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A novel 4-methylene-3-borahomoadamantane: 1,1-organoboration of an alkyn-1-ylsilane using 1-boraadamantane

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1,1-Dibromo-2,2-bis(trimethylsilylethynyl)ethene (2) reacts with two equivalents of 1-boraadamantane (1) by 1,1-organoboration of both trimethylsilylethynyl groups to give a triene 3 bearing two 4-methylene-3-borahomoadamantane moieties in terminal positions. The triene was characterized by one- and two-dimensional ^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR spectroscopy in solution and X-ray structural analysis in the solid state. The planes of the C=C double bond are strongly twisted against each other as a result of the bulky substituents, and the surroundings of the boron atoms deviate from the ideal trigonal planar geometry owing to the tension in the tricyclic frameworks. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: alkyn-1-ylsilanes; organoboration; 1-boraadamantane; NMR; multinuclear; X-ray

INTRODUCTION

1-Boraadamantane **1** is the most reactive trialkylborane[1–3] and therefore it is an attractive reagent in organometallic synthesis. The boron atom in **1** is highly electrophilic, since it occupies the position much better suited for a tetrahedral than a trigonal planar centre. This can be exploited in 1,1-organoboration reactions[4] with alkyn-1-ylsilanes, as has been shown previously.[5–8] Trialkylboranes other than **1** react with alkyn-1-ylsilanes sluggishly after prolonged periods of heating up to 100 °C.[4] In contrast, **1** reacts with alkyn-1-ylsilanes already at room temperature to give selectively novel alkenes in essentially quantitative yield (Scheme 1). In analogy to the comparable chemistry of alkyn-1-yl tin compounds,[9–13] it is proposed that the reaction proceeds by cleavage of the Si−C ≡ bond via a short-lived zwitterionic alkyn-1-ylborate-like intermediate A to the alkenes of type B, representing 4-methylene-3-borahomoadamantanes. The stereochemistry shown for B, with the boryl and silyl groups in *cis*-positions, is frequently observed, although the bulky groups may encounter steric repulsion.

So far only two compounds related to B have been characterized by direct structural methods (Scheme 2). The stereochemistry in C[7] is the same as in B, and the sum of bond angles at the boron atoms is less than 360°, indicating the strain enforced by the fairly rigid tricyclic framework. In the case of D,[8] the distortion from trigonal planar surroundings of the boron atom is even stronger because of an electron-deficient Si−H−B bridge.

In the present work, we report another example of a structurally characterized alkene of type B containing the 3-methylene-4-borahomoadamantane system. Furthermore, a fairly complete NMR-spectroscopic data set for this polycyclic system is presented, allowing for the straightforward solution-state identification of this particular structural unit in future studies. The reaction of the 1,1-dibromo-2,2-bis(trimethylsilylethynyl)ethene, **2**, with 1-boraadamantane, **1**, studied here shows that 1-boraadamantane is suitable for 1,1-organoboration of complex polyynes bearing terminal silyl groups.[14–18]

RESULTS AND DISCUSSION

1,1-Dibromo-2,2-bis(trimethylsilylethynyl)ethene **2** is readily available,[15,16] and reacts with two equivalents of 1-boraadamantane, **1**, in benzene at room temperature to give the triene **3** (Scheme 3) in essentially quantitative yield as a

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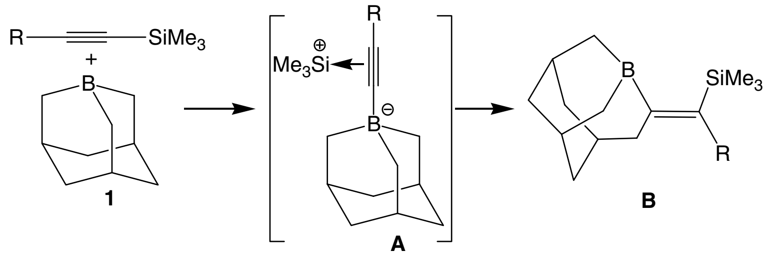
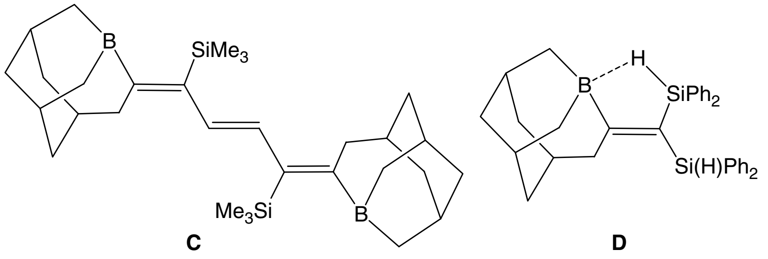


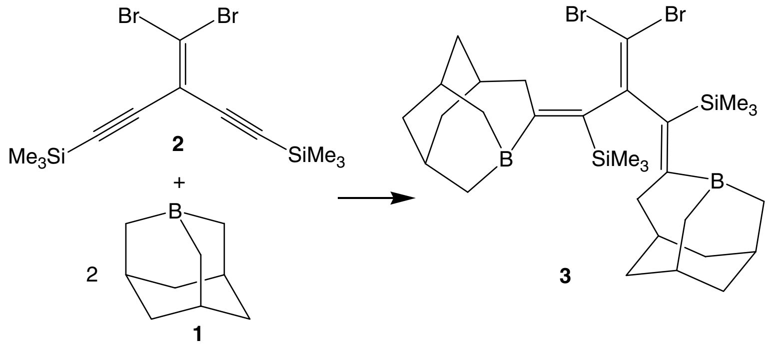
Scheme 1. 1-Boraadamantane in 1,1-organoboration of alkyn-1-yl(trimethyl)silanes.



sum of bond angles at boron atoms 355.8°

sum of bond angles at boron atom 349.6°

Scheme 2. Structurally characterized[7,8] (X-ray analysis) alkenes of type B.



Scheme 3. 1,1-Organoboration using 1-boraadamantane **1** of 1,1-dibromo-2,2-bis(trimethylsilylethynyl)ethene **2**.

colourless, air-sensitive crystalline solid. Recrystallization of **3** from toluene gave crystals suitable for X-ray analysis.

Crystal structure of the triene 3

The molecular structure of **3** is shown in Fig. 1. The planes containing the C=C bonds are strongly twisted against each other [torsion angles C3–C11–C12–C13 = −70.0(9)° and C13–C12–C11′–C3′ = −74.1(7)]. The surroundings of the boron atoms deviate from the usual trigonal planar geometry (sum of bond angles at the boron atoms: 355.1° and 355.9°), similar to the finding for C[7] (Scheme 2). The BC_2 planes of the 4-methylene-3-borahomoadamantane units are twisted against the B–C=C planes [C4–B1–C10–/B1–C3–C11 95.7(7)° and C4′–B2–C10/B2–C3–C11′ 90.8(7)°]. The bonds C4–C5 [154.5(8) pm] and C7–C10 [155.8(8) pm] in the tricyclic systems tend to be slightly longer than other C–C distances [e.g. C5–C6 153.4(9) pm]. This elongation can be explained by the effect of hyperconjugation[19,20] involving these C–C σ bond and the formally empty boron p_z orbital.[21,22]

NMR spectroscopy

The proposed structure of the triene **3** in solution follows conclusively from the consistent set of NMR data (^1H, ^{11}B, ^{13}C, ^{29}Si NMR) as given in the Experimental section. The molecule **3** is chiral both in the solid state and in solution. Restricted rotation of the alkenyl groups bearing the organometallic substituents is indicated by the diastereotopic nature of the carbon atoms C(9,10), C(6,8) and C(5,11) (Fig. 2). It is also shown in Fig. 2 that the ^{13}C NMR spectra were recorded with a sufficient signal-to-noise ratio

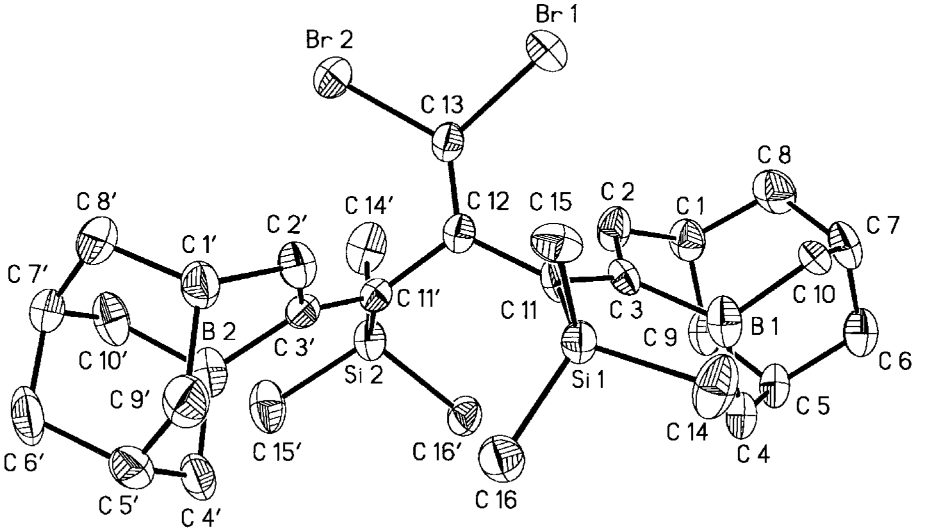


Figure 1. ORTEP plot (50%) of the molecular structure of the triene **3** (hydrogen atoms have been omitted). Selected bond lengths (pm) and angles (deg): Br1–C13 192.0(6), C12–C13 131.4(9), C3–C11 134.2(7), Si1–C11 188.9(5), Si1–C14 189.7(6), B1–C3 157.7(9), B1–C4 158.1(12), B1–C10 159.1(9), C2–C3 153.7(8), C1–C2 155.3(8), C4–C5 154.5(8), C7–C10 155.8(8), C5–C6 153.4(9); Br1–C3–Br2 109.9(3), C11–C12–C13 122.9(5), C11′–C12–C13 119.4(5), Si1–C11–C12 117.1(4), C3–C11–C12 123.1(5), C3′–C11′–C12 122.4(5), C2–C3–C11 123.6(5), C2′–C3′–C11′ 121.8(6), B1–C3–C11 128.1(5), C11′–C3′–B2 131.0(6), C3–B1–C4 120.9(6), C3–B1–C10 119.5(7), C4–B1–C10 115.5(5), C3′–B2–C4′ 120.5(5), C3′–B2–C10′ 118.8(7), C4′–B2–C10′ 115.8(5).

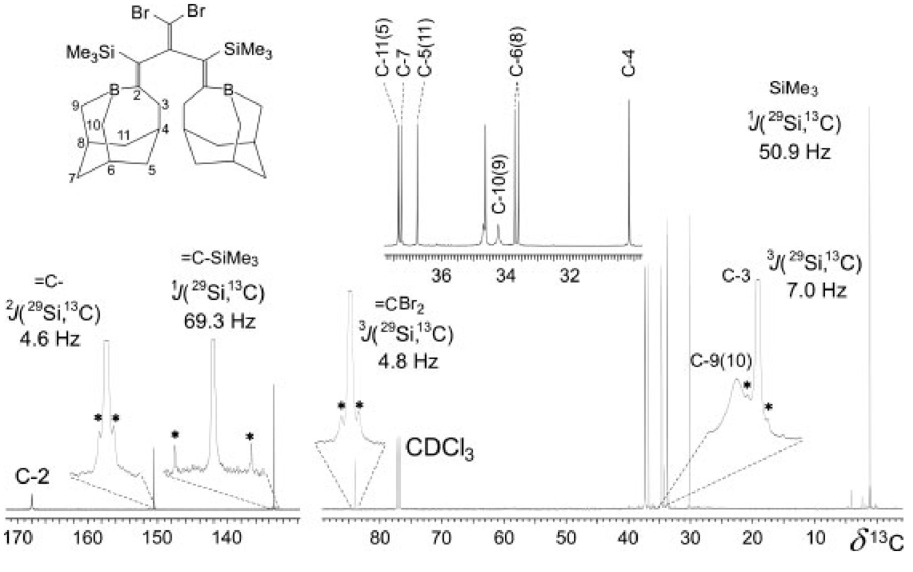


Figure 2. 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of the triene **3**. Note the broad ^{13}C NMR signals of carbon atoms bonded to boron[24]. ^{29}Si satellites are marked by asterisks.

for observing ^{29}Si satellite signals corresponding to the coupling constants $J(^{29}Si,^{13}C)$.[23,24] This is extremely helpful for assignment purposes. The assignment of the ^{13}C NMR signals is further supported by the typically broad NMR signals for boron-bonded ^{13}C nuclei.[25] The observation of ^{29}Si satellites corresponding to $^3J(^{29}Si,^{13}C)$ for the methylene carbon atom C(3) linked to the C=C bond aids the assignment of the ^1H NMR spectra using the information from relevant two-dimensional $^{13}C/^1H$ HETCOR (Fig. 3), $^1H/^1H$ COSY and NOESY spectra.

The observation of ^{13}C satellites corresponding to the coupling constants $^1J(^{13}C,^{13}C)$ for $^{13}CH_2$ and ^{13}CH NMR signals for the tricyclic frameworks are of interest concerning hyperconjugative interactions. Thus, the magnitude of the data $^1J(^{13}C,^{13}C)$ lies in the expected range (33–34 ± 1 Hz[26]) except for those ^{13}C nuclei where the C–C σ

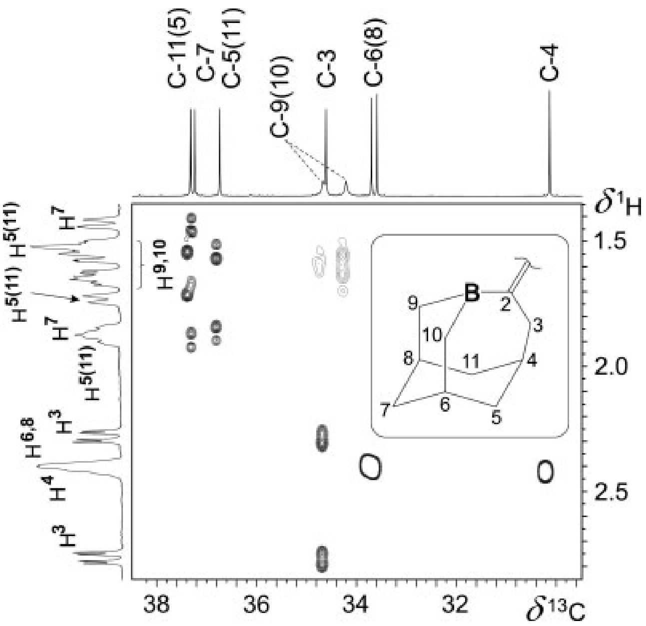


Figure 3. Contour plot of the 125.8 MHz ^{13}C/^{1}H HETCOR experiment (with ^{1}H decoupling of non-geminal protons in F$_2$) of the triene **3** (aliphatic region) based on $^{1}J(^{13}\text{C},^{1}\text{H}) = 140$ Hz (number of scans 32, time domain size 2048 × 512, processed size 2048 × 1024). Projections in F$_1$ and F$_2$ are taken from the normal one-dimensional NMR experiments.

bonds are involved in hyperconjugation with the boron p$_z$ orbital. The reduced magnitude of these coupling constants $^{1}J(^{13}\text{C},^{13}\text{C})$ (24 ± 1 Hz) compares favourably with the elongation of these C–C bonds as well as with the findings for 1-boraadamantane $\{^{1}J[^{13}\text{C}(2),^{13}\text{C}(3)] = 18.5$ Hz and $^{1}J[^{13}\text{C}(3),^{13}\text{C}(4)] = 32.6$ Hz},[22] where this effect is even more pronounced.

CONCLUSIONS

The highly reactive 1-boraadamantane can be used for the 1,1-organoboration of complex silylated polyynes under mild reaction conditions, in contrast with other triorganoboranes. Apparently, the surroundings of the boron atoms in 4-methylene-3-borahomoadamantane always deviate from trigonal planar geometry.

EXPERIMENTAL

General

All preparative work and the handling of the samples were carried out observing necessary precautions to exclude traces of air and moisture. Solvents were carefully dried and distilled in an atmosphere of argon, and oven-dried glassware was used throughout. 1-Boraadamantane **1**[1,2] and 1,1-dibromo-2,2-bis(trimethylsilylethynyl)ethane **2**[15] were prepared following the literature procedures {**2**: ^{1}H NMR (500.1 MHz): $\delta^{1}\text{H} = 0.21$ (Me$_3$Si). ^{13}C NMR (125.8 MHz): $\delta^{13}\text{C} = -0.1$ [Me$_3$Si, $^{1}J(^{29}\text{Si},^{13}\text{C}) = 56.6$ Hz]; 101.2 [≡ C-, $^{2}J(^{29}\text{Si},^{13}\text{C}) = 15.1$ Hz]; 103.5 [≡ C-Si, $^{1}J(^{29}\text{Si},^{13}\text{C}) = 79.9$ Hz]; 111.6 (=C-); 115.5 (=CBr$_2$); ^{29}Si NMR (99.4 MHz): $\delta^{29}\text{Si} = -15.9$}. NMR measurements of solutions (5–10% in C$_6$D$_6$) in 5 mm (o.d.) tubes at 23 °C: DRX 500: ^{1}H, ^{13}C^{11}B, ^{29}Si NMR (refocused INEPT[27,28] based on $^{2,3}J(^{29}\text{Si},^{1}\text{H}) = 7$ Hz). ^{1}H/^{1}H COSY, ^{1}H/^{1}H NOESY and ^{1}H/^{13}C HETCOR spectra[29–31] were measured using pulse programs from the Bruker program library. ^{1}H/^{1}H COSY: number of scans, 8; time domain size, 1024 × 1024; processed size, 2048 × 2048; ^{1}H/^{1}H NOESY: number of scans, 16; time domain size, 1024 × 102; processed size, 2048 × 2048; mixing time, 0.8 s; ^{1}H/^{13}C HETCOR: details are given in the caption to Fig. 3. Chemical shifts are given relative to Me$_4$Si [δ^{1}H (C$_6$D$_5$H) = 7.15, ±0.02; δ^{13}C (C$_6$D$_6$) = 128.0, ±0.05; $\delta^{29}\text{Si} = 0$, ±0.02, for $\Xi(^{29}\text{Si}) = 19.867184$ MHz; $\delta^{11}\text{B} = 0$, ±0.3, for external BF$_3$-OEt$_2$ with $\Xi(^{11}\text{B}) = 32.083971$ MHz]. Melting point (uncorrected): Büchi 510 melting point apparatus.

Reaction of 1,1-dibromo-2,2-bis(trimethylsilylethynyl)ethene 2 with 1-boraadamantane 1

To the solution of 0.113 g (3.0 mmol) of the enediyne **2** in benzene (1 ml) the solution of boraadamantane **1** (0.08 g, 6.0 mmol) in benzene (1 ml) was added at room temperature. A slightly exothermic reaction took place immediately, by which the triene **3** was formed almost quantitatively (monitored by ^{29}Si NMR). Volatile materials were removed at reduced pressure, and the remaining solid was crystallized from toluene at −30 °C to give crystals suitable for X-ray measurement.

2-(Dibromomethylidene)-1,3-bis(trimethylsilyl)-1,3-bis(1-boratricyclo[9.1^{1,6}.1^{4,8}]undec-2-ylidene)propane **3**: m.p. 216–218 °C; ^{1}H NMR (500.1 MHz): $\delta^{1}\text{H} = 0.13$ (s, 18H, SiMe$_3$); 1.43 [d, 1H, H-7, $^{2}J(^{1}\text{H},^{1}\text{H}) = 13.8$ Hz]; 1.5–1.6 [m, 4H, H-5(11), H-9(10)]; 1.6–1.7 [m, 2H, H-5(11), H9(10)]; 1.73 [dtt, 1H, H-5(11), $^{2}J(^{1}\text{H},^{1}\text{H}) = 12.7$ Hz, $^{3}J(^{1}\text{H},^{1}\text{H}) = 2.3$ Hz, $^{3}J(^{1}\text{H},^{1}\text{H}) = 2.1$ Hz]; 1.8–1.9 [m, 2H, H-5(11), H-7]; 2.28 [dd, 1H, H-3, $^{2}J(^{1}\text{H},^{1}\text{H}) = 17.3$ Hz, $^{3}J(^{1}\text{H},^{1}\text{H}) = 4.3$ Hz]; 2.4 (m, 3H, H-4,6,8); 2.76 [dd, 1H, H-3, $^{2}J(^{1}\text{H},^{1}\text{H}) = 17.3$ Hz, $^{3}J(^{1}\text{H},^{1}\text{H}) = 4.4$ Hz]. ^{13}C NMR (125.8 MHz): $\delta^{13}\text{C} = 1.1$ [Me$_3$Si, $^{1}J(^{29}\text{Si},^{13}\text{C}) = 50.9$ Hz]; 30.2 (C-4), 33.6 (C-6,8), 33.7 (C-8,6), 34.2 (broad, C-9,10), 34.6 [C-3, $^{3}J(^{29}\text{Si},^{13}\text{C}) = 7.0$ Hz], 34.7 (broad, C-10,9), 36.7 (C-5,11), 37.2 (C-7), 37.3 (C-11,5), 84.0 [=CBr$_2$, $^{3}J(^{29}\text{Si},^{13}\text{C}) = 4.8$ Hz]; 133.3 [=C–Si, $^{1}J(^{29}\text{Si},^{13}\text{C}) = 69.3$ Hz]; 150.5 [=C–, $^{2}J(^{29}\text{Si},^{13}\text{C}) = 4.6$ Hz]; 168.0 (broad, C-2). ^{11}B NMR (160.5 MHz): $\delta^{11}\text{B} = 77.2$. ^{29}Si NMR (99.4 MHz): $\delta^{29}\text{Si} = -2.5$.

X-Ray structural analysis of the triene 3

The X-ray crystal structural analysis of **3** was carried out on a single crystal, 0.16 × 0.18 × 0.26 mm^3, fixed in a sealed capillary at 293(2) K using a STOE IPDS I system; λ:

0.71073 Å. $C_{30}H_{48}B_2Br_2Si_2$, $M = 646.30$, Crystal system triclinic, space group P-1, $a = 10.654(2)$ Å, $b = 11.325(2)$ Å, $c = 13.663(3)$ Å, $\alpha = 97.60(3)^\circ$, $\beta = 102.17(3)^\circ$, $\gamma = 92.70(3)^\circ$, $V = 1592.5(5)$ Å^3, $Z = 2$, $\mu = 2.638$ mm^{-1}, $\theta_{max} = 25.9^\circ$. Reflections collected = 7769, independent reflections = 4735 [R_{int} = 0.065]. Data/parameters: 4735/325. GoF on $F^2 = 0.93$. Final R indices [3009 data with $I > 2\sigma(I)$]: $R = 0.057$ $wR^2 = 0.133$; R indices (all data): $R = 0.094$, $wR^2 = 0.148$. CCDC deposition no. 602111.

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