Supplementary Material (ESI) for Chemical Communications

Identification of An Intermediate in the Deboronation of *ortho*-Carborane. Adduct of *ortho*-Carborane with Two Nucleophiles on One Boron Atom

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Supporting Information

General

Reaction of 1-Bromo-*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. ^{1}H- -NMR spectra were recorded on a JEOL JNM-GX400, and chemical shifts are expressed in ppm relative to tetramethylsilane. ^{11}B-NMR spectra were recorded on a JEOL JNM-A500 spectrometer, by using BF_3-Et_2O (15% v/v in $CDCl_3$) 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*-Caroborane (**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 CH_2Cl_2, and dried over $MgSO_4$. After evaporation, the residue was chromatographed on silica gel (CH_2Cl_2 : *n*-hexane 4:1) to give **6a** (422 mg, 99%).

Compound **6a**: Colorless prisms (CH_2Cl_2); mp 148°C; ^{1}H-NMR (acetone-d_6) 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); ^{11}B-NMR (acetone-d6) d 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 $C_{12}H_{21}B_{10}BrN_2$: 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-mrthylpyridine or 4-methylpyridine, respectively.

Compound **6c**: Colorless prisms (CH_2Cl_2-*n*-hexane); mp 146-147°C; ^{1}H-NMR (acetone-d_6) δ 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) δ 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_2Cl_2-*n*-hexane); mp 143-144°C; ^{1}H-NMR (acetone-d_6) δ 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) δ 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_2Cl_2-*n*-hexane); mp 181-182°C; ^{1}H-NMR (acetone-d_6) δ 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) δ 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 $C_{12}H_{20}B_{10}Br_2N_2$: C, 31.32; H, 4.38; N, 6.09. Found: C, 31.37; H, 4.43; N, 6.03.

Compound **7b**: Colorless prisms (CH_2Cl_2-*n*-hexane); mp 145-146°C; ^{1}H-NMR (acetone-d_6) δ 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) δ 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 $C_{12}H_{18}B_{10}Br_2Cl_2N_2$: C, 27.24; H, 3.43; N, 5.30. Found: C, 27.11; H, 3.37; N, 5.24.

Compound **8d**: Colorless prisms (CH_2Cl_2-*n*-hexane); mp 78-80°C; ^{1}H-NMR (acetone-d_6) δ 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); ^{11}B-NMR (acetone-d_6) δ -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 $C_8H_{19}B_9BrN$: C, 31.36; H, 6.25; N, 4.57. Found: C, 31.36; H, 5.98; N, 4.85.