Identification of An Intermediate in the Deboronation of \textit{ortho}-Carborane.

Adduct of \textit{ortho}-Carborane with Two Nucleophiles on One Boron Atom

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Supporting Information

General

Reaction of 1-Bromo-\textit{ortho}-carborane (4) with pyridine

Physicochemical data of compounds 6 – 8
Experimental

General  Melting points were determined by using a Yanagimoto hot-stage melting point apparatus and are uncorrected. Elemental analyses were carried out in the Microanalytical Laboratory, Faculty of Pharmaceutical Sciences, The University of Tokyo, and were within ±0.3% of the theoretical values. ¹H- NMR spectra were recorded on a JEOL JNM-GX400, and chemical shifts are expressed in ppm relative to tetramethylsilane. ¹¹B-NMR spectra were recorded on a JEOL JNM-A500 spectrometer, by using BF₃-Et₂O (15% v/v in CDCl₃) as reference. X-ray data were collected on a Bruker Smart1000 CCD detector. The crystal structure was solved by direct methods SHELXS-97 (Sheldrick, 1997) and refined by full-matrix least-squares SHELXL-97 (Sheldrick, 1997). Mass spectra were measured on JEOL JMS-SZ 102A (EI).

Ortho-Carborane (1) was purchased from Katchem s. r. o., Czech Republic. 1-Bromo-ortho-carborane (4) and 1,2-dibromo-ortho-carborane (5) were prepared by the method described in the reference 10.

Reaction of 1-Bromo-ortho-carborane (4) with pyridine (Run 1 in Table 1)
A solution of 1-bromo-ortho-carborane (4, 250 mg, 1.12 mmol) in pyridine (1.5 ml) was stirred at room temperature for 20 h. The reaction mixture was poured into 2 M hydrochloric acid, extracted with CH₂Cl₂, and dried over MgSO₄. After evaporation, the residue was chromatographed on silica gel (CH₂Cl₂ : n-hexane 4:1) to give 6a (422 mg, 99%).

Compound 6a: Colorless prisms (CH₂Cl₂); mp 148°C; ¹H-NMR (acetone-d₆) δ 8.96 (dd, 2 H, J = 1.5, 5.1 Hz), 8.92 (dd, 2 H, J = 1.5, 5.1 Hz), 8.35 (tt, 1 H, J = 1.5, 7.7 Hz), 8.34 (tt, 1 H, J = 1.5, 7.7 Hz), 7.92 (dd, 2 H, J = 5.1, 7.7 Hz), 7.90 (dd, 2 H, J = 5.1, 7.7 Hz), -3.0 (br s, 1 H), 0 - 4.0 (br m, 10 H); ¹¹B-NMR (acetone-d₆) δ 8.32 (s 1 B), -6.28 (d, 1 B), -10.19 (d, 1 B), -10.98 (d, 1 B), -13.08 (d, 1 B), -17.63 (d, 1 B), -19.26 (d, 1 B), -19.60 (d, 1 B), -26.12 (s 1 B), -34.49 (d, 1 B); Anal. Calcd for C₁₂H₂₁B₁₀BrN₂: C, 37.80; H, 5.55; N, 7.35. Found: C, 37.70; H, 5.45; N, 7.23.
Compounds 6c and 6d were similarly obtained from the reaction of 1-bromo-ortho-carborane (4) with 3-methylpyridine or 4-methylpyridine, respectively.

**Compound 6c:** Colorless prisms (CH$_2$Cl$_2$-n-hexane); mp 146-147°C; $^1$H-NMR (acetone-$d_6$) $\delta$ 8.78 (m, 4 H), 8.13 (t, 2 H, $J$ = 5.9 Hz), 7.79 (t, 1 H, $J$ = 7.7 Hz), 7.75 (t, 1 H, $J$ = 5.9 Hz), 2.48 (s, 3 H), 2.47 (s, 3 H), -2.93 (br s, 1 H), 0 - 4.50 (br m, 10 H); $^{11}$B-NMR (acetone-$d_6$) $\delta$ 7.11 (s 1 B), -7.31 (d, 1 B), -11.26 (d, 1 B), -12.23 (d, 1 B), -14.11 (d, 1 B), -18.85 (d, 1 B), -20.37 (d, 1 B), -20.79 (d, 1 B), -27.07 (s, 1 B), -35.54 (d, 1 B); Anal. Calcd for C$_{14}$H$_{25}$B$_{10}$BrN$_2$: C, 41.08; H, 6.15; N, 6.84. Found: C, 41.29; H, 6.24; N, 6.83.

**Compound 6d:** Colorless prisms (CH$_2$Cl$_2$-n-hexane); mp 143-144°C; $^1$H-NMR (acetone-$d_6$) $\delta$ 8.75 (d, 2 H, $J$ = 6.6 Hz), 8.70 (d, 2 H, $J$ = 6.6 Hz), 7.69 (d, 2 H, $J$ = 6.6 Hz), 7.68 (d, 2 H, $J$ = 6.6 Hz), 2.57 (s, 3 H), 2.56 (s, 3 H), -2.97 (br s, 1 H), 0 - 4.50 (br m, 10 H); $^{11}$B-NMR (acetone-$d_6$) $\delta$ 7.36 (s 1 B), -6.99 (d, 1 B), -10.94 (d, 1 B), -11.68 (d, 1 B), -13.83 (d, 1 B), -18.47 (d, 1 B), -20.09 (d, 1 B), -20.46 (d, 1 B), -26.51 (s, 1 B), -35.23 (d, 1 B); Anal. Calcd for C$_{14}$H$_{25}$B$_{10}$BrN$_2$: C, 41.08; H, 6.15; N, 6.84. Found: C, 40.94; H, 5.91; N, 6.95.

Compounds 7a, 7b and 8d were similarly obtained from the reaction of 1,2-dibromo-ortho-carborane (5) with pyridine, 3-chloropyridine, or 4-methylpyridine, respectively. In the case of 8d, the crude mixture was purified by recrystallization without silica gel column chromatography.

**Compound 7a:** Colorless prisms (CH$_2$Cl$_2$-n-hexane); mp 181-182°C; $^1$H-NMR (acetone-$d_6$) $\delta$ 8.96 (d, 4 H, $J$ = 5.1 Hz), 8.40 (t, 2 H, $J$ = 7.7 Hz), 7.97 (dd, 4 H, $J$ = 7.3. 6.6 Hz), -2.76 (br s, 1 H), 0 - 4.50 (br m, 9 H); $^{11}$B-NMR (acetone-$d_6$) $\delta$ 7.07 (s 1 B), -7.43 (d, 3 B), -17.54 (d, 4 B), -27.94 (s, 1 B), -34.62 (d, 1 B); Anal. Calcd for C$_{12}$H$_{20}$B$_{10}$Br$_2$N$_2$: C, 31.32; H, 4.38; N, 6.09. Found: C, 31.37; H, 4.43; N, 6.03.

**Compound 7b:** Colorless prisms (CH$_2$Cl$_2$-n-hexane); mp 145-146°C; $^1$H-NMR (acetone-$d_6$) $\delta$ 9.10 (s, 2H), 8.95 (d, 2 H, $J$ = 5.9 Hz), 8.44 (d, 2 H, $J$ = 7.0 Hz), 7.99 (t, 2 H, $J$ = 5.9 Hz), -2.81 (br s, 1 H), 0 - 4.40 (br m, 9 H); $^{11}$B-NMR (acetone-$d_6$) $\delta$ 6.70 (s 1 B), -8.52 (d, 3 B), -18.46 (d, 4
B), -29.21 (s, 1 B), -35.56 (d, 1 B); Anal. Calcd for C\textsubscript{12}H\textsubscript{18}B\textsubscript{10}Br\textsubscript{2}Cl\textsubscript{2}N\textsubscript{2}: C, 27.24; H, 3.43; N, 5.30. Found: C, 27.11; H, 3.37; N, 5.24.

Compound 8d: Colorless prisms (CH\textsubscript{2}Cl\textsubscript{2}-n-hexane); mp 78-80°C; \textsuperscript{1}H-NMR (acetone-\textit{d}\textsubscript{6}) \(\delta\) 11.42 (br s, 1 H), 8.90 (d, 2 H, \(J = 6.2\) Hz), 8.06 (d, 2 H, \(J = 5.9\) Hz), 2.75 (s, 3 H), 2.25 (s, 1 H), -2.83 (br s, 1 H), -0.5 – 3.30 (br m, 9 H); \textsuperscript{11}B-NMR (acetone-\textit{d}\textsubscript{6}) \(\delta\) -9.33 (d, 1 B), -13.32 (d, 1 B), -13.86 (d, 1 B), -16.22 (d, 1 B), -20.52 (d, 1 B), -22.52 (d, 1 B), -22.90 (d, 1 B), -34.20 (d, 1 B), -37.56 (d, 1 B); Anal. Calcd for C\textsubscript{8}H\textsubscript{19}B\textsubscript{9}BrN: C, 31.36; H, 6.25; N, 4.57. Found: C, 31.36; H, 5.98; N, 4.85.