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1-Boraadamantane: reactivity towards mono-1-alkynyltin, -germanium and -silicon compounds — synthesis of 4-methylene-3-borahomoadamantanes

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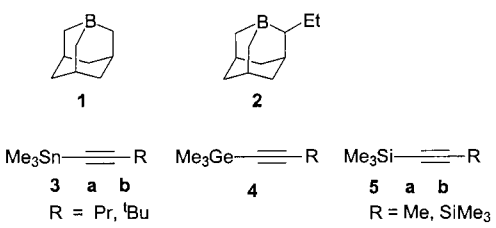
Abstract

The reaction of 1-boraadamantane **1** with 1-alkynyltin (**3**), -germanium (**4**), and -silicon compounds (**5**) leads to enlargement of the tricyclic system by formation of 4-methylene-3-borahomoadamantanes (**6**–**9**). These are 1,1-organoboration reactions which proceed by cleavage of the M–C≡ bond (M = Sn, Ge, Si). There is evidence for 1,1-deorganoboration which apparently take place much more readily than for non-cyclic analogues, most likely as the result of the strained tricyclic system. When 2-ethyl-1-boraadamantane (**2**) is used, again 3-borahomoadamantanes are formed, the isomers **15**–**18**. The product distribution is sensitive to steric effects. However, it appears that the B–C(H)Et bond in **2** is slightly more reactive than the B–CH_2 bonds. All products were characterised by ^{1}H-, ^{11}B-, ^{13}C-, ^{29}Si- and ^{119}Sn-NMR.

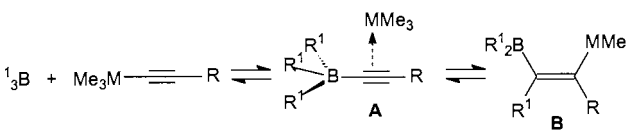
Keywords: Boraadamantane; Boranes; 3-Borahomoadamantanes; 1,1-Organoboration; NMR

1. Introduction

1-Boraadamantane **1** [1] possesses a rather high Lewis acidity when compared with other cyclic or non-cyclic trialkylboranes. Although any boron atom with co-ordination number three strongly prefers trigonal planar surroundings, the fairly rigid tricyclic system of 1-boraadamantane would accommodate more readily a boron atom with tetrahedral surroundings. In this context the reactivity of **1** towards 1-alkynyltin, -germanium and -silicon compounds is of interest. It is known that such alkyne derivatives react with triorganoboranes by 1,1-organoboration under very mild (Sn), mild (Ge) and harsh (Si) reaction conditions [2]. These reactions proceed via cleavage of the M–C≡ bond, formation of alkynylborate-like intermediates of type **A** [2,3], and finally one organyl group is transferred from boron to the neighboured alkynyl carbon atom to give **B**, in which the boryl and the fragment M are in *cis*-positions at the C=C bond. An intermediate of type **A** should be favoured in the case of **1** where the boron atom is ready to become tetra co-ordinate.



Scheme 1.



In bicyclic trialkylboranes, such as 9-alkyl-9-borabicyclo[3.3.1]nonanes, it was found that enlargem-ent of the bicyclic ring system and transfer of the exocyclic alkyl group may compete with each other [4]. In the

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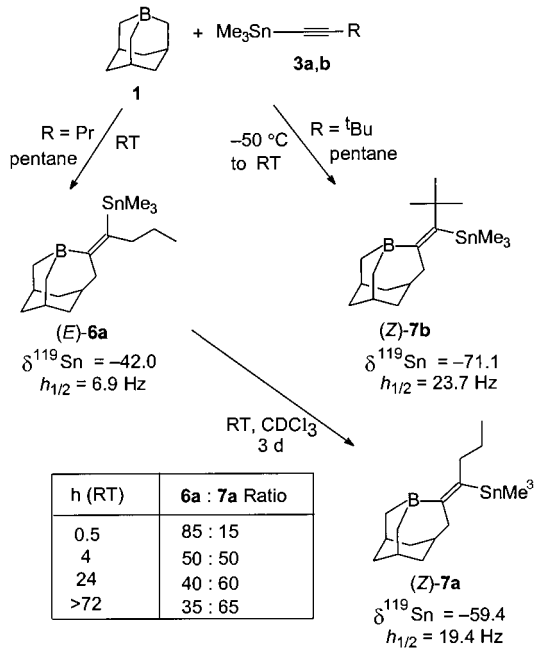


Scheme 2.

case of **1**, there is no choice, and 1,1-organoboration should lead to 4-methylene-3-borahomoadamantanes. Considering the high reactivity of **1** towards nucleophilic reagents, one can expect that even the reaction of **1** with 1-alkynylsilanes is fast, in strong contrast to other trialkylboranes. In Scheme 1, the 1-boraadamantanes **1** and **2** are shown together with 1-alkynyltin (**3**), -germanium (**4**), and -silicon compounds (**5**) used in this work. These are the first attempts to make use of 1-boraadamantanes in 1,1-organoboration reactions. The emphasis here is therefore not on isolating new compounds on a preparative scale but rather on exploring the scope of the reaction by application of multinuclear NMR methods.

2. Results and discussion

*2.1. Reactions of 1-boraadamantane **1** with the 1-alkynyltin compounds **3a**,**b***

1-Boraadamantane **1** reacts with 1-alkynyltin compounds under very mild conditions, starting at -50°C. The results are summarised in Scheme 2. In the case of **3a**, the first product is **6a** with *E*-configuration, the same stereochemistry (see **B**) which is usually encountered if e.g. triethylborane is used for 1,1-organoboration. Interestingly, **6a** rearranges slowly into **7a** with *Z*-configuration. In the case of corresponding alkenes obtained by using triethylborane instead of **1**, this process takes place only for R = H (in the presence of THF); for other groups R, it requires a much longer time (sometimes months), and the mechanisms of the rearrangement may be completely different. It has been noted on several occasions that 1,1-organoboration is a reversible reaction [2]. Because of the ring strain induced by the boron atom with trigonal planar surroundings in the tricyclic framework of compounds of type **6** or **7**, the 1,1-organoboration is more readily reversible, and the structure of the final product is the result of thermodynamic control. This is also indicated by the selective formation of **7b** which possesses *Z*-configuration. In contrast, the reaction of triethylborane with **3b** gives selectively the corresponding alkene with *E*-configuration (δ ^{119}Sn -54.6). Chemical shifts δ ^{119}Sn and line widths $h_{1/2}$ of the ^{119}Sn-NMR signals (given in Scheme 2; see also Fig. 1) are convenient tools to assign the *E*- or *Z*-configuration. The ^{119}Sn nuclear shielding is always lower in the *E*-isomer [e.g. (*E*)-$Et_2B(Et)C{=}C(Me)SnMe_3$ with δ ^{119}Sn -47.5 and (*Z*)-isomer with δ ^{119}Sn -55.6 [5]]. The broader ^{119}Sn-NMR signal must be assigned to the tin atom in *trans*-position with respect to the boron atom [5,6], since the line widths reflect the partially relaxed scalar coupling $^3J(^{119}Sn,^{11}B)$, the absolute magnitude of the *trans*-coupling being larger than that of the *cis*-cou-

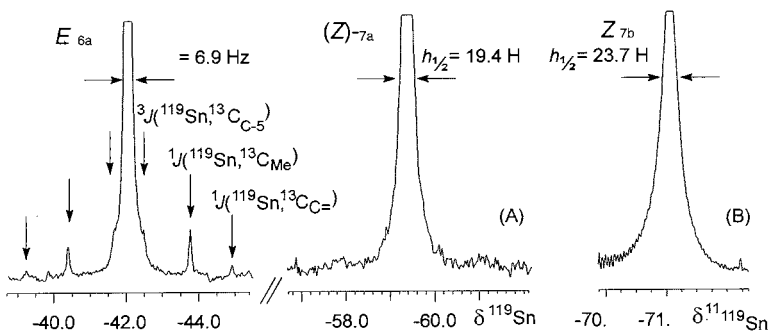
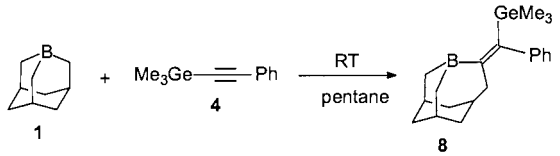
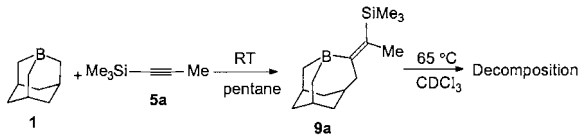


Fig. 1. 93.3 MHz ^{119}Sn{^{1}H}-NMR spectra, showing the influence of the *E*-(^{11}B and ^{119}Sn in *cis*-positions) and *Z*-configuration (^{11}B and ^{119}Sn in *trans*-positions) on the line width. (A) ^{119}Sn-NMR signals (at 298 K) of the mixture containing the products **6a** and **7a** of the reaction of **1** with **3a**. The ^{13}C satellites for **6a** are indicated by arrows. The assignment of the signals is based on the magnitude of $^nJ(^{119}Sn,^{13}C)$ measured from ^{13}C-NMR spectra. (B) 93.3 MHz ^{119}Sn-NMR spectrum (at 298 K) of **7b**.



Scheme 3.



Scheme 4.

Scheme 5.

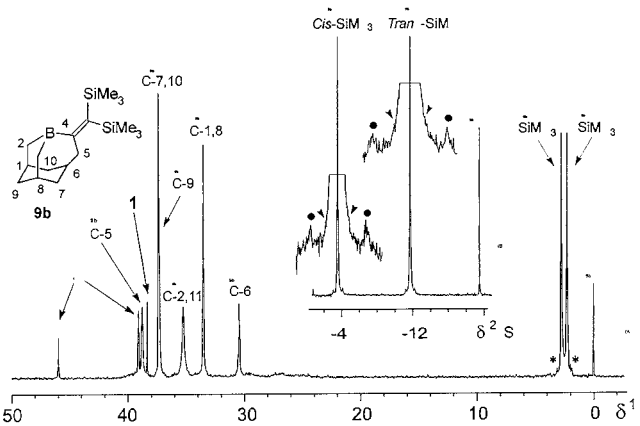


Fig. 2. The reaction solution obtained from the reaction of **1** with **5b** (ratio 1:1) (after 2 h at room temperature in $CDCl_3$) contains the equilibrium mixture of **1**, **5b** and **9b** (ratio 1:1:8). (A) 75.5 MHz $^{13}C\{^1H\}$-NMR spectrum (high field region) (the ^{29}Si satellites for $^1J(^{29}Si, ^{13}C_{Me})$ are marked by asterisks). (B) 49.7 MHz ^{29}Si-NMR (refocused INEPT, ^1H decoupled) spectrum corresponding to (A) (the ^{13}C satellites for $^1J(^{29}Si, ^{13}C_{Me})$ are marked by filled circles, the ^{29}Si satellites for $^2J(^{29}Si,^{29}Si)$ are marked by arrows; they are not well resolved owing to broadening of the ^{29}Si resonances as a result of partially relaxed ^{29}Si–^{11}B coupling [5] and dynamic effects described in the text).

pling (see Fig. 1). Similarly, further proof comes from the magnitude of coupling constants $|^3J(^{119}Sn,^{13}C)_{cis}| < |^3J(^{119}Sn,^{13}C)_{trans}|$ [6] (see Table 1; the data $|^3J(^{119}Sn,^{13}C)_{cis}| < |^3J(^{119}Sn,^{13}C)_{trans}|$ for the (*Z*)- and (*E*)-isomers of $Et_2B(Et)C{=}C(Me)SnMe_3$ [5] are 70.8 and 82.8 Hz, respectively; in **7b** with *Z*-configuration: $|^3J(^{119}Sn,^{13}C)_{cis}| = 60.8$ Hz and for (*E*)-$Et_2B(Et)C{=}C$-(^{t}Bu)$SnMe_3$ a value of 107.4 Hz has been measured for $|^3J(^{119}Sn,^{13}C)_{trans}|$).

2.2. Reaction of 1-boraadamantane **1** with phenylethynyl(trimethyl)germanium **4**

A smooth reaction takes place at room temperature between **1** and **4** (Scheme 3) to give a single product **8** in quantitative yield. The *E*-configuration of **8** is assigned on the basis of $^1H/^1H$ NOE difference spectra (spatial proximity of the aryl and the CH_2 groups at the C=C bond).

2.3. Reactions of 1-boraadamantane **1** with the 1-alkynylsilanes **5a**,**b**

The compound **9a** with *E*-configuration is formed selectively and quantitatively already at room temperature from the reaction of **1** with **5a** (Scheme 4). The analogous reaction with Et_3B requires heating at least for 24 h in boiling Et_3B (ca. 100°C), and there is no quantitative conversion of **5a** [7]. According to AM1 calculations [8], the (*E*)-isomer **9a** is more stable by 3.5 kcal mol^{-1} than the isomer with *Z*-configuration which is not formed.

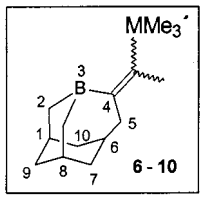
Bis(trimethylsilyl)ethyne **5b** was selected since it does not react at all with Et_3B. The alkene $Et_2B(Et)C{=}C(SiMe_3)_2$, analogous to **9b**, which would have been the expected product, can be prepared by other methods, and is known to decompose into **5b** and Et_3B at elevated temperatures [9]. However, as shown in Scheme 5, the reaction of **5b** with **1** takes place already under mild conditions. At room temperature the equilibrium between **9b** and the starting materials lies to ca. 80% on the side of **9b**.

NMR spectra (see Fig. 2 and Table 1) clearly indicate that the exchange of **9a** with **1** and **5b** is slow on the NMR time scale. However, treatment of such equilibrated mixtures with bis(trimethylstannyl)ethyne leads to the formation of **10** and gives back **5b**, and with pyridine the adduct **11** and again **5b** are obtained (Scheme 6). In contrast, the 1,1-organoboration is less reversible in the case of **9a** which does not react with pyridine to give the adduct **11**. By comparison of the structures of **9a** and **9b**, it is conceivable that the increased steric crowding in **9b** helps to lower the barrier for 1,1-deorganoboration. Differences in the properties of **9b** and **10** can be traced to the more labile Sn–C= as compared with the Si–C= bonds. Thus, **10** exhibits more dynamic features than **9b**, and this will be discussed elsewhere in more detail [10].

2.4. Reactions of the borahomoadamantanes **9a**,**b** with methanol

Organometallic-substited alkenes bearing a boryl and a $SiMe_3$ group in *cis*-positions at the C=C bond are

Table 1
^{13}C-, ^{119}Sn-, ^{29}Si- and ^{11}B-NMR data [a] of the 4-(1-MMe_3-1-R)-methylene-3-borahomoadamantanes (**6**–**10**)



R/No	M = Sn				M = Ge	M = Si	
	Pr (*E*)-**6a** [b]	Pr (*Z*)-**7a** [c]	^{t}Bu (*Z*)-**7b** [d]	$SnMe_3$ **10** [e]	Ph (*E*)-**8** [f]	Me(*Z*)-**9a** [g]	$SiMe_3$**9b** [h]
Mme_3	−8.3 [313.1]	−8.2 [315.9]	−4.5 [309.9]	−7.1 (*trans*) [305.4][10.0] −6.7 (*cis*) [301.7][11.1]	−1.0	−0.9 (49.6)	2.3 (br) (49.6), 2.8 (br) (49.6)
M–C=	136.5 [527.0]	137.5 [485.6]	148.9 [505.0]	133.7 [348.2][306.5]	144.7	127.0 (71.1)	133.4 (br) (55.3)
B–C=	163.4 [br]	164.9 [br]	158.6 [br]	187.4 [39.3][23.8]	161.2 [br]	163.8 [br]	186.0 [br]
C-5	33.0 [82.0]	42.1 [64.5]	40.4 [60.8]	43.2 [134.5][114.4]	34.0	33.3 (7.6)	38.8 (br)
C-6	30.5	30.7	30.7	30.1	30.1	30.2	30.4 (br)
C-7,10	37.1	37.2	37.5	36.5	36.9	37.2	37.4 (br)
C-1,8	34.9	34.9	33.1	34.2	34.1	34.0	33.5 (br)
C-9	37.4	37.3	37.15	36.8	37.0	37.3	37.3 (br)
C-2,11	36.7 [br]	36.7 [br]	35.5 [br]	36.0	36.4 [br]	36.1 [br]	35.3 [br]
δ ^{119}Sn or δ ^{29}Si	−42.0 [i] [528.5] [313.4] [80.4]	−59.4 [j]	−71.1 [k]	−51.7 (*trans*) [305.2]{942.9} −28.8 (*cis*) [302.0]{942.9}		−4.6 (71.2) (49.9)	−11.3 (*trans*) (49.9) −3.2 (*cis*) (49.5)
δ ^{11}B	80.5	81.5	74.3	79.4	80.5	79.2	77.3

[a] In $CDCl_3$; coupling constants $^nJ(^{119}Sn,^{13}C)$ are given in brackets; coupling constants $^nJ(^{29}Si,^{13}C) \pm 0.5$ Hz are given in parentheses; coupling constants $^2J(^{119}Sn,^{119}Sn)$ are given in curved brackets; [br] denotes broad ^{13}C resonances of boron-bound carbon atoms; (br) denotes broad ^{13}C resonances due to dynamic effects.

[b] Other δ ^{13}C data: 13.9, 23.2 [13.7], 35.1 [59.6] (CH_3–CH_2–CH_2–).

[c] Other δ ^{13}C data: 14.1, 24.7 [16.1], 37.4 [67.2] (CH_3–CH_2–CH_2–).

[d] Other δ ^{13}C data: 29.1, 32.2 [21.9] ($C(CH_3)_3$).

[e] 243 K; further details in Ref. [10].

[f] Other δ ^{13}C data: 124.7 (C_p), 127.8, 128.0 ($C_{o,m}$), 138.4 (C_i).

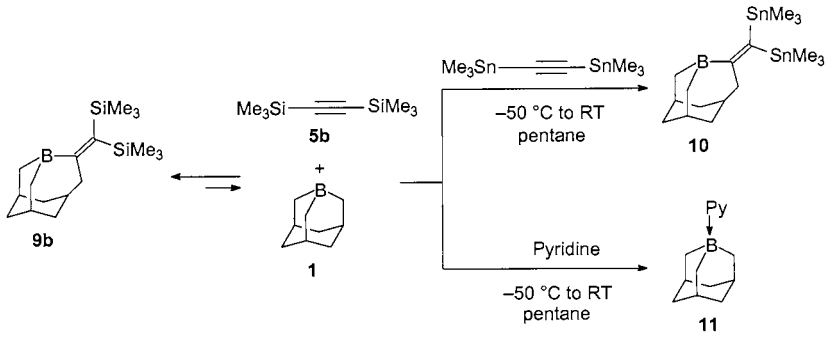
[g] Other δ ^{13}C data: 14.9 (Me).

[h] $^2J(^{29}Si,^{29}Si) < 20$ Hz; ca. 85% in $CDCl_3$.

[i] $h_{1/2} = 6.9$ Hz (at 298 K); at 263 K: δ $^{119}Sn = -40.6$ [526.8], [312.8].

[j] $h_{1/2} = 19.4$ Hz (at 298 K); at 263 K: δ $^{119}Sn = -59.0$ [485.5], [316.2].

[k] $h_{1/2} = 23.7$ Hz (at 298 K); at 233 K: δ $^{119}Sn = -70.3$ [504.0], [309.0], [60.4].



Scheme 6.

known to react with methanol not only by protolytic cleavage of the B–C= bond but addition and rearrangement may also take place [11]. The present results indicate that the latter process appears to be preferred under conditions stabilising an intermediate in which methanol is co-ordinated to the boron atom. Scheme 7 shows that a small amount of **12** is formed which is the product of methanolysis of **1**, and the major product is the new tricyclic compound **13**.

When the equilibrated mixture containing **1**, **5b** and the 1,1-organoboration product **9b** is cooled to -50°C before methanol is added, compound **14**, analogous to **13**, is formed as the major product along with a small amount of **12**. When the same reaction is carried out at room temperature, the amount of **12** markedly increases. This indicates the presence of a temperature dependent equilibrium, and that the rates of the reaction of **1** and **9b** with methanol are distinctively different at different temperatures (Scheme 8).

The proposed structures of **13** and **14** are based on the consistent set of NMR data (Table 2). Already from the reaction mixtures it is clear that the boron atom is linked to two aliphatic carbon atoms and one oxygen atom (δ ^{11}B values in the typical range [12]), and δ ^{29}Si data show that the $SiMe_3$ groups are no longer linked to olefinic carbon atoms [13]. Final proof comes from the ^{1}H- and ^{13}C-NMR data.

2.5. Reactions of 2-ethyl-1-boraadamantane **2** with the 1-alkynylstannane **3b** and the 1-alkynylsilane **5a**

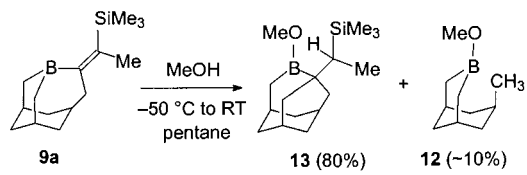
2-Ethyl-1-boraadamantane **2** offers two slightly different types of B–C bonds for 1,1-organoboration. If the course of the reaction (Scheme 9) of **2** with **3b** is controlled by steric factors, it can be expected that the products **15b** and **16b** with *Z*-configuration are preferred, as was already found for **7b** (Scheme 2). Then a further steric control arises because of repulsion between the ethyl substituent and the $SnMe_3$ group. This explains why the formation of **16b** is preferred.

As for **9a** (Scheme 4), the products **17a** and **18a** from the reaction of **2** with **5a** possess *E*-configuration, and they are formed in an approximate ratio of 1:1. If the two types of B–C bonds would not differ in reactivity, a 1:2 ratio is expected. Therefore, in spite of the increased steric crowding, the B–C(H)Et-bond in **2** appears to be more reactive than the B–CH_2-bonds in the 1,1-organoboration reaction shown in the lower half of Scheme 9. This is supported by AM1 calculations [8], which show that the energies of **17a** and **18a** are almost identical.

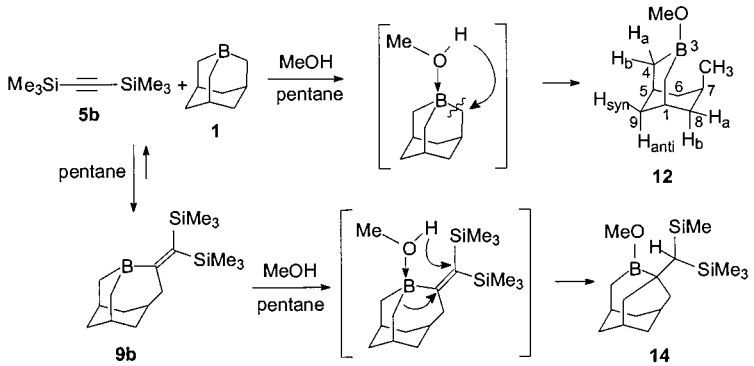
The mixtures of the products **15b**/**16b** and **17a**/**18a** were analysed by NMR spectroscopy (Table 3). Since the ^{13}C- and ^{1}H-NMR spectra show complicated patterns except for the MMe_3 regions, the ^{119}Sn- and ^{29}Si-NMR spectra which show consistently only two signals for each of the mixtures are particularly valuable in this context. The small differences in the δ^{119}Sn (**15b**, **16b**) and δ^{29}Si data (**17a**, **18a**) indicate that these mixtures do not contain (*E*)/(*Z*)-isomers but isomers with respect to the position of the ethyl substituent. The *Z*-configuration of **15b** and **16b** and the *E*-configuration of **17a** and **18a** is deduced by comparison with the δ^{119}Sn value for **7b** and the δ ^{29}Si value for **9a** (Table 1).

3. Conclusions

1-Boraadmantanes are much more reactive in 1,1-organoboration reactions than other cyclic or noncyclic trialkylboranes. Thus, the enlargement of the tricyclic ring system is easy to achieve. By selecting suitable combinations of substituents at the C≡C bond of the alkynes, stable compounds can be prepared selectively and in high yield. If there are two MMe_3

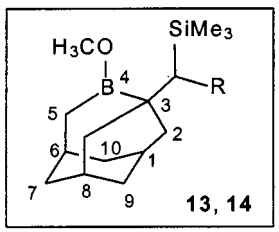


Scheme 7.



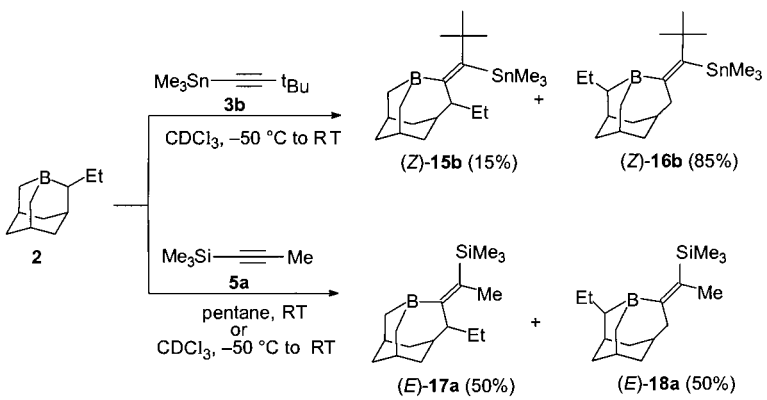
Scheme 8.

Table 2
^{13}C-, ^{29}Si- and ^{11}B-NMR data [a] of the 3-(1-R-1-trimethylsilyl)methyl-4-methoxy-4-boratricyclo[4.3.1.1^{3,8}]undecanes **13** and **14**



Compound	δ ^{13}C					δ ^{29}Si	δ ^{11}B
	$SiMe_3$	B–C	CH	CH_2	OCH_3		
13, R = Me [b]	0.2 (49.6)	27.8 [br] 29.8 [br]	27.1, 28.9, 29.0, 29.1	35.9, 36.8, 37.5, 38.0, 39.3	52.5	4.2 (49.9)	54.4
14, R = $SiMe_3$	4.0 (50.5)	[br] 34.9 [br]	25.5 (*C*$SiMe_3$) (C-6) 29.4 (C-1,8)	(C-9) 38.5 ($2CH_2$) 41.8 ($2CH_2$)	52.7	0.4 (50.0)	54.4

[a] In $CDCl_3$; coupling constants $^nJ(^{119}Si,^{13}C) \pm 0.5$ Hz are given in parentheses; [br] denotes broad ^{13}C resonances of boron-bound carbon atoms.
[b] Other δ ^{13}C data: 10.4 (Me).



Scheme 9.

groups present, 1,1-deorganoboration becomes a prominent feature, most likely because of steric repulsion and considerable strain in the tricyclic system. Clearly, the new homoboraadamantanes are attractive compounds for further transformations, including 1,1-organoboration reactions. The result of the 'simple' methanolysis reaction studied here already shows that the chemistry of these compounds is less predictable than for many other triorganoboranes.

4. Experimental

4.1. 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 (1-boraadamantane **1** [1b], 2-Et-1-boraadamantane **2** was liberated from the adduct **2**-NMe_3 by treatment with Et_2O–BF_3 [1,14], and alkyne derivatives **3**, **4** and **5** [15]). NMR measurements: Bruker ARX 250: ^{1}H-, ^{11}B-, ^{13}C-, ^{119}Sn-NMR (refocused INEPT [16] based on $^2J(^{119}Sn,^1H)$ ca. 50 Hz), ^{29}Si-NMR (refocused INEPT based on $^2J(^{29}Si,^1H) = 7$ Hz); chemical shifts are given with respect to Me_4Si [δ ^{1}H ($CHCl_3$–$CDCl_3$) = 7.24; δ ^{13}C ($CDCl_3$) = 77.0; δ ^{29}Si = 0 for $\Xi(^{29}Si) = 19.867184$ MHz]; external Me_4Sn [δ ^{119}Sn = 0 for $\Xi(^{119}Sn) = 37.290665$ MHz]; external BF_3–OEt_2 [δ ^{11}B = 0 for $\Xi(^{11}B) = 32.083971$ MHz].

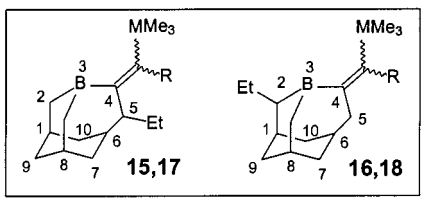
4.2. Reactions of 1-boraadamantane *1* with 1-alkynyltin, 1-alkynylgermanium and 1-alkynylsilicon compounds *3*–*5a*; general procedure:

To a solution of **1** (approximately 1–2 mmol) in pentane (2 ml) the equimolar amount of **3**, **4** or **5a** dissolved in 1 ml of pentane was added in one portion at room temperature (r.t.) or −50°C (for **3b**). After stirring the solution for 0.5–1 h at r.t., the solvent was removed in vacuo (8–9 Torr). According to the NMR data, several products such as **7b**, **8** and **9a** are formed selectively in high purity and can be used for further transformations. All compounds are left as colourless, extremely air- and moisture-sensitive oils.

Compound **6a**: (*E*)-4-(1-trimethylstannyl)butylideno-3-borahomoadamantane. ^{1}H-NMR ($CDCl_3$, 298 K, *J*/Hz): δ [$^nJ(^{119}Sn,^1H)$] = 0.03 [51.7] (s, 9H, Me_3Sn), 0.93 (t, 3H, Me, 7.3), 1.25–1.50 (m, 7H), 1.55 (m, 1H), 1.60–1.70 (m, 3H), 1.8–1.9 (m, 2H), 2.28 (m, 4H), 2.43 (m, 2H).

Compound **7b**: (*Z*)-4-(2,2-dimethyl-1-trimethylstannyl)propylideno-3-borahomoadamantane. ^{1}H-NMR

Table 3
^{13}C-, ^{119}Sn-, ^{29}Si- and ^{11}B-NMR data [a] of the 5-ethyl- (**15**, **17**) and 2-ethyl-4-(1-MMe_3-1-R)-methylene-3-borahomoadamantanes (**16**, **18**)



	M = Sn, R = ^{t}Bu				M = Si, R = Me	
	(*Z*)-**15b** [b]		(*Z*)-**16b** [c]		(*E*)-**17a** [d]	(*E*)-**18a** [d]
Temperature (K)	298	243	298	243	298	298
MMe_3	−4.4 [n.o.]	−4.7 [n.o.]	−4.5 [309.1]	−4.9 [307.8]	0.8 (50.4)	−1.2 (50.5)
M–C=	149.3 [508.0]	148.4	149.9 [505.0]	148.8 [500.7]	129.0 (70.8)	127.0 (71.7)
B–C=	158.4 [br]	158.4	155.8 [br]	155.7	168.0 [br]	161.2 [br]
C-5	47.3 [n.o.]	47.0 [n.o.]	40.3 [59.9]	40.1 [59.7]	40.6 (7.0)	38.45 (7.9)
C-6	30.6	29.9	30.8	30.1	30.2 or 30.8	
CH_3·(Et)	13.6	13.3	12.7	12.3	11.7 or 13.1	
CH_2·(Et)	24.3	23.7	22.9	22.4	25.6	22.8
C-2	n.o.	n.o.	43.9 [br]	42.8	39.8 [br]	45.9 [br]
δ ^{119}Sn or δ ^{29}Si	−71.4	−70.9	−71.2 [e]	−70.8 [308.5]	−4.8 (50.5) or −4.6 (50.5)	
δ ^{11}B	76.5				79.7	
% in mixture	15		85		50	50

[a] In $CDCl_3$; coupling constants $^nJ(^{119}Sn,^{13}C)$ are given in brackets; coupling constants $^nJ(^{29}Si,^{13}C) \pm 0.5$ Hz are given in parentheses; [br] denotes broad ^{13}C resonances of boron-bound carbon atoms; n.o. = not observed.

[b] Other δ ^{13}C signals are not assigned owing to overlap with signals for **16b** and impurities.

[c] Other δ ^{13}C data (at 298 K): 31.4 (CMe_3), 31.6 [22.7] ($C(CH_3)_3$), 32.3 (CH), 33.1 (CH), 35.1 (CH_2), 36.6 (br., C-11), 37.1 (CH_2), 38.0 (CH_2); other δ ^{13}C data (at 243 K): 31.3, 31.5 ($C(CH_3)_3$), 32.5 (CH), 33.7 (CH), 35.5 (CH_2), 35.7 (C-11), 36.5 (CH_2), 37.7 (CH_2).

[d] Other δ ^{13}C data: 14.8 (6.4) (**18a**: CH_3–C=), 15.9 (6.4) (**17a**: CH_3C=), 31.1 (**17a**: CH_2), 31.9 (**17a**: CH_2), 32.9 (**17a**: CH_2), 33.0 (**17a**: br., C-11), 34.0 (CH), 34.3 (CH), 34.8 (CH), 35.8 (CH_2), 36.7 (**18a**: br., C-11), 36.8 (CH), 36.9 (CH_2), 38.5 (CH_2).

[e] $h_{1/2} = 25.5$ Hz (at 298 K).

($CDCl_3$, 298 K, J/Hz): δ [$^nJ(^{119}Sn,^1H)$] = 0.24 [48.4] (s, 9H, Me_3Sn), 1.00 (s, 9H, $(CH_3)_3C$), 1.30–1.55 (m), 1.55–1.70 (m), 1.80–2.0 (m), 2.20 (d, 2H, H-5, 3.8), 2.15–2.35 (m, 3H).

Compound **8**: (*E*)-4-(1-trimethylgermyl)benzylideno-3-borahomoadamantane. ^{1}H-NMR ($CDCl_3$, 298 K, J/Hz): δ = 0.09 (s, 9H, Me_3Ge), 1.25–1.45 (m), 1.45–1.6 (m), 1.65–1.9 (m), 2.04 (d, 2H, H-5, 5.6), 2.15 (m, 1H), 2.45 (m, 2H), 6.98–7.50 (m, 3H, Ph), 7.11–7.20 (m, 2H, Ph).

Compound **9a**: (*E*)-4-(1-trimethylsilyl)ethylideno-3-borahomoadamantane. ^{1}H-NMR ($CDCl_3$, 298 K, J/Hz): δ = 0.05 (s, 9H, Me_3Si), 1.25–1.55 (m, 8H), 1.60–1.70 (m, 1H), 1.63 (s, 3H, CH_3C=), 1.80–1.90 (m, 1H), 2.13 (d, 2H, H-5, 4.0), 2.25–2.40 (m, 3H).

Compound **9b**: 4,4-Bis(trimethylsilyl)methylene-3-borahomoadamantane. ^{1}H-NMR ($CDCl_3$, 298 K, J/Hz): δ = 0.0 (s, 9H, Me_3Si), 0.19 (s, 9H, Me_3Si), 1.40–1.55 (m), 1.55–1.75 (m), 1.75–1.95 (m, 2H), 2.20–2.40 (m, 5H).

4.3. (E)/(Z)-Isomerisation of (E)-4-(1-trimethylstannyl)butylideno-3-borahomoadamantane **6a**

The (*E*)-isomer **6a** (2 mmol in 1 ml $CDCl_3$) isomerises into the (*Z*)-isomer **7a** (65%) at r.t. within three days. For the mixture containing **6a**/**7a** all NMR spectra indicate that there are no further impurities.

Compound **7a:** (*Z*)-4-(1-trimethylstannyl)butylideno-3-borahomoadamantane. ^{1}H-NMR ($CDCl_3$, 298 K, J/Hz): δ [$^nJ(^{119}Sn,^1H)$] = 0.16 [52.1] (s, 9H, Me_3Sn), 0.86 (t, 3H, Me, 7.26), 1.20–1.60 (m), 1.6–1.7 (m), 1.89–1.90 (m), 2.05–2.20 (m, 5H), 2.35–2.50 (m, 1H).

4.4. Reaction of the tricyclic compound **9b** with bis(trimethylstannyl)ethyne

To a solution of **9b** (2 mmol) in $CDCl_3$ (1 ml) the equimolar amount of bis(trimethylstannyl)ethyne in $CDCl_3$ (1 ml) was added at r.t. The reaction mixture was stirred for 0.5 h. The progress of the reaction was monitored by ^{29}Si- and ^{119}Sn-NMR spectroscopy. The resulting mixture contained **5b** and **10**; all NMR spectra indicate there are no further impurities.

Compound **10**: 4,4-Bis(trimethylstannyl)methylene-3-borahomoadamantane. ^{1}H-NMR ($CDCl_3$, 298 K, J/Hz): δ [$^nJ(^{119}Sn,^1H)$] = 0.12 [46.6] (s, 18H, Me_3Sn), 0.80–2.2 (m), 2.40 (m) (see Table 1 for ^{13}C-NMR data at low temperature; details will be given elsewhere [10]).

4.5. Reaction of the tricyclic compound **9b** with pyridine

To a solution of **9b** (2 mmol) in pentane (2 ml) the equimolar amount of pyridine in pentane (2 ml) was added at −50°C; the mixture was warmed to r.t. and stirred for 2 h. After removal of all volatile material in vacuo (0.1 Torr), the residue was purified by recrystallization from pentane–CH_2Cl_2 to give the known [1,17] pyridine adduct of 1-boraadamantane (**11**).

Compound **11**: 1-Boraadamantane-pyridine adduct: ^{13}C-NMR ($CDCl_3$, 298 K): δ = 32.9 (C-3,5,7), 40.2 (C-4,6,10), 125.0 ($C_{3,5}$-py), 138.5 (C_4-py), 144.8 ($C_{2,6}$-py). ^{11}B-NMR ($CDCl_3$, 298 K): δ = −3.7.

4.6. Reaction of the tricyclic compounds **9** with methanol: general procedure

A solution of methanol (1 ml) in pentane (2 ml) was added dropwise to a solution of **9** (2 mmol) in pentane (2 ml) at −50°C. After stirring the mixture for 0.5 h at r.t., all volatile material was removed in vacuo (15 Torr). The residue contains the mixtures of the compounds **12**/**13** or **12**/**14** as colourless oils, and all NMR spectra indicate that there are no further impurities. The compound **12** has already been described [1a,18].

Compound **12**: 3-Methoxy-7α-methyl-3-borabicyclo[3.3.1]nonane. ^{1}H-NMR ($CDCl_3$, 298 K, J/Hz): δ = 0.85 (m, 2H, H-2β,4β), 0.91 (d, 3H, CCH_3, 5.2), 1.05 (m, 2H, H-2α, 4α), 1.14 (m, 2H, H-6α, 8α), 1.36 (m, 1H, H-9*syn*), 1.59 (m, 1H, H-9*anti*), 1.70–1.90 (m, 3H, H-7, H-6β,8β), 2.13 (m, 2H, H-1,5), 3.6 (s, 3H, OCH_3). ^{13}C-NMR ($CDCl_3$, 298 K): δ = 24.4 (C–CH_3), 25.4 (C-7), 27.1 (C-1,5), 34.2 (C-9), 39.1 (C-6,8), 52.7 (OCH_3). ^{11}B-NMR ($CDCl_3$, 298 K): δ = 54.5.

Compound **13**: 3-(1-Trimethylsilyl)ethyl-4-methoxy-4-boratricyclo[4.3.1.1^{3,8}]undecane. ^{1}H-NMR ($CDCl_3$, 298 K): δ [$^nJ(^{29}Si,^1H)$] = 0.08 (6.3) (s, 9H, Me_3Si), 0.50–0.65 (m), 0.80–0.90 (m), 0.87 (m, Me–C), 1.0–1.7 (m), 1.8–2.15 (m), 3.57 (s, 3H, OCH_3).

Compound **14**: 3,3-Bis(trimethylsilyl)methyl-4-methoxy-4-boratricyclo[4.3.1.1^{3,8}]undecane. ^{1}H-NMR ($CDCl_3$, 298 K, J/Hz): δ [$^nJ(^{29}Si,^1H)$] = 0.05 (6.0) (18H, Me_3Si), 0.73 (s, 1H, CH–Si), 0.94 (m, 2H), 1.1 (m, 2H), 1.2–2.15 (m), 3.58 (s, 3H, OCH_3).

4.7. Reactions of the 2-ethyl-1-boraadamantane **2** with the 1-alkynylstannane (**3b**) and 1-alkynylsilane (**5a**): general procedure

To a solution of **2** (2 mmol) in $CDCl_3$ (1 ml) the equimolar amount of **3b** or **5a** in 1 ml of $CDCl_3$ was added in one portion at −50°C; the mixture was warmed to r.t. The mixtures contained **15b**/**16b** or **17a**/**18a**; ^{13}C-, ^{119}Sn- and ^{29}Si-NMR spectra (see Table 3) indicated that no other compounds were present.

Compounds **15b**, (*Z*)-5-Ethyl-4-(2,2-dimethyl-1-trimethylstannyl)propylideno-3-borahomoadamantane and **16b**, (*Z*)-2-ethyl-4-(2,2-dimethyl-1-trimethylstannyl)propylideno-3-borahomoada-mantane. Selected ^{1}H-NMR data ($CDCl_3$, 298 K): δ [$^nJ(^{119}Sn,^1H)$] = 0.188 [50.7] (**16b**: s, Me_3Sn), 0.191 (**15b**: s, Me_3Sn), 0.83 (t,

CH_3CH_2), 0.85–0.93 (m), 0.95 (**15b**: s, $(CH_3)_3C$), 0.97 (**16b**: s, $(CH_3)_3C$), 1.20–1.65 (m), 1.7–1.95 (m), 2.00–2.4 (m).

Compounds **17a**, (*E*)-5-Ethyl-4-(1-trimethylsilyl)-ethylideno-3-borahomoadamantane and **18a**, (*E*)-2-ethyl-4-(1-trimethylsilyl)ethylideno-3-borahomoadamantane. Selected ^{1}H-NMR data ($CDCl_3$, 298 K): $\delta = -0.055$ (s, Me_3Si), -0.051 (s, Me_3Si), 0.75–0.95 (m), 1.20–1.65 (m), 1.71 (s, CH_3C=), 1.80–2.40 (m).

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