Hydroboration and Haloboration of Propyne and 1-Butyne

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Dedicated to Prof. Donald S. Matteson

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Hydroboration, Haloboration, Boron

Hydroboration of propyne and 1-butyne with $HBCl_2$ obtained from BCl_3 and Me_3SiH in equimolar amounts leads to 1,1-bis(dichloroboryl)alkanes **1**. When BCl_3 is used in excess, no 1,1-bis(dichloroboryl)alkanes **1** but E-1-dichloroborylalkene **2** besides E-1-dichloroboryl-2-chloro-alk-1-ene **3** are formed. Other by-products are tris(2-chloro-alk-1-ene-1-yl)borane **4** and bis(2-chloro-alk-1-ene-1-yl)chloroborane **5**. The reaction of **3** with catechol and the formation of pyridine adducts of **4** and **5** lead to crystalline products. The composition of the products was determined by NMR spectroscopy, MS spectrometry and X-ray structure analyses of **6a**, **6b**, **7a** and **8b**.

Introduction

In 1976 the first double hydroboration of terminal alkynes with $HBCl_2$ was reported by H. C. Brown and N. Ravindran using $HBCl_2 \cdot OEt_2/BCl_3$ [1] as hydroboration reagent [2]. Because hydroboration reactions with Me_3SiH/BCl_3 are more convenient [3], acetylene [4], 3,3-dimethyl-1-butyne [5, 6], phenylacetylene [7], and mesitylacetylene [7] have been hydroborated according to this method. Zhao *et al.* [8] observed that 1-octyne and 1-hexyne undergo both monohydroboration and chloroboration when the alkyne was reacted with $HBCl_2 \cdot SMe_2$ in a 1.4 : 1 ratio at –20 °C in the presence of BCl_3. At 0 °C double hydroboration took place preferentially [8]. The bromoboration of 1-hexyne, investigated by Blackborow [9], shows that Z- or E-bromo-hex-1-ene-1-yldibromoborane (I), Z,E- and Z,Z-bis(2-bromo-hex-1-ene-1-yl)bromoborane (II) and Z,Z,Z-tris(2-bromo-hex-1-ene-1-yl)borane (III) can be prepared by addition of a stoichiometric amount of 1-hexyne to tribromoborane. The Z-I, Z,Z-II and Z,Z,Z-III isomers, respectively, are formed preferentially. In the case of chloroboration no definite results regarding the preferred configurations of chlorohexenyldichloroborane, bis(chlorohexenyl)chloroborane and tris(chlorohexenyl)borane were reported because of difficulties in determining the configuration of the hexenylboranes [9].

We report here on the hydroboration of propyne and 1-butyne with BCl_3 and Me_3SiH in equimolar amounts, which leads to the expected 1,1-bis-(dichloroboryl)alkanes **1**, whereas the reaction of propyne with BCl_3 and Me_3SiH in the molar ratio 1.25 : 1 forms a product mixture of monohydroborated and haloborated compounds. Furthermore the chloroboration products of propyne and 1-butyne were investigated. This included substitution reactions of the organo-chloroborane products to obtain crystalline derivatives, suitable for X-ray structure analyses.

Results and Discussion

Synthesis and reactivity of organo-chloroboranes

Hydroboration of propyne and 1-butyne with equimolar amounts of Me_3SiH and BCl_3 at –78 °C in pentane leads to the products **1a** and **1b**, respectively, in good yields. The NMR spectra of **1a** are in agreement with the reported data [6]. The ^1H, ^{11}B and ^{13}C NMR spectra of **1b** exhibit the expected

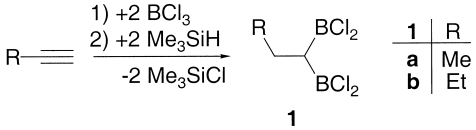

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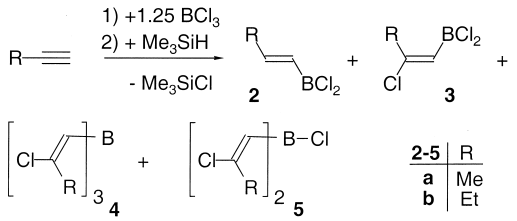
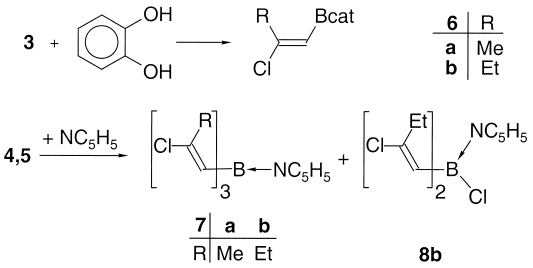
Table 1. Crystal data and structure refinement for **6a**, **7a**, **6b**, and **8b**.

	6a	**7a**	**6b**	**8b**
Empirical formula	$C_9H_8BClO_2$	$C_{14}H_{17}BCl_3N$	$C_{10}H_{10}BClO_2$	$C_{13}H_{17}BCl_3N$
Formula weight	194.42	316.46	208.44	304.44
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$
Unit cell dims: a [Å]	11.075(7)	9.2888(4)	5.3239(3)	8.2252(4)
b [Å]	5.449(2)	9.9593(5)	16.5545(9)	9.4989(5)
c [Å]	15.337(10)	17.5772(8)	11.3143(6)	10.6474(5)
α [°]	90	90	90	105.541(1)
β [°]	100.21(5)	90	94.070(1)	99.737(1)
γ [°]	90	90	90	96.955(1)
Volume [Å^3]	910.8(9)	1626.1(1)	994.7(1)	777.7(1)
Z	4	4	4	2
Calcd. density [g/cm^3]	1.418	1.293	1.392	1.300
Absorp. coeff. [mm^{-1}]	0.38	0.55	0.350	0.571
$F(000)$	400	656	432	316
Crystal size [mm]	0.08×0.12×0.42	0.28×0.30×0.38	0.45×0.30×0.29	0.48×0.37×0.30
Temperature [K]	173	173	190	190
Θ_{max} [°]	28.35	28.27	32.24	32.40
Unique reflections	(8422)	3865	3303	5146
Observed refls [$I > 2\sigma(I)$]	(6709)	3551	2836	4432
Parameters	151	240	170	231
Final $R1$ [$I > 2\sigma(I)$]	0.0562	0.0286	0.0352	0.0369
Final $wR2$	0.1802	0.0711	0.1039	0.1058
Largest diff. peak/hole [e/Å^3]	+0.44/–0.34	+0.28/–0.13	+0.40/–0.22	+1.06/–0.60





signals (for details see experimental section). An EI mass spectrum of **1b** shows the molecular ion peak [M$^+$] at $m/z = 218$.

Both hydroboration **2** and chloroboration products **3** and **4** are obtained in the reaction of propyne and 1-butyne, respectively, with BCl_3 and Me_3SiH in the molar ratio 1.25 : 1. The isolation of the compounds **2** and **3** is difficult because of similar boiling points. Compounds **3** and **4** are also formed in absence of Me_3SiH in excellent yields. Depending on how long propyne or 1-butyne, respectively, is bubbled through the reaction solution, the product ratio of monoalkenylated to trisalkenylated borane varies. In the case of 1-butyne, the appearance of E,E-bis(2-chloro-but-1-ene-1yl)chloroborane (**5b**) is observed. It is surprising that no indication is found for the existence of bis(propenyl)-chloroborane (**5a**) which also should be formed as intermediate during the chloroboration of three molecules of propyne. Heating of compound **3** leads to the symmetrical product **4** with elimination of BCl_3.

In order to have evidence for the exact configuration the products **3**, **4** and **5b** were reacted with catechol or pyridine to obtain crystalline derivatives appropriate for X-ray structure analyses. Compounds **3a**, **b** gave the substitution products **6a**, **b**, while **4** and **5b** yielded the donor-acceptor compounds **7a**, **7b** and **8b**.

The crystal structure analyses reveal that the monoalkenylated **6a** and **6b**, the bisalkenylated **8b** and the trisalkenylated compound **7a** have E configuration. Most probably the kinetically preferred

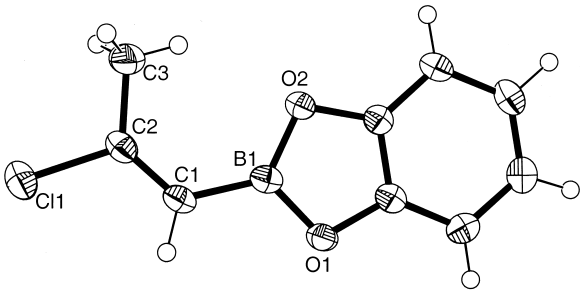


Fig. 1. Structure of **6a** in the crystal; selected bond lengths [Å] and angles [°]: B1-C1 1.532(2), C1-C2 1.320(2), C2-Cl1 1.760(2), C2-C3 1.483(3), B1-O1 1.392(2), B1-O2 1.396(2), C1-B1-O1 121.8(1), C1-B1-O2 127.7(2), O1-B1-O2 110.6(1).

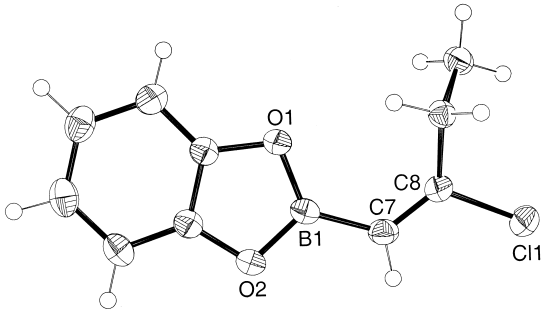


Fig. 2. Structure of **6b** in the crystal; selected bond lengths [Å] and angles [°]: B1-C7 1.534(2), C7-C8 1.317(2), C8-Cl1 1.757(1), B1-O1 1.395(1), B1-O2 1.395(1), C7-B1-O1 127.1(1), C7-B1-O2 121.8(1), O1-B1-O2 111.1(1).

Z-isomers are formed first at low temperature. Under distillation conditions the activation energy necessary for isomerisation is supplied, so that finally the thermodynamically most stable E-configurated products are formed. The olefinic protons of **3b**, **4b**, **5b**, **6b**, **7b** and **8b** would be expected to show a triplet pattern, however, the fine structures were not well resolved and therefore the resonances were treated as "singlets".

Crystal structures of **6a**, **6b**, **7a** *and* **8b**

To elucidate the structures, X-ray diffraction studies were carried out (crystal data and structure refinement parameters for **6a**, **6b**, **7a** and **8b** are presented in Table 1). The colorless crystals of **6a**, grown at –30 °C from a solution in dichloromethane, belong to the monoclinic system, space group $P2_1/n$. The molecular structure is shown in Fig. 1. The coordination of the boron atom is trigonal planar.

A single crystal of **6b** was grown from a solution in dichloromethane at 20 °C. **6b** crystallizes in the monoclinic space group $P2_1/n$. The molecular structure is shown in Fig. 2. For all distances and bonding angles no significant differences in comparison to the structural data of **6a** are observed.

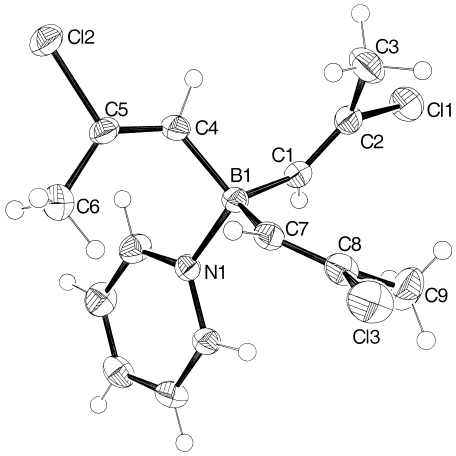


Fig. 3. Structure of **7a** in the crystal; selected bond lengths [Å] and angles[°]: B1-C1 1.627(2), B1-C4 1.627(2), B1-C7 1.623(2), B1-N1 1.646(2), C1-C2 1.319(2), C4-C5 1.324(2), C7-C8 1.324(2), C2-Cl1 1.785(2), C5-Cl2 1.777(1), C8-Cl3 1.782(2), C1-B1-N1 103.8(1), C4-B1-N1 108.6(1), C7-B1-N1 108.1(1), C1-B1-C4 110.9(1), C1-B1-C7 116.5(1), C4-B1-C7 108.6(1).

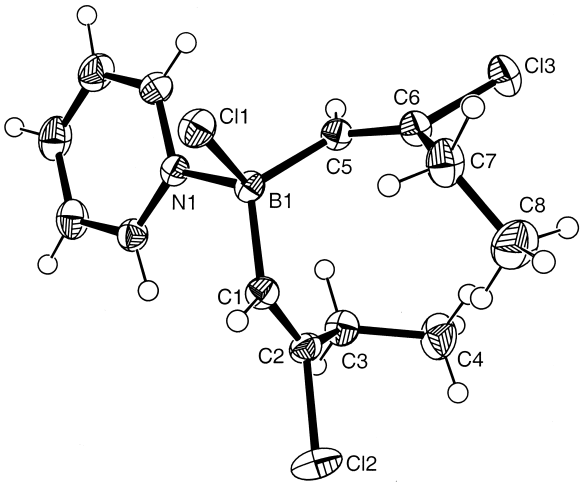


Fig. 4. Structure of **8b** in the crystal; selected bond lengths [Å] and angles[°]: B1-C1 1.603(2), B1-C5 1.606(2), B1-Cl1 1.923(1), B1-N1 1.617(2), C1-C2 1.331(2), C5-C6 1.331(2), C2-Cl2 1.771(1), C6-Cl3 1.778(1), C1-B1-C5 116.1(1), C1-B1-N1 111.8(1), C5-B1-N1 107.7(1), C1-B1-Cl1 107.2(1), C5-B1-Cl1 110.7(1), N1-B1-Cl1 102.5(1).

Crystals of **7a** and **8b** were grown from toluene at –30 °C. **7a** crystallizes in the orthorhombic space group $P2_12_12_1$, while **8b** belongs to the triclinic

space group $P\bar{1}$. The molecular structures are shown in Figs 3 and 4. The coordination of the boron atoms is distorted tetrahedral. The B-N distances (1.646 and 1.617 Å) are in agreement with those found in other pyridine adducts [10, 11].

Experimental Section

All experiments were performed under argon using the Schlenk technique. Solvents were dried, distilled and saturated with nitrogen. Glassware was dried with a heat-gun under high vacuum. – ^{1}H, ^{13}C and ^{11}B NMR: Bruker DRX 200 spectrometer, $Et_2O{\cdot}BF_3$ was used as the external standard for ^{11}B NMR. As internal references for ^{1}H and ^{13}C NMR spectra the signals of the deuterated solvents were used and calculated for TMS. The mass spectra were measured on a ZAB-2F VH Micromass CTD spectrometer (EI and HR-EI techniques) and on a Jeol MS station JMS 700 (EI, and HR-EI techniques). – Melting points (uncorrected) were measured with a Büchi apparatus using capillaries which were filled under argon or nitrogen and sealed.

*1,1-*B*is(dichloroboryl)butane (***1b***)*

Dried 1-butyne is bubbled at –78 °C through a solution of 76 g (0.65 mol) of BCl_3 in 250 ml of pentane. At the same time a solution of 48.3 g (0.65 mol) of trimethylsilane in 50 ml of pentane is added slowly via a dropping funnel so that almost all 1-butyne passing through the solution is absorbed. Then the reaction mixture is allowed to warm to 20 °C. After removal of the pentane at 50 mbar the residue is distilled to yield 61.1 g of **1b** (85.8%). – B. p. 85 °C/200 mbar. – ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 0.91 (t, ^{3}J = 7.2 Hz, 3 H, CH_2CH_3), 1.32 (m, 2 H, CH_2CH_3), 1.94 (m, 2 H, B_2CHCH_2), 2.62 (m, 1 H, B_2CHCH_2). – ^{13}C{^{1}H} NMR (50.32 MHz, $CDCl_3$): δ = 14.3 (CH_2CH_3), 24.9 (CH_2CH_3), 32.9 (B_2CHCH_2), 49 (br., B_2CHCH_2). – ^{11}B NMR (64.21 MHz, $CDCl_3$): δ = 60.3. – MS (EI, 70 eV): *m*/z (%) = 218 (1) [M^+], 183 (3) [M^+ - Cl], 102 (100) [M^+ - Cl - BCl_2], 81 (89) [BCl_2^+], 43 (66) [$C_3H_7^+$], 29 (67) [$C_2H_5^+$].

*E-1-*D*ichloroboryl-prop-1-ene (***2a***), E-1-dichloroboryl-2-chloro-prop-1-ene (***3a***) and E,E,E-tris(2-chloro-prop-1-ene-1-yl)borane (***4a***)*

Dried propyne is bubbled at –78 °C through a solution of 67 g (0.55 mol) of BCl_3 in 150 ml of pentane. At the same time a solution of 29.0 g (0.39 mol) of trimethylsilane in 50 ml of pentane is added slowly via a dropping funnel so that almost all propyne passing through the solution is absorbed. Then the reaction mixture is allowed to warm to 20 °C. After removal of the pentane at 50 mbar the residue is distilled to yield 38.4 g of **2a** (55.1%), 12.3 g of **3a** (13.7%) and 5.4 g of **4a** (4.0%). **2a**: B. p. 40 °C / 200 mbar. – ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 1.98 (dd, ^{3}J = 6.6 Hz, ^{4}J = 1.5 Hz, 3 H, $CHCH_3$), 6.08 (dq, ^{3}J = 17.2 Hz, ^{4}J = 1.5 Hz, 1 H, BCH), 7.10 - 7.29 (m, 1 H, $CHCH_3$). – ^{13}C{^{1}H} NMR (50.32 MHz, $CDCl_3$): δ = 22.0 ($CHCH_3$), 132 (br., BCH), 160.8 ($CHCH_3$). – ^{11}B NMR (64.21 MHz, $CDCl_3$): δ = 52.5. – MS (EI, 70 eV): *m*/z (%) = 122 (23) [M^+], 86 (100) [$C_3H_4BCl^+$].

3a: B. p. 65 °C / 200 mbar. – ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 2.60 (d, ^{4}J = 0.8 Hz, 3 H, $CClCH_3$), 6.22 (q, ^{4}J = 0.8 Hz, 1 H, BCH). – ^{13}C{^{1}H} NMR (50.32 MHz, $CDCl_3$): δ = 26.4 ($CClCH_3$), 128 (br., BCH), 162.9 ($CClCH_3$). – ^{11}B NMR (64.21 MHz, $CDCl_3$): δ = 50.5. – MS (EI, 70 eV): *m*/z (%) = 156 (15) [M^+], 120 (54) [M^+ - HCl], 81 (100) [BCl_2^+]. – HR-MS (EI): *m*/z = 155.9504 (M^+), calcd. $^{12}C_3{}^{1}H_4{}^{11}B_1{}^{35}Cl_3$: 155.9472 ($\Delta$ = 3.3 mmu).

4a: B. p. 120 °C / 200 mbar. – ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 2.32 (d, ^{4}J = 0.6 Hz, 9 H, $CClCH_3$), 6.3 (br., 3 H, BCH). – ^{13}C{^{1}H} NMR (50.32 MHz, $CDCl_3$): δ = 26.4 ($CClCH_3$), 134 (br., BCH), 152.3 ($CClCH_3$).- ^{11}B NMR (64.21 MHz, $CDCl_3$): δ = 54.7. – MS (EI, 70 eV): *m*/z (%) = 236 (1) [M^+], 196 (18) [M^+ - C_3H_4], 161 (33) [M^+ - C_3H_4Cl], 41 (100) [$C_3H_5^+$]. – HR-MS (EI): *m*/z = 236.0071 (M^+), calcd. $^{12}C_9{}^{1}H_{12}{}^{11}B_1{}^{35}Cl_3$: 236.0045 ($\Delta$ = 2.6 mmu).

Alternative synthesis of **3a** *and* **4a**

Dried propyne is bubbled at –78 °C through a solution of 47.3 g (0.4 mol) of BCl_3 in 250 ml of pentane for 1 h. Then the reaction mixture is allowed to warm to 20 °C. An ^{11}B NMR spectrum of the crude product shows that only **3a** is formed. Then pentane is removed in a vacuum and the residue is purified by distillation to give 42.7 g of **3a** (67.6%) and 5.7 g of **4a** (6.0%).

*E-1-*D*ichloro-2-chloro-but-1-ene (***3b***), E,E-bis(2-chloro-but-1-ene-1-yl)chloro-borane (***5b***) and E,E,E-tris(2-chloro-but-1-ene-1-yl)borane (***4b***)*

Dried 1-butyne is bubbled at –78 °C through a solution of 47.3 g (0.4 mol) of BCl_3 in 250 ml of pentane for 3 h. Then the reaction mixture is allowed to warm to 20 °C. After removal of pentane at 50 mbar the residue is distilled to yield 54.8 g of **3b** (79.1%, B. p. 88 °C / 160 mbar) and 4.3 g of **5b** (4.7%, B. p. 52 °C / 0.05 mbar). A third fraction is obtained at 90 - 100 °C / 0.05 mbar consisting of 3.17 g of **5b** (3.5%) and 2.22 g of **4b** (2.0%). The separation of **4b** from **5b** was not possible (yield determined by ^{11}B NMR). **3b**: B. p. 88 °C/160 mbar. – ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 1.23 (t, ^{3}J = 7.4 Hz, 3 H, CH_2CH_3), 2.93 (q, ^{3}J = 7.4 Hz, 2 H, CH_2CH_3), 6.24 (s, 1 H, BCH). – ^{13}C{^{1}H} NMR (50.32 MHz, $CDCl_3$): δ = 13.0 (CH_2CH_3),

32.0 (CH_2CH_3), 127 (br., BCH), 169.1 ($CClCH_2$). – ^{11}B NMR (64.21 MHz, $CDCl_3$): δ = 50.4. – MS (EI, 70 eV): *m*/z (%) = 170 (6) [M^+], 155 (1) [M^+ - CH_3], 134 (7) [M^+ - HCl], 98 (16) [M^+ - 2HCl], 81 (76) [BCl_2^+], 54 (100) [$C_4H_6^+$], 36 (90) [HCl^+]. – HR-MS (EI): *m*/z = 169.9636 (M^+), calcd. $^{12}C_4{}^1H_6{}^{11}B_1{}^{35}Cl_3$: 169.9628 ($\Delta$ = 0.8 mmu).

5b: B. p. 52 °C/0.05 mbar. – ^1H NMR (200.13 MHz, $CDCl_3$): δ = 1.21 (t, ^3J = 7.4 Hz, 6 H, CH_2CH_3), 2.79 (q, ^3J = 7.4 Hz, 4 H, CH_2CH_3), 6.22 (s, 2 H, BCH). - $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ = 13.1 (CH_2CH_3), 32.4 (CH_2CH_3), 130 (br., BCH), 163.3 ($CClCH_2$). – ^{11}B NMR (64.21 MHz, $CDCl_3$): δ = 53.7. - MS (EI, 70 eV): *m*/z (%) = 224 (14) [M^+], 189 (24) [M^+ - Cl], 134 (100) [M^+ - H - C_4H_6Cl], 98 (97) [M^+ - H - HCl - C_4H_6Cl], 54 (91) [$C_4H_6^+$]. – HR-MS (EI): *m*/z = 224.0837 (M^+), calcd. $^{12}C_8{}^1H_{12}{}^{11}B_1{}^{35}Cl_3$: 224.0878 ($\Delta$ = 4.1 mmu).

4b: ^1H NMR (200.13 MHz, $CDCl_3$): δ = 1.15 (t, ^3J = 7.4 Hz, 9 H, CH_2CH_3), 2.59 (q, ^3J = 7.4 Hz, 6 H, CH_2CH_3), 6.25 (s, 3 H, BCH). - $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ = 13.1 (CH_2CH_3), 32.6 (CH_2CH_3), 134 (br., BCH), 157.7 ($CClCH_2$). - ^{11}B NMR (64.21 MHz, $CDCl_3$): δ = 52.7. - MS (EI, 70 eV): *m*/z (%) = 277 (8) [M^+ - H], 243 (27) [M^+ - Cl], 215 (16) [M^+ + H - Cl - C_2H_5], 189 (60) [M^+ - C_4H_6Cl], 161 (40) [M^+ + H - C_4H_6Cl - C_2H_5], 99 (63) [$C_4H_5ClB^+$] 55 (100) [$C_4H_7^+$]. - HR-MS (EI): *m*/z = 278.0600 (M^+), calcd. $^{12}C_{12}{}^1H_{18}{}^{11}B_1{}^{35}Cl_3$: 278.0633 ($\Delta$ = 3.3 mmu).

*E-1-[1,3,2-*B*enzodioxaborol-2-yl]-2-chloro-prop-1-ene* (**6a**)

Catechol (110 mg, 1 mmol) is dissolved in 20 ml of CH_2Cl_2 and 160 mg (1 mmol) of **3a** is added dropwise at –60 °C. After the solution is allowed to warm to 20 °C, CH_2Cl_2 is removed in a vacuum to give 169 mg of colorless **6a** (85.4%). – M. p. 48 °C. – ^1H NMR (200.13 MHz, $CDCl_3$): δ = 2.52 (d, ^4J = 0.7 Hz, 3 H, $CClCH_3$), 5.86 (q, ^4J = 0.7 Hz, 1 H, BCH), 7.18-7.20 (m, 4 H, C_6H_4). - $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ = 26.5 ($CClCH_3$), 112.6, 123.1, 148.1 (C_6H_4), 153 (br., BCH), 156.0 ($CClCH_3$). - ^{11}B NMR (64.21 MHz, $CDCl_3$): δ = 30.0. - MS (EI, 70 eV):*m*/z (%) = 194 (28) [M^+], 154 (100) [M^+ - C_3H_4]. - HR-MS (EI): *m*/z = 194.0304 (M^+), calcd. $^{12}C_9{}^1H_8{}^{11}B_1{}^{35}Cl_1{}^{16}O_2$: 194.0306 ($\Delta$ = 0.2 mmu).

*E-1-[1,3,2-*B*enzodioxaborol-2-yl]-2-chloro-but-1-ene* (**6b**)

Catechol (1.10 g, 10 mmol) is dissolved in 80 ml of CH_2Cl_2 and 1.71 g (10 mmol) of **3b** is added dropwise at -60 °C. After the solution is allowed to warm to 20 °C, CH_2Cl_2 is removed in a vacuum to yield 1.90 g of colorless **6b** (91.3%). – M. p. 28 °C – ^1H NMR (200.13 MHz, $CDCl_3$): δ = 1.24 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 2.89 (q, ^3J = 7.4 Hz, 2 H, CH_2CH_3), 5.86 (s, 1 H, BCH), 7.00 - 7.25 (m, 4 H, C_6H_4). – $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ = 13.2 (CH_2CH_3), 32.3 (CH_2CH_3), 112.5, 122.8, 147.8 (C_6H_4), 159 (br., BCH), 162.2 ($CClCH_2$). – ^{11}B NMR (64.21 MHz, $CDCl_3$): δ = 29.9. – MS (EI, 70 eV): *m*/z (%) = 208 (13) [M^+], 173 (2) [M^+ - Cl], 154 (100) [M^+ - C_4H_6], 144 (7) [M^+ - Cl - C_2H_5], 119 (2) [$C_6H_4O_2B^+$]. – HR-MS (EI): *m*/z = 208.0465 (M^+), calcd. $^{12}C_{10}{}^1H_{10}{}^{11}B_1{}^{35}Cl_1{}^{16}O_2$: 208.0468 ($\Delta$ = 0.3 mmu).

E,E,E-Tris(2-chloro-prop-1-ene-1-yl)borane-pyridine adduct (**7a**)

The solution of 0.51 g (2.1 mmol) of **4a** in 20 ml of pentane is cooled to –10 °C and 0.17 g (2.1 mmol) of pyridine is added dropwise. After the solution is allowed to warm to 20 °C, pentane is removed in a vacuum to yield 0.64 g of colorless **7a** (94.1%). – M. p. 78 °C. – ^1H NMR (200.13 MHz, $CDCl_3$): δ = 1.95 (d, ^4J = 0.8 Hz, 9 H, $CClCH_3$), 5.84 (q, ^4J = 0.8 Hz, 3 H, BCH), 7.66 (m, 2 H, py-H), 8.07 (m, 1 H, py-H), 8.66 (m, 2 H, py-H). – $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ = 24.4 ($CClCH_3$), 138 (br., BCH), 145.7 ($CClCH_3$), 126.1, 135.0, 140.9 (py-C). – ^{11}B NMR (64.21 MHz, $CDCl_3$): δ = –3.3.

*E,E-*B*is(2-chloro-but-1-ene-1-yl)chloroborane-pyridine adduct* (**8b**)

The solution of 1.03 g (4.6 mmol) of **5b** in 30 ml of pentane is cooled to –10 °C and 0.36 g (4.6 mmol) of pyridine is added dropwise. After the solution is allowed to warm to 20 °C, pentane is removed in a vacuum to yield 1.27 g of colorless **8b** (91.2%). – M. p. 72 °C. – ^1H NMR (200.13 MHz, $CDCl_3$): δ = 1.03 (t, ^3J = 7.3 Hz, 6 H, CH_2CH_3), 2.39 (q, ^3J = 7.3 Hz, 4 H, CH_2CH_3), 5.87 (s, 2 H, BCH), 7.71 (m, 2 H, py-H), 8.13 (m, 1 H, py-H), 8.90 (m, 2 H, py-H). – $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ = 12.3 (CH_2CH_3), 30.9 (CH_2CH_3), 135 (br., BCH), 144.7 ($CClCH_2$), 126.0, 135.0, 142.0 (py-C). – ^{11}B NMR (64.21 MHz, $CDCl_3$): δ = 2.5.

E,E,E-Tris(2-chloro-but-1-ene-1-yl)borane-pyridine adduct (**7b**)

The solution of 1.00 g of the mixture of **4b** and **5b**, containing 0.51 g (1.83 mmol) of **4b**, in 30 ml of pentane is cooled to –10 °C and 0.31 g (3.9 mmol) of pyridine is added dropwise. After the solution is allowed to warm to 20 °C, pentane is removed in a vacuum to yield 1.23 g of the product mixture of **7b** and **8b** which contains 0.51 g (77.7%) of colorless **7b**. **7b**: ^1H NMR (200.13 MHz, $CDCl_3$): δ = 0.93 (t, ^3J =7.3 Hz, 9 H, CH_2CH_3), 2.17 (q, ^3J = 7.3 Hz, 6 H, CH_2CH_3), 5.89 (s, 3 H, BCH), 7.58 (m, 2 H, py-H), 8.04 (m, 1 H, py-H), 8.68 (m, 2 H, py-H). –

$^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ = 12.1 (CH_2CH_3), 31.0 (CH_2CH_3), 141 (br., BCH), 144.7 ($CClCH_2$), 126.0, 141.5, 145.6 (py-C). – ^{11}B NMR (64.21 MHz, $CDCl_3$): δ = –4.2.

Crystal structure determinations of **6a**, **6b**, **7a**, **8b**

A summary of the crystal data and details of the structure determinations is given in Table 1. Data were collected on a Bruker AXS area detector Smart 1000 (Mo-K_α-radiation, λ = 0.71073 Å, ω-scans) at low temperature. Data were corrected for Lp- and absorption effects (semi-empirical, SADABS [12]). The structures were solved by direct methods and refined by full-matrix least-squares methods based on F^2 (SHELXTL) [13]. The crystals of **6a** were twinned. A data set of non-overlapped and exactly overlapped reflections of both components was prepared using the program GEMINI [14]. The structure was refined using the TWIN option in SHELXL97 [15]. The ethyl group in **6b** is disordered. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in difference Fourier syntheses and refined with isotropic displacement parameters (with exception for those of the disordered ethyl group in **6b**, which were inserted in calculated positions and refined using a riding model). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-176330 (**6a**), -176331 (**6b**), -176332 (**7a**), -176333 (**8b**).

Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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