

Electronic Supplementary Information

For

Synthesis of a Bicyclic Diborane by Selective Boron Carbon Bond Formation

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Experimental Section

General Considerations

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 CaH₂ under dry argon and storage over molecular sieves. CD₂Cl₂ were degassed by three freeze-pump-thaw cycles and stored over molecular sieves. I₂B₂Mes₂¹ was prepared according to published procedures. NEt₃ was purchased from Acros Organics and stored over molecular sieves. NMR spectra were acquired on a Bruker Avance 500 (¹H: 500.1 MHz, ¹¹B: 160.4 MHz, ¹³C: 125.7 MHz) FT-NMR spectrometer. ¹H, ¹³C and ¹³C{¹H} NMR spectra were referenced to external TMS *via* the residual protons of the solvent (¹H) or the solvent itself (¹³C). ¹¹B{¹H} NMR spectra were referenced to external BF₃·OEt₂. Microanalyses (C, H, N) were performed on a Leco Instruments elemental analyzer, type CHNS 932.

Preparation of 1: A solution of NEt₃ (16.4 mg, 0.16 mmol, 2.6 eq.) in pentane (0.5 mL) was added to solid I₂B₂Mes₂ (32.0 mg, 0.06 mmol). The mixture was stored over night at room temperature affording a viscous material. The precipitate consisting of yellow, crystalline **1** and colorless [Et₃NH][I]² was diluted with pentane (5 mL) and the flask shaken. Since **1** settled down faster than [Et₃NH][I], [Et₃NH][I] and the supernatant could be removed by decantation to leave analytically pure **1**. Gradual sedimentation was repeated three times. All batches of **1** were combined and all volatiles were removed *in vacuo* to afford **1** (16.4 mg, 0.03 mmol, 54%) as a yellow powder.

¹H NMR (500.1 MHz, CD₂Cl₂, 300 K, TMS): δ = 6.89 (s, 1H; CH_{arom.}), 6.75 (s, 1H; CH_{arom.}), 6.72 (s, 2H, CH_{arom.}), 3.88–3.77 (m, 1H; NCH₂), 3.65–3.56 (m, 1H; NCH₂), 3.55–3.45 (m, 1H; NCH₂), 3.38–3.29 (m, 1H; NCH₂), 3.15–3.06 (m, 1H; NCH₂), 3.05–2.95 (m, 1H; NCH₂), 2.84 (s, 3H; NMe₂), 2.72–2.37 (m br, 6H; CH₃, Mes), 2.23 (s, 3H; CH₃, Mes), 2.20 (s, 3H; CH₃, Mes), 2.16–2.11 (m, 1H; NCH₂), 2.15–1.80 (m br, 6H; CH₃, Mes), 2.09 (s, 3H; CH₃, Mes), 1.76–1.65

(m, 1H; NCH_2), 1.23–1.13 (m, 3H; NCH_2CH_3), 0.86–0.76 ppm (m, 3H; NCH_2CH_3); $^{11}\text{B}\{^1\text{H}\}$ NMR (160.4 MHz, CD_2Cl_2 , 300 K, $\text{BF}_3\cdot\text{OEt}_2$): $\delta = 41.5$ (s br; BC), 30.7 ppm (s br; BN); $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CD_2Cl_2 , 300 K, TMS): $\delta = 144.1$ (s; C_q), 142.4 (s; C_q), 137.9 (s; C_q), 137.5 (s; C_q), 137.0 (s; C_q), 136.1 (s; C_q), 130.1 (s, 2C; CH), 129.8 (s, 1C; CH), 128.7 (s, 1C; CH), 62.8 (s, 1C; NCH_2), 53.6 (s, 1C; NCH_2), 45.5 (s, 1C; NCH_2), 28.0 (s, 1C; CH_3 , Mes), 27.6 (s, 2C; CH_3 , Mes), 24.8 (s, 1C; CH_3 , Mes), 24.5 (s, 1C; BCH_2), 20.9 (s, 1C; CH_3 , Mes), 20.7 (s, 1C; CH_3 , Mes), 9.66 ppm (s, 2C; NCH_2CH_3); elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{36}\text{B}_2\text{IN}$ (487.06): C 59.18, H 7.45, N 2.88; found: C 58.94, H 7.53, N 3.01.

Crystal structure determination

The crystal data of **1** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated Mo_Kα radiation. The structure was solved using direct methods, refined with the Shelx software package³ and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealised geometric positions. The crystal was a pseudo-merohedral twin with domains rotated by 180.0 ° around real axis [1.000 0.000 0.000]. The BASF parameter was refined to 35%.

Crystal data for **1**: C₂₄H₃₆B₂IN, $M_r = 487.06$, colourless block, 0.19×0.18×0.11 mm³, Triclinic space group *P*-1, $a = 8.3238(17)$ Å, $b = 8.5956(17)$ Å, $c = 16.157(3)$ Å, $\alpha = 95.40(3)^\circ$, $\beta = 90.39(3)^\circ$, $\gamma = 104.22(3)^\circ$, $V = 1115.1(4)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.451$ g·cm⁻³, $\mu = 1.446$ mm⁻¹, $F(000) = 500$, $T = 100(2)$ K, $R_1 = 0.0222$, $wR^2 = 0.0743$, 4363 independent reflections [$2\theta \leq 52.76^\circ$] and 262 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-912614 (**1**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Theoretical Calculations

Initial geometry optimization on *R,R*-**1**_{OPT} were done with the Turbomole 5.10 program working on a cluster of Linux workstations.⁴ The final optimization was performed with the Gaussian03 program package using DFT methods.⁵ The three hybrid functional B3LYP using 6-31G(d,p) basis set for H, C, B, N and 6-311G(d,p) I was applied.⁶⁻⁸ The orbitals were plotted by using the program Molekel (Version 4.3).⁹ The ¹¹B NMR chemical shifts were referenced to idealized B₂H₆.

B₂H₆:

$$\delta_{exp.}(\text{B}_2\text{H}_6) = 16.6 \text{ ppm.}$$

$$\delta_{ISOTROPIC}(\text{B}_2\text{H}_6) = 95.3765 \text{ ppm.}$$

R,R-**1**_{OPT}:

$$\delta_{ISOTROPIC}(\text{B1}) = 80.9053 \text{ ppm}$$

$$\delta_{ANISOTROPIC}(\text{B1}) = 31.0712 \text{ ppm.}$$

$$\delta_{ISOTROPIC}(\text{B2}) = 59.5186 \text{ ppm}$$

$$\delta_{ANISOTROPIC}(\text{B2}) = 52.4579 \text{ ppm.}$$

Cartesian coordinates for *R,R*-**1**_{OPT}:

B	-0.65083100	-0.41431300	0.16677800	C	2.38268700	-0.02798100	0.29778800
B	0.99987300	-0.81806800	0.44775400	C	2.55236600	1.07311900	-0.60443800
I	-0.08223700	-1.58277300	-2.06922300	C	3.53676300	-0.35697900	1.08945600
N	-1.47229800	-1.64791500	1.00842000	C	3.77851300	1.74128700	-0.71442700
C	-0.49923600	-2.81270100	1.01756200	C	4.73519100	0.35292400	0.95231900
C	0.91207900	-2.26608800	1.16785600	C	4.89165000	1.39866800	0.04532600
C	-1.64285900	-1.12148200	2.42042300	H	3.85650300	2.56495400	-1.42109600
C	-2.16291800	-2.10836800	3.46751800	H	5.57896700	0.07584800	1.58077700
C	-2.79095100	-2.16941600	0.46977400	C	-2.89629900	0.47597600	-2.02186000
C	-4.03390800	-1.32006300	0.72653500	H	-2.98300100	-0.58253900	-1.78383700
H	-0.61747200	-3.31471200	0.05821100	H	-3.86448100	0.81456800	-2.40297800
H	-0.80232100	-3.51287300	1.80062500	H	-2.17439600	0.54362800	-2.84150100
H	1.13502000	-2.14275500	2.23425400	C	-3.52786100	4.86064200	0.24254100
H	1.62814700	-3.00621800	0.79859100	H	-3.14899500	5.53147100	-0.53856100
H	-2.30217700	-0.25696000	2.34795800	H	-4.60433200	4.74902400	0.07429100
H	-0.66685500	-0.75044700	2.73017000	H	-3.38475500	5.36265000	1.20382800
H	-2.33847000	-1.55039600	4.39277800	C	-0.07990700	1.81778100	2.15397000
H	-1.44413300	-2.89780200	3.69943200	H	0.37637800	2.78849000	2.37009900
H	-3.10879000	-2.57739800	3.18596100	H	-0.50780800	1.45987600	3.09934300
H	-2.93864500	-3.16279300	0.90734000	H	0.72365100	1.14134500	1.86674800

H	-2.62800100	-2.31404500	-0.59921800	C	3.58690400	-1.44024800	2.15408700
H	-4.85929200	-1.75415800	0.15336200	H	3.44051300	-2.44321800	1.74651800
H	-3.91111800	-0.28559300	0.40830900	H	4.56501600	-1.43282000	2.64198800
H	-4.33426900	-1.32401900	1.77750200	H	2.84048100	-1.29373900	2.94137100
C	-1.45893300	0.98092500	0.09900200	C	6.21059200	2.11419400	-0.11393800
C	-2.47096600	1.33817500	-0.84905200	H	6.84286300	1.61503200	-0.85946800
C	-1.14271100	1.97373000	1.07927000	H	6.06848200	3.14620700	-0.44927000
C	-3.12019900	2.57579300	-0.77094800	H	6.77290100	2.13437100	0.82500300
C	-1.82481200	3.19913900	1.11583100	C	1.47673900	1.58726100	-1.53318500
C	-2.82197200	3.52683400	0.20496600	H	1.41351800	0.97363000	-2.43753100
H	-3.88493000	2.80546200	-1.51030200	H	0.48786900	1.59033000	-1.08245200
H	-1.55281400	3.92005900	1.88453800	H	1.70647600	2.61106300	-1.84380200

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