{29}Si{^{1}H} NMR (refocused INEPT[18]) spectra of the reaction solutions obtained from the reactions of triallylborane **4** with the enedyines **1** (A: products **14**, **15** from reactions in a 1:1, and **16**–**18** in a 1:2 molar ratio) and **2** (B: products **9** and **10** from reactions in a 1:1 molar ratio only; coupling constants $^1J(^{29}\mathrm{Si},^{13}\mathrm{C}{=})$ are given in parentheses. Except for the signals of the starting materials and spurious signals of unidentified impurities all other signals belong to products of 1,1- and 1,2-allylboration (see Scheme 2 and Scheme 3). In both **16** and **18**, the two silicon atoms are chemically equivalent. Note the large shift difference for silicon atoms in geminal (low frequency) and vicinal (*cis*) position (high frequency) with respect to the $\mathrm{All_2B}$ group.



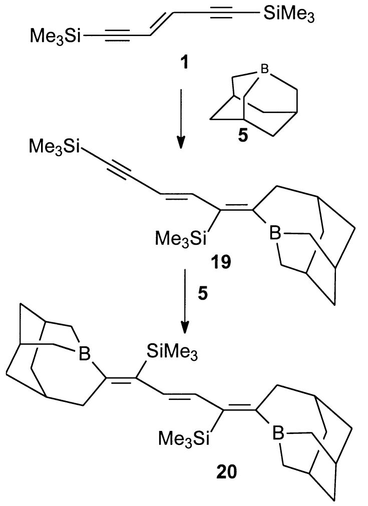
Scheme 2. Reactions of **2** with **4**.

bicyclo[2.2.2]oct-2-ene derivative **25** is formed quantitatively. This is reminiscent of the products observed from the reaction of two equivalents of **5** with di(1-alkynyl)silanes and -stannanes.[9] The structure of **25** in solution follows conclusively from the NMR data (see Figure 3 for the ^{13}C NMR spectrum, and Table 2 for a comparison of the ^{13}C NMR data of **25** with those for a related derivative[9]). Single crystals, however of low quality, were obtained for **25**, and the X-ray structural analysis at least confirmed the proposed structure also for the solid state.

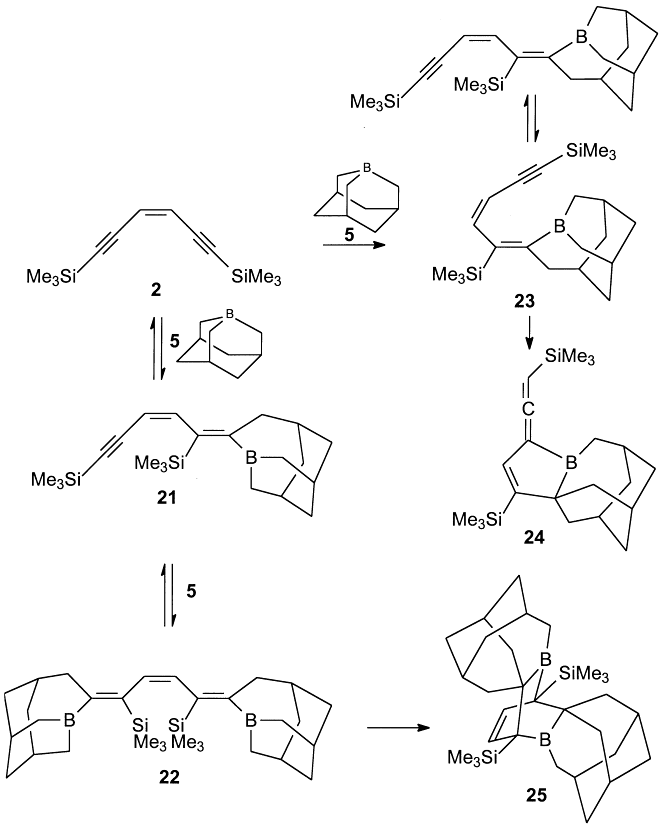
The formation of both **24** and **25** can be ascribed to the strongly Lewis-acidic character of the boron atoms in the respective precursor molecules, in which the boron atoms are part of a 4-methylene-3-borahomoadamantane system. According to the results of the X-ray structural analysis of **20**, in agreement with the calculated structure of the parent compound **20a**, the surroundings of the boron atom deviate from a trigonal-planar geometry, although the pyramidal character is less pronounced than in 1-boraadamantane (vide infra). Thus, the energy of activation for an intramolecular attack of electron-rich sites such as the trimethylsilyl-substituted alkynyl or alkenyl carbon atoms is reduced and further rearrangements can take place.



Scheme 3. Reactions of **1** with **4**.



Scheme 4. Reaction of **1** with **5**.



Scheme 5. Reaction of **2** with **5**.

X-ray structural analysis of the 4-methylene-3-borahomoadamantane derivative 20[10] and of the 6,8-diborabicyclo[2.2.2]oct-2-ene derivative 25: The molecular structure of **20** is shown in Figure 4, together with selected bond lengths and angles. The six carbon atoms of the triene system, the two boron and two silicon atoms are all in one plane within experimental error (mean deviation 1.4 pm). There are very few molecular structures reported for hexa-1,3,5-triene derivatives.[11] All bond lengths are in the expected range when compared with those in 1,6-bis[bis(trimethylsilylamino)]-1,6-diphenyl-hexa-1,3,5-triene[11] and with Et_3B.[12] The C–C bonds in the tricyclic system are slightly elongated which points towards effects arising from hyperconjugation.[12] According to the arrangement of the B-C(2)-C(9)-C(10) unit with respect to the plane B-C(1)-C(11) C–B(pp)π interactions are negligible. Most noteworthy, the surroundings of the boron atoms deviate from trigonal-planar geometry, since the sum of bond angles around the boron atoms is only 355.8° instead of 360°, usually encountered in triorganoboranes. This is in agreement with the calculated gas-phase structure of the related parent compound **20a** (vide infra). Considerable distortions of the bond angles at the terminal C–C double bond occur in the vicinity of the boron atoms: C(11)-C(1)-B 130.60(19)°, and B-C(1)-C(2) 107.38(17)°. The corresponding data for the calculated structure of the parent compound **20a** (128.0°, 110.8°) suggest that this is not an effect of the Me_3Si groups in **20**.

In spite of several attempts to grow better crystals of **25**, the quality of the single crystals were insufficient to obtain crystal data with high accuracy as was possible in the case of **20**, and therefore, structural parameters will not be discussed. However, the structural features of **25**, as proposed on the basis of NMR data in solution, could be confirmed. There are two independent molecules in the unit cell which differ only slightly in their parameters. The molecular structure is shown in Figure 5.

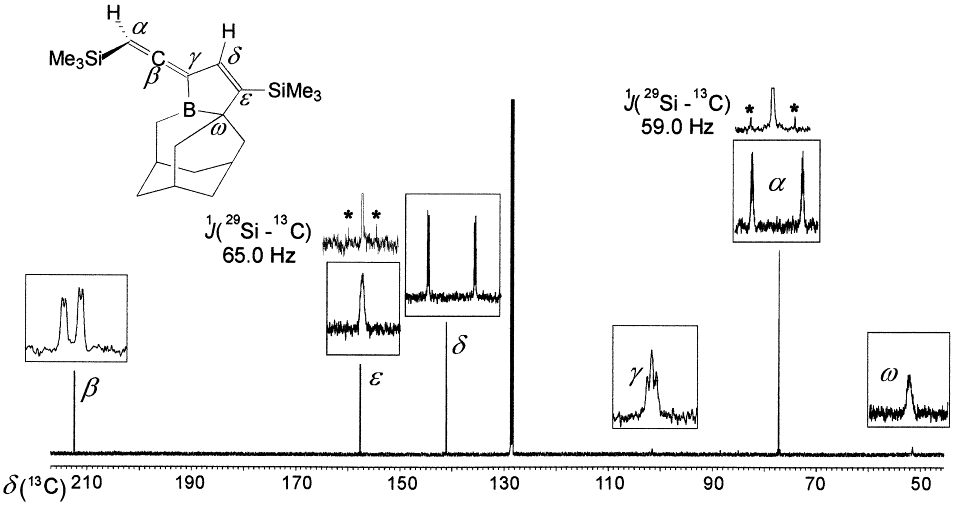


Figure 2. 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum (high-field region is omitted) of compound **24** (in C_6D_6, 23 ± 1 °C). The ^1H-coupled, ^{11}B-decoupled ^{13}C NMR signals are shown in rectangular frames. The broad ^{13}C NMR signals, typical of ^{13}C nuclei linked to the quadrupolar ^{11}B nucleus,[19] are readily assigned (ω, γ), and one of the olefinic and one of the terminal allenic ^{13}C resonance signals are accompanied by ^{29}Si satellites (marked by asterisks) according to $^1J(^{29}Si,^{13}C)$ with a characteristic magnitude.[20] The ^{13}C NMR signal of the central allenic carbon atom is found at typically high frequency.[21]

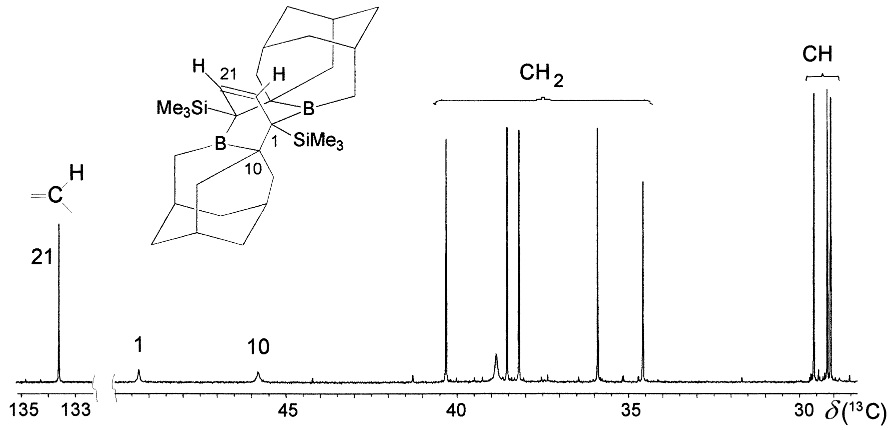
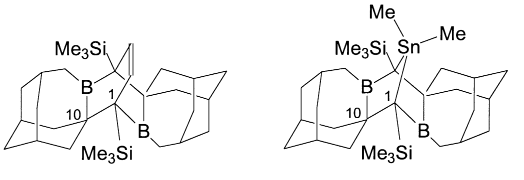


Figure 3. 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum (see also Table 2) of the 6,8-diborabicyclo[2.2.2]oct-2-ene derivative **25** (in C_6D_6, 23 ± 1 °C). All thirteen pairs of carbon atom types are different in their surroundings, giving rise to 13 ^{13}C NMR signals, of which 12 belong to four-coordinate carbon atoms and one represents the olefinc carbon atoms ($^{13}C(SiMe_3)$ not shown). There are three broad signals typical of ^{13}C linked to ^{11}B,[19] of which one represents a CH_2 group and the other two quaternary carbon atoms. Of the latter, the narrower signal at higher frequency is that of the bridgehead carbon atom bearing both silicon and boron, whereas the broader signal at lower frequency is assigned to C(10). The differential broadening[19] can be traced to the different magnitude of $^{13}C-^{11}B$ scalar coupling which is smaller, and therefore more efficiently averaged, in the case of C(1) with the Me_3Si group as an additional electropositive substituent (numbering according to IUPAC rules).

Quantum-chemical calculations of 1-boraadamantane (5), 4-methylene-3-borahomoadamantane and 6,8-diboranorbornene: In the absence of direct structural information on 1-boraadamantane (**5**), the optimized geometry based on ab initio MO calculations (RB3LYP/6-311**G[13]) (Figure 6) indicate that the surroundings of the boron atom are pyramidal. The GIAO-calculated ^{11}B chemical shift[14] is correctly predicted (in agreement with the experimental data) with respect to that of trimethylborane (calculated at the same level of theory). This also applies to the $\delta(^{13}C)$ values (Table 3) which indicates that the structural data for **5**, **20a** and **25a** are fairly reliable.

Table 2. Comparison of ^{11}B, ^{29}Si and relevant ^{13}C NMR data for **25** and **26**[9]



25 **26**

	$\delta(^{11}B)$	$\delta(^{29}Si)$	$\delta(^{13}C)(1)$	$\delta(^{13}C)(10)$
25	81.5	– 0.5 [49.4]	49.3	45.8
26	84.9	– 3.5 [49.0]	51.4	44.1

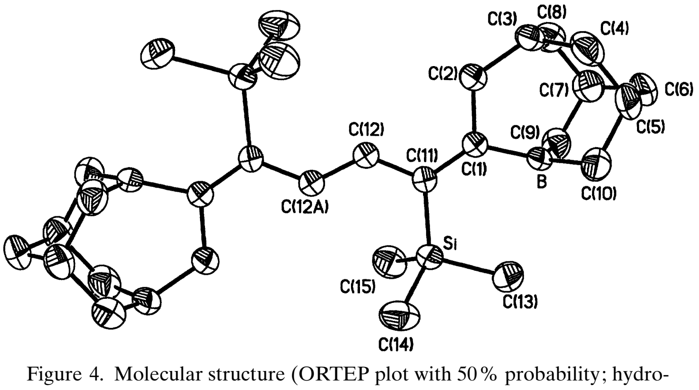


Figure 4. Molecular structure (ORTEP plot with 50% probability; hydrogen atoms have been omitted for clarity) of the triene **20**. Selected bond lengths [pm] and angles [°]: B–C(1) 155.5(3), B–C(9) 155.4(1), B–C(10) 156.8(4), C(1)–C(11) 135.8(3), C(11)–C(12) 146.6(3), C(12)–C(12A) 134.2(4), C(2)–C(3) 155.0(3), C(3)–C(4) 153.6(4), C(4)–C(5) 153.0(4), C(5)–C(6) 153.1(4), C(5)–C(10) 155.2(3), Si–C(11) 187.8(2), Si–C(13) 186.3(3), Si–C(14) 186.7(3), Si–C(15) 186.4(3); C(1)-B-C(9) 119.8(2), C(1)-B-C(10) 120.8(2), C(9)-B-C(10) 115.2(2), B-C(1)-C(2) 107.38(17), C(11)-C(1)-B 130.60(19), C(11)-C(1)-C(2) 121.99(19), C(1)-C(11)-C(12) 120.31(19), C(1)-C(11)-Si 119.66(16).

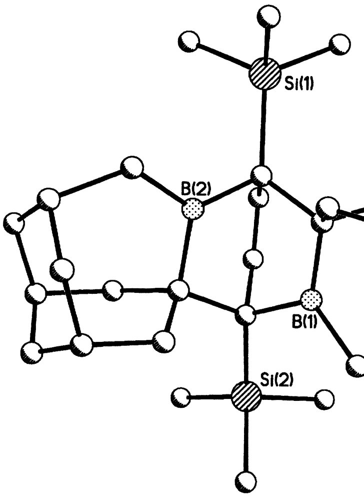
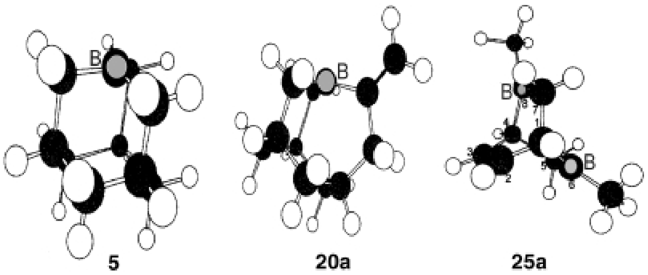


Figure 5. Molecular structure of the diborabicyclo[2.2.2]octene derivative **25** (see text).



5 **20a** **25a**

Figure 6. Optimized (RB3LYP/6–311**G) geometries of 1-boraadamantane (**5**), 4-methylene-3-borahomoadamantane (**20a**), and 6,8-dimethyl-6,8-diborabicyclo[2.2.2]oct-2-ene (**25a**). Selected bond lengths [pm] and angles [°]: **5**: B–C 156.9, C(B)–C 158.9, C–C 155.0; C-B-C 116.4; Σ(C-B-C) 349.2. **20a**: B–C 157.3, B–C= 155.4, C=C 134.1, C(B)–C 157.6, =C(B)–C 155.8, Σ(C-B-C) 355.7. **25a**: B(6)–C(1) 159.1, B(6)–C(5) 157.7, B(6)–C(Me) 156.8, C(1)–C(2) 152.1, C(2)–C(3) 134.8, C(3)–C(4) 152.1, C(4)–C(5) 157.9; C(1)-B(6)-C(Me) 123.7, C(1)-B(6)-C(5) 111.6, C(5)-B(6)-C(Me) 124.7; Σ(C-B-C) 360.0.

Table 3. Calculated (GIAO) and experimental chemical shifts $\delta(^{11}B)$ and $\delta(^{13}C)$ of 1-boraadamantane, 4-methylene-3-boraadamantane, and 6,8-diborabicyclo[2.2.2]oct-2-ene.

	$\delta(^{11}B)$ (calcd)	$\delta(^{11}B)$ (exp.)	$\delta^{13}C$(calcd)	$\delta(^{13}C)$ (exp.)
Me_3B	86.0	86.0	11.8	14.0
1-boraadamantane **5**	82.6	82.6	39.2 (BCH_2)	39.7
			51.0 (CH)	45.1
			37.8 (CH_2)	38.5
4-methylene-3-borahomoadamantane	80.2 (**20a**)	78.3 (**20**)	36.6 (BCH_2)	36.6
			169.8 (BC=)	166.4
			107.0 (=CH_2)	–
6,8-Me_2–6,8-diborabicyclo[2.2.2]oct-2-ene	81.5 (**25a**)	81.2 (**25**)	44.4 ($C^{1,4}$)	49.3
			29.6 ($C^{5,7}$)	45.8
			138.4 (HC=CH)	133.6

The optimized geometry of 4-methylene-3-borahomoadamantane **20a** (Figure 6) agrees very well with the relevant experimental structural data for **20**. In particular, the sum of the bond angles at the boron atom is identical in **20** and **20a**. The accuracy of the X-ray structural data for **25** is insufficient for a meaningful comparison with the optimized geometry of **25a**. As expected, the sum of bond angles at the boron atoms in **25a** is exactly 360°, as the result of two wide exocyclic and a more acute endocyclic C-B-C bond angle.

Conclusion

1-Boraadamantane is extremely reactive in 1,1-organoboration reactions when compared with triethylborane, and is even more reactive than triallylborane. The 4-methylene-3-borahomoadamantane derivatives which are formed by the 1,1-organoboration still contain a rather Lewis-acidic boron atom, as indicated by the results of the X-ray structural analysis of **20** with nonplanar surroundings of the boron atom, and this is confirmed by the optimized geometry according to ab initio MO calculations. Deorganoboration also takes place readily providing access to configurations at the C=C bond which invite further intramolecular reactions leading to novel types of polycyclic compounds such as the allene **24** and the first 6,8-diboranorbornene derivative **25**.

Experimental Section

General: The preparation and the handling of all compounds were carried out in an atmosphere of dry argon, and carefully dried solvents were used throughout. Starting material were prepared as described (alkyne derivatives **1** and **2**,[15] triethylborane,[16] triallylborane,[3, 17] and 1-boraadamantane (**5**)[6]). NMR measurements: Bruker ARX 250, Bruker DRX 500: ^{1}H(J(H,H) coupling constants given in Hz), ^{11}B, ^{13}C (J(Si,C) coupling constants given in Hz), ^{29}Si NMR (refocused INEPT[18] based on $^{2}J(^{29}Si,^{1}H_{Me})$ ca. 7 Hz; J(Si, Si) coupling constants given in Hz), chemical shifts are given with respect to Me_4Si ($\delta(^{1}H)$ ($CHCl_3/CDCl_3$) = 7.24; $\delta(^{13}C)$ ($CDCl_3$) = 77.0; $\delta(^{29}Si) = 0$ for $\Xi(^{29}Si) = 19.867184$ MHz); external BF_3–OEt_2 ($\delta(^{11}B) = 0$ for $\Xi(^{11}B) = 32.083971$ MHz). IR spectra: Perkin Elmer, Spectrum 2000 FTIR. EI-MS: Finnigan MAT 8500 (ionization energy 70 eV; direct inlet); the *m/z* data refer to the isotopes ^{1}H, ^{11}B, ^{12}C, ^{28}Si. Melting or decomposition points: Büchi 510 melting point apparatus. All ab initio MO calculations were carried out by using the Gaussian 98 package.[13, 14]

Reaction of triethylborane (3) with the enediynes 1 and 2; general procedure: A solution of the enediyne (**1** or **2**, ca. 0.7 mmol) in a tenfold excess of Et_3B was heated at reflux (ca. 100 °C) for two days; then unreacted borane was removed in vacuo. The oily residues were analyzed by NMR spectroscopy. The enediynes were transformed quantitatively into the respective products by 1,1-ethylboration.

Reaction of triallylborane (4) with the enediynes 1 and 2; general procedure: Two equivalents of All_3B were added to a solution of the enediyne **1** or **2** (ca. 0.7 mmol) in C_6D_6 (0.5 mL) and the mixtures were kept at room temperature for two days. NMR analysis showed that the enediynes were converted quantitatively into new products as a result of 1,1- and 1,2-allylboration. ^{29}Si NMR spectra (Figure 1), recorded immediately after mixing of the compounds, reveal that **1** and **2** have not reacted completely with All_3B under these conditions.

Reaction of 1-boraadamantane (5) with the enediynes 1 and 2; general procedure: A solution of enediyne **1** or **2** (1 or 2 equivalents, RT) in C_6D_6 (0.5 mL) was added to a solution of 1-boraadamantane **5** (ca. 0.5 mmol) in C_6D_6 (0.5 mL). The first products were formed immediately. Heating (80 °C, 6 h) of the solutions of **5** with one and two equivalents of **2** led to quantitative formation of compounds **24** and **25**, respectively.

6: ^{1}H NMR: $\delta = 0.14$ (s, 9H, Me_3Si, 6.5), 0.40 (s, 9H, Me_3Si, 7.0), 0.85 (t, 3H, Et, 7.6), 1.03 (t, 6H, Et, 7.2), 1.24 (q, 4H, Et_2B, 7.2), 1.89 (q, 2H, Et, 7.6), 5.98 (d, 1H, =CH, 16.5), 7.44 (d, 1H, =CH, 16.5, 7.1{Si}); ^{11}B NMR: $\delta = 81.4$.

7: ^{1}H NMR: $\delta = 0.35$ (s, 18H, Me_3Si, 6.5), 1.15 (t, 6H, Et, 7.5), 1.16 (t, 12H, Et_2B, 7.2), 1.38 (q, 8H, Et_2B, 7.2), 2.22 (q, 4H, Et, 7.5), 6.97 (s, 2H, =CH–, 2.7{Si}); ^{11}B NMR: $\delta = 81.4$.

8: ^{1}H NMR: $\delta = 0.24$ (s, 9H, Me_3Si, 6.6), 0.32 (s, 9H, Me_3Si, 6.8), 1.05 (t, 3H, Et, 7.6), 1.22 (t, 6H, Et, 7.6), 1.43 (q, 4H, Et, 7.6), 2.25 (qd, 2H, Et, 7.6, 0.8), 5.61 (d, 1H, =CH, 11.4), 6.42 (dt, 1H, =CH, 11.4, 0.8); ^{11}B NMR: $\delta = 84.1$.

9: ^{1}H NMR: $\delta = 0.21$ (s, 9H, Me_3Si, 6.4), 0.31 (s, 9H, Me_3Si, 6.6), 2.39 (d, 4H, CH_2B, 7.5), 3.09 (dq, 2H, CH_2, 7.1, 1.3), 5.0–5.1 (m, 6H, =CH_2), 5.57 (d, 1H, CH, 11.4), 5.9–6.2 (m, 3H, –CH=), 6.32 (dt, 1H, CH, 11.4, 1.3); ^{11}B NMR: $\delta = 83.1$.

10: ^{1}H NMR: $\delta = 0.20$ (s, 9H, Me_3Si, 6.6), 0.27 (s, 9H, Me_3Si, 7.0), 2.29 (d, 4H, CH_2B, 7.7), 3.49 (dt, 2H, CH_2, 6.3, 1.6), 5.0–5.1 (m, 6H, =CH_2), 5.52 (d, 1H, CH, 12.3), 5.9–6.2 (m, 3H, –CH=), 6.57 (d, 1H, CH, 12.3); ^{11}B NMR: $\delta = 81.2$.

19: ^{1}H NMR: $\delta = 0.21$ (s, 9H, Me_3Si, 6.5), 0.41 (s, 9H, Me_3Si, 7.0), 1.2–2.6 (m, 15H, boraadamantane), 6.02 (d, 1H, =CH–, 16.6), 7.45 (d, 1H, =CH–, 16.6, [7.9]); ^{11}B NMR: $\delta = 78.3$.

20: M.p. 159–161 °C; ^{1}H NMR: $\delta = 0.45$ (s, 18H, Me_3Si, [6.2]), 1.2–2.6 (m, 30H, boraadamantane), 7.14 (s, 2H, =CH–); ^{11}B NMR: $\delta = 78.3$.

21: ^{1}H NMR: $\delta = 0.28$ (s, 9H, Me_3Si, 6.6), 0.32 (s, 9H, Me_3Si, 7.1), 1.4–2.5 (m, 15H, boraadamantane), 5.62 (d, 1H, =CH, 11.4), 6.45 (dt, 1H, =CH, 11.4, 1.8); ^{11}B NMR: $\delta = 79.9$.

22: ^{1}H NMR: $\delta = 0.30$ (s, 9H, Me_3Si, 6.3), 1.4–2.5 (m, 15H, boraadamantane), 6.15 (s, 2H, =CH); ^{11}B NMR: $\delta = 79.9$.

24: M.p. 74–77 °C; ^{1}H NMR: $\delta = 0.26$ (s, 9H, Me_3Si, 6.8), 0.37 (s, 9H, Me_3Si, 6.4), 1.6–1.7 (m, 4H, boraadamantane), 1.76 (ddd, 1H, CH_2, 12.3, 5.2, 1.9), 1.84 (ddd, 1H, CH_2, 12.3, 5.2, 2.4), 1.93 (d, 2H, CH, 2.7), 2.1–2.2 (m, 4H, boraadamantane), 2.24 (dd, 2H, CH_2, 13.7, 4.1), 2.36 (ddd, 1H, CH, 10.9, 10.9, 4.1, 1.2), 5.11 (s, 1H, =CH); 6.93 (s, 1H, =CH, [5.1]); ^{13}C NMR: $\delta = 0.2$ (Me_3Si, 53.3), 1.7 (Me_3Si, 51.1), 29.7 (CH), 30.2 (CH), 30.3 (CH), 32.4 (br., CH_2B), 36.4 (CH_2), 37.3 (CH_2), 37.5 (CH_2), 39.0 (CH_2), 39.1 (CH_2), 51.5 (br., CB), 77.2 (=C(H)–Si, 59.0), 101.5 (br., =CB), 141.1 (=CH), 157.7 (=CSi, 65.0), 212.5 (=C=); ^{29}Si NMR: $\delta = -9.2$, -3.7; ^{11}B

NMR: $\delta = 82.2$; IR: $\tilde{\nu} = 1914$ (ν(C=C)$_{as}$) cm^{-1}; EI-MS: *m/z* (%): 354 (37) [M^+], 73 (100) [Me_3Si^+].

25: M.p. 82 – 87 °C (decomp); ^{1}H NMR: $\delta = 0.29$ (s, 18 H, Me$_3$Si, 6.2), 1.30 (d, 2 H, CH$_2$, 13.4), 1.36 (d, 2 H, CH$_2$, 14.6), 1.44 – 1.53 (m, 6 H), 1.60 (m, 2 H), 1.66 (m, 2 H), 1.8 – 2.0 (m, 12 H), 2.1 – 2.2 (m, 4 H), 5.94 (s, 2 H, =CH–); ^{13}C NMR: $\delta = 3.3$ (Me$_3$Si, 49.4), 29.1, 29.2, 29.6, 34.3, 35.9, 38.2, 38.6, 38.9 (br., CH$_2$B), 40.3, 45.8 (br.), 49.3 (br.), 133.6 (=CH–); ^{29}Si NMR: $\delta = -0.5$; ^{11}B NMR: $\delta = 81.2$; EI-MS: *m/z* (%):488 (17) [M^+], 414 (15) [$M^+ - H - Me_3Si$], 73 (100) [Me_3Si^+].

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[10] X-ray crystallographic investigation of **20**: 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 hydrogen atoms are at calculated positions. All hydrogen atoms were refined by applying the riding model with fixed isotropic temperature factors. $C_{30}H_{50}B_2Si_2$: a colorless irregular crystal with dimensions $0.22 \times 0.15 \times 0.12$ mm crystallizes in the monoclinic space group $P2_1/c$ with the lattice parameters $a = 1091.50(12)$, $b = 1078.01(8)$, $c = 1300.14(14)$ pm, $\beta = 104.907(8)^\circ$, $V = 1478.3(3) \times 10^6$ pm^3, $Z = 2$, $\mu = 0.137$ mm^{-1}; a total of 4276 reflections collected in the range $2.5^\circ \leq \vartheta \leq 27.5^\circ$, 3364 reflections independent, 2120 assigned to be observed ($I \geq 2\sigma(I)$), full-matrix least squares refinement against F^2 with 155 parameters converged at $R1/wR2$ values of 0.053/0.123; the max./min. residual electron density was $2.41/-1.70 \times 10^{-6}$ e pm^{-3}. CCDC-169999 (**20**) contains the supplementary crystallographic data (excluding structure factors) for the structure reported in this paper. These data can be can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

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