SUPPORTING INFORMATIONS of SYNTHESES and STRUCTURES

A Stable Neutral Diborene Containing a B=B Double Bond

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All reactions were performed under purified argon using Schlenk techniques and an inert atmosphere drybox (M-Braun LabMaster 130). Chemicals were purchased from Aldrich and used as received. NHC carbene ligand, :C{N(2,6-$Pr^i_2C_6H_3$)CH}$_2$, was prepared according to the reported method.[1] Solvents were dried and distilled under argon from Na/benzophenone prior to use. Elemental analyses were performed by Complete Analysis Laboratories, Inc. (CALI; Parsippany, NJ). ^{1}H NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer and ^{11}B NMR spectra were recorded on a Varian Unity Inova 500 MHz spectrometer. X-ray intensity data for **1-4** were collected on a Bruker SMART APEX II X-ray diffractometer system with graphite-monochromated Mo K radiation (λ = 0.71073 Å), using the -scan technique.

Compound 1. NHC carbene ligand (4.82 g, 12.40 mmol) was added to a flask containing 80 mL of hexane at ambient temperature. After the slurry was stirred about 5 min., BBr_3 (3.41 g, 13.61 mmol) was added into the flask. The mixture was stirred over 1 day and then filtered. The white residue was vacuumed over night, leading to the white powder **1** (7.69 g, 97.0% yield). **1** was recrystallized from toluene to obtain X-ray quality colorless block crystals. Mp: gradually decomposed and melt at 346 °C. ^{1}H NMR (C_6D_6): δ 0.95 [d, 12H, CH(CH_3)$_2$], 1.43 [d, 12H, CH(CH_3)$_2$], 2.86 [m, 4H, CH(CH$_3$)$_2$], 6.31 (s, 2H, CH), 7.05 (d, 4H, Ar-H), 7.19 (t, 2H, Ar-H). ^{11}B NMR (C_6D_6): δ -16.46 (s, $w_{1/2}$ = 48 Hz). Anal. Calcd (found) for $C_{27}H_{36}N_2B_1Br_3$: C, 50.74 (50.70); H, 5.68 (5.80). Crystal data for **1**: $C_{27}H_{36}N_2B_1Br_3$, fw = 639.12, monoclinic, $P2_1/n$ (No. 14), a = 10.1936(5) Å, b = 19.8023(9) Å, c = 14.7695(7) Å, β = 100.6100(10)º, V = 2930.4(2) Å^3, Z = 4, R1 = 0.0464 for 3818 data ($I > 2\sigma(I)$), wR_2 = 0.1360 (all data).

Compound 2. 80 mL of Et_2O was added to a flask containing **1** (2.84 g, 4.437 mmol) and KC_8 (5.40 g, 40.00 mmol) at ambient temperature. After vigorous stirring for 6 days, the red solution was filtered. The filtrate was concentrated to 2 mL and then kept at ambient temperature. Over 2 days, colorless block crystals of **2** (0.14 g, 7.9% yield) formed. Mp: 249 °C. ^{1}H NMR (C_6D_6): 1.05 [d, 24H, CH(CH_3)$_2$], 1.22 [d, 24H, CH(CH_3)$_2$], 2.93 [m, 8H, CH(CH$_3$)$_2$], 6.21 (s, 4H, CH), 7.07 (d, 8H, Ar-H), 7.22 (t, 4H, Ar-H). ^{11}B NMR (C_6D_6): -31.62 (s with shoulders, $w_{1/2}$ = 188 Hz). Anal. Calcd (found) for $C_{54}H_{76}N_4B_2$: C, 80.79 (80.54); H, 9.54 (9.50). Crystal data for **2**: $C_{54}H_{76}N_4B_2$, fw = 802.80, monoclinic, $P2_1/n$ (No. 14), a = 12.8024(17) Å, b = 14.372(2) Å, c = 14.466(2) Å, β = 110.296(2)°, V = 2496.4(6) Å^3, Z = 2, R1 = 0.0532 for 3593 data ($I > 2\sigma(I)$), wR_2 = 0.1548 (all data).

Compound 3. 70 mL of Et_2O was added to a flask containing **1** (2.65 g, 4.146 mmol) and KC_8 (3.00 g, 22.22 mmol) at ambient temperature. After stirring for 3.5 days, filtering and solvent removal in vacuo, the purple residue was extracted with 20 mL of a 1:1 toluene/hexane solvent mixture. Considerable solid crystallized after concentration. Dissolution by warming and standing overnight at ambient temperature gave orange-red

sheet-like crystals of **3**. More **3** crystallized after further concentration (0.20 g, 12.0% yield). Mp: 237 °C. ^{1}H NMR (C_6D_6): 1.12 [d, 24H, CH(CH_3)$_2$], 1.14 [d, 24H, CH(CH_3)$_2$], 2.90 [m, 8H, CH(CH$_3$)$_2$], 6.14 (s, 4H, CH), 7.07 (d, 8H, Ar-H), 7.25 (t, 4H, Ar-H). ^{11}B NMR (C_6D_6): 25.30 (br s, $w_{1/2}$ = 946 Hz). Anal. Calcd (found) for $C_{54}H_{74}N_4B_2$: C, 80.99 (80.89); H, 9.31 (9.50). Crystal data for **3**: $C_{54}H_{74}N_4B_2$, fw = 800.79, orthorhombic, $P2_12_12_1$ (No. 19), a = 12.3979(16) Å, b = 21.067(3) Å, c = 39.689(5) Å, V = 10366(2) Å^3, Z = 8, R1 = 0.0792 for 2804 data ($I > 2\sigma(I)$), wR_2 = 0.1861 (all data).

Compound 4. NHC carbene ligand (2.98 g, 7.669 mmol) was added to a flask containing 50 mL of hexane at ambient temperature. After the slurry was stirred about 5 min., BH_3•THF (1.0 M in THF, 7.80 mL, 7.800 mmol) was added into the flask. The mixture was stirred over 1 day and then the solvent was removed in vacuo. The residue, recrystallized in CH_2Cl_2, gave colorless crystals of **4** (2.93 g, 95.1% yield). Mp: decomposed and melt at 273 °C. ^{1}H NMR (C_6D_6): δ 1.10 [d, 12H, CH(CH_3)$_2$], 1.41 [d, 12H, CH(CH_3)$_2$], 2.72 [m, 4H, CH(CH$_3$)$_2$], 6.31 (s, 2H, CH), 7.12 (d, 4H, Ar-H), 7.24 (t, 2H, Ar-H). ^{11}B NMR (C_6D_6): δ -35.38 (q, J_{BH} = 83.38 Hz). Anal. Calcd (found) for $C_{27}H_{39}N_2B_1$: C, 80.58 (80.49); H, 9.77 (9.74). Crystal data for **4**: $C_{27}H_{39}N_2B_1$, fw = 402.41, monoclinic, $P2_1/n$ (No. 14), a = 19.622(3) Å, b = 6.9958(12) Å, c = 20.174(4) Å, β = 101.398(2)°, V = 2714.7(8) Å^3, Z = 4, R1 = 0.0703 for 2634 data ($I > 2\sigma(I)$), wR_2 = 0.2079 (all data).

Reference:

(1) Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523-14534.

Figures of the Structures of Compound **1** and **4**

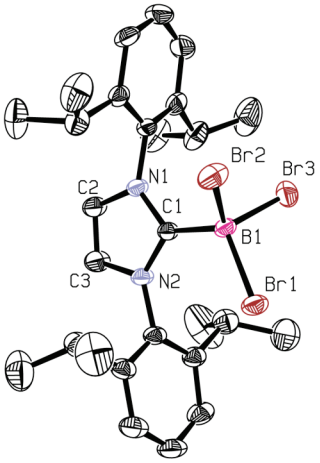

Figure **1**. Molecular Structure of Compound **1**.

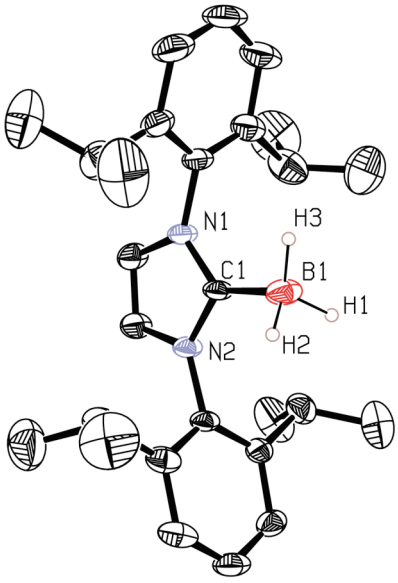

Figure **2**. Molecular Structure of Compound **4**.