1,2-Hydroboration of Alkyn-1-yldichlorosilanes using Triethylborane

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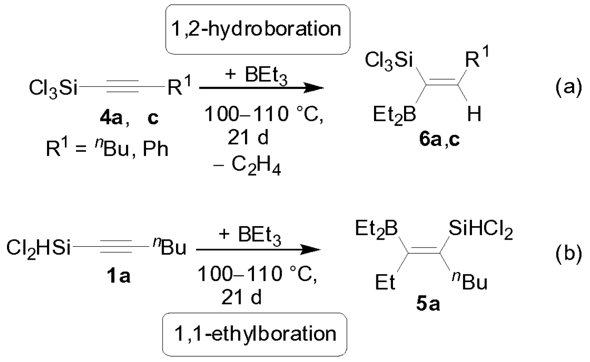
Triethylborane, BEt_3, can act as a 1,2-hydroborating reagent towards alkyn-1-ylsilanes, depending on the nature of the silane. A mechanism is proposed invoking hydrogen transfer from the β-carbon of one ethyl group, quite different from the 1,2-hydroboration mechanism using tri-*n*-propylborane, B^nPr_3. The structure of the products has been confirmed by comparison with that obtained using 9-borabicyclo[3.3.1]nonane, 9-BBN, as a well established 1,2-hydroborating reagent. All products have been characterized by a consistent set of NMR data (^1H, ^{11}B, ^{13}C and ^{29}Si NMR). The molecular structure of (*Z*)-1-dichlorosilyl-1-[9-(9-borabicyclo[3.3.1]nonyl)]-2-phenylethene has been determined by single crystal X-ray diffraction.

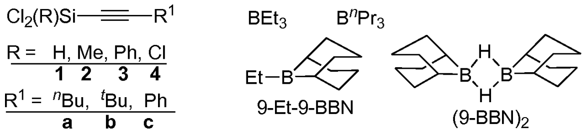
Key words: Alkynes, Alkenes, Triethylborane, 9-BBN, Silanes, Hydroboration, NMR

Introduction

Triethylborane, BEt_3, has been considered for a long time as thermally robust [1 – 6], and 1,2-dehydroboration, common for many other trialkylboranes, to give ethene and Et_2BH *via* β-hydrogen elimination had not been observed [1, 5, 6]. This is in strong contrast with tri-*n*-propylborane, B^nPr_3, which slowly forms propene and $^nPr_2BH$ at temperatures > 80 °C [4]. So far, we have used BEt_3 frequently for 1,1-ethylboration reactions of organometallic-substituted alkynes [7, 8]. In order to induce 1,1-ethylboration reactions of alkyn-1-ylsilanes, heating of a large excess of BEt_3 with the respective alkyn-1-ylsilane was required for prolonged periods of time at about 100 °C. Although this led to cleavage of the B–C(Et) bond, evidence for 1,2-dehydroboration and/or formation of ethene was missing [9 – 12]. Recently, however, we observed [13] that trichloro(hexyn-1-yl)silane, $Cl_3Si–C≡C–^nBu$, and trichloro(phenylethynyl)silane, $Cl_3Si–C≡C–Ph$, react with BEt_3 by 1,2-hydroboration and elimination of ethene (Scheme 1a). In contrast, the reaction of dichloro(hexyn-1-yl)silane, $Cl_2(H)Si–C≡C–^nBu$, with BEt_3 (Scheme 1b) affords the 1,1-ethylboration product in essentially quantitative yield [12].



Scheme 1. BEt_3 as a 1,2-hydroborating reagent (a) *versus* BEt_3 in 1,1-ethylboration (b).



Scheme 2. Alkyn-1-ylsilanes and boranes used in this study.

The stereo- and regioselective 1,2-hydroboration (Scheme 1a) was readily confirmed, since the reaction of $Cl_3Si–C≡C–^nBu$ with B^nPr_3 or 9-borabicyclo[3.3.1]nonane, 9-BBN, gave the analogous products [13]. In the present study, we have investigated the reactivity of alkyn-1-yl(dichloro)silanes $Cl_2(R)Si–C≡C–R^1$ towards various triorganoboranes (Scheme 2). It was hoped to reveal the relative influence of R and R^1 on the reaction type, 1,1-organoboration *versus* 1,2-hydroboration.

Results and Discussion

Alkyn-1-ylsilanes

The alkyn-1-yl(chloro)silanes **1** – **4** were prepared [12 – 14] from the reactions of $RSiCl_3$ with the alkynyl

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Table 1. ^{11}B, ^{13}C and ^{29}Si NMR data[a] of the alkenes **6**–**8**.

	δ^{13}C(BC=)	δ^{13}C(C=)	δ^{13}C(R^1)	δ^{13}C(BEt$_2$)	δ^{11}B	δ^{29}Si
6a[b]	145.1(br) [88.2]	154.9	35.5, 31.3, 22.6, 14.3	21.7 (br), 8.9	82.8	−7.8
6a’	n. o. (br)	164.8	33.6, 31.0, 22.5, 14.1	n. o. (br), 9.0	82.8	−5.8
6c[b]	147.0 (br) [90.5]	151.6	138.2 (*i*), 129.6 (*o*), 128.5 (*m*), 129.3 (*p*)	21.3 (br), 8.9	83.8	−0.5
6c’	147.8 (br)	161.1	137.9 (*i*), 129.6 (*o*), 128.7 (*m*) 130.4 (*p*)	21.6 (br), 8.9	83.0	−6.9
7c	147.8 (br)	164.1	140.1 (*i*), 129.5 (*o*), 128.4 (*m*), 132.6 (*p*)	21.7 (br), 9.4	86.8	−7.7
8c	141.9 (br) [78.5]	160.8	138.0 (*i*) [7.1], 129.6 (*o*), 130.3 (*p*), 128.7 (*m*)	34.5, 31.3 (br), 23.6 (BBN)	82.4	−6.4

[a] Measured in C$_6$D$_6$ at 23 °C; (br) indicates a broad NMR signal owing to partially relaxed ^{13}C-^{11}B scalar coupling [15]; some coupling constants $J(^{29}\text{Si},^{13}\text{C})$ [±0.4 Hz] are given in square brackets; [b] data from ref. [13].

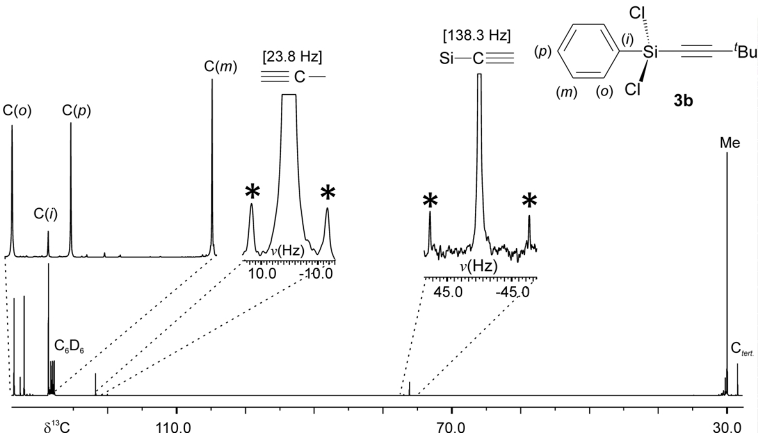
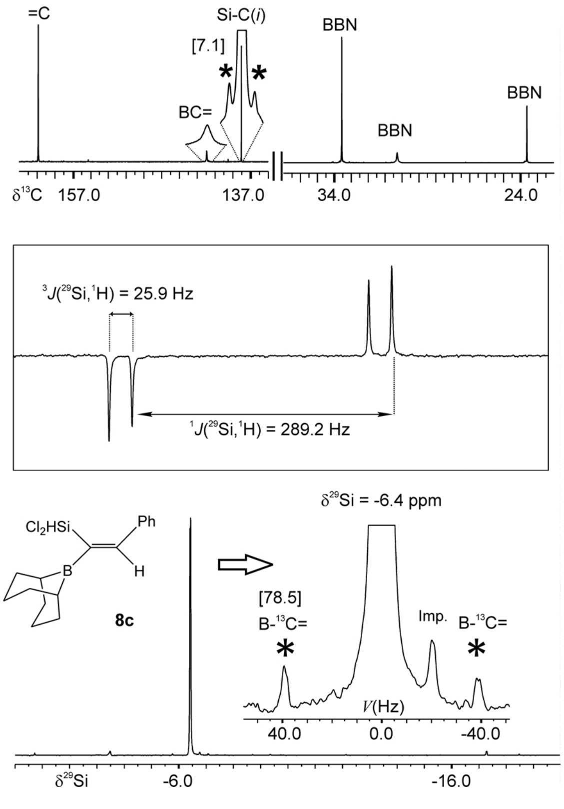


Fig. 1. 100.5 MHz ^{13}C{^{1}H} NMR spectrum of 3,3-dimethylbutyn-1-yl(dichloro)(phenyl)silane **3b** in C$_6$D$_6$; in expanded parts satellites are marked by asterisks and correspond to $^1J(^{29}\text{Si},^{13}\text{C})$ and $^2J(^{29}\text{Si},^{13}\text{C})$.

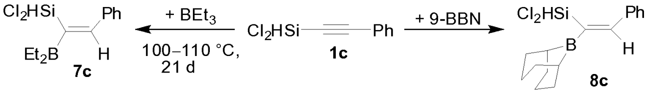


←— Fig. 2. NMR spectra of the alkene **8c** in C$_6$D$_6$ [expanded parts show satellite signals, marked by asterisks, corresponding to $J(^{29}\text{Si},^{13}\text{C})$]: Upper trace: Part of the 100.5 MHz ^{13}C{^{1}H} NMR spectrum. Middle trace (inserted): 59.6 MHz ^{1}H-coupled ^{29}Si NMR spectrum (INEPT [20]). Lower trace: ^{29}Si{^{1}H} NMR spectrum (INEPT [20]).

lithium reagents Li–C≡C–^{n}Bu (**a**), Li–C≡C–^{t}Bu (**b**) or Li–C≡C–Ph (**c**), characterized by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy (*e. g.* Fig. 1) and purified by fractional distillation.

*Reaction of dichloro(phenylethynyl)silane **1c** with triethylborane*

According to Scheme 1b [12], it was expected that the reaction of **1c** with BEt$_3$ proceeds *via* 1,1-ethylboration. However, it was found that the exchange of R^1 = ^{n}Bu in **1a** against R^1 = Ph in **1c** caused a complete reversal of the reaction to give the 1,2-hydroboration product **7c** instead in essentially quantitative yield. A small amount (< 10 %) of **7c’**, the (*E*)-isomer, was formed along with **7c**. The structure of **7c** follows conclusively from the consistent set of NMR data (Table 1). The analogous 1,2-hydroboration product **8c** was obtained from **1c** using 9-BBN as the 1,2-hydroborating reagent (Scheme 3). The NMR data of **8c** (Ta-



Scheme 3. Reaction of dichloro(phenylethynyl)silane **1c** with BEt_3 and with 9-BBN affording the analogous product.

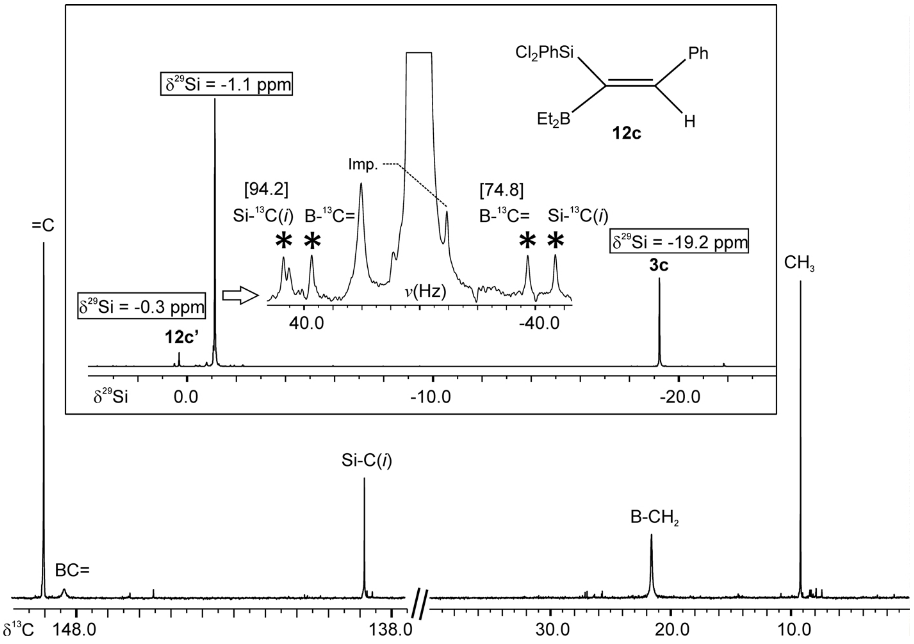
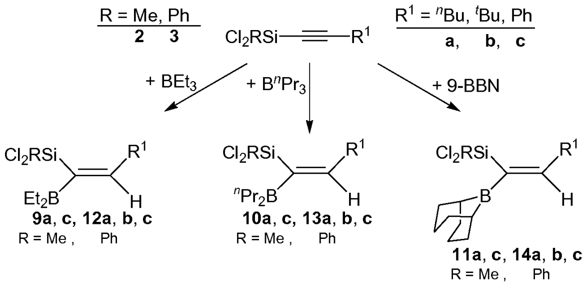


Fig. 3. 100.5 MHz $^{13}C\{^1H\}$ NMR spectrum of **12c**, showing the typical pattern in the olefinic region and two signals for the BEt_2 group. The absence of other ^{13}C(alkyl) NMR signals clearly rules out 1,1-ethylboration. Insert: $^{29}Si\{^1H\}$ NMR spectrum (refocused INEPT [20]) of the reaction solution (after addition of C_6D_6) containing the alkene **12c** and some of the dichloro(phenyl)(phenylethynyl)silane **3c** along with a small amount of the (*E*)-isomer **12c'**. Satellites are marked by asterisks and correspond to $J(^{29}Si,^{13}C)$ as indicated.

ble 1, Fig. 2) correspond to those of **7c**, and **8c** was also characterized in the solid state by X-ray diffraction (*vide infra*).

*Reactions of alkyn-1-yl(dichloro)(organo)silanes **2** and **3** with triethyl- and tri-n-propylborane and with 9-BBN*

From these reactions, the alkenes **9** and **12** are formed in high yield (Scheme 4, Fig. 3), accompanied by small amounts ($<$ 10 %) of the corresponding (*E*)-isomers. The analogous reactions with B^nPr_3, under milder conditions, afford the alkenes **10** and **13** as mixtures with the respective (*E*)-isomers in variable amounts (up to 30 %), and a small amount of dialkenyl(*n*-propyl)boranes. The 1,2-hydroboration of **2** and **3** with 9-BBN gives the pure alkenes **11** and **14** in essentially quantitative yield. The NMR data (Tables 2 and 3) are in agreement with the proposed structures.



Scheme 4. Reactions of alkyn-1-yl(dichloro)organosilanes **2** and **3** with BEt_3, B^nPr_3 and 9-BBN leading mainly to alkenes with analogous structures.

*Reactions of dichloro(hexyn-1-yl)(phenyl)silane **3a** and trichloro(hexyn-1-yl)silane **4a** with 9-ethyl-9-borabicyclo[3.3.1]nonane*

9-Ethyl-9-borabicyclo[3.3.1]nonane, 9-Et-9-BBN, usually does not undergo 1,2-dehydroboration or decomposition at temperatures $<$ 150 °C even after pro-

Table 2. ^{11}B, ^{13}C and ^{29}Si NMR data[a] of the alkenes **9 – 11**.

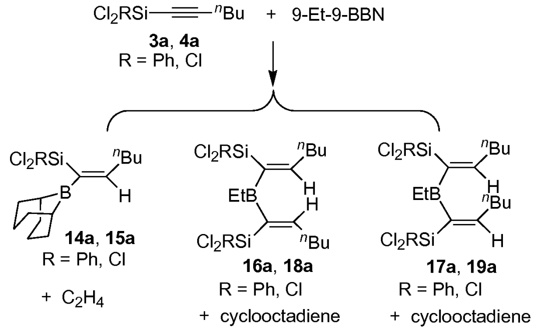
	δ ^{13}C(BC=)	δ ^{13}C(C=)	δ ^{13}C(R^1)	δ ^{13}C(Si-Me)	δ ^{13}C(BR$_2$)	δ ^{11}B	δ ^{29}Si
9a	147.1 (br)	150.5	35.5, 31.7, 22.7, 14.2	8.5 [67.8]	21.7 (br), 9.0 (BEt$_2$)	83.2	12.7
9c	151.4 (br) [72.7]	147.5	139.3 [*i*, 6.8], 132.6 (*o*), 128.9 (*p*), 128.6 (*m*)	7.2 [69.4]	21.2 (br), 9.0 (BEt$_2$)	83.6	12.4
10a	147.6 (br)	151.0	35.4, 31.7, 22.7, 14.2	8.7 [67.6]	32.8 (br), 18.8, 17.6 (B^{n}Pr$_2$)	82.9	13.0
10a’	145.7 (br)	161.2	35.5, 31.7, 22.1, 14.1	7.5	32.8 (br), 18.9, 17.7 (B^{n}Pr$_2$)	82.9	14.6
10c	152.2 (br)	147.6	139.8, 139.8, 132.6, 130.2	6.2 [70.9]	32.3 (br), 18.8, 17.4 (B^{n}Pr$_2$)	82.8	14.0
10c’	151.4 (br)	146.7	128.6, 128.5, 129.1, 128.9[b]	7.2 [69.2]	30.1 (br), 18.5, 17.4 (B^{n}Pr$_2$)	82.8	14.3
11a	143.6 (br) [76.2]	163.8	35.3, 31.4, 22.7, 14.1	9.2 [66.5]	34.4, 31.5 (br), 23.4 (BBN)	81.3	16.2
11c	147.6 (br) [76.7]	156.7	139.5 (*i*), 129.6 (*p*), 129.1 (*o*), 128.5 (*m*)	8.0 [68.8]	34.7, 31.8 (br), 23.6 (BBN)	82.9	15.8

[a] Measured in C_6D_6 at 23 °C; (br) indicates a broad NMR signal owing to partially relaxed ^{13}C-^{11}B scalar coupling [15]; some coupling constants $J(^{29}\text{Si},^{13}\text{C})$ [±0.4 Hz] are given in square brackets; [b] phenyl carbons without assignment.

Table 3. ^{11}B, ^{13}C and ^{29}Si NMR data[a] of the alkenes **12 – 14**.

	δ ^{13}C(BC=)	δ ^{13}C(C=)	δ ^{13}C(R^1)	δ ^{13}C(BR$_2$)	δ ^{11}B	δ ^{29}Si
12a[b]	145.6 (br) [74.2]	152.5	36.0, 31.4, 22.6, 14.1	22.0 (br), 9.1 (BEt$_2$)	83.5	−0.4
12a’[c]	144.2 (br)	162.3	36.2, 33.3, 22.2, 13.6	20.8 (br), 9.4 (BEt$_2$)	83.5	1.4
12b[d]	139.4 (br) [77.2]	159.1	38.0, 29.9	21.9 (br), 9.4 (BEt$_2$)	82.1	−1.0
12c	148.3 (br) [74.8]	149.0 [18.7]	138.8, 133.6, 133.7, 132.7, 132.1, 128.7, 128.1, 127.8[e]	21.6 (br), 9.2 (BEt$_2$)	83.6	−1.2
13a[f]	146.1 (br)	152.9	35.9, 31.4, 22.6, 14.1	32.9 (br), 18.9, 17.7 (B^{n}Pr$_2$)	82.5	−0.2
13a’[g]	145.2 (br)	151.5	36.1,31.1, 22.6, 14.0	33.4(br), 19.0, 17.8 (B^{n}Pr$_2$)	82.5	1.3
13b[h]	140.1 (br)	159.2	38.0 [5.1], 30.1	33.0 (br), 19.1, 17.8 (B^{n}Pr$_2$)	82.4	−1.0
13b’[i]	138.9 (br)	159.0	38.2, 30.2	33.0, 19.0, 17.7 (B^{n}Pr$_2$)	82.4	−1.1
13c	149.3 (br) [74.8]	149.1 [74.8]	138.9, 133.6, 132.3, 131.1, 129.1, 128.7	32.7 (br), 19.0, 17.9 (B^{n}Pr$_2$)	80.2	−1.2
13c’	148.6 (br)	148.3	128.2, 128.1[e]	32.7, 18.6, 17.7 (B^{n}Pr$_2$)	80.2	0.1
14a[j]	141.6 (br)	164.8	35.3, 30.9, 22.4, 13.9	34.0, 31.2 (br), 23.0 (BBN)	82.7	3.4
14b[k]	139.5 (br) [80.1]	170.9	37.8 [4.4], 30.1	34.9, 32.4 (br), 23.5 (BBN)	82.3	2.4
14c[j]	143.9 (br)	158.6 [79.2]	125.4 (*i*), 129.4(*o*), 127.9(*m*), 132.7(*p*)	34.3, 31.6 (br), 23.1(BBN)	83.6	2.2

[a] Measured in C_6D_6 at 23 °C; (br) indicates a broad NMR signal owing to partially relaxed ^{13}C-^{11}B scalar coupling [15]; some coupling constants $J(^{29}\text{Si},^{13}\text{C})$ [±0.4 Hz] are given in square brackets; [b] other ^{13}C NMR data: δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = 135.1 [91.8] (*i*), 133.7 (*o*), 131.6 (*p*), 128.6 (*m*) (Si-Ph); [c] other ^{13}C NMR data: δ = 134.7 (*i*), 133.7 (*o*), 131.2 (*p*), 128.4 (*m*) (Ph); [d] other ^{13}C data: δ = 136.5 (*i*), 133.6 (*o*), 131.5 (*p*), 128.5 (*m*) (Si-Ph); [e] Ph carbons without assignment; [f] other ^{13}C data: δ = 133.7 (*i*), 133.6 (*o*), 132.1 (*p*), 128.6 (*m*) (Ph); [g] other ^{13}C NMR data: δ = 133.8 (*i*), 133.6 (*o*), 131.6 (*p*), 128.6 (*m*) (Ph); [h] other ^{13}C data: δ [$J(^{29}\text{Si}, ^{13}\text{C})$] = 136.4 [93.7] (*i*), 133.6 (*o*), 132.8 (*m*), 128.5 (*p*) [Si-Ph]; [i] due to low concentration other carbons could not be assigned correctly; [j] data taken from ref. [16]; [k] other ^{13}C data: δ = 136.6 [92.7] (*i*), 133.8 (*o*), 131.4 (*p*), 128.5 (*m*) [Ph].



Scheme 5. Reactions of dichloro(hexyn-1-yl)(phenyl)silane **3a** and trichloro(hexyn-1-yl)silane **4a** with 9-ethyl-9-borabicyclo[3.3.1]nonane affording exclusively 1,2-hydroboration products.

longed periods of heating without a solvent [5]. However, in the presence of the alkyn-1-ylsilanes **3a** or **4a** reactions take place to give mixtures of three products, *viz.* **14a/ 16a/ 17a** and **15a/ 18a/ 19a**, respectively (Scheme 5). The different alkenes are readily identified by their consistent NMR data sets (Table 4, Fig. 4). Two alkenes are formed in major quantity by 1,2-hydroboration and loss of cyclooctadiene, and the minor component results from 1,2-hydroboration and elimination of ethene.

Mechanism

There is no doubt in the case of B^{n}Pr$_3$ that it slowly decomposes upon heating > 80 °C *via* 1,2-dehydroboration into propene and ^{n}Pr$_2$BH which then reacts with alkynes or alkenes in the usual way as a 1,2-hydroborating reagent [3, 4]. In contrast, even under much more harsh conditions, BEt$_3$ or 9-Et-9-BBN do not undergo elimination of ethene to give dialkylboron hydrides Et$_2$BH or 9-BBN. Nevertheless, BEt$_3$ and 9-Et-9-BBN act as hydroborating reagents in the

Table 4. ^{11}B, ^{13}C and ^{29}Si NMR data[a] of the alkenes **15 – 18**.

	δ ^{13}C(BC=)	δ ^{13}C(C=)	δ ^{13}C(R^1)	δ ^{13}C(BEt$_2$/BBN)	δ ^{11}B	δ ^{29}Si
15a	144.1 (br)	162.2	35.9, 31.1, 22.6, 14.0	19.9 (br), 9.1	83.2	1.2
16a	n. a.	164.8	35.6, 31.0, 22.7, 14.0	20.2 (br), 8.9	82.2	−5.9
17a	145.5, 143.3	166.0, 152.6	36.2, 35.9, 31.4, 30.8, 22.8, 22.5, 14.2, 14.1	19.9 (br), 10.5	83.2	1.6, −0.6
18a	n. a.	167.9, 154.9	35.9, 35.5, 31.3, 30.7, 22.8, 22.6, 14.1, 14.0	20.2 (br), 10.3	82.2	−7.8, −5.6

[a] Measured in C_6D_6 at 23 °C; n. a. denotes not assigned; (br) indicates a broad NMR signal owing to partially relaxed ^{13}C-^{11}B scalar coupling [15].

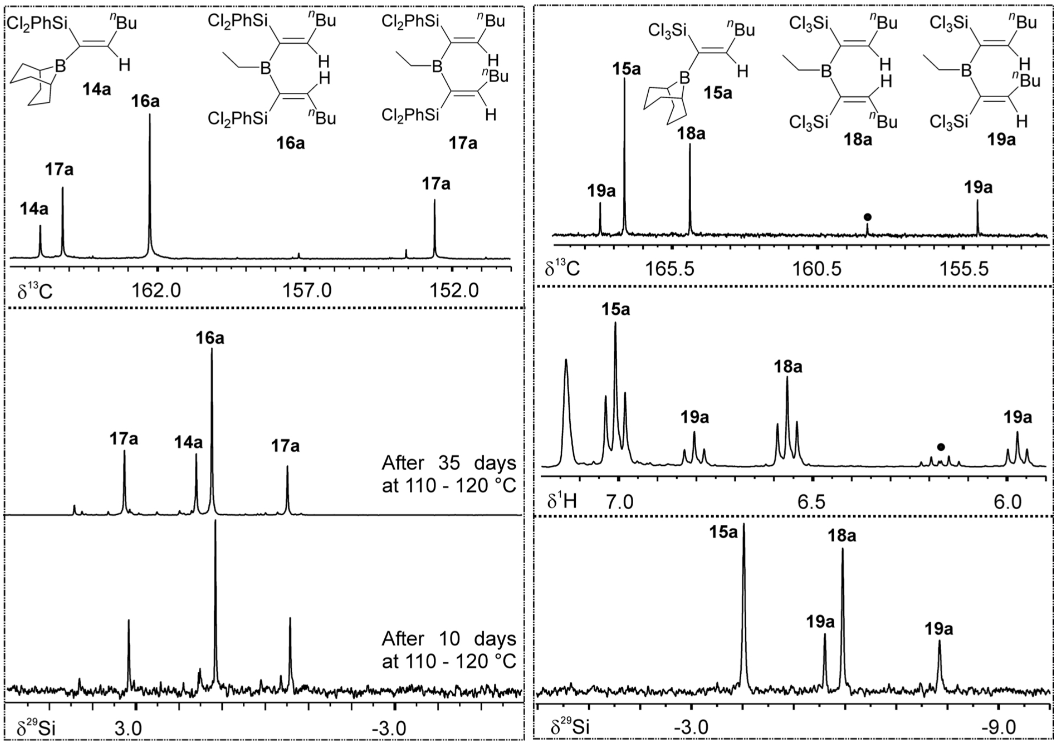
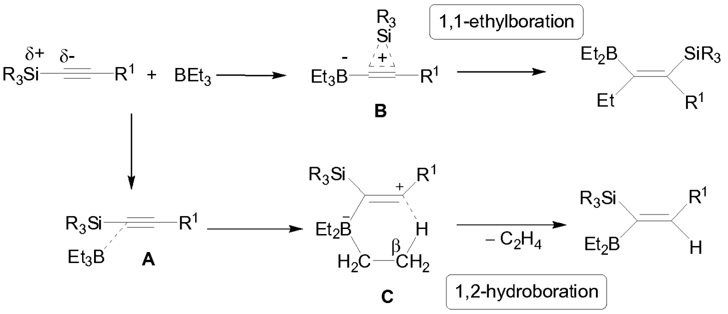


Fig. 4. NMR spectra of the mixtures (in C_6D_6) obtained from the reactions shown in Scheme 5. Upper traces: Olefinic regions (=CH) of the 100.5 MHz, ^{13}C{^{1}H} NMR spectra for the mixtures of **14a**/ **16a**/ **17a** and **15a**/ **18a**/ **19a**. Middle trace (right): 400 MHz ^{1}H(=CH) NMR spectrum for the mixture of compounds **17a**/ **18a**/ **19a**. Middle trace (left) and lower trace: 59.6 MHz ^{29}Si{^{1}H} of the mixtures **14a**/ **16a**/ **17a** and **15a**/ **18a**/ **19a** solution in C_6D_6.

presence of certain alkyn-1-ylsilanes. An explanation is offered in Scheme 6, where the first interaction (**A**) between the borane and the alkyn-1-ylsilane is the same for 1,1-ethylboration and 1,2-hydroboration. Cleavage of the Si–C≡ bond leads to a borate-like zwitterionic intermediate **B** [7] and finally to 1,1-ethylboration [7 – 12]. If the Si–C≡ bond is particularly strong, cleavage of this bond does not occur, leaving alternative routes for the subsequent steps. In particular for substituents R^1 capable of delocalizing a positive charge (*e. g.* R^1 = Ph), an intermediate **C** is stabilized, and transfer of a hydrogen atom from the β-carbon atom is favored to give the 1,2-hydroboration product accompanied by elimination of ethene. Compelling evidence for the influence of R^1 is provided by comparison of the reaction of **1a** (Scheme 1b, 1,1-ethylboration) and **1c** with BEt$_3$ (Scheme 3, 1,2-hydroboration). The β-hydrogen transfer in Scheme 6 reminds of the processes proposed for limiting the chain lengths of polymers, in the chemistry of aluminum alkyls [17]. It may also be important in the catalyzed high-temperature alkane isomerization of alkanes caused by carbenium ions [18] which are isoelectronic with boranes.



Scheme 6. Proposed mechanism for the reactivity of BEt_3 as a hydroborating agent towards certain alkyn-1-ylsilanes in competition with 1,1-ethylboration.

*X-Ray structural analysis of the alkene **8c***

The molecular structure of the alkene **8c** is shown in Fig. 5 together with selected structural parameters. The main structural features are similar to those already published for similar alkenes [16, 19]. The CBC plane of the 9-borabicyclo[3.3.1]nonyl group is twisted by 37°, and the Ph plane (C11–C16) by 41.9°, against the Si(B)C=C plane. The surroundings of the boron atom are trigonal planar within the experimental error. Thus, the structure of **8c** does not indicate Si–Cl···B or Si–H···B interactions in the solid state in spite of the spatial proximity of the silyl and boryl groups. This has been observed previously [16, 19] and is consistent with the absence of such interactions in solution. As for other structural constraints, marked Si–H···B interactions have been observed both in the solid state and in solution [21].

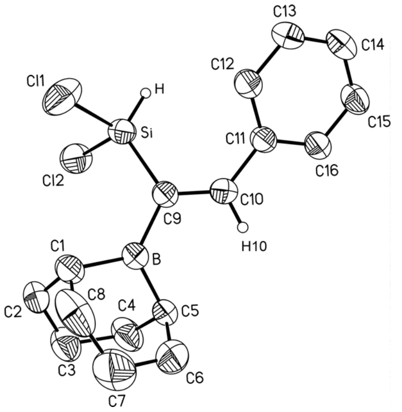


Fig. 5. Molecular structure of **8c** (ORTEP, displacement ellipsoids at the 40 % probability level; hydrogen atoms omitted for clarity except those attached to Si and C=C which were drawn as spheres with arbitrary radius). Selected bond lengths (pm) and angles (deg.): Cl1–Si 203.7(2), Cl2–Si 206.2(2), Si–C9 185.1(3), C9–C10 134.8(4), C10–C11 147.8(4), C11–C12 138.7(4), B–C1 157.3(5), B–C5 154.8(5), B–C9 156.9(5); C9–Si–Cl1 113.8(1), C9–Si–Cl2 107.6(1), Cl1–Si–Cl2 106.3(1), C10–C9–B 117.4(3), C10–C9–Si 122.4(2), B–C9–Si 120.1(2), C9–C10–C11 130.5(3), C12–C11–C10 123.3(3), C5–B–C9 124.0(3), C5–B–C1 110.6(3), C9–B–C1 125.4(3).

Experimental Section

All preparative work was carried out by observing necessary precautions to exclude traces of oxygen and moisture. Tetrachlorosilane, trichlorosilane, trichloro(methyl)silane, trichloro(phenyl)silane, 1-hexyne, 3,3-dimethylbut-1-yne, ethynylbenzene, *n*-butyllithium in hexane (1.6 M), triethylborane (BEt_3), and 9-borabicyclo[3.3.1]nonane (9-BBN) were used as commercial products without further purification. NMR spectra: Varian Inova 300 and 400 spectrometers (23 °C), both equipped with multinuclear units, using C_6D_6 solutions (*ca.* 5 – 10 % v/v) in 5 mm tubes. Chemical shifts are given with respect to $SiMe_4$ [δ^1H (C_6D_5H) = 7.15, δ^{13}C (C_6D_6) = 128.0, δ^{29}Si = 0 for $SiMe_4$ with $\Xi(^{29}Si)$ = 19.867187 MHz], and δ^{11}B = 0 for BF_3-OEt_2 with $\Xi(^{11}B)$ = 32.083971 MHz. ^{29}Si NMR spectra were recorded using the refocused INEPT pulse sequence with ^{1}H decoupling [20], based either on $^1J(^{29}Si,^1H) \approx 280$ Hz or $^3J(^{29}SiC{=}C^1H) \approx$ 25 – 35 Hz (after optimization of the refocusing delay). Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet (data for ^{1}H, ^{11}B, ^{12}C, ^{35}Cl, ^{28}Si).

*Synthesis of silanes **1**, **2**, **3** and **4***

A suspension of $R^1C{\equiv}CLi$ (R^1 = ^{n}Bu, ^{t}Bu, Ph; 25 mmol) in hexane (60 mL) was freshly prepared, and the solution was cooled to −78 °C. Then the respective chlorosilane was added (in 6 – 8 fold excess) slowly with constant stirring. The reaction mixture was warmed to r. t. and kept stirring for 3 – 4 h. Insoluble materials were filtered off, and volatiles were removed in a vacuum. The colorless oily residue was identified as a mixture of silanes, from which the pure desired silanes were obtained by fractional distillation. **3b**: b. p. 74 – 76 °C (2×10^{-2} mbar). – ^{1}H NMR (400 MHz): δ = 0.9 (s, 9H, ^{t}Bu), 7.1, 7.4 (m, m, 5H, Si-Ph). – ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 132.7 [80.2] (*i*-C), 133.3 (*o*-C), 132.2 (*p*-C), 128.6 (*m*-C) (Ph-Si); 121.8 [23.8] (≡C); 76.2 [138.3] (Si–C≡); 30.0, 28.5 (^{t}Bu). – ^{29}Si NMR: δ = −19.8. For the other silanes see refs. [12, 13].

*Hydroboration of the dichloro(phenylethynyl)silane **1c** with BEt$_3$ and 9-BBN*

An NMR tube was charged with dichloro(phenylethynyl)silane **1c** (0.37 g, 1.8 mmol) and BEt$_3$ was added in excess. The tube was sealed and kept at 110 – 120 °C for 3 d. The reaction was monitored from time to time by ^{29}Si NMR. After the reaction was complete, the NMR tube was cooled in liquid nitrogen and was opened carefully. All the volatiles were removed, and the oily compound left was identified as **7c** (yield 80 %). – ^{1}H NMR (400 MHz): δ = 0.9, 1.4 (t, q, 6H, 4H, BEt$_2$), 5.6 (s, 1H, $^1J(^{29}\text{Si},^1\text{H})$ = 292.4 Hz, Si–H), 6.9 – 7.1 (m, 5H, 1H, Ph, =C–H). The reaction conditions for the synthesis of **8c** were less harsh. An NMR tube was charged with the silane **1c** (0.568 g, 2.83 mmol) dissolved in C$_6$D$_6$, and 9-BBN (0.356 g, 2.83 mmol) was added in one portion. The reaction mixture was heated at 80 – 100 °C for 30 min. The oily liquid was characterized as **8c**, the yield being approximately 99 % from NMR spectroscopy. **8c** (yield after recrystallization 91 %; m. p. = 42 – 45 °C). – ^{1}H NMR (400 MHz): δ = 1.4 – 2.2 (m, 14H, BBN), 5.8 (s, 1H, $^1J(^{29}\text{Si},^1\text{H})$ = 289.2 Hz, SiH), 7.2, 7.4 (m, m, 5H, Ph), 8.1 (s, 1H, $^3J(^{29}\text{Si},^1\text{H})$ = 25.9 Hz, =CH).

*Hydroboration of the alkyn-1-yl(dichloro)(methyl)silanes **2** with BEt$_3$, B^{n}Pr$_3$ and 9-BBN*

Silane **2a** (0.32 g, 1.6 mmol) was given into an NMR tube, and BEt$_3$ (0.8 mL) as solvent was added, after which the NMR tube, was sealed. The reaction mixture was kept at 110 – 120 °C for 19 d. After the reaction was completed, the NMR tube was cooled in liquid N$_2$, opened, warmed to r. t., and volatile materials were removed in a vacuum. The oily residue was identified as **9a** (yield 85 % from ^{1}H NMR spectra). An analogous procedure was adopted for the synthesis of **9c**, **10a** and **10c** (except for the reaction time): **9c** (14 d), **10a** (7 d) and **10c** (10 d). In the case of hydroboration with 9-BBN, the reaction was complete after 4 – 8 h at r. t. in THF or after 15 min in C$_6$D$_6$ at 80 °C.

9a: ^{1}H NMR (400 MHz): δ = 0.7 (s, 3H, Si-Me, $^2J(^{29}\text{Si},^1\text{H})$ = 7.4 Hz), 1.2, 1.0 (m, t, 10H, BEt$_2$), 2.2, 1.1, 0.8 (q, m, t, 9H, ^{n}Bu), 5.9 (t, 1H, =CH, $^3J(^{29}\text{Si},^1\text{H})$ = 26.7 Hz, $^3J(^1\text{H}, ^1\text{H})$ = 7.4 Hz). – EI-MS: *m/z* (%) = 265 (36) [M]$^+$, 250 (11) [M–Me]$^+$, 229 (27) [M–Cl]$^+$, 207 (15) [M–Bu]$^+$, 196 (10) [M–BEt$_2$]$^+$, 151 (12) [M–Si(Me)Cl$_2$]$^+$, 43 (87) [C$_3$H$_7$]$^+$, 41 (100) [C$_3$H$_5$]$^+$.

9c: ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, SiMe, $^2J(^{29}\text{Si},^1\text{H})$ = 8.6 Hz), 1.2, 0.8 (q, t, 10H, BEt$_2$), 6.8 – 7.0 (m, 5H, Ph), 6.7 (s, 1H, =CH, $^3J(^{29}\text{Si},^1\text{H})$ = 26.3 Hz). – EI-MS: *m/z* (%) = 185 (29) [M]$^+$, 270 (35) [M–CH$_3$]$^+$, 257 (30) [M–C$_2$H$_5$]$^+$, 216 (11) [M–BEt$_2$]$^+$, 207 (69), 171 (27) [M–MeSiCl$_2$]$^+$, 113 (82), 102 (32), 103 (47), 91 (100).

10a: ^{1}H NMR (400 MHz): δ = 0.7 (s, 3H, $^2J(^{29}\text{Si},^1\text{H})$ = 7.4 Hz, SiMe), 0.8, 1.3, 2.2 (t, m, q, 9H, Bu), 1.0, 1.3 (t, m, 14H, B^{n}Pr$_2$), 6.0 (t, 1H, $^3J(^1\text{H},^1\text{H})$ = 7.5 Hz, $^3J(^{29}\text{Si},^1\text{H})$ = 34.7 Hz, =CH).

10a’: ^{1}H NMR (400 MHz): δ = 0.6 (s, 3H, $^2J(^{29}\text{Si}, ^1\text{H})$ = 7.6 Hz, Si-Me), 0.8, 1.3, 2.4 (t, m, q, 9H, Bu), 1.0, 1.3 (t, m, 14H, B^{n}Pr$_2$), 6.5 (t, 1H, $^3J(^1\text{H},^1\text{H})$ = 7.5 Hz, $^3J(^{29}\text{Si},^1\text{H})$ = 32.7 Hz, =CH).

10c: ^{1}H NMR (400 MHz): δ = 0.39 (s, 3H, $^2J(^{29}\text{Si}, ^1\text{H})$ = 7.5 Hz, SiMe), 1.0, 1.4, 1.6 (t, m, m, B^{n}Pr$_2$), 6.9 – 7.4 (m, Ph, =CH).

10c’: ^{1}H NMR (400 MHz): δ = 0.38 (s, 3H, SiMe), 1.0, 1.4, 1.6 (t, m, m, B^{n}Pr$_2$), 6.9 – 7.4 (m, Ph).

11a: ^{1}H NMR (400 MHz): δ = 7.0 (t, 1H, =CH, $^3J(^1\text{H},^1\text{H})$ = 7.2 Hz), 2.4, 1.1 – 1.3, 0.8 (q, m, t, 9H, ^{n}Bu), 1.3 – 1.9 (m, 14H, BBN), 0.6 (s, 3H, Si-Me). – EI-MS: *m/z* (%) = 317 (35) [M]$^+$, 316 (91) [M–H]$^+$, 281 (5) [M–Cl]$^+$, 274 (22) [M–C$_3$H$_7$]$^+$, 260 (12) [M–Bu]$^+$, 113 (63), 110 (43), 67 (100).

11c: ^{1}H NMR (400 MHz): δ = 0.1 (s, 3H, SiMe, $^2J(^{29}\text{Si}, ^1\text{H})$ = 7.3 Hz), 1.1 – 1.9 (m, 14H, 9-BBN), 7.6 (s, 1H, =CH, $^3J(^{29}\text{Si},^1\text{H})$ = 25.6 Hz), 6.8 – 7.1 (m, 5H, Ph). – EI-MS: *m/z* (%) = 337 (37) [M]$^+$, 336 (99) [M–H]$^+$, 258 (41), 223 (100) [M–MeSiCl$_2$]$^+$, 216 (71) [M–C$_8$H$_{14}$B]$^+$, 201 (44), 181 (28), 165 (52), 138 (37), 113 (18) [Si(Cl)$_2$Me]$^+$.

*Hydroboration of the alkyn-1-yl(dichloro)(phenyl)silanes **3** with BEt$_3$, B^{n}Pr$_3$ and 9-BBN*

Silane **3a** (0.26 g, 1.0 mmol) and BEt$_3$ (0.8 mL) as solvent were mixed in an NMR tube and after sealing the tube, the reaction mixture was kept at 110 – 120 °C for 19 d. Then the NMR tube was cooled in liquid nitrogen, opened, and volatile materials were removed in a vacuum. The oily residue was identified as a mixture of **12a** and **12a’** (9 : 1; according to the NMR spectra). The alkenes **12b**, **c** and **13a**, **b**, **c** were obtained in the same way, except for the reaction time: **12b** (30 d; only 40 % of the reactants were converted into products), **12c** (26 d), **13a** (2 d), **13b** (15 d), and **13c** (10 d). The hydroboration of **3b** was carried out with 9-BBN at 100 – 110 °C in toluene and was complete after 1 h.

12a: ^{1}H NMR (400 MHz): δ = 2.1, 0.8 – 1.1, 0.4 (m, m, t, 9H, ^{n}Bu), 0.8 – 1.1, 0.8 (m, t, 10H, BEt$_2$), 5.8 (t, 1H, =CH $^3J(^1\text{H},^1\text{H})$ = 7.4 Hz, $^3J(^{29}\text{Si},^1\text{H})$ = 24.3 Hz), 6.8 – 7.5 (m, 5H, SiPh).

12a’: ^{1}H NMR (400 MHz): δ = 1.8, 0.8 – 1.1, 0.4 (m, m, t, 9H, ^{n}Bu), 0.8 – 1.1, 0.6 (m, t, 10H, BEt$_2$), 5.6 (t, 1H, =CH $^3J(^1\text{H},^1\text{H})$ = 7.4 Hz), 6.8 – 7.5 (m, 5H, SiPh).

12b: ^{1}H NMR (400 MHz): δ = 0.9 (s, 9H, ^{t}Bu), 1.0, 1.4 (t, q, 10H, BEt$_2$), 7.0, 7.7 (m, 5H, 5H, SiPh), 6.1 (s, 1H, =CH, $^3J(^{29}\text{Si},^1\text{H})$ = 30.8 Hz).

12c: ^{1}H NMR (400 MHz): δ = 1.5, 1.1 (q, t, 10H, BEt$_2$), 6.8 – 7.8 (m, 5H, 5H, 1H, SiPh, Ph, =CH). – EI-MS: *m/z* (%) = 347 (5) [M]$^+$, 346 (9) [M–H]$^+$, 332 (8) [M–CH$_4$]$^+$, 316 (32) [M–C_2H_5]$^+$, 317 (79) [M–C_2H_6]$^+$, 278 (15) [M–BEt_2]$^+$, 271 (74) [M–C_6H_6]$^+$, 270 (13) [M–C_6H_5]$^+$, 178 (100) [C_8H_8BClSi]$^+$, 171 (12) [M–$SiCl_2Ph$]$^+$.

13a: ^{1}H NMR (400 MHz): δ = 2.0, 1.0 – 1.4, 0.5 (m, m, t, 9H, ^{n}Bu), 1.0 – 1.4, 0.8 (m, t, 14H, B^{n}Pr$_2$), 6.9 – 7.6 (m, 5H, SiPh), 5.9 (t, 1H, =CH, $^3J(^1H,^1H)$ = 7.4 Hz).

13a': ^{1}H NMR (400 MHz, C_6D_6): δ = 2.1, 1.0 – 1.4, 0.5 (m, m, t, 9H, Bu), 1.0 – 1.4, 0.7 (m, t, 14H, B^{n}Pr$_2$), 6.9 – 7.6 (m, 5H, SiPh), 5.8 (t, 1H, =CH, $^3J(^1H,^1H)$ = 7.4 Hz).

13b: ^{1}H NMR (400 MHz): δ = 0.9 (s, 9H, ^{t}Bu), 0.9, 1.3 – 1.4 (t, m, 14H, B^{n}Pr$_2$), 5.8 (s, 1H, =CH, $^3J(^{29}Si,^1H)$ = 30.9 Hz), 7.1, 7.7 (m, m, 5H, Ph).

13b': ^{1}H NMR (400 MHz): δ = 5.81 (s, =CH).

13c: ^{1}H NMR (400 MHz): δ = 6.8 – 7.2, 7.4 (m, m, Ph, SiPh, =CH), 0.9, 1.5, (t, m, 14H, B^{n}Pr$_2$).

14b: ^{1}H NMR (400 MHz): δ = 1.1 (s, 9H, ^{t}Bu), 1.3 – 1.9 (m, 14H, BBN), 7.0 (s, 1H, =CH, $^3J(^{29}Si,^1H)$ = 29.5 Hz), 7.1, 7.7 (m, m, 5H, SiPh).

*Reaction of dichloro(hexyn-1-yl)(phenyl)silane **3a** and trichloro(hexyn-1-yl)silane **4a** with 9-Et-9-BBN*

A mixture of the silane **3a** and 9-Et-9-BBN was sealed in an NMR tube which was kept at 110 – 120 °C. After 30 d the NMR tube was opened, and volatile materials were removed in a vacuum. The components of the oily residue were identified as a mixture of compounds **14a**, **15a** and **16a** (ratio 15 : 60 : 25). The same procedure was followed for the synthesis of **17a**, **18a** and **19a** (ratio 60 : 30 : 10) except that 40 d of heating was necessary to achieve sufficient conversion of reactants into products.

16a: ^{1}H NMR (400 MHz): δ = 6.63 (t, 2H, =CH).

17a: ^{1}H NMR (400 MHz): δ = 6.91, 5.98 (t, t, 1H, 1H, =CH).

18a: ^{1}H NMR (400 MHz): δ = 6.57 (t, 2H, =CH).

19a: ^{1}H NMR (400 MHz): δ = 6.81, 5.98 (t, t, 1H, 1H, =CH).

*X-Ray structural analysis of **8c***

The X-ray crystal structural analysis of **8c** was carried out for a single crystal fixed in a sealed capillary at 293(2) K using a Stoe IPDS I system; MoK_α radiation, λ = 0.71073 Å. $C_{16}H_{20}BCl_2Si$, M_r = 322.12, crystal size: 0.22 × 0.15 × 0.12 mm^3, crystal system: triclinic, space group $P\bar{1}$, a = 7.5130(15), b = 9.755(2), c = 12.508(3) Å, α = 92.44(3)°, β = 98.85(3)°, γ = 110.66(3)°, V = 842.9(3) Å^3, Z = 2, D_{calc} = 1.269 mg m^{-3}, μ(MoK_α) = 0.443 mm^{-1}, F(000) = 338 e, $\theta_{min/max}$ = 2.24 – 26.08°, index ranges: $-9 \le h \le 9$, $-11 \le k \le 9$, $-15 \le l \le 14$, 5126 collected reflections, 3039 independent reflections, R(int) = 0.041, completeness to θ = 26.08°: 91.0 %, data/parameters: 3039 / 182, goodness-of-fit on F^2: 0.844, final R indices [$I > 2\ \sigma(I)$] 3781: $R1$ = 0.0543, $wR2$ = 0.1502; R indices (all data): $R1$ = 0.0951, $wR2$ =0.1345; largest difference peak and hole: 0.43 and −0.25 e Å^{-3}.

Structure solution and refinement were accomplished using SHELXTL (version 5.1) [22]. CCDC 696258 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc. cam.ac.uk/ data_request/cif.

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