

1,1-VINYLBORATION AND 1,1-ETHYLBORATION OF DI(ALKYN-1-YL)SILANES: SYNTHESIS OF NEW SILOLES

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Dedicated to Professor Jaromír Plešek on the occasion of his 75th birthday in recognition of his outstanding contributions to boron chemistry.

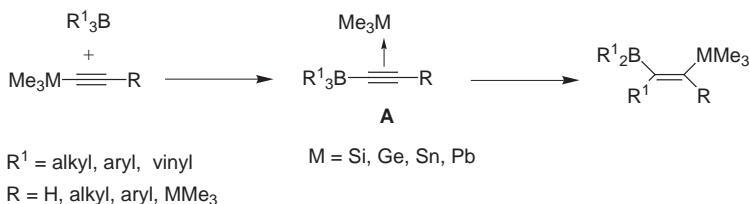
Triethylborane (**1**) or trivinylborane (**2**) reacts with di(alkyn-1-yl)methylsilanes, MeSiH(C≡C-R)₂ **3** [R = Bu (**a**), *t*-Bu (**b**), SiMe₃ (**c**)], to give the novel chiral 1-silacyclopenta-2,4-dienes (siloles) **4a–4c** or **5a–5c**, respectively, by twofold 1,1-organoboration. Similarly, di(alkyn-1-yl)dimethylsilane Me₂Si(C≡C-*t*-Bu)₂ **3d** reacts with **2** to give the silole **5d**. These are the first applications of **2** in 1,1-organoboration reactions. All products are characterized by multinuclear magnetic resonance (¹H, ¹¹B, ¹³C, ²⁹Si NMR).

Keywords: Boranes; Organoboration; Alkynes; Silanes; Siloles; Multinuclear NMR spectroscopy.

Numerous applications of triethylborane (**1**) or of its derivatives have been described¹, whereas applications of trivinylborane (**2**) in organic synthesis have received scant attention². Although **2** is readily accessible by the reaction of boron trihalides with tetravinyllead^{3a} or tetravinyltin^{3b,3c}, it requires careful handling in order to avoid rapid decomposition. In any case, **2** should be an attractive reagent in 1,1-organoboration reactions of alkyn-1-yl metal compounds^{4,5} which have been described extensively for triethylborane (**1**). We have made now the first attempt to study the reactivity of trivinylborane (**2**) towards some di(alkyn-1-yl)silanes of type **3** and to compare it with that of **1**. The objective was to obtain 1-silacyclopenta-2,4-diene derivatives (siloles) with a novel pattern of substituents, *e.g.* a hydrido function at the silicon atom and/or a vinyl group in position 4.

Usually, 1,1-organoboration of alkyn-1-yl metal compounds works by cleavage of an M–C≡ bond and formation of an alkynylborate-like intermediate^{4–6} **A** (Scheme 1). In this intermediate, the transfer of a vinyl group

(R¹) from boron to the adjacent alkynyl carbon atom is expected to create a diene, in which the divinylboryl group occupies an allylic position, ready for allylic rearrangement⁷.



SCHEME 1

If there is a second alkynyl group linked to M, the intermolecular 1,1-organoboration may be followed by an intramolecular 1,1-organoboration to give metallacyclopenta-2,4-dienes (metalloles), and we have shown previously that 1,1-dimethylsiloles can be prepared selectively and in high yields by 1,1-ethylboration of di(alkyn-1-yl)dimethylsilanes (e.g. **3d**)^{5,8}. This procedure is more straightforward than most other routes to siloles⁹.

EXPERIMENTAL

General Methods

All compounds were handled under dry argon, using carefully dried solvents; all conditions were observed in order to exclude air and moisture. Triethylborane (**1**) (Schering) was used as a commercial product, and the other starting materials such as trivinylborane (**2**) and the di(alkyn-1-yl)dimethylsilane (**3d**) were prepared according to slightly modified literature procedures^{3,10}. The synthesis of bis(hex-1-yn-1-yl)methylsilane (**3a**), bis(3,3-dimethylbut-1-yn-1-yl)methylsilane (**3b**), and bis(trimethylsilylethynyl)methylsilane (**3c**) was achieved by the reaction of the respective chlorosilanes with lithium alkynides in the usual way^{10,11}; and details will be described elsewhere¹². NMR measurements: Bruker ARX 250 and DRX 500 [¹H, ¹¹B, ¹³C NMR, and ²⁹Si NMR (refocused INEPT¹³)]. Chemical shifts (δ, ppm) are given with respect to Me₄Si [^δ¹H (CHCl₃/CDCl₃) = 7.24, (C₆D₅H) 7.15; ^δ¹³C (CDCl₃) = 77.0, (C₆D₆) 128.0; ^δ²⁹Si = 0 for Ξ(²⁹Si) = 19.867184 MHz], BF₃·Et₂O [^δ¹¹B = 0; for Ξ(¹¹B) = 32.083971 MHz]. Coupling constants (*J*) are given in Hz. IR spectra: Perkin-Elmer, Spectrum GX FT-IR. EI-MS: Finnigan MAT 8500 (ionisation energy 70 eV; direct inlet); the *m/z* data refer to the isotopes ¹H, ¹¹B, ¹²C, ²⁸Si.

Preparation of Trivinylborane (**2**)

Boron tribromide (25.1 g, 100 mmol) was added dropwise to pure tetravinyltin (26.3 g, 100 mmol) at 0 °C within 30 min, and then the mixture was allowed to stay at ambient temperature for 12 h. Volatile products were removed *in vacuo* and trapped in a precooled

(-78 °C) flask. NMR spectra showed that this material was trivinylborane (yield >90 and >95% pure) which was used without any further purification.

Synthesis of Siloles 4. General Procedure

The respective di(alkyn-1-yl)methylsilane **3** (20 mmol) was mixed with triethylborane (5.42 g, 55 mmol), and the mixture was heated at reflux for 24 h. After cooling to room temperature, the excess of Et₃B was removed *in vacuo* and the siloles were obtained in quantitative yield as colorless oils. Compound **4a** could be distilled under reduced pressure (83–85 °C/0.133 Pa). The compounds **4b**, **4c** decompose at the attempt of distillation.

2,5-Dibutyl-3-(diethylboryl)-4-ethyl-1-methylsilole (4a). ¹H NMR (250 MHz, C₆D₆): δ¹H [*J*(²⁹Si, ¹H)] = 0.28 (d, *J*(H,H) = 4.2, 3 H, SiMe); 2.06, 0.90 (m, t, 5 H, 4-Et); 1.35, 1.0 (m, t, 10 H, BEt₂); 2.28, 2.04, 1.50, 0.93 (m, 18 H, 2,5-Bu); 4.66 [183.1] (q, *J*(H,H) = 4.2, 1 H, SiH). IR: ν(Si-H) = 2 108 cm⁻¹. EI-MS, *m/z* (%): 304 (100) [M⁺], 275 (82) [M⁺ - Et].

2,5-Di-tert-butyl-3-(diethylboryl)-4-ethyl-1-methylsilole (4b). ¹H NMR (250 MHz, C₆D₆): δ¹H [*J*(²⁹Si, ¹H)] = 0.37 (d, *J*(H,H) = 4.1, 3 H, SiMe); 2.2, 0.94 (m, t, 5 H, 4-Et); 1.36, 1.01 (m, t, 10 H, BEt₂); 1.23, 1.01 (s, s, 18 H, 2,5-*t*-Bu); 4.9 [183.8] (q, *J*(H,H) = 4.2, 1 H, SiH).

3-(Diethylboryl)-4-ethyl-1-methyl-2,5-bis(trimethylsilyl)silole (4c). ¹H NMR (250 MHz, C₆D₆): δ¹H [*J*(²⁹Si, ¹H)] = 0.33 (d, *J*(H,H) = 4.0, 3 H, SiMe); 2.12, 0.96 (m, t, 5 H, 4-Et); 1.40, 1.35, 0.99 (m, m, t, 10 H, BEt₂); 0.24, 0.15 (s, s, 18 H, 2,5-SiMe₃); 4.90 [183.8] (q, *J*(H,H) = 4.1, 1 H, SiH).

2,5-Dibutyl-4-ethyl-1-methylsilole (6a)

Ethanolamine (1.25 mmol) was added in one portion to a solution of **4a** (1.25 mmol) in THF (10 ml) at room temperature. An exothermic reaction was observed, and the mixture was stirred for 2 h. Then THF was removed *in vacuo* and a white precipitate formed when pentane (5 ml) was added. The solution was decanted, centrifuged, decanted again, and pentane was removed *in vacuo*. The silole **6a** was left as a colorless oil (83%). ¹H NMR (250 MHz, C₆D₆): δ¹H [*J*(²⁹Si, ¹H)] = 0.19 (d, *J*(H,H) = 4.2, 3 H, SiMe); 2.13, 0.95 (q, t, 5 H, 4-Et); 2.20, 1.35, 0.86 (m, m, m, 18 H, 2,5-Bu); 4.24 [185.2] (q, *J*(H,H) = 4.2, 1 H, SiH).

Reactions of Trivinylborane (2) with Silanes 3a–3d. General Procedure

A mixture of trivinylborane (**2**) and the respective silane (2 : 1 mole ratio on 0.2–0.5 g scale) was heated at 100–110 °C for 1–2 h. Then all volatile material was removed *in vacuo*, and siloles **5a–5d** were left as major products (≥90%) as yellowish oils. Under these reaction conditions, decomposition of **2** also takes place and therefore an excess of **2** is required; the decomposition products of **2** are not well soluble in organic solvents (e.g. in benzene) and can be removed by filtration.

2,5-Dibutyl-3-(divinylboryl)-1-methyl-4-vinylsilole (5a). ¹H NMR (500 MHz, C₆D₆): δ¹H [*J*(²⁹Si, ¹H)] = 0.40 (d, *J*(H,H) = 4.3, 3 H, MeSi); 2.58, 2.46, 2.3, 1.4–1.6, 0.99, 0.94 (dt, dt, m, m, t, t, *J*(H,H) = 14.2, 7.9, 14.2, 7.7, 7.4, 7.4, 18 H, 2,5-Bu); 4.78 [185.4] (q, *J*(H,H) = 4.3, 1 H, SiH); 6.69, 5.14, 5.07 (dd, d, d, *J*(H,H) = 17.5, 11.2, 17.5, 11.2, 3 H, 4-vinyl); 6.88, 6.33, 6.23 (dd, dd, dd, *J*(H,H) = 19.3, 12.7, 19.3, 4.2, 12.7, 4.2, 6 H, B(CH=CH₂)₂). IR: ν(Si-H) = 2 182 cm⁻¹. EI-MS, *m/z* (%): 271 (100) [M⁺ - C₂H₃].

2,5-Di-tert-butyl-3-(divinylboryl)-1-methyl-4-vinylsilole (5b). ¹H NMR (500 MHz, C₆D₆): δ¹H [*J*(²⁹Si, ¹H)] = 0.61 [7.0] (d, *J*(H,H) = 4.3, 3 H, MeSi); 1.37, 1.26 (s, s, 18 H, 2,5-*t*-Bu); 4.98

[176.6] (q, $J(\text{H,H}) = 4.3$, 1 H, SiH); 6.6, 5.0–5.1 (m, m, 3 H, 4-vinyl); 6.89, 6.85, 6.30, 6.26, 6.18, 6.16 (dd, dd, dd, dd, dd, $J(\text{H,H}) = 19.2$, 12.7, 19.3, 12.8, 19.3, 4.2, 19.2, 4.2, 12.8, 4.2, 12.7, 4.2, 6 H, $\text{B}(\text{CH}=\text{CH}_2)_2$). EI-MS, m/z (%): 312 (35) $[\text{M}^+]$, 297 (62) $[\text{M}^+ - \text{CH}_3]$.

3-(Divinylboryl)-1-methyl-2,5-bis(trimethylsilyl)-4-vinylsilole (5c). ^1H NMR (500 MHz, C_6D_6): $\delta^1\text{H}$ [$J(^{29}\text{Si}, ^1\text{H})$] = 0.39 [6.3], 0.27 [6.6] (s, s, 18 H, 2,5- Me_3Si); 0.52 [7.0] (d, $J(\text{H,H}) = 4.2$, 3 H, MeSi); 5.08 [187.4] (q, $J(\text{H,H}) = 4.2$, 1 H, SiH); 6.86, 5.29, 5.15 (dd, d, d, $J(\text{H,H}) = 17.6$, 11.4, 17.6, 11.4, 3 H, 4-vinyl); 6.90, 6.26, 6.13 (br, br, br, 6 H, $\text{B}(\text{CH}=\text{CH}_2)_2$).

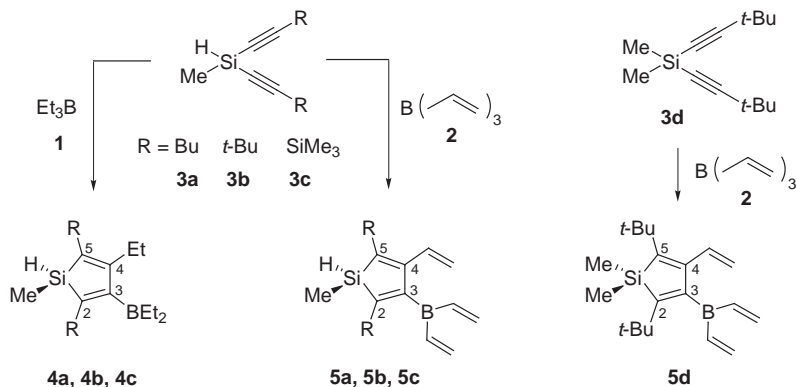
2,5-Di-tert-butyl-3-(divinylboryl)-1,1-dimethyl-4-vinylsilole (5d). ^1H NMR (500 MHz, C_6D_6): $\delta^1\text{H}$ [$J(^{29}\text{Si}, ^1\text{H})$] = 0.59 [6.4] (s, 6 H, Me_2Si); 1.38, 1.26 (s, s, 18 H, 2,5-*t*-Bu); 6.64, 5.1 (dd, m, $J(\text{H,H}) = 18.7$, 11.1, 3 H, 4-vinyl); 6.92, 6.31, 6.17 (dd, dd, dd, $J(\text{H,H}) = 19.2$, 12.8, 19.2, 4.2, 12.8, 4.2, 6 H, $\text{B}(\text{CH}=\text{CH}_2)_2$).

RESULTS AND DISCUSSION

Reaction of Di(alkyn-1-yl)silanes **3** with Triethylborane (**1**) and Trivinylborane (**2**)

1,1-Ethylboration of di(alkyn-1-yl)dimethylsilanes (type **3d**) or tetra(alkyn-1-yl)silanes and other poly(alkyn-1-yl)polysilanes has opened the route to numerous siloles⁸, a useful alternative to other methods⁹. Since di(alkyn-1-yl)methylsilanes **3a–3c** are readily available^{11,12}, 1,1-organoboration may give access to chiral siloles bearing a hydrido function at the silicon atom. Therefore, these alkynes were treated with triethylborane (**1**) and with trivinylborane (**2**) in order to find out whether the Si–H function changes the product distribution of 1,1-ethylboration. For comparison with the known reaction of **1** with **3d**^{8a}, the analogous reaction of **2** with **3d** was studied.

The results are summarized in Scheme 2. The 1,1-ethylboration of **3a–3c** proceeds in the same way as has been observed previously for **3d**^{8a}. The



SCHEME 2

methylsilanes **3a–3c** were found to be somewhat more reactive than corresponding dimethylsilanes, and the reactions were complete after 12–24 h of heating in triethylborane as a solvent. The chiral siloles **4a–4c** were isolated in high yields. The 1,1-vinylboration of **3d** and of silanes **3a–3c** also affords siloles **5d** and **5a–5c**, for the first time with a vinyl group in position 4. Trivinylborane (**2**) is considerable more reactive than triethylborane. In general, the reactions of **2** with **3** were complete after 1–2 h at 100–110 °C without solvent.

The proposed structure of the siloles **4** and **5** follows from the consistent NMR data set, of which the ^{13}C NMR spectra in the olefinic region are particularly instructive (Fig. 1). Since it was possible to determine the coupling constants $^1J(^{29}\text{Si}, ^{13}\text{C})$ from ^{29}Si satellite signals, the assignment of the $^{13}\text{C}(2,4,5)$ signals is straightforward, and the broad $^{13}\text{C}(3)$ NMR signal, as the result of partially relaxed scalar ^{13}C – ^{11}B coupling, is typical of a carbon atom linked to boron (^{11}B : $I = 3/2$)¹⁴. The ^{11}B , ^{13}C and ^{29}Si NMR data of the siloles are given in Table I. ^1H NMR data are listed in the Experimental. The ^{11}B chemical shifts are in the typical region for triorganoboranes with small or negligible $\text{CB}(\text{pp})\pi$ interactions (siloles **4**)¹⁵ or weak $\text{C}(\text{vinyl})\text{B}(\text{pp})\pi$ interactions (siloles **5**). This means that the average orientation of the CCB plane of the BR_2 groups in the siloles is perpendicular to the plane of the

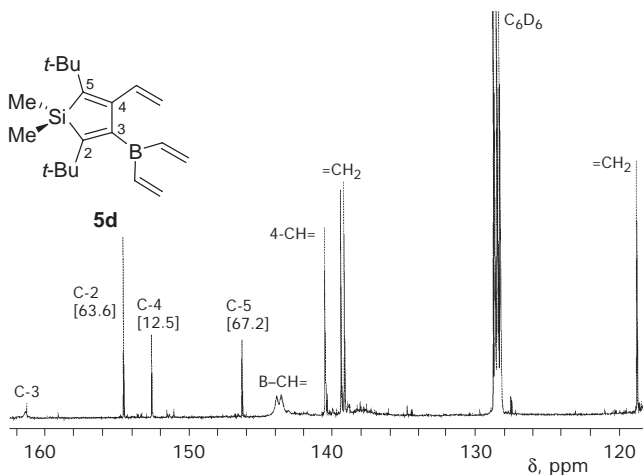


FIG. 1

^{13}C NMR spectra (at 125.8 MHz) of silole **5b** showing the range for olefinic C atoms. The $J(^{29}\text{Si}, ^{13}\text{C})$ are given in brackets. Note the broad ^{13}C signals for the C atoms linked to B. As a result of hindered rotation about the $\text{C}(3)$ –B bond the vinyl groups linked to boron are chemically non equivalent

TABLE I
¹¹B, ¹³C and ²⁹Si NMR data^a of siloles 4–6

Nucleus	4a	6a	5a	4b	5b	4c	5c	5d
¹³ C(2)	139.4 (64.4)	143.6 (63.3)	145.9 (62.6)	150.2 (64.2)	154.6 (63.3)	144.7 (43.7)	150.7 (42.7)	155.7 (63.1)
¹³ C(3)	168.2 (br)	144.5 (9.1)	163.3 (br)	165.3 (br)	161.5 (br)	186.6 (br)	181.4 (br)	159.9 (br)
¹³ C(4)	155.7 (11.6)	153.7 (8.4)	153.5 (11.0)	154.8 (12.3)	152.6 (12.5)	172.2 (8.6, 11.2)	168.6 (11.0, 9.1)	151.4 (10.6)
¹³ C(5)	135.2 (69.0)	133.6 (68.1)	141.3 (68.1)	143.5 (68.1)	146.4 (67.2)	136.8 (49.4)	142.9 (48.9)	147.2 (68.2)
¹³ C(BR ₂)	22.7 (br), 9.2	–	143.1 (br), 140.8	22.5 (br), 10.1	143.9 (br), 143.6 (br), 139.4, 139.2	22.7 (br), 9.4	143.5 (br), 141.4 (br)	143.8 (br), 138.7
¹³ C(4-Et) (4-vinyl)	23.4, 14.0	23.8, 13.5	134.2, 117.5	26.6, 15.1	140.5, 118.7	30.3, 15.5	139.8, 119.1	141.1 (7.1), 118.6
¹³ C(2,5-R)	34.9, 34.4, 32.7, 28.8, 24.6, 23.3, 14.3, 13.7	34.9, 34.4, 32.0, 28.8, 23.3, 23.1, 14.3, 14.2	35.1 (7.7), 34.6, 33.1 (7.0), 30.1, 23.8, 23.7, 14.8, 14.7	35.8, 35.1, 33.1, 32.9	36.9 (6.5), 35.7 (6.3), 34.4, 32.9	1.57 (51.6), 1.56 (51.3)	2.7 (51.6), 1.8 (52.1)	37.1 (6.6), 35.7 (6.1), 34.2, 32.6
¹³ C(Si-Me)	–5.9 (47.5)	–6.7 (48.3)	–5.6 (48.0)	–2.3 (47.3)	–2.42 (47.5)	–4.6 (46.7)	–4.5 (47.5)	0.6 (47.6)
¹¹ B	87.0	–	63.0	87.7	63.5	87.0	63.5	63.3
²⁹ Si	–15.9	–16.9	–14.2	–15.2	–15.0	+6.5 ^b	+6.8 ^c	+7.0

^a In C₆D₆ (23 ± 1 °C); ¹J(²⁹Si,¹³C) are in parentheses (±0.2 Hz); (br) denotes the broadened ¹³C NMR signal of the carbon atom of a C–B bond. ^b Me₃Si groups: δ²⁹Si –10.4, –10.9; ²J(²⁹Si(1), ²⁹Si) = 10.3 and 10.5 Hz; ¹J(²⁹Si, ¹³C(2)) = 63.5 Hz; ¹J(²⁹Si, ¹³C(5)) = 62.4 Hz. ^c Me₃Si groups: δ²⁹Si –9.89, –9.91; ²J(²⁹Si(1), ²⁹Si) = 9.6 and 10.1 Hz; ¹J(²⁹Si, ¹³C(2)) = 62.4 Hz; ¹J(²⁹Si, ¹³C(5)) = 60.9 Hz.

silole ring, as shown by hindered rotation about the C(3)–B bond (see Fig. 1). In all reactions, ^{29}Si NMR spectra proved very useful for monitoring the progress of the reactions and for the determination of the final product distribution (Fig. 2). The $^{29}\text{Si}(1)$ nuclear deshielding in **4c** and **5c** (when compared with **4a**, **4b** and **5a**, **5b**) is due to the presence of SiMe_3 groups in positions 2 and 5, as has been observed previously⁸.

It appears that 1,1-vinylboration of the di(alkyn-1-yl)silanes is not accompanied by allylic rearrangement. Therefore, it is concluded that the first intermolecular 1,1-vinylboration, which leads to **B**, is followed by a fast second intramolecular 1,1-organoboration *via* the zwitterionic intermediate **C**^{5,6} to give the siloles **5**, before allylic rearrangements⁷ become competitive. In the case of the reaction of **3d** with **2**, small quantities of other products (<10%) are formed, some of which possess an allene structure. These can be formed if allylic rearrangement occurs in the intermediate of type **B** if the conversion into **C** is slow. The bulky *t*-Bu groups in **3d** may be responsible for slow reactions. It is remarkable that five-membered rings are formed selectively both in 1,1-ethylboration and in 1,1-vinylboration. There is no indication of the presence of 1,4-silaboracyclohexa-2,5-dienes which might result from transfer of a second vinyl group starting from **C**.

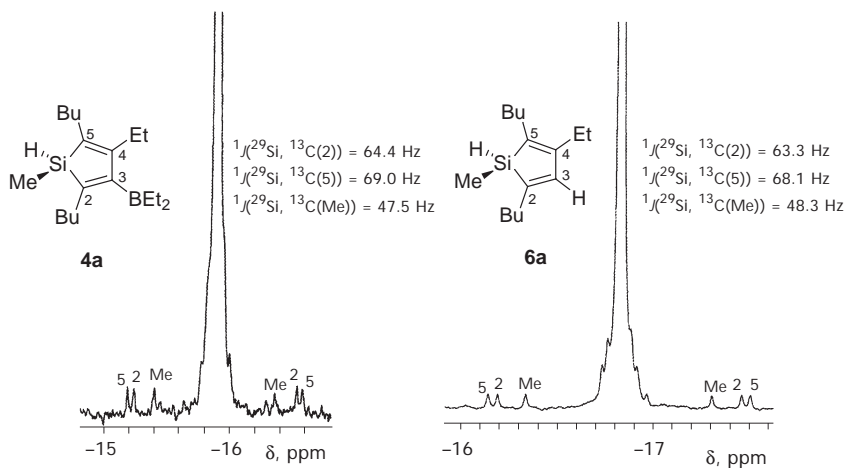
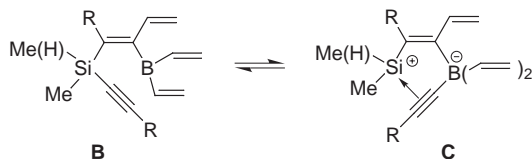


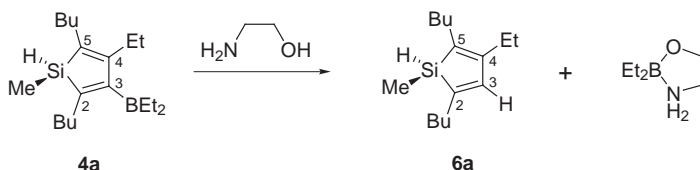
FIG. 2

^{29}Si NMR spectra (at 49.7 MHz) of siloles **4a** and **6a** (ca 10% in C_6D_6 , at 23 ± 1 °C) showing the ^{13}C satellites for $^1J(^{29}\text{Si}, ^{13}\text{C})$, recorded by the refocused INEPT pulse sequence with ^1H decoupling¹³; polarization transfer was based on $^1J(^{29}\text{Si}, ^1\text{H}) = 185$ (result of 128 transients, repetition time 8 s, acquisition time 6 s). The ^{29}Si NMR signal of **6a** is somewhat sharper than that of **4a** since there is no boryl group which causes some broadening of the ^{29}Si signal of **4a** owing to partially relaxed scalar ^{29}Si – ^{11}B coupling^{14c}

Apparently, other potential reaction pathways such as alkynyl/vinyl exchange, play a minor role.



Treatment of **4a** with ethanolamine leads to cleavage of the B–C(3) bond, and the silole **6a** is obtained as a colorless liquid (Scheme 3). The analogous reaction of **4a** with methanol or ethanol either in excess or in a 1 : 1 mole ratio gives complex mixtures of compounds since the cleavage of the B–C(3) bond and attack at the Si–H function, together with Si–C(2,5) bond cleavage, take place at the same time.



SCHEME 3

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