Supporting Information

Unexpected Cluster Formation upon Hydroboration of a Neutral Diborene with 9-BBN

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Experimental Section

General Procedure:

All manipulations were conducted either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Solvents were purified by distillation from Na/K alloy under dry argon immediately prior to use. C_6D_6 was degassed by three freeze-pump-thaw cycles and stored over molecular sieves. **1a,b** were prepared according to published procedures.[1] NMR spectra were acquired on a Bruker Avance 400 FT-NMR spectrometer (^{1}H: 400.1 MHz, ^{11}B: 100.6 MHz) or a Bruker Avance 500 FT-NMR spectrometer (^{1}H: 500.1 MHz, ^{11}B: 160.5 MHz, ^{13}C: 125.8 MHz, ^{29}Si: 99.4 MHz). ^{1}H, ^{13}C{^{1}H} and ^{29}Si NMR spectra were referenced to external TMS *via* the residual protons of the solvent (^{1}H) or the solvent itself (^{13}C). ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$. Microanalyses (C, H, N) were performed on a Leco Instruments elemental analyzer, type CHNS 932.

Synthesis of 2a:

A solution of 9-BBN (63.9 mg, 262 µmol) in toluene (10 mL) was added to a solution of diborene **1a** (100 mg, 262 µmol) in toluene (10 mL). After stirring for 72 h at room temperature the solution turned yellow. All volatiles were removed in *vacuo* and the crude product washed with hexane (2 x 20 mL). **2a** was isolated as a yellow solid (83 mg, 198 µmol, 76%) after recrystallization from a benzene/hexane solution.

^{1}H NMR (500.1 MHz, C_6D_6, 297 K): δ = 1.56 - 2.77 (m, 14H, C*H*$_2$/C*H*-9BBN), 3.20 (s, 6H, C*H*$_3$-IMe), 3.42 (s, 6H, C*H*$_3$-IMe) 5.53 (s, 2H, C*H*-IMe), 5.86 (s, 2H, C*H*-IMe), 6.53 (m, 1H, C*H*-thienyl), 6.92 (dd, $^3J_{H\text{-}H}$ = 4.8 Hz, $^3J_{H\text{-}H}$ = 3.2 Hz, 1H, C*H*-thienyl), 6.96 (dd, $^3J_{H\text{-}H}$ = 4.8 Hz, $^4J_{H\text{-}H}$ = 0.8 Hz, 1H, C*H*-thienyl); **^{13}C{^{1}H} NMR** (125.8 MHz, C_6D_6, 297 K): δ = 36.03, 38.11 (*C*H$_3$), 26.15, 27.15, 33.98 (*C*H$_2$), 21.39, 118.44, 119.19, 120.46, 124.99, 126.42 (*C*H),

131.42 (C_q); **^{11}B NMR** (160.5 MHz, C_6D_6, 297 K): δ = −31.8 (br), −23.2, 5.08 (br). **Elemental analysis** (%) calcd. for $C_{25}H_{43}B_3N_4SSi$: C 62.91; H 8.40; N 13.34; S 7.63. Found: C 63.11; H 8.42; N 11.26; S 8.48.

NMR data of 3a:

^{1}H NMR (400.1 MHz, C_6D_6, 297 K): δ = 1.74 - 2.02 (m, 12H, C*H*$_2$-9-BBN), 2.15 - 2.25 (m, 2H, C*H*-9-BBN), 7.01 (m, 1H, C*H*-thienyl), 7.44 (m, 1H, C*H*-thienyl), 7.72 (m, 1H, C*H*-thienyl); **^{11}B NMR** (100.6 MHz, C_6D_6, 297 K): δ = 72.8.

Synthesis of 2b:

A solution of 9-BBN (46.6 mg, 191 µmol) in toluene (10 mL) was added to a solution of diborene **1b** (100 mg, 191 µmol) in toluene (10 mL). After stirring for 72 h at room temperature the solution turned yellow. All volatiles were removed in *vacuo* and the crude product washed with hexane (2 x 20 mL). **2b** was isolated as a yellow solid (55 mg, 94.7 µmol, 49%) after recrystallization from a benzene/hexane solution.

^{1}H NMR (500.1 MHz, C_6D_6, 297 K): δ = 0.33 (s, 9H, Si(C*H*$_3$)$_3$), 1.76 - 2.73 (m, 14H, C*H*$_2$/C*H*-9BBN), 3.19 (s, 6H, C*H*$_3$-IMe), 3.42 (s, 6H, C*H*$_3$-IMe) 5.55 (s, 2H, C*H*-IMe), 5.86 (s, 2H, C*H*-IMe), 6.54 (m, 1H, C*H*-thienyl), 7.12 (d, $^3J_{H\text{-}H}$ = 3.2 Hz, 1H, C*H*-thienyl); **^{13}C{^{1}H} NMR** (125.8 MHz, C_6D_6, 297 K): δ = 0.00 (Si(*C*H$_3$)$_3$), 34.90, 37.07 (*C*H$_3$), 24.93, 25.96, 35.50 (*C*H$_2$), 23.81, 117.39, 118.25, 125.47, 132.96 (*C*H), 131.42 (C_q); **^{29}Si NMR** (99.4 MHz, C_6D_6, 297 K): δ = −10.2; **^{11}B NMR** (160.5 MHz, C_6D_6, 297 K): δ = −30.7 (br), −22.0, 5.75 (br). **Elemental analysis** (%) calcd. for $C_{25}H_{43}B_3N_4SSi$: C 61.00; H 8.81; N 11.38; S 6.51. Found: C 60.93; H 8.65; N 11.05; S 7.87.

NMR data of 3b:

^{1}H NMR (400.1 MHz, C_6D_6, 297 K): δ = 0.27 (s, 9H, Si(CH_3)$_3$), 1.84 - 2.05 (m, 12H, CH_2-9-BBN), 2.27-2.33 (m, 2H, CH-9-BBN), 7.37 (d, $^{3}J_{H\text{-}H}$ = 3.3 Hz, 1H, CH-thienyl), 7.88 (d, $^{3}J_{H\text{-}H}$ = 3.4 Hz, 1H, CH-thienyl); **^{11}B NMR** (100.6 MHz, C_6D_6, 297 K): δ = 73.9.

Crystal structure determination of 2a,b

The crystal data of **2a,b** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using direct methods, refined with the SHELX software package (G. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112–122) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms (except H111 and H2) were assigned to idealised geometric positions. The highest residual electron density was set to H111 and H2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. 1007674 (**2a**) and 1007675 (**2b**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S1: Crystal data for 2a,b

Data	**2a**	**2b**
Empirical formula	$C_{22}H_{35}B_3N_4S$	$C_{25}H_{43}B_3N_4SSi$
Formula weight ($g \cdot mol^{-1}$)	420.03	491.21
Temperature (K)	100(2)	100(2)
Radiation, λ (Å)	$Mo_{K\alpha}$ 0.71073	$Mo_{K\alpha}$ 0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/n$
Unit cell dimensions		
a (Å)	10.76(1)	12.667(5)
b (Å)	14.57(1)	14.559(7)
c (Å)	14.66(1)	15.099(6)
α (°)	90.00	90.00
β (°)	97.11(2)	94.37(1)
γ (°)	90.00	90.00
Volume ($Å^3$)	2281(4)	2777(2)
Z	4	4
Calculated density ($Mg \cdot m^{-3}$)	1.223	1.175
Absorption coefficient (mm^{-1})	0.159	0.181
F(000)	904	1060
Theta range for collection	1.40 to 26.37°	1.95 to 26.81°
Reflections collected	16235	41976
Independent reflections	6666	5870
Minimum/maximum transmission	0.6454/0.7454	0.6526/0.7454
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / parameters / restraints	6666 / 597 / 115	5870 / 322 / 0

Goodness-of-fit on F^2	0.982	1.062
Final R indices [I>2σ(I)]	R_1 = 0.0527, wR^2 = 0.1064	R_1 = 0.0371, wR^2 = 0.0941
R indices (all data)	R_1 = 0.0975, wR^2 = 0.1244	R_1 = 0.0488, wR^2 = 0.1025
Maximum/minimum residual electron density (e·Å^{-3})	0.346 / –0.257	0.393 / –0.251

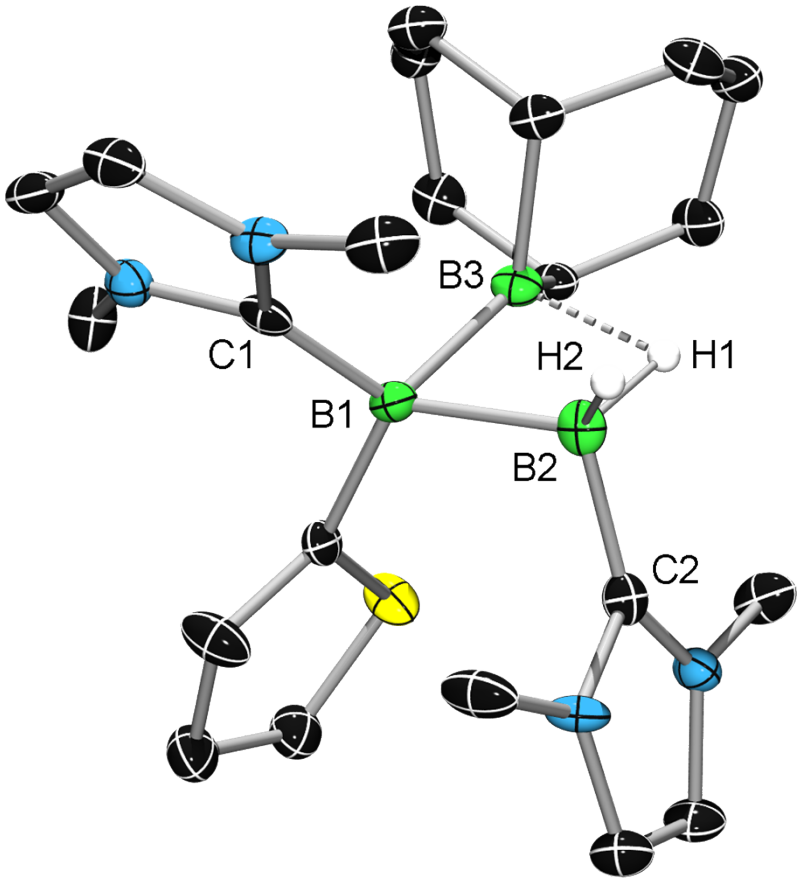

Fig. 1. Molecular structure of **2a** the solid state. Hydrogen atoms (except H1 and H2, which were crytallographically located) have been omitted for clarity. Ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: B1–B2 1.799(7), B2–B3 1.933(7), B1–B3 1.720(6), B1–C1 1.596(6), B2–C2 1.581(6), B2–H1 1.25(3), B2–H2 1.10(3), B3–H1 1.58(4), B2–B1–B3 66.7(3), B1–B3–B2 58.7(3), B3–B2–B1 54.6(3).

References

(1) Braunschweig, H.; Dewhurst, R. D.; Hörl, C.; Phukan, A. K.; Pinzner, F.; Ullrich, S. *Angew. Chem. Int. Ed.* **2014**, *53*, 3241-3244.