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Synthesis of Halogen-Substituted Borolanes and 2,3-Dihydro-1*H*-boroles by Reactions of Aluminacarbocycles with Boron Trichloride and Boron Tribromide

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Abstract—A selective procedure has been developed for the synthesis of 1-chloro(bromo)-substituted borolanes and 2,3-dihydro-1*H*-boroles by reaction of aluminacarbocycles with boron trihalides BX_3 (X = Cl, Br). 3-Substituted 1-chloro(bromo)borolanes and 2,3-dihydro-1*H*-boroles have been isolated as individual substances, and their structure has been determined.

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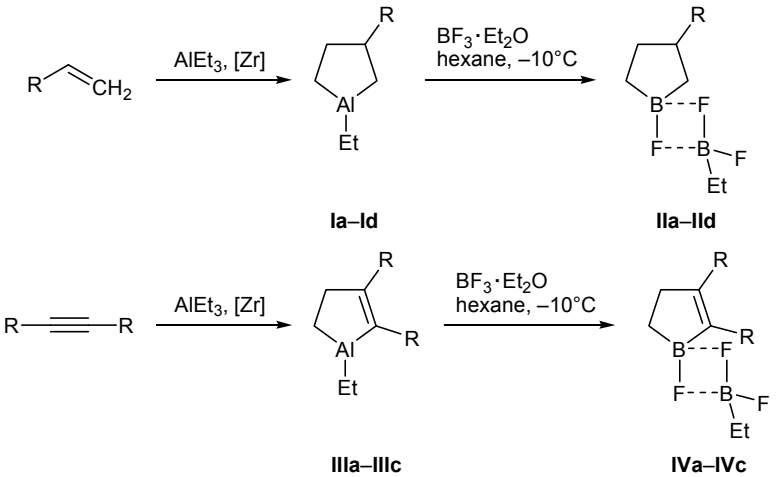
We have recently synthesized [1, 2] for the first time 1-fluoro-substituted borolanes **II** and 2,3-dihydro-1*H*-boroles **IV** by reactions of aluminacarbocycles (aluminacyclopentanes **I** and aluminacyclopent-2-enes **III**) with boron trifluoride–diethyl ether complex (Scheme 1). The products were isolated as molecular complexes with $EtBF_2$. In continuation of these studies in the present work we examined reactions of 3-alkyl-1-ethylaluminacyclopentanes **Ia**–**Ic** and 1-ethyl-2,3-dialkylaluminacyclopent-2-enes **IIIa**–**IIIc** [3−5] with BCl_3 and BBr_3 with a view to obtain other halogen-substituted boracyclanes.

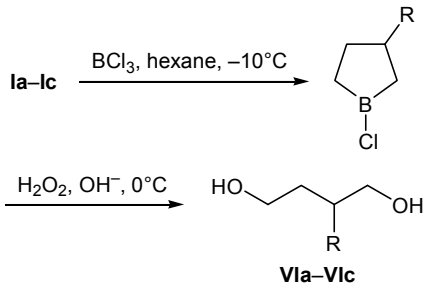
Compounds **Ia**–**Ic** were successfully involved in exchange reaction with BCl_3. The reaction of 3-butyl-1-ethylaluminacyclopentane (**Ia**) with 2 equiv of BCl_3 in hexane over a period of 0.5 h and subsequent treatment of the reaction mixture with hydrogen peroxide afforded diol **VIa**, which indirectly indicated formation of borolane **Va** (Scheme 2). By vacuum distillation under dry argon we isolated a yellow fuming (on exposure to air) liquid with bp 70°C (17 mm). The product was identified as 3-butyl-1-chloroborolane (**Va**) on the basis of its ^1H, ^{13}C, and ^{11}B NMR spectra (Scheme 2).

Scheme 1.



I, **II**, R = Bu (**a**), C_6H_{13} (**b**), C_8H_{17} (**c**), $PhCH_2$ (**d**); **III**, **IV**, R = Et (**a**), Pr (**b**), Bu (**c**); [Zr] = Cp_2ZrCl_2.

Scheme 2.

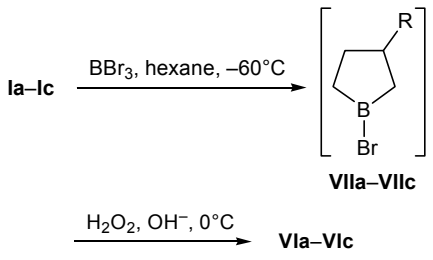


R = Bu (**a**), C_6H_{13} (**b**), C_8H_{17} (**c**).

Unlike 3-butyl-1-fluoroborolane (**IIa**) isolated previously, which is stable only as a molecular complex with $EtBF_2$ [1], 3-butyl-1-chloroborolane (**Va**) was an individual substance. Its ^1H, ^{13}C, and ^{11}B NMR spectra lacked signals assignable to $EtBCl_2$, and the molecular weight of **Va** determined by cryoscopy was *M* 154 (calculated 158.48). The boron signal in the ^{11}B NMR spectrum of **Va** in $CDCl_3$ was located at δ_B 93.4 ppm, which is close to the corresponding signal of fluoro-substituted analog **IIa** (δ_B 92.9 ppm) [1]. The positions of signals from protons and carbon nuclei in the boracyclopentane ring and butyl group in the ^1H and ^{13}C NMR spectra of **IIa** and **Va** were almost identical [1]. Analogous results were obtained in the transmetalation of 3-hexyl- and 3-octylaluminacyclopentanes **Vb** and **Vc** [3] with BCl_3 (Scheme 2).

In order to compare the reactivities of BCl_3 and BBr_3 in transmetalation of aluminacyclopentanes and synthesize 1-bromo-substituted borolanes 3-alkyl-1-ethylaluminacyclopentanes **Ia**–**Ic** were brought into reaction with BBr_3. The reactions of **Ia**–**Ic** with BBr_3 were accompanied by vigorous heat evolution; therefore, the reaction mixtures were cooled to −60°C. We tried to obtain 1-bromo-3-butylborolane (**VIIa**) by reaction of 3-butyl-1-ethylaluminacyclopentane (**Ia**) with BBr_3 under the developed conditions (hexane, 0.5 h, −60°C). After treatment of the reaction mixture with hydrogen peroxide in alkaline medium we isolated 2-butylbutane-1,4-diol (**VIa**) in nearly quantitative yield (~90%), which indicated intermediate formation of 1-bromo-3-butylborolane (**VIIa**) (Scheme 3). However, all attempts to isolate and identify compound **VIIa** as pure substance were unsuccessful. It decomposed during vacuum distillation.

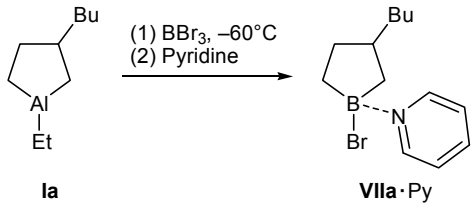
Scheme 3.



R = Bu (**a**), C_6H_{13} (**b**), C_8H_{17} (**c**).

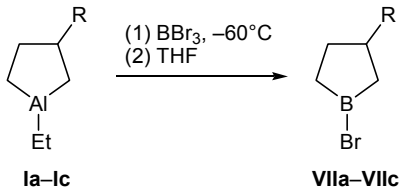
Taking into account that boron compounds form fairly strong molecular complexes with electron pair donors such as ethers, sulfides, and amines [6−10], 1-bromo-3-butylborolane (**VIIa**) was subjected to vacuum distillation in the presence of pyridine. We thus succeeded in isolating pyridine complex **VIIa**·Py (Scheme 4). The structure of **VIIa**·Py was reliably proved by multinuclear NMR spectroscopy. The boron nucleus resonated in the ^{11}B NMR spectrum of **VIIa**·Py at δ_B 5.0 ppm ($CDCl_3$), which corresponded to tetragonal configuration of bonds at the boron atom [11] due to formation of a strong complex with pyridine molecule.

Scheme 4.



When the reaction was carried out with THF instead of pyridine, we isolated 72% of pure 1-bromo-3-butylborolane (**VIIa**) which contained no THF molecule (Scheme 5). In the ^{11}B NMR spectrum of **VIIa** ($CDCl_3$), the boron signal appeared at δ_B 92.5 ppm, i.e., in the same region as in the spectra of 3-butyl-1-fluoro- and -1-chloroborolanes **IIa** and **Va** (δ_B 92.9 and 93.4 ppm, respectively).

Scheme 5.



R = Bu (**a**), C_6H_{13} (**b**), C_8H_{17} (**c**).

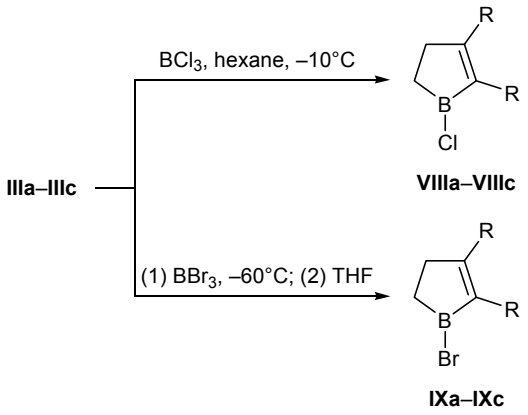
Presumably, the formation of fairly weak associates **VIIa**$\cdots THF_n$ stabilizes borolane **VIIa** and prevents its thermal decomposition during vacuum distillation. On the other hand, distillation of **VIIa**$\cdots THF_n$ is accompanied by decomposition of these associates with

liberation of free molecules **VIIa** which are stable in an argon atmosphere. Likewise, we synthesized individual bromo-substituted borolanes **VIIb** and **VIIc** (Scheme 5).

The complexation of **VIIa** with pyridine induces an appreciable upfield shift of the boron signal in the ^{11}B NMR spectrum (δ_B 5.0 ppm in pyridine-d_5), whereas association of **VIIa** with tetrahydrofuran involves only a weak dative interaction (δ_B 83.2 ppm in THF-d_8), i.e., in the latter case the boron atom retains trigonal bond configuration [11].

Our previous results on transmetalation of aluminacyclopent-2-enes with the aid of $BF_3 \cdot Et_2O$ [2] prompted us to study Al–B exchange in the series of aluminacyclopent-2-enes by the action of BCl_3 and BBr_3 with a view to obtain substituted 1-chloro(bromo)-2,3-dihydro-1*H*-boroles. The reaction of aluminacyclopent-2-enes **IIIa**–**IIIc** with 2 equiv of BCl_3 (hexane, –10°C, 30 min) afforded 75–85% of pure 4,5-dialkyl-1-chloro-2,3-dihydro-1*H*-boroles **VIIIa**–**VIIIc** (Scheme 6). We succeeded in isolating 1-bromo-2,3-dihydro-1*H*-boroles **IXa**–**IXc** (yield 70–80%) only when THF was added to the reaction mixture before vacuum distillation, as in the synthesis of 1-bromo-substituted borolanes **VIIa**–**VIIc** (Scheme 5).

Scheme 6.



R = Et (**a**), Pr (**b**), Bu (**c**).

In summary, the one-pot procedure proposed by us for the transformation of aluminacyclopentanes and aluminacyclopent-2-enes generated *in situ* into the corresponding borolanes and dihydroboroles by the action of boron trifluoride–diethyl ether complex and boron halides (BCl_3, BBr_3) provides a simple and efficient synthetic route to 1-fluoro(chloro, bromo)borolanes and 1-fluoro(chloro, bromo)-2,3-dihydro-1*H*-boroles which are important intermediate products for organic and organometallic synthesis.

EXPERIMENTAL

All reactions with organometallic reagents were carried out under dry argon. Commercially available 98% $AlEt_3$, a 1 M solution of BCl_3 in hexane, 99.9% BBr_3, and symmetrically substituted acetylenes were used without additional purification. Hexane was distilled over Al(*i*-Bu)$_3$. One-dimensional (^{1}H, ^{13}C, ^{11}B) and two-dimensional homo- (COSY) and heteronuclear (HSQC, HMBC) NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400.13 (^{1}H), 100.62 (^{13}C), and 128.33 MHz (^{11}B). The ^{1}H and ^{13}C chemical shifts were measured relative to tetramethylsilane as internal reference, and the ^{11}B chemical shifts were determined relative to $BF_3 \cdot Et_2O$. The molecular weights of organoboron compounds were determined by cryoscopy in benzene according to standard procedure [12] under argon using a glass three-necked cell and a Beckmann thermometer (accuracy ±0.005°C). The oxidation of boracyclanes with hydrogen peroxide in alkaline medium was accomplished according to the procedure described in [1, 2]. The spectral parameters and physical constants of compounds **VIa**–**VIc** were consistent with those reported in [1, 3]. The elemental compositions were determined using a Carlo Erba 1106 analyzer.

3-Alkyl-1-chloroborolanes Va–Vc and 4,5-dialkyl-1-chloro-2,3-dihydro-1*H*-boroles VIIIa–VIIIc (*general procedure*). A 50-mL glass reactor was charged under dry argon under stirring at 0°C in succession with 5 mL of hexane, 0.5 mmol of Cp_2ZrCl_2, 10 mmol of the corresponding alkene or acetylene, and 12 mmol of $AlEt_3$. The mixture was stirred for 8 h at 20–22°C and cooled to –10°C, and 24 mmol BCl_3 (1 M solution in hexane) was added dropwise. The mixture was allowed to warm up to room temperature and stirred for 30 min, the solvent was evaporated, and the residue was distilled under reduced pressure in a stream of argon.

3-Butyl-1-chloroborolane (Va). Yield 1.1 g (70%), yellow liquid, bp 70°C (17 mm). ^{1}H NMR spectrum, δ, ppm: 0.49 m (1H, 2-H), 0.70–0.98 m (4H, 5-H, CH_3), 1.12 m (1H, 4-H), 1.19–1.39 m (6H, CH_2), 1.47 m (1H, 5-H), 1.61 d.d (1H, 2-H, J = 17.7, 5.9 Hz), 1.78 m (1H, 3-H), 1.95 m (1H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 14.29, 23.14, 27.25 (C^5), 31.00, 33.49 (C^4), 35.37 (C^2), 37.66, 41.55 (C^3). ^{11}B NMR spectrum: δ_B 93.4 ppm ($w_{1/2}$ = 0.24 kHz). Found, %: C 59.95; H 11.00. M 154. $C_8H_{16}BCl$. Calculated, %: C 60.63; H 10.18. M 158.48.

1-Chloro-3-hexylborolane (Vb). Yield 1.4 g (75%), yellow liquid, bp 78°C (17 mm). ^{1}H NMR spectrum, δ, ppm: 0.44 d.d (1H, 2-H, J = 18.2, 10.4 Hz), 0.74 m (1H, 5-H), 0.89 t (3H, CH_3, J = 7.2 Hz), 1.02–1.10 m (1H, 4-H), 1.22–1.38 m (11H, 5-H, CH_2), 1.48 d.d (1H, 2-H, J = 18.2, 6.4 Hz), 1.62 m (1H, 3-H), 1.89 m (1H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 14.54, 23.64, 27.93 (C^5), 29.64, 30.72, 33.01, 34.55 (C^4), 35.00 (C^2), 39.05, 42.65 (C^3). ^{11}B NMR spectrum: δ_B 92.9 ppm ($w_{1/2}$ = 0.30 kHz). Found, %: C 65.11; H 9.85. M 185. $C_{10}H_{20}BCl$. Calculated, %: C 64.39; H 10.81. M 186.53.

1-Chloro 3-octylborolane (Vc). Yield 1.46 g (68%), yellow liquid, bp 92°C (10 mm). ^{1}H NMR spectrum, δ, ppm: 0.49 d.d (1H, 2-H, J = 17.7, 11.2 Hz), 0.83 m (1H, 5-H), 0.92 t (3H, CH_3, J = 7.5 Hz), 1.13 m (1H, 4-H), 1.22–1.39 m (14H, CH_2), 1.47 d.d (1H, 5-H, J = 18.6, 6.5 Hz), 1.62 d.d (1H, 2-H, J = 18.6, 6.5 Hz), 1.77 m (1H, 3-H), 1.93 m (1H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 14.21, 22.83, 27.32 (C^5), 28.78, 29.54, 29.88, 30.21, 32.09, 33.49 (C^4), 35.54 (C^2), 38.02, 41.59 (C^3). ^{11}B NMR spectrum: δ_B 92.3 ppm ($w_{1/2}$ = 0.39 kHz). Found, %: C 65.50; H 10.88. M 213. $C_{12}H_{24}BCl$. Calculated, %: C 67.16; H 11.27. M 214.58.

1-Chloro-4,5-diethyl-2,3-dihydro-1*H*-borole (VIIIa). Yield 1.33 g (85%), yellow liquid, bp 60°C (8 mm). ^{1}H NMR spectrum, δ, ppm: 0.99 t (3H, 4-$CH_2C\mathbf{H}_3$, J = 7.5 Hz), 1.13 t (3H, 5-$CH_2C\mathbf{H}_3$, J = 7.5 Hz), 1.33 m (2H, 2-H), 2.22 q (2H, 4-CH_2, J = 7.5 Hz), 2.24 q (2H, 5-CH_2, J = 7.5 Hz), 2.52 m (2H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 12.77, 14.70, 19.23, 22.80 (C^2), 24.84, 34.42 (C^3), 139.80 (C^4), 188.03 (C^5). ^{11}B NMR spectrum: δ_B 69.3 ppm ($w_{1/2}$ = 0.30 kHz). Found, %: C 61.02; H 8.50. M 150. $C_8H_{14}BCl$. Calculated, %: C 61.41; H 9.02. M 156.46.

1-Chloro-4,5-dipropyl-2,3-dihydro-1*H*-borole (VIIIb). Yield 1.38 g (75%), yellow liquid, bp 73°C (10 mm). ^{1}H NMR spectrum, δ, ppm: 0.92 t (3H, 4-$CH_2CH_2C\mathbf{H}_3$, J = 8.0 Hz), 0.97 t (3H, 5-$CH_2CH_2C\mathbf{H}_3$, J = 8.0 Hz), 1.23 m (2H, 2-H), 1.32 sext (2H, 4-$CH_2C\mathbf{H}_2$, J = 8.0 Hz), 1.54 sext (2H, 5-$CH_2C\mathbf{H}_2$, J = 8.0 Hz), 2.17 t (2H, 4-CH_2, J = 8.0 Hz), 2.35 t (2H, 5-CH_2, J = 8.0 Hz), 2.42 m (2H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 14.54 (CH_3), 21.71 (C^2), 21.97, 24.03, 29.83, 33.43, 36.40 (C^3), 148.30 (C^5), 183.99 (C^4). ^{11}B NMR spectrum: δ_B 81.2 ppm ($w_{1/2}$ = 0.29 kHz). Found, %: C 66.01; H 9.50. M 178. $C_{10}H_{18}BCl$. Calculated, %: C 65.09; H 9.83. M 184.51.

4,5-Dibutyl-1-chloro--2,3-dihydro-1*H*-borole (VIIIc). Yield 1.59 g (75%), yellow liquid, bp 85°C (6 mm). ^{1}H NMR spectrum, δ, ppm: 0.90–1.00 m (6H, CH_3), 1.30–1.40 m (8H, 2-H, CH_2), 1.52 quint (2H, CH_2, J = 8.0 Hz), 2.21 t (2H, CH_2, J = 8.0 Hz), 2.42 t (2H, CH_2, J = 8.0 Hz), 2.51 m (2H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 14.06, 14.15, 22.88 (C^2), 23.00, 23.11, 26.20, 30.56, 31.89, 32.48, 35.04 (C^3), 146.13 (C^5), 187.11 (C^4). ^{11}B NMR spectrum: δ_B 69.4 ppm ($w_{1/2}$ = 0.3 kHz). Found, %: C 66.33; H 10.98. M 202. $C_{12}H_{22}BCl$. Calculated, %: C 67.80; H 10.43. M 212.56.

3-Alkyl-1-bromoborolanes VIIa–VIIc and 4,5-dialkyl-1-bromo-2,3-dihydro-1*H*-boroles IXa–IXc (*general procedure*). A 50-mL glass reactor was charged under dry argon under stirring at 0°C in succession with 5 mL of hexane, 0.5 mmol Cp_2ZrCl_2, 10 mmol of the corresponding alkene or acetylene, and 12 mmol of $AlEt_3$. The mixture was stirred for 8 h at 20–22°C and cooled to –60°C, 24 mmol of BBr_3 was added dropwise, the mixture was stirred for 30 min at 0°C, 1 mL of THF was added, and the mixture was allowed to warm up to room temperature. Hexane and THF were evaporated, and the residue was distilled under reduced pressure in a stream of argon.

1-Bromo-3-butylborolane (VIIa). Yield 1.46 g (72%), colorless liquid, bp 85°C (16 mm). ^{1}H NMR spectrum, δ, ppm: 0.46 d.d (1H, 2-H, J = 17.9, 12.0 Hz), 0.73–0.95 m (4H, 5-H, CH_3), 1.11 m (1H, 4-H), 1.21–1.50 m (7H, 5-H, CH_2), 1.59 d.d (1H, 2-H, J = 17.9, 6.0 Hz), 1.75 m (1H, 3-H), 1.92 m (1H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 14.23, 23.11, 27.19 (C^5), 32.34, 33.45 (C^4), 35.51 (C^2), 37.63, 41.52 (C^3). ^{11}B NMR spectrum: δ_B 92.5 ppm ($w_{1/2}$ = 0.24 kHz). Found, %: C 51.05; H 8.50. M 201. $C_8H_{16}BBr$. Calculated, %: C 47.35; H 7.95. M 202.94.

1-Bromo-3-hexylborolane (VIIb). Yield 1.5 g (65%), colorless liquid, bp 80°C (6 mm). ^{1}H NMR spectrum, δ, ppm: 0.46 d.d (1H, 2-H, J = 18.2, 10.4 Hz), 0.81 m (1H, 5-H), 0.93 t (3H, CH_3, J = 7.5 Hz), 1.08–1.15 m (1H, 4-H), 1.30–1.40 m (11H, 5-H, CH_2), 1.53 d.d (1H, 2-H, J = 18.5, 6.9 Hz), 1.70 m (1H, 3-H), 1.95 m (1H, 4-H). ^{13}C NMR spectrum, δ_C, ppm: 14.22, 23.32, 27.41 (C^5), 29.30, 30.99, 32.99, 32.99, 34.18 (C^4), 35.15 (C^2), 38.91, 41.98 (C^3). ^{11}B NMR spectrum: δ_B 91.9 ppm ($w_{1/2}$ = 0.25 kHz). Found, %: C 50.63; H 7.98. M 229. $C_{10}H_{20}BBr$. Calculated, %: C 51.99; H 8.73. M 230.99.

1-Bromo-3-octylborolane (VIIc). Yield 1.42 g (55%), colorless liquid, bp 94°C (4 mm). ^{1}H NMR spectrum, δ, ppm: 0.47 d.d (1H, 2-H, J = 17.4, 11.3 Hz), 0.75 m (1H, 5-H), 0.83 t (3H, CH_3, J = 7.2 Hz), 1.09 m (1H, 4-H), 1.20–1.49 m (15H, 5-H, CH_2), 1.58 d.d (1H, 2-H, J = 17.4, 7.2 Hz), 1.75 m (1H, 3-H), 1.89–1.93 m (1H, 4-H). ^{13}C NMR spec-

trum, δ_C, ppm: 14.15, 22.74, 27.17 (C^5), 29.44, 29.76, 30.08, 31.99 (2C), 33.41 (C^4), 35.50 (C^2), 37.91, 41.48 (C^3). ^{11}B NMR spectrum: δ 93.7 ppm ($w_{1/2}$ = 0.28 kHz). Found, %: C 53.81; H 9.95. *M* 252. $C_{12}H_{24}BBr$. Calculated, %: C 55.64; H 9.34. *M* 259.04.

1-Bromo-4,5-diethyl-2,3-dihydro-1*H*-borole (IXa). Yield 1.6 g (80%), colorless liquid, bp 77°C (10 mm). ^1H NMR spectrum, δ, ppm: 1.06 t (3H, 5-CH_2CH_3, *J* = 7.7 Hz), 1.10 t (3H, 4-CH_2CH_3, *J* = 7.7 Hz), 1.22 m (2H, 2-H), 2.10 q (2H, 4-CH_2, *J* = 7.7 Hz), 2.20 q (2H, 5-CH_2, *J* = 7.7 Hz), 2.42 m (2H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 13.00, 13.25, 19.71, 20.44, 21.70 (C^2), 35.87 (C^3), 141.52 (C^5), 182.96 (C^4). ^{11}B NMR spectrum: δ_B 81.06 ppm ($w_{1/2}$ = 0.26 kHz). Found, %: C 46.31; H 6.88. *M* 201. $C_8H_{14}BBr$. Calculated, %: C 47.82; H 7.02. *M* 200.92.

1-Bromo-4,5-dipropyl-2,3-dihydro-1*H*-borole (IXb). Yield 1.7 g (75%), colorless liquid, bp 85°C (10 mm). ^1H NMR spectrum, δ, ppm: 0.99 t (3H, 4-$CH_2CH_2CH_3$, *J* = 8.5 Hz), 1.08 t (3H, 5-$CH_2CH_2CH_3$, *J* = 8.5 Hz), 1.35 m (2H, 2-H), 1.42 sext (2H, 4-CH_2CH_2, *J* = 8.5 Hz), 1.56 sext (2H, 5-CH_2CH_2, *J* = 8.5 Hz), 2.11 t (2H, 4-CH_2, *J* = 8.5 Hz), 2.30–2.40 m (4H, 3-H, 5-CH_2). ^{13}C NMR spectrum, δ_C, ppm: 14.13, 14.54, 21.22 (C^2), 22.50, 23.90, 30.83, 33.55, 37.48 (C^3), 148.05 (C^5), 185.56 (C^4). ^{11}B NMR spectrum: δ_B 82.00 ppm ($w_{1/2}$ = 0.28 kHz). Found, %: C 53.06; H 7.90. *M* 220. $C_{10}H_{18}BBr$. Calculated, %: C 52.45; H 7.92. *M* 228.97.

1-Bromo-4,5-dibutyl-2,3-dihydro-1*H*-borole (IXc). Yield 1.8 g (70%), colorless liquid, bp 107°C (4 mm). ^1H NMR spectrum, δ, ppm: 0.75–0.93 m (6H, CH_3), 1.14 m (2H, 2-H), 1.16–1.34 m (6H, CH_2), 1.40 quint (2H, CH_2, *J* = 8.0 Hz), 2.09 t (2H, CH_2, *J* = 8.0 Hz), 2.28 t (2H, CH_2, *J* = 8.0 Hz), 2.33 m (2H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 14.07, 14.18, 21.65 (C^2), 23.13 (2C), 27.33, 30.91, 32.43, 33.18, 36.39 (C^3), 147.90 (C^5), 181.97 (C^4). ^{11}B NMR spectrum: δ_B 81.8 ppm ($w_{1/2}$ = 0.26 kHz). Found, %: C 55.30; H 7.99. *M* 252. $C_{12}H_{22}BBr$. Calculated, %: C 56.07; H 8.63. *M* 257.02.

Pyridinium 1-bromo-3-butylborolan-1-ide (VIIa·Py). A 50-mL glass reactor was charged under dry argon under stirring at 0°C in succession with 5 mL of hexane, 0.5 mmol Cp_2ZrCl_2, 10 mmol of hex-1-ene, and 12 mmol of $AlEt_3$. The mixture was stirred for 8 h at 20–22°C, 10 mL of hexane was added, the mixture was cooled to –60°C, 24 mmol of BBr_3 was added dropwise, and the mixture was stirred for 30 min at 0°C. Pyridine, 72 mmol, was then added, the mixture was allowed to warm up to room temperature, hexane and excess pyridine were evaporated, and the residue was distilled under reduced pressure in a stream of argon. Yield 1.84 g (52%), light yellow liquid, bp 90°C (2 mm). ^1H NMR spectrum, δ, ppm: 0.08 t (1H, 2-H, *J* = 11.7 Hz), 0.35–0.45 m (2H, 5-H), 0.88 t (3H, CH_3, *J* = 7.8 Hz), 0.90–1.00 m (2H, 2-H, 4-H), 1.20–1.38 m (6H, CH_2), 1.55 m (1H, 3-H), 1.74 m (1H, 4-H); 7.56 t (2H, *J* = 8.0 Hz), 7.96 t (1H, *J* = 8.0 Hz), and 8.64 br.s (2H, $w_{1/2}$ = 13.23 kHz) (pyridine). ^{13}C NMR spectrum, δ_C, ppm: 14.71, 22.42 (C^5), 24.18, 32.13 (C^2), 32.34, 36.59 (C^4), 39.95, 43.85 (C^3); 125.78, 139.78, and 147.53 (pyridine). ^{11}B NMR spectrum: δ_B 5.0 ppm. Found, %: C 54.99; H 7.48; N 4.85. *M* 279. $C_{13}H_{21}BBrN$. Calculated, %: C 55.36; H 7.51; N 4.97. *M* 282.03.

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