ELECTROPHILIC HALOGENATION OF *nido*-5,6-C$_2$B$_8$H$_{12}$

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Room-temperature chlorination of the dicarbaborane *nido*-5,6-C$_2$B$_8$H$_{12}$ (**1**) with CCl$_4$ in the presence of anhydrous AlCl$_3$ yielded a mixture of 7-Cl-5,6-C$_2$B$_8$H$_{11}$ (7-Cl-**1**) (yield 34%), 4-Cl-5,6-C$_2$B$_8$H$_{11}$ (4-Cl-**1**) (yield 20%), 3-Cl-5,6-C$_2$B$_8$H$_{11}$ (3-Cl-**1**) (yield 21%), and 3,4-Cl$_2$-5,6-C$_2$B$_8$H$_{10}$ (3,4-Cl$_2$-**1**) (yield 26%), while a trisubstituted derivative, 3,4,7-Cl$_3$-5,6-C$_2$B$_8$H$_9$ (3,4,7-Cl$_3$-**1**) (yield 80%), was isolated as a sole product at reflux. Bromination of compound **1** with elemental Br$_2$ in the presence of Al powder at ambient temperature in CS$_2$ gave a mixture of 7-Br-5,6-C$_2$B$_8$H$_{11}$ (7-Br-**1**) (yield 31%) and 4,7-Br$_2$-5,6-C$_2$B$_8$H$_{10}$ (4,7-Br$_2$-**1**) (yield 52%). The most selective was AlCl$_3$-catalyzed iodination of **1** in refluxing benzene, which resulted in the formation of 7-I-5,6-C$_2$B$_8$H$_{11}$ (7-I-**1**) (yield 85%). Although performed under different conditions, the experiments point to the following order of reactivity of individual positions in **1** in electrophilic halogenation: 7 > 4 > 3. Individual compounds were isolated and purified by liquid chromatography and characterized by mass spectrometry and NMR spectroscopy (^{11}B, ^{1}H) combined with two-dimensional [^{11}B-^{11}B]-COSY and ^{1}H-{^{11}B(selective)} NMR techniques. Various NMR effects of halo-substitution are discussed for the series of monosubstituted 7-X-5,6-C$_2$B$_8$H$_{11}$ (7-X-**1**) compounds (X = Cl, Br, and I).

Keywords: Boranes; Carboranes; Dicarbaboranes; Electrophilic substitutions; Halogenations; NMR spectroscopy.

The ten-vertex dicarbaborane *nido*-5,6-C$_2$B$_8$H$_{12}$ (**1**), known since 1971 [1], has so far been employed as an extremely useful starting material for a variety of boron-cluster compounds containing two carbon vertices, such as [*nido*-C$_2$B$_8$H$_{10}$]$^{2-}$, *closo*-1,2-C$_2$B$_8$H$_{10}$, *arachno*-6,9-C$_2$B$_8$H$_{14}$, and ligand derivatives of the *arachno*-LC$_2$B$_8$H$_{12}$ type (where L = amines)[2–4]. Insertion of carbon atoms into the structure of **1** generated a series of 11-vertex *nido*-tricarbaboranes (derivatives of C$_3$B$_8$H$_{11}$$^-$)[5] and twelve-vertex *arachno* tetracarbaboranes of the C$_4$B$_8$H$_{14}$ structure[6]. Incorporation of other main-group elements[7–9] into **1** led to the isolation of the phoshadicarbaborane *nido*-PC$_2$B$_8$H$_{11}$, thiadicarbaborane *nido*-SC$_2$B$_8$H$_{10}$, and to the twelve-vertex *arachno* azatricarbaborane NC$_3$B$_8$H$_{11}$Me. Metal incorporation reactions between **1** and organometallic complexes generated a series of the eleven-vertex *closo*-

metalladicarbaboranes of the $MC_2B_8H_{10}$ type[10]. Preliminary results on electrophilic bromination, iodination and deuteration of **1** were published 25 years ago[11]. These halogenation reactions were performed under conditions similar to those employed earlier for other neutral carboranes[12] and boranes[13]. In this paper, we report full experimental details and a more complete set of halo derivatives of carborane **1**. These were isolated from specific substitution reactions of carborane **1** that lead to halo-substitution at three different boron positions of the cage.

RESULTS AND DISCUSSION

Halogenations of dicarbaborane *nido*-5,6-$C_2B_8H_{12}$ (**1**) under electrophilic conditions[12,13a], similar to those employed for the halogenation of *arachno*-6,9-$C_2B_8H_{14}$ or *nido*-$B_{10}H_{14}$, afforded mono-, di-, and trisubstituted derivatives, depending on the nature of the halogenation agent and temperature. Thus, a room-temperature reaction of compound **1** with CCl_4 in the presence of anhydrous $AlCl_3$ gave a mixture of 7-Cl-5,6-$C_2B_8H_{11}$ (7-Cl-**1**) (yield 34%), 4-Cl-5,6-$C_2B_8H_{11}$ (4-Cl-**1**) (yield 20%), 3-Cl-5,6-$C_2B_8H_{11}$ (3-Cl-**1**) (yield 21%), and 3,4-Cl_2-5,6-$C_2B_8H_{10}$ (3,4-Cl_2-**1**) (yield 26%). When the same reaction was performed at reflux, a trisubstituted derivative, 3,4,7-Cl_3-5,6-$C_2B_8H_9$ (3,4,7-Cl_3-**1**) (yield 80%), was isolated as a sole product. Bromination of compound **1** with elemental Br_2 in the presence of Al powder in CS_2 at room temperature gave 7-Br-5,6-$C_2B_8H_{11}$ (7-Br-**1**) (yield 31%) and 4,7-Br_2-5,6-$C_2B_8H_{10}$ (4,7-Br_2-**1**) (yield 52%), while $AlCl_3$-catalyzed iodination with I_2 in refluxing benzene gave only 7-I-5,6-$C_2B_8H_{11}$ (7-I-**1**) (yield 85%). Individual compounds could be isolated and purified by repeated liquid chromatography in CH_2Cl_2-hexane mixtures.
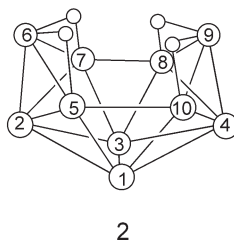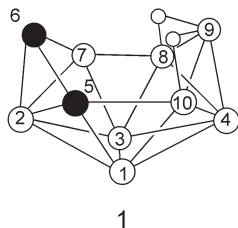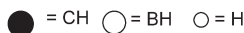

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TABLE I
NMR Data

Compound	Nucleus	Chemical shifts
5,6-$C_2B_8H_{12}$[a] **(1)**	^{11}B[b,c]	6.5 (d, 154, B7), 5.1 (d, 161, B1), 3.3 (d, 154, B8), –2.8 (d, 142, B3), –3.7 (d, 150, B9), –10.0 (d, 158/34, B10), –27.1 (d, 177, B2), –39.1 (d, 154, B4), all [^{11}B-^{11}B]-COSY cross-peaks observed
	$^1H\{^{11}B\}$[b,d]	6.48 (s, H6), 4.99 (s, H5), 3.54 (s, H1), 3.53 (s, H7), 3.14 (s, H9), 3.13 (s, H8), 2.95 (s, H3), 2.63 (s, H10), 1.05 (s, H2), 0.78 (s, H4), –2.21 (s, μH9,10), –2.47 (s, μH8,9)
7-Cl-5,6-$C_2B_8H_{11}$ **(7-Cl-1)**	^{11}B[b,c]	16.3 (s, –, B7) [9.8][e], 8.5 (d, ca. 160, B1), 6.7 (d, ca. 160, B8), –0.6 (d, ca. 160, B3), –1.1 (d, ca. 160, B9), –8.5 (d, 155, B10), –25.3 (d, 180, B2), –39.0 (d, 156, B4), all [^{11}B-^{11}B]-COSY cross-peaks observed
	$^1H\{^{11}B\}$[b,d]	6.20 (s, H6), 4.74 (s, H5), 3.57 (s, H1), 3.34 (s, H9), 3.29 (s, H8), 3.18 (s, H3), 2.66 (s, H10), 1.49 (s, H2), 0.80 (s, H4), –1.81 (s, μH9,10), –2.02 (s, μH8,9)
3-Cl-5,6-$C_2B_8H_{11}$ **(3-Cl-1)**	^{11}B[b,c]	10.95 (s, –, B3) [13.8]e, 7.8 (d, ca. 152, B1,7), 4.0 (d, 158, B8), –5.1 (d, 156, B9,10), –26.4 (d, 184, B2), –36.6 (d, 159, B4), all [^{11}B-^{11}B]-COSY cross-peaks observed
	$^1H\{^{11}B\}$[b,d]	6.20 (s, H6), 4.86 (s, H5), 4.02 (s, H7), 3.83 (s, H1), 3.41 (s, H8), 3.17 (s, H9), 2.80 (s, H10), 1.18 (s, H2), 0.96 (s, H4), –1.97 (s, μH9,10/8,9)
4-Cl-5,6-$C_2B_8H_{11}$ **(4-Cl-1)**	^{11}B[b,c]	7.3 (d, 153, B7), 6.5 (d, 159, B1), 4.1 (d, 159, B8), –0.8 (d, 149, B3), –3.2 (d, 147, B9), –10.0 (d, 159, B10), –21.9 (s, –, B4) [17.2][e], –27.0 (d, 184, B2), all [^{11}B-^{11}B]-COSY cross-peaks observed
	$^1H\{^{11}B\}$[b,d]	6.39 (s, H6), 5.14 (s, H5), 3.61 (s, H7), 3.83 (s, H1), 3.56 (s, H8), 3.51 (s, H9), 3.01 (s, H10), 1.17 (s, H2), –1.59 (s, μH9,10), –1.81 (s, μH8,9)
3,4-Cl_2-5,6-$C_2B_8H_{10}$ **(3,4-Cl_2-1)**	^{11}B[b,c]	11.1 (s, –, B3) [13.9][e], 8.8 (d, ca. 165, B7), 8.3 (d, ca. 153, B1), 4.6 (d, 159, B8), –4.0 (d, ca. 160, B9), –5.6 (d, ca. 160, B10), –20.8 (s, –, B4) [18.3][e], –26.0 (d, 180, B2), -all [^{11}B-^{11}B]-COSY cross-peaks observed, except B7–B8 and B8–B9
	$^1H\{^{11}B\}$[b,d]	6.15 (s, H6), 4.94 (s, H5), 4.12 (s, H7), 3.91 (s, H1), 3.63 (s, H8), 3.56 (s, H9), 3.14 (s, H10), 1.30 (s, H2), –1.30 (s, μH9,10/8,9)
3,4,7-Cl_3-5,6-$C_2B_8H_9$ **(3,4,7-Cl_3-1)**	^{11}B[b,c]	14.7 (s, –, B7)[8.2][e], 10.3 (s, –, B3) [13.1][e], 9.2 (s, ca.160, B1), 4.5 (d, 159, B8), –2.2 (d, 164, B9), –6.0 (d, 159, B10), –21.6 (s, –, B4) [17.5]e, –25.3 (d, 183, B2), all [^{11}B-^{11}B]-COSY cross-peaks observed
	$^1H\{^{11}B\}$[b,d]	6.14 (s, H6), 5.00 (s, H5), 3.90 (s, H1), 3.65 (s, H9), 3.39 (s, H8), 2.96 (s, H10), 1.44 (s, H2), –0.65 (s, μH9,10), –0.80 (s, μH8,9)
7-Br-5,6-$C_2B_8H_{11}$ **(7-Br-1)**	^{11}B[b,c]	9.6 (s, –, B7) [3.1][e], 7.4 (d, ca. 160, B1), 5.9 (d, ca. 160, B8), –0.9 (d, ca. 160, B3), –2.4 (d, ca. 160, B9), –9.4 (d, 156/33, B10), –26.3 (d, 183, B2), –39.4 (d, 158, B4), all [^{11}B-^{11}B]-COSY cross-peaks observed
	$^1H\{^{11}B\}$[b,d]	6.39 (s, H6), 4.90 (s, H5), 3.50 (s, H1), 3.34 (s, H8,9), 3.29 (s, H3), 2.64 (s, H10), 1.49 (s, H2), 0.86 (s, H4), –1.84 (s, μH9,10), –1.99 (s, μH8,9)
4,7-Br_2-5,6-$C_2B_8H_{10}$ **(4,7-Br_2-1)**	^{11}B[b,c]	9.9 (s, –, B7) [3.4][e], 8.5 (d, 174, B1), 6.4 (d, 177, B8), 0.9 (d, 155, B3), –1.8 (d, 168, B9), –8.9 (d, 156, B10), –25.6 (d, 180, B2), –29.8 (s, –, B4) [9.3][e], all [^{11}B-^{11}B]-COSY cross-peaks observed
	$^1H\{^{11}B\}$[b,d]	6.39 (s, H6), 5.09 (s, H5), 3.84 (s, H1,8), 3.60 (s, H3), 3.04 (s, H9), 3.01 (s, H10), 1.64 (s, H2), –1.11 (s, μH9,10), –1.25 (s, μH8,9)
7-I-5,6-$C_2B_8H_{11}$ **(7-I-1)**	^{11}B[b,c]	6.9 (d, 162, B1,8), 0.0 (d, 150, B3), –2.8 (d,164, B9), –4.4 (s, –, B7) [–9.9][e], –9.5 (d, 156, B10), –26.0 (d, 183, B2), –36.4 (d, 159, B4), all [^{11}B-^{11}B]-COSY cross-peaks observed
	$^1H\{^{11}B\}$[a,c]	6.63 (s, H6), 5.10 (s, H5), 3.52 (s, H8), 3.43 (s, H3), 3.37 (s, H1), 3.30 (s, H9), 2.61 (s, H10), 1.51 (s, H2), 0.94 (s, H4), –1.90 (s, μH9,10/8,9)

[a] Measured under the same conditions for comparison. [b] In $CDCl_3$. [c] $\delta(^{11}B)$ (multiplicity, $^1J_{BH}$ in Hz, assignment). [d] $\delta(^1H)$ (multiplicity, assignment). [e] $\Delta\alpha$ value at the substituted site (in square brackets).

Mass spectra of all compounds exhibit theoretical cut-offs in their molecular envelops. The compounds isolated were also characterized by ^{11}B and ^{1}H NMR spectroscopy (see Table I). The use two-dimensional [^{11}B-[11]B]-COSY [14] and ^{1}H-{[11]B(selective)}[15] NMR techniques led to complete assignments of all [11]B and ^{1}H resonances to individual BH cluster units. The ^{11}B NMR spectra of all the isolated compounds consist of eight different resonances, of which those of the substituted boron vertices are singlets, while others are doublets due to $^1J(BH)$ coupling. Table I (values in square brackets) also shows [11]B chemical shift changes induced by individual halogens at the substituted sites ($\Delta\alpha$) ($\Delta\alpha = \delta_s - \delta_p$, where subscripts s and p refer to the substituted and parent compounds[16], respectively). It can be readily seen that the shielding decreases in the expected[16] order I > Br > Cl. Inspection of Table I also suggests that shielding by halogens in individual substituted vertices decreases remarkably in the order 7 > 3 > 4. Figure 1 shows that the plot of chemical shift changes $\Delta\alpha$ for the monosubstituted derivatives 7-X-**1** (X = Cl, Br, and I) at the substituted B7 site versus the corresponding characteristics for the structurally similar 5-X-$B_{10}H_{13}$ compounds (5-X-**2**)[13] is essentially linear, which reflects a similar shielding behaviour in the ten-vertex *nido* series of boron-cluster compounds (for similar correlations, see ref.[17]).

A characteristic feature of the ^{1}H NMR spectra of all the derivatives of **1** isolated is the presence of two broad low-field singlets, attributed to H6 and
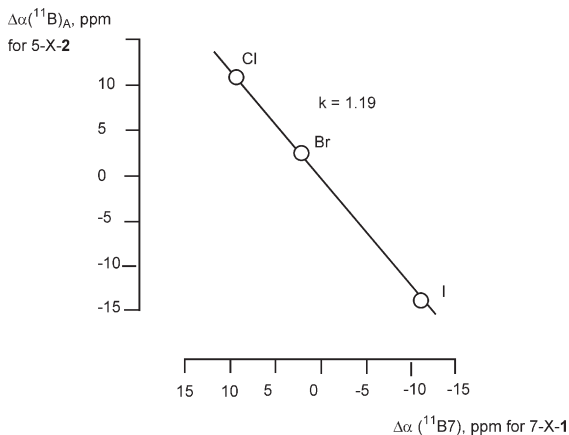

FIG. 1
Plot of $\Delta\alpha(^{11}B7) = \delta(^{11}B7)_s - \delta(^{11}B7)_p$ vs $\Delta\alpha(^{11}B5) = \delta(^{11}B5)_s - \delta(^{11}B5)_p$ chemical shift changes for compounds 7-X-5,6-$C_2B_8H_{11}$ (7-X-**1**) and 5-X-$B_{10}H_{13}$ (5-X-**2**, data from ref.[13]) (X = Cl, Br, and I; subscripts s and p relate to the substituted and parent compounds, respectively)

H5 protons, and of two broad high-field resonances of two nonequivalent μ-H8,9 and μ-H9,10 hydrogen bridges[18]. In addition to these resonances, the ^{1}H-{^{11}B} NMR spectra show singlet signals due to unsubstituted BH units. Another interesting NMR correlation is shown in Fig. 2, which demonstrates linear relationship between $\Delta\alpha(^{11}B7)$ and $\Delta\beta(^1H6)$ parameters for the monosubstituted derivatives 7-X-**1** (where X = Cl, Br, and I), which means that the ^{1}H shift of the hydrogen on the C6 vertex is proportionally affected by the type of the halogen on the neighbouring B7 atom (β-effect)[16].
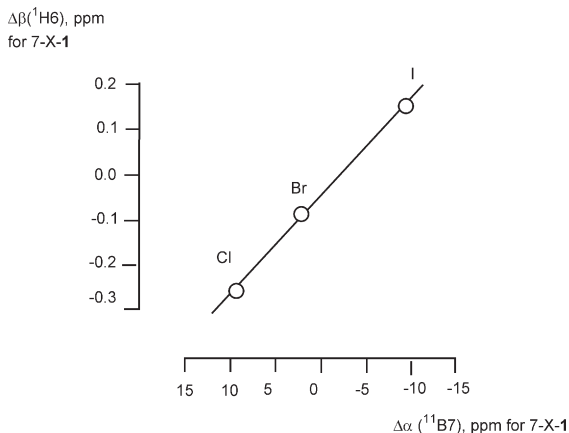

FIG. 2
Linear correlation between $\Delta\alpha(^{11}B7) = \delta(^{11}B7)_s - \delta(^{11}B7)_p$ and $\Delta\beta(^1H6) = \delta(^1H6)_s - \delta(^1H6)_p$ chemical shift changes for the monosubstituted derivatives 7-X-**1** (X = Cl, Br, and I; subscripts s and p relate to the substituted and parent compounds, respectively)

CONCLUSION

We have shown that halogenations of the dicarbaborane *nido*-5,6-C$_2$B$_8$H$_{12}$ (**1**) under electrophilic conditions resulted in the formation of mono-, di-, and trisubstituted derivatives. A typical feature of all the halogenations discussed above is the formation of 7-substituted compounds (7-X-**1**, where X = Cl, Br, and I), further halogenations occur in positions 4 or 3, depending on the halogenation agent. Although performed under different conditions, the experiments established the following order of reactivities of positions in **1** in electrophilic halogenation: 7 > 4 > 3, which is in agreement with the previously reported results of electrophilic deuteration[11]. It was also established that shielding by halogens in individual substituted vertices decreases sharply in the order 7 > 3 > 4. We hope that the halo de-

rivatives of **1** will serve as halogen-labelled compounds in mechanistic studies of cluster rearrangements, complex formation, and also in other areas of carborane chemistry.

EXPERIMENTAL

General

All reactions were carried out using standard vacuum or inert-atmosphere techniques as described by Shriver[19], although some operations, such as column LC, were carried out in air. The starting carborane **1** was prepared according to the literature[20]. Fluka dichloromethane and hexane were dried over CaH_2 and freshly distilled before use. Other chemicals were of reagent or analytical grade and were used as purchased. Column chromatography was carried out using silica gel (Aldrich, 130–270 mesh) as stationary phase. The purity of chromatographic fractions was checked by analytical TLC on Silufol (silica gel on aluminum foil; detection by I_2 vapour, followed by 2% aqueous $AgNO_3$ spray). Low-resolution mass spectra were obtained using a Finnigan MAT Magnum ion-trap quadrupole mass spectrometer equipped with a heated inlet option, as developed by Spectronex AG, Basel, Switzerland (70 eV, EI ionisation). ^1H and ^{11}B NMR spectroscopy was performed at 9.4 T on a Varian Mercury 400 instrument. The $[^{11}B-^{11}B]$-COSY [14] and ^1H-$\{^{11}B(\text{selective})\}$ [15] NMR experiments were made essentially as described earlier[18]. Chemical shifts are given in ppm referenced to high-frequency (low field) of Ξ = 32.083971 MHz (nominally $F_3B \cdot OEt_2$ in $CDCl_3$) for ^{11}B (± 0.5 ppm) and Ξ = 100 MHz ($SiMe_4$) for ^1H (quoted ± 0.05 ppm), Ξ being defined as in ref.[21] Solvent resonances were used as internal secondary standards. NMR data for all the compounds isolated are listed in Table I.

7-Cl-*nido*-5,6-$C_2B_8H_{11}$ (7-Cl-**1**), 3-Cl-*nido*-5,6-$C_2B_8H_{11}$ (3-Cl-**1**), and
3,4-Cl_2-*nido*-5,6-$C_2B_8H_{10}$ (3,4-Cl_2-**1**)

A solution of compound **1** (123 mg, 1 mmol) in CCl_4 (20 ml) was treated with anhydrous $AlCl_3$ (66 mg, 0.5 mmol) and the mixture was stirred at room temperature for 4 h. The mixture was then carefully treated with water (20 ml) at 0 °C and the CCl_4 layer evaporated to dryness. The residual solid was then separated by LC on a silica gel column (2.5 × 35 cm) using hexane–CH_2Cl_2 (3:1) mixture as a mobile phase. Three main fractions of R_F 0.50, 0.25, 0.20, and 0.15 were evaporated to dryness and identified by ^{11}B NMR as 7-Cl-**1** (53 mg, 34%), 4-Cl-**1** (32 mg, 20%), 3-Cl-**1** (33 mg, 21%), and 3,4-Cl_2-**1** (50 mg, 26%), respectively. Analytical samples were obtained by slow evaporation of hexane solutions as white crystals.

7-Cl-**1**: m.p. 144 °C. MS, *m/z*: 159 (5%, M$^+$), 154 (100%). For $C_2H_{11}B_8Cl$ (157.0) calculated: 15.30% C, 7.06% H; found: 15.20% C, 6.91% H.

4-Cl-**1**: m.p. 134 °C. MS, *m/z*: 159 (5%, M$^+$). For $C_2H_{11}B_8Cl$ (157.0) calculated: 15.30% C, 7.06% H; found: 15.10% C, 7.11% H.

3-Cl-**1**: m.p. 130 °C. MS, *m/z*: 159 (5%, M$^+$), 154 (100%). For $C_2H_{11}B_8Cl$ (157.0) calculated: 15.30% C, 7.06% H; found: 15.16% C, 7.13% H.

3,4-Cl_2-**1**: m.p. 162 °C. MS, *m/z*: 194 (5%, M$^+$), 188 (100%). For $C_2H_{10}B_8Cl_2$ (192.5) calculated: 12.48% C, 5.24% H; found: 11.86% C, 5.32% H.

3,4,7-Cl$_3$-*nido*-5,6-C$_2$B$_8$H$_9$ (3,4,7-Cl$_3$-**1**)

A solution of compound **1** (123 mg, 1 mmol) in CCl$_4$ (20 ml) was treated with anhydrous AlCl$_3$ (66 mg, 0.5 mmol) and the mixture was heated at reflux for 2 h. The mixture was then carefully treated with water (20 ml) at 0 °C and the CCl$_4$ layer evaporated to dryness. The residual solid was then separated by LC on a silica gel column (2.5 × 35 cm) using hexane–CH$_2$Cl$_2$ (3:1) mixture as a mobile phase. The main fraction of R_F 0.05 was evaporated to dryness and identified by ^{11}B NMR as 3,4,7-Cl$_3$-**1** (181 mg, 80%). Analytical samples were obtained by crystallization from hot hexane as white crystals. 3,4,7-Cl$_3$-**1**: m.p. 178 °C. MS, *m/z*: 232 (1%, M$^+$), 225 (100%). For C$_2$H$_9$B$_8$Cl$_3$ (225.9) calculated: 10.63% C, 4.02% H; found: 10.76% C, 4.15% H.

7-Br-*nido*-5,6-C$_2$B$_8$H$_{11}$ (7-Br-**1**) and 4,7-Br$_2$-*nido*-5,6-C$_2$B$_8$H$_{10}$ (4,7-Br$_2$-**1**)

A solution of compound **1** (123 mg, 1 mmol) in CS$_2$ (20 ml) was treated with Al powder (20 mg) and Br$_2$ (240 mg, 1.5 mmol; dropwise), and the mixture was stirred at room temperature for 4 h. The mixture was then carefully treated with water (20 ml) at 0 °C and CH$_2$Cl$_2$ (20 ml) under stirring. The CH$_2$Cl$_2$ layer was evaporated to dryness and the residual solid was then separated by LC on a silica gel column (2.5 × 35 cm) using hexane–CH$_2$Cl$_2$ (3:1) mixture as a mobile phase. The main fractions of R_F 0.36 and 0.16 were evaporated to dryness and identified by ^{11}B NMR as 7-Br-**1** (73 mg, 36%) and 4,7-Br$_2$-**1** (146 mg, 52%), respectively. Analytical samples were obtained by crystallization from hexane solutions as white crystals.

7-Br-**1**: m.p. 152 °C. MS, *m/z*: 204 (35%, M$^+$), 201 (100%). For C$_2$H$_{11}$B$_8$Br (201.5) calculated: 11.92% C, 5.50% H; found: 11.85% C, 5.41% H.

4,7-Br$_2$-**1**: m.p. 174 °C. MS, *m/z*: 284 (20%, M$^+$), 281 (100%). For C$_2$H$_{10}$B$_8$Br$_2$ (280.4) calculated: 8.57% C, 3.59% H; found: 8.62% C, 3.60% H.

7-I-*nido*-5,6-C$_2$B$_8$H$_{11}$ (7-I-**1**)

A solution of compound **1** (123 mg, 1 mmol) in benzene (20 ml) was treated with anhydrous AlCl$_3$ (33 mg, 0.25 mmol) and I$_2$ (888 mg, 3.5 mmol), and the mixture was stirred at room temperature for 2 h. The mixture was then carefully treated with water (20 ml) at 0 °C and CH$_2$Cl$_2$ (20 ml) under stirring. The CH$_2$Cl$_2$ layer was evaporated to dryness and the residual solid then separated by LC on a silica gel column (2.5 × 35 cm) using hexane–CH$_2$Cl$_2$ (3:1) mixture as a mobile phase. The main fraction of R_F 0.15 was evaporated to dryness and identified by ^{11}B NMR spectroscopy as 7-I-**1** (211 mg, 85%). Analytical samples were obtained by crystallization from hexane solutions as white crystals. 7-I-**1**: m.p. 165 °C. MS, *m/z*: 250 (50%, M$^+$), 249 (100%). For C$_2$H$_{11}$B$_8$I (248.5) calculated: 9.67% C, 4.46% H; found: 9.83% C, 4.52% H.

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