Supplementary Information

Formation of an Air-Stable Diborane via a Stepwise BH₃ Addition of Pyrido[1,2-*a*]isoindole with H₂ Evolution

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Contents

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1. General Considerations.

All solvents were freshly distilled over sodium metal and stored under nitrogen prior to use. All starting materials were purchased from Sigma-Aldrich Chemicals Corp and Energy Chemical. All reactions were carried out under a nitrogen atmosphere, either using Schlenk/vacuum line techniques or in a glove box. Melting points were performed using a Huazhi HMZ-2A melting point apparatus. The ^{1}H, ^{11}B, and ^{13}C NMR spectra were recorded on Bruker Avance 400 and 500 MHz spectrometers. High-resolution mass spectrometry (HRMS) was performed using an Micromass GCT TOF-EI mass spectrometer. Pyrido[1,2-*a*]isoindole (**A**) were prepared using methods described in the literature.[1,2]

2. Synthesis and Characterisation
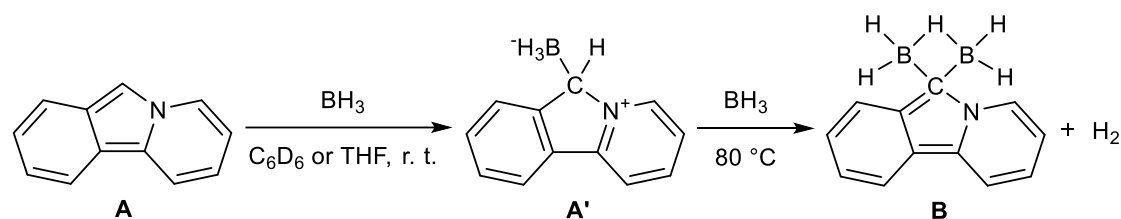
Scheme S1. Synthesis of **B**.

NMR Scale Reaction: To a solution of **A** (0.042 g, 0.25 mmol) in deuterated benzene (0.75 mL) in a J-Young NMR tube was added borane dimethylsulfide (Me$_2$S·BH$_3$; 0.75 mmol) at room temperature in the glovebox. The resulting mixture was immediately taken for an NMR scan, in which the intermediate **A'** can be monitored in the spectra. Subsequently, the reaction was warmed to 80 °C and monitored by ^{1}H NMR until the substrate and the intermediate **A'** were fully consumed. Crystals suitable for X-ray diffraction experiments were obtained from slow evaporation of the original NMR solution in the glovebox as colourless crystals.

Preparation Scale Reaction: To a solution of **A** (0.17 g, 1.0 mmol) in ultra-dry THF (5 mL) in a sealed tube was added borane dimethylsulfide (Me$_2$S·BH$_3$; 3 mmol) or borane tetrahydrofuran (Me$_2$S·THF; 3 mmol) at room temperature in the glovebox. The sealed tube was transferred out and heat up to 80 °C for 4 hours. The volatiles were

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removed in *vacuo* with 1 mL THF left, and the product was filtered by adding hexanes in the glovebox as white solid.

^{1}H NMR (500 MHz, C$_6$D$_6$) δ (ppm) 8.17 (1 H, d, $^3J_{HH}$ = 6.6 Hz, C*H*), 7.88 (1 H, d, $^3J_{HH}$ = 8.1 Hz, C*H*), 7.49 (1 H, d, $^3J_{HH}$ = 8.0 Hz, C*H*), 7.37 (1 H, t, $^3J_{HH}$ = 7.6 Hz, C*H*), 7.09 (1 H, t, $^3J_{HH}$ = 7.5 Hz, C*H*), 6.97 (1 H, d, $^3J_{HH}$ = 8.4 Hz, C*H*), 6.64 (1 H, t, $^3J_{HH}$ = 7.7 Hz, C*H*), 6.24 (1 H, t, $^3J_{HH}$ = 6.8 Hz, C*H*), 3.20–1.69 (4 H, br, m, B*H$_2$*), 1.04–0.66 (1 H, br, m, B-*H*-B).

^{1}H{^{11}B} NMR (500 MHz, C$_6$D$_6$) δ (ppm) 8.18 (1 H, d, $^3J_{HH}$ = 6.6 Hz, C*H*), 7.87 (1 H, d, $^3J_{HH}$ = 8.1 Hz, C*H*), 7.50 (1 H, d, $^3J_{HH}$ = 8.0 Hz, C*H*), 7.37 (1 H, t, $^3J_{HH}$ = 7.6 Hz, C*H*), 7.09 (1 H, t, $^3J_{HH}$ = 7.5 Hz, C*H*), 6.96 (1 H, d, $^3J_{HH}$ = 6.7 Hz, C*H*), 6.63 (1 H, t, $^3J_{HH}$ = 6.4 Hz, C*H*), 6.25 (1 H, t, $^3J_{HH}$ = 5.8 Hz, C*H*), 2.66 (2 H, d, $^2J_{HH}$ = 4.7 Hz, B*H$_2$*), 2.22 (2 H, d, $^2J_{HH}$ = 9.6 Hz, B*H$_2$*), 0.86 (1 H, p, $^2J_{HH}$ = 9.7 Hz, B-*H*-B).

^{11}B NMR (128 MHz, C$_6$D$_6$) δ (ppm) -18.6 (t, $^1J_{BH}$ = 126.5 Hz).

^{11}B{^{1}H} NMR (160 MHz, C$_6$D$_6$) δ (ppm) -19.5.
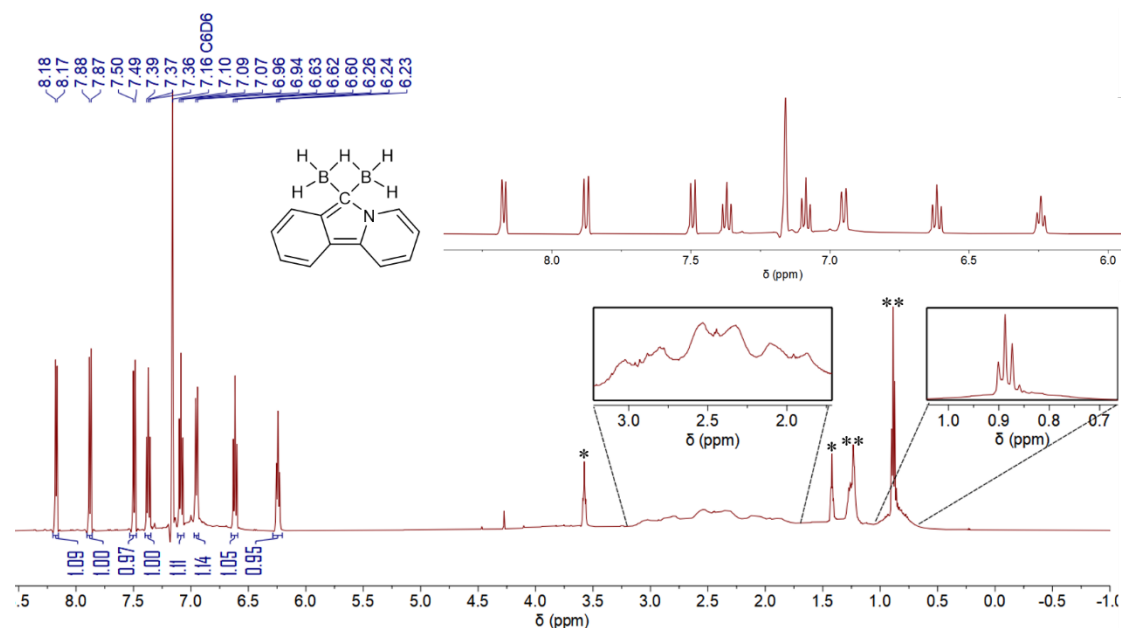
^{13}C NMR (101 MHz, C$_6$D$_6$) δ (ppm) 156.9, 131.9, 131.7, 131.4, 124.7, 123.2, 122.1, 120.6, 120.1, 119.2, 117.1. Boron-bonded carbon signal was not observed.

HRMS (EI) Found: 193.1230. Calcd. for C$_{12}$H$_{13}$B$_2$N: 193.1234. (See Section 3.4 for details).

Melting Point: 174.21–177.51 °C (under N$_2$); 178.00–178.60 °C (under air).

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3. NMR Spectra and HRMS

3.1 ¹H NMR (500 MHz, C₆D₆) Spectrum of B.

Figure S1. ¹H NMR spectra of **B** in C₆D₆. * mark the THF impurities, which was not able to remove even under vacuum overnight. ** indicate residual signals after *n*-hexane removal. Insets: top right: expanded aromatic region; centre: H (BH₂); centre right: H (B–H–B) partially merged with the *n*-hexane signals.

3.2 ¹H{¹¹B} NMR (500 MHz, C₆D₆) Spectrum of B.
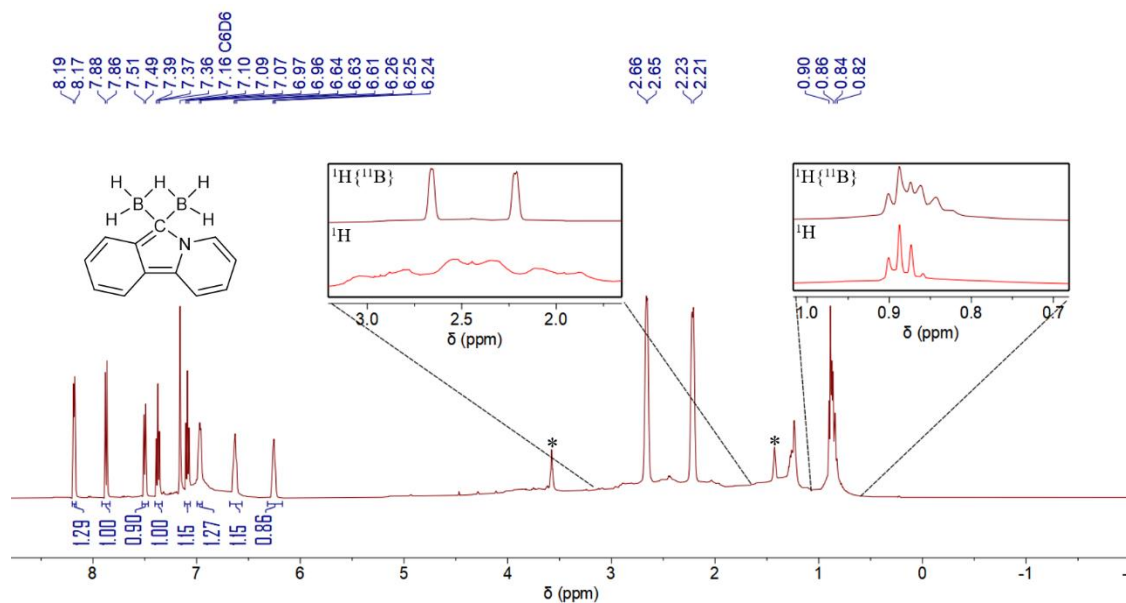
Figure S2. ¹H{¹¹B} NMR spectra of **B** in C₆D₆. * indicate the THF impurities, which was not able to remove even under vacuum overnight. Insets: centre: H (BH₂) signals in the ¹H and ¹H{¹¹B} spectra; centre right: H (B–H–B) signals in the ¹H and ¹H{¹¹B} spectra.

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3.3 ¹¹B NMR spectrum (128 MHz, C₆D₆) of Compound B
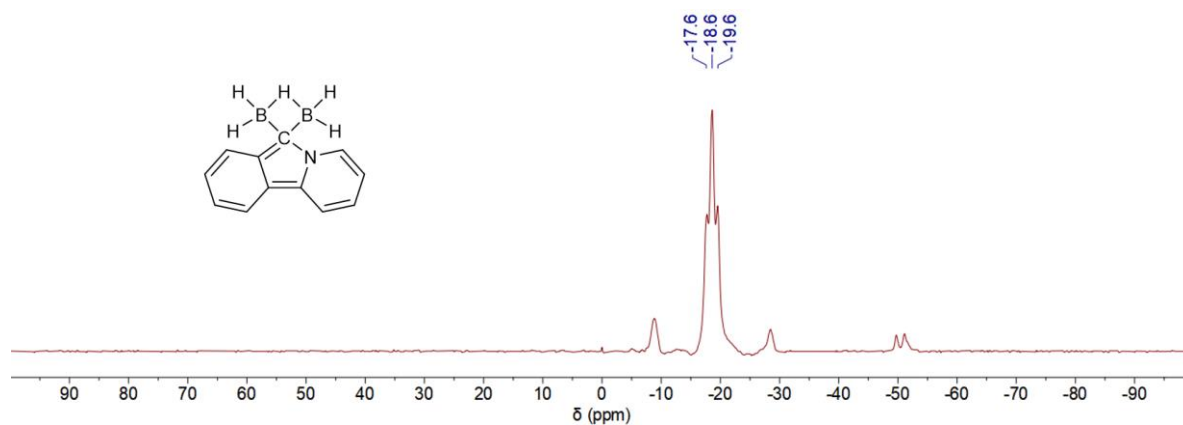
Figure S3.

3.4 ¹¹B {¹H}NMR spectrum (160 MHz, C₆D₆) of Compound B
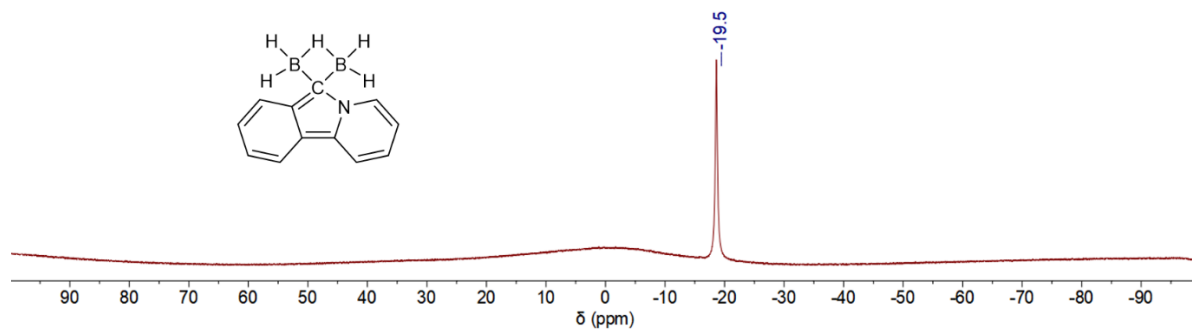
Figure S4.

3.5 ¹³C NMR spectrum (101 MHz, C₆D₆) of Compound B
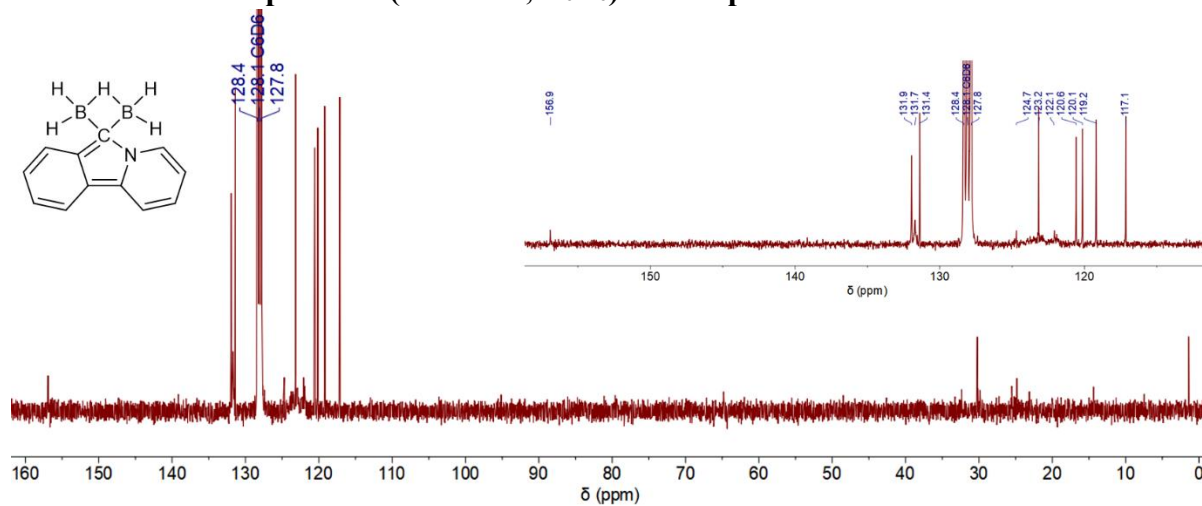
Figure S5.

3.6 High-Resolution Mass Spectrometry

SWG20141015-DY-C259

SWG20141015-DY-C259 (1.584) Is (1.00,1.00) C12H13B2N

TOF MS EI+
5.98e12

EI MODEL

193.1239

192.1272

194.1268

191.1307

SWG20141015-DY-C259 95 (1.584)

TOF MS EI+
92.2

193.1230

188.0963

192.1270

189.1011

190.1110

191.1058

194.2264

196.2322

197.2589

199.1864

202.1045

m/z
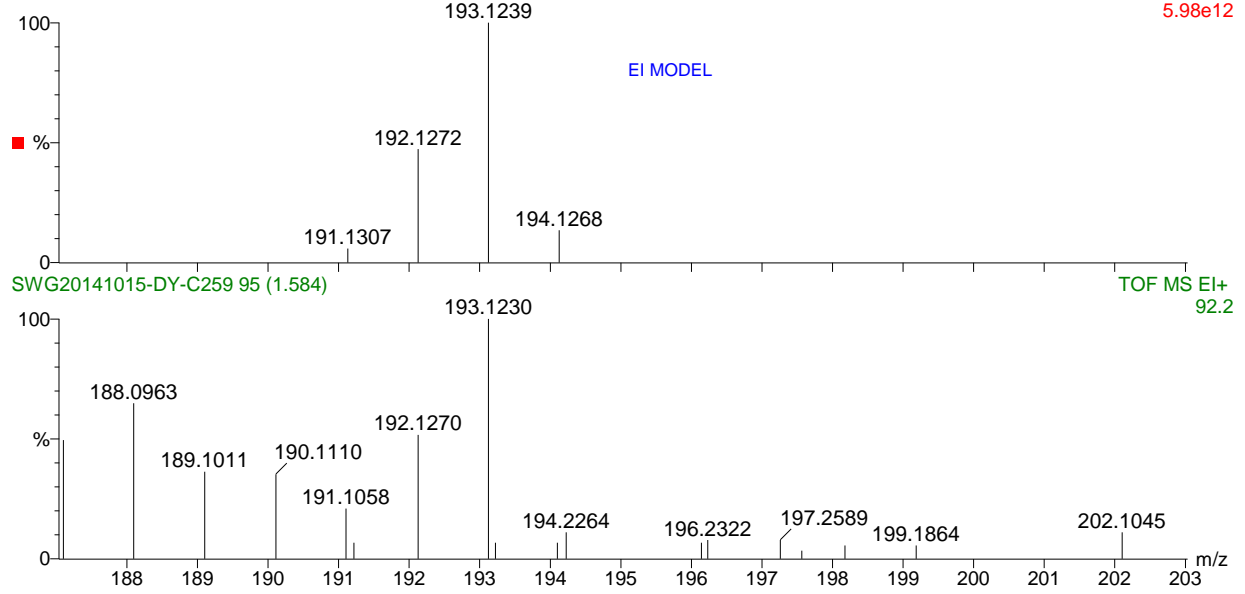
Figure S6.

SWG20141015-DY-C259

SWG20141015-DY-C259 95 (1.584)

$[M - BH_3]^+$
179.1007

TOF MS EI+
462

$[M - B_2H_4]^+$
167.0802

$[M - B_2H_5]^+$
166.0865

180.1025

57.0642

84.0841

193.1230
M^+

95.0853

111.1202

139.0603

130.0811

205.1248

232.1379

257.2654

m/z
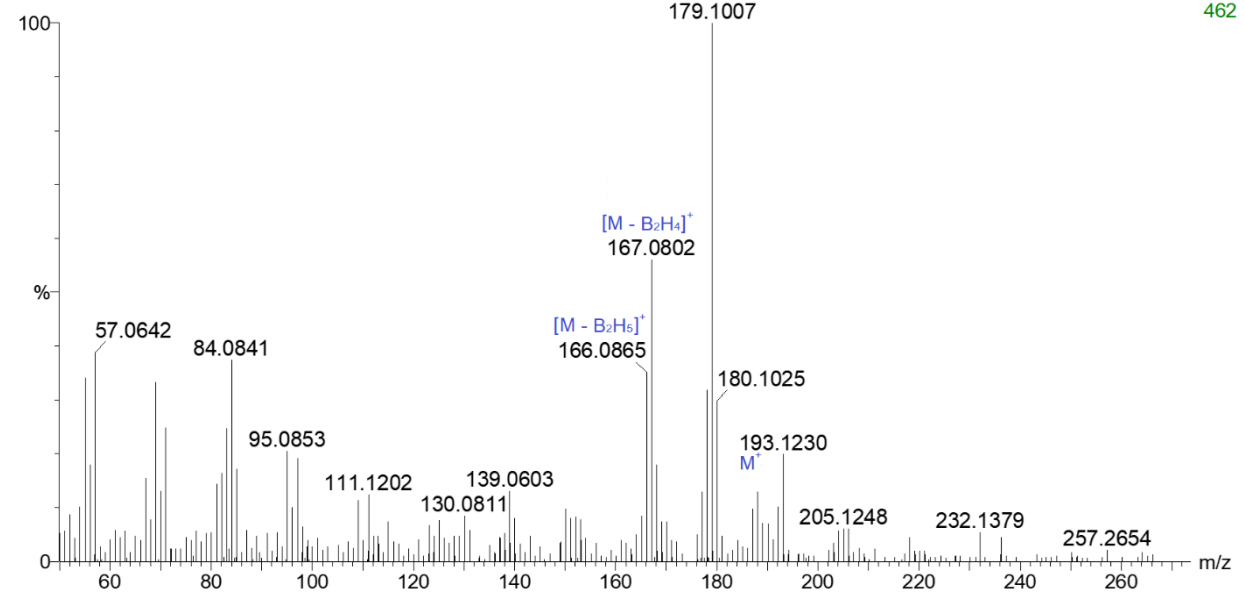
Figure S7.

4. X-ray Crystallographic Analysis

Single crystals of compounds **A** and **B** were obtained by recrystallisation from THF and hexane at 298 K. Data were collected on a Bruker AXS Apex II single-crystal X-ray diffractometer with graphite-monochromated Mo Kα radiation, operating at 50 kV and 30 mA at 180 K. Data were processed on a PC with the aid of the Bruker SHELXTL software package (version 6.14)[3] and corrected for absorption effects. All structures were solved by direct methods. The crystals of **A** belong to the orthorhombic space group Pnma while those of **B** belong to the triclinic space group P -1. The molecules of **A** possess a crystallographically imposed mirror plane with 0.5 molecule in the asymmetric unit. As a consequence, the nitrogen atom (N(1)) and the carbon atom (C(2)) are disordered over the two symmetry related sites. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated, and their contributions in structural factor calculations were included. The details of crystallographic data can be found in the supporting information. Molecular graphics were generated using Olex2 v1.2.[4]
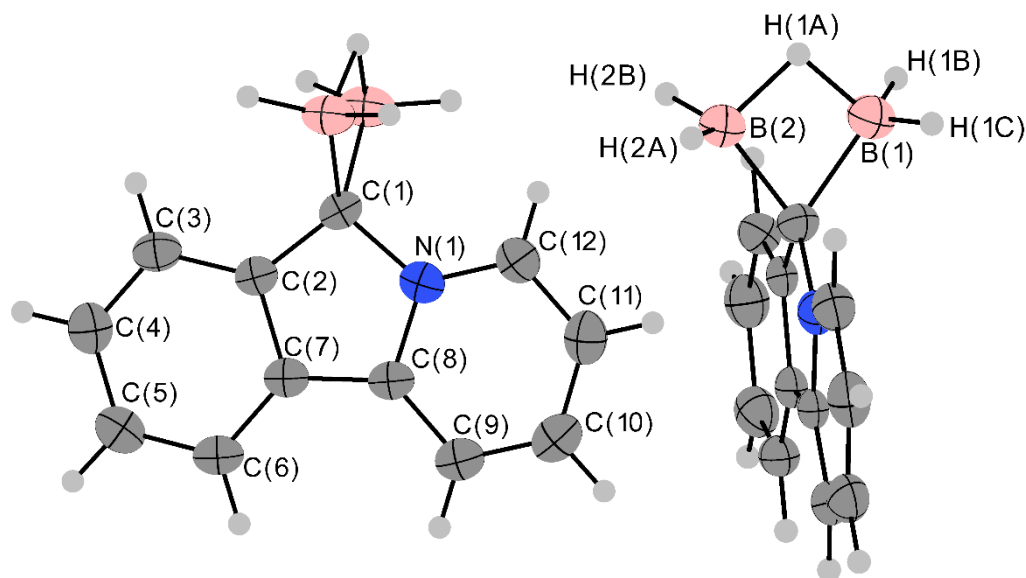
Figure S8. Atom numbering for **B**.

Table S1. Crystal data and structural refinement for **B**.

Identification code	**B**
Empirical formula	C12 H13 B2 N
Formula weight (g/mol)	192.85
T (K)	180(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	$a = 6.995(5)$ Å $\quad \alpha = 69.122(5)°$
	$b = 8.942(6)$ Å $\quad \beta = 89.652(6)°$
	$c = 9.230(6)$ Å $\quad \gamma = 83.064(6)°$
Volume (Å^3)	535.1(6)
Z	2
Density (g/cm^3)	1.197
Absorption coefficient (mm^{-1})	0.067
F(000)	204
Crystal size (mm^3)	$0.05 \times 0.06 \times 0.2$
Theta range for data collection	2.73–25.50°
Index ranges	-8 < h < 7, -10 < k < 10, -10 < l < 10
Reflections collected	2653
Independent reflections	1080
Completeness to theta = 24.992°	83.6%
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares F^2
Data/restraints/parameters	1574/0/151
Goodness- of-fit on F^2	1075
Final R indices [I > 2 sigma(I)]	R1 = 0.0562, wR2 = 0.1147
R indices (all data)	R1 = 0.0964, wR2 = 0.1351
Largest diff. peak and hole (e/Å^3)	0.118; -0.192

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **B**. U(eq) is defined as one third of the trace of the orthogonalised U$_{ij}$ tensor.

Atom (No.)	x	y	z	U(Eq)
N(1)	0.2842(3)	0.8421(3)	1.0089(3)	0.0316(6)
C(1)	0.2801(4)	0.8577(3)	0.8462(3)	0.0311(7)
C(2)	0.2427(3)	1.0318(3)	0.7655(3)	0.0270(6)
C(3)	0.2262(4)	1.1217(3)	0.6077(3)	0.0354(7)
H(3)	0.2382	1.0695	0.5341	0.042
C(4)	0.1920(4)	1.2873(3)	0.5591(3)	0.0396(7)
H(4)	0.1807	1.3490	0.4511	0.048
C(5)	0.1737(4)	1.3668(3)	0.6656(3)	0.0393(7)
H(5)	0.1501	1.4812	0.6293	0.047
C(6)	0.1896(3)	1.2797(3)	0.8227(3)	0.0342(7)
H(6)	0.1769	1.3327	0.8956	0.041

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C(7)	0.2252(3)	1.1111(3)	0.8725(3)	0.0288(6)
C(8)	0.2512(3)	0.9900(3)	1.0257(3)	0.0283(6)
C(9)	0.2488(4)	0.9979(3)	1.1737(3)	0.0348(7)
H(9)	0.2243	1.0992	1.1865	0.042
C(10)	0.2821(4)	0.8580(4)	1.3010(3)	0.0416(8)
H(10)	0.2812	0.8620	1.4024	0.050
C(11)	0.3173(4)	0.7097(4)	1.2806(3)	0.0409(7)
H(11)	0.3413	0.6129	1.3686	0.049
C(12)	0.3176(4)	0.7026(3)	1.1345(3)	0.0359(7)
H(12)	0.3409	0.6016	1.1211	0.043
B(1)	0.1709(5)	0.7301(5)	0.7978(5)	0.0435(9)
B(2)	0.4396(5)	0.7434(4)	0.7905(5)	0.0414(9)
H(1A)	0.321(4)	0.650(3)	0.767(3)	0.050
H(1B)	0.086(4)	0.784(3)	0.684(3)	0.050
H(1C)	0.107(4)	0.637(3)	0.902(3)	0.050
H(2A)	0.541(4)	0.658(3)	0.891(3)	0.050
H(2B)	0.500(4)	0.807(3)	0.674(3)	0.050

Table S3. Selected bond lengths (Å) and angles (°) for **B**.

Bond lengths			
C(1)–N(1)	1.458(4)	C(1)–C(2)	1.458(3)
C(2)–C(7)	1.404(5)	C(7)–C(8)	1.439(3)
C(8)–N(1)	1.378(4)	C(1)–B(1)	1.632(6)
C(1)–B(2)	1.627(5)	B(1)···B(2)	1.897(5)
C(12)–N(1)	1.363(3)	C(2)–C(3)	1.388(4)
B(1)–H(1A)	1.29(3)	B(2)–H(1A)	1.32(3)
B(1)–H(1B)	1.13(3)	B(1)–H(1C)	1.15(2)
B(2)–H(2A)	1.15(2)	B(2)–H(2B)	1.13(3)
Angles			
B(1)–C(1)–B(2)	71.2(2)	B(1)–H(1A)–B(2)	94(2)
B(1)–C(1)–N(1)	118.1(2)	B(2)–C(1)–N(1)	118.5(2)
B(1)–C(1)–C(2)	122.9(2)	B(2)–C(1)–C(2)	122.6(2)
C(2)–C(1)–N(1)	102.7(3)	C(1)–N(1)–C(8)	111.9(2)
C(7)–C(8)–N(1)	107.3(3)	C(2)–C(7)–C(8)	107.7(2)
C(1)–C(2)–C(7)	110.4(2)	C(1)–C(2)–C(3)	130.0(3)
C(1)–N(1)–C(12)	126.8(3)	C(8)–N(1)–C(12)	121.3(3)
C(2)–C(3)–C(7)	119.6(2)		

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Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **B**. The anisotropic displacement factor exponent takes the form: $-2\,^2\,[h^2\,a^{*2}\,U_{11} + ... + 2\,h\,k\,a^*\,b^*\,U_{12}\,]$.

Atom (No.)	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	0.0229(13)	0.0334(15)	0.0406(15)	-0.0154(11)	0.0016(9)	-0.0048(9)
C(1)	0.0304(16)	0.0366(18)	0.0297(17)	-0.0163(12)	0.0017(11)	-0.0033(11)
C(2)	0.0170(14)	0.0343(16)	0.0331(17)	-0.0154(13)	0.0012(10)	-0.0055(10)
C(3)	0.0305(17)	0.0404(19)	0.041(2)	-0.0220(15)	0.0001(12)	-0.0047(12)
C(4)	0.0333(18)	0.042(2)	0.0395(19)	-0.0092(14)	-0.0026(12)	-0.0048(12)
C(5)	0.0307(17)	0.0355(18)	0.051(2)	-0.0149(15)	-0.0036(13)	-0.0016(12)
C(6)	0.0255(16)	0.0400(18)	0.044(2)	-0.0235(14)	-0.0006(12)	-0.0026(11)
C(7)	0.0181(14)	0.0346(18)	0.0374(17)	-0.0172(13)	0.0016(11)	-0.0045(11)
C(8)	0.0162(14)	0.0359(17)	0.0381(18)	-0.0192(13)	0.0022(10)	-0.0051(10)
C(9)	0.0240(16)	0.0440(19)	0.0423(19)	-0.0218(15)	0.0020(12)	-0.0070(12)
C(10)	0.0319(18)	0.058(2)	0.040(2)	-0.0228(17)	0.0027(13)	-0.0101(13)
C(11)	0.0329(18)	0.047(2)	0.0377(19)	-0.0078(14)	0.0004(12)	-0.0097(13)
C(12)	0.0316(17)	0.0354(18)	0.0398(19)	-0.0119(14)	0.0008(12)	-0.0057(12)
B(1)	0.038(2)	0.044(2)	0.058(3)	-0.0296(19)	0.0015(17)	-0.0060(15)
B(2)	0.037(2)	0.042(2)	0.054(2)	-0.0281(18)	0.0055(16)	-0.0079(15)

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5. Computational Details

5.1 Mechanistic analysis

DFT calculations were performed using the Gaussian 09 suite of programs[5] on the High Performance Computing Virtual Laboratory (HPCVL) at Queen's University. Geometry optimisations (without constraints) and frequency calculations were performed using the hybrid DFT-D2 functional ωB97XD, which has been proposed as a promising functional for obtaining accurate data for main group thermochemistry, kinetics, and non-covalent interactions.[6] The basis set used for all calculations was 6-31G(d,p). Transition state structures were located with potential energy surface scans and optimised using the opt = (ts, noneigentext, calcfc) algorithm,[7] and confirmed to be maxima through vibrational frequency analysis (one true imaginary frequency). Additionally, intrinsic reaction coordinate (IRC) calculations were performed to connect the obtained transition states with their corresponding "start" and "end" geometries along the imaginary frequency normal mode.[8]

The cartesian coordinates are given in Å, together with the atom symbols, point groups, and total electronic energies at the 6-31G(d,p) level of theory.

Table S5. A + 2 BH$_3$; E_{tot} = -570.488404:

Atom	x	y	z
C	3.46875200	-0.01036000	-0.50444100
C	3.28061500	1.38259200	-0.26936300
C	2.04039700	1.91897400	-0.05170700
C	0.91262700	1.05560700	-0.05915300
C	1.10944800	-0.35328300	-0.25363600
C	2.40669500	-0.87314700	-0.50135400
H	4.47106000	-0.38653600	-0.67880900
H	4.15006500	2.03293400	-0.26855600
H	1.91410000	2.98348000	0.11633900
H	2.54934000	-1.93596300	-0.66840600
C	-0.45311100	1.28322000	0.08117200
H	-1.00990300	2.18876100	0.26091400
C	-2.43711300	-0.18347500	0.05212100
C	-2.89240500	-1.45718800	-0.08867100
C	-1.98791700	-2.52710300	-0.31907900
C	-0.64576800	-2.26705800	-0.39365900
C	-0.17203900	-0.95152500	-0.24777900

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H	-3.07323500	0.67296400	0.23405200
H	-3.95777200	-1.63948100	-0.01525800
H	-2.36245300	-3.53790400	-0.42894400
H	0.07799200	-3.05808800	-0.55373400
N	-1.08981700	0.07849700	-0.03623700
B	1.29981300	-0.89222700	2.23786100
H	0.19549900	-0.49009200	2.46964600
H	1.47596100	-2.06676800	2.07847300
H	2.23707800	-0.16477700	2.38239100
B	-4.16483600	3.40166400	-0.06591700
H	-4.71276800	4.45629800	-0.16995300
H	-3.08562900	3.23786200	-0.55468400
H	-4.69659100	2.50712400	0.52376000

Table S6. A' + BH₃; E_{tot} = -570.523817:

Atom	x	y	z
C	-3.06940000	-1.47316800	-0.03325200
C	-3.44978200	-0.12303900	0.04633000
C	-2.50975200	0.89249900	0.13032600
C	-1.16057800	0.54587200	0.12122400
C	-0.78547400	-0.80188300	0.03964200
C	-1.73171500	-1.82717200	-0.03259600
H	-3.83236900	-2.24191900	-0.08898900
H	-4.50606400	0.12667000	0.05140700
H	-2.80522200	1.93156200	0.22011000
H	-1.43163800	-2.86902000	-0.08731600
C	0.03092500	1.40514400	0.25494200
H	0.13716100	2.20363700	-0.49630300
C	2.42659100	0.73286300	0.14460100
C	3.35820900	-0.27625700	0.07605600
C	2.92443200	-1.60681700	0.00023400
C	1.57345000	-1.89733200	-0.00885800
C	0.65819600	-0.84650800	0.04356300
H	2.66127300	1.78376900	0.25159500
H	4.41192000	-0.03008900	0.09706200
H	3.65227900	-2.40947600	-0.04312000
H	1.21088300	-2.91677100	-0.05718100
N	1.11663300	0.43120500	0.11171300
H	1.21587700	2.80051600	1.72113300
H	-0.80206400	2.95609100	1.79390000
H	0.12088800	1.33139800	2.60359200
B	0.14938400	2.19770500	1.74574200
B	0.22445300	1.87247400	-2.50868700
H	1.30610700	2.37562200	-2.40159000

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H	0.13209500	0.68517000	-2.60909500
H	-0.74735600	2.55829400	-2.61575100

Table S7. TS1'; E_{tot} = -570.481049:

Atom	x	y	z
C	-2.95875800	-0.77317700	-0.60920800
C	-3.14212900	0.63291400	-0.44878300
C	-2.08489200	1.47322400	-0.22867800
C	-0.77921200	0.92368000	-0.16006600
C	-0.59641700	-0.47505500	-0.32133800
C	-1.69568600	-1.32832300	-0.55266500
H	-3.81404700	-1.39638500	-0.84399900
H	-4.14909100	1.03400700	-0.49578800
H	-2.23376600	2.53953300	-0.09629300
H	-1.55071600	-2.39073000	-0.71554700
C	0.47502600	1.53241100	0.05888200
H	0.84724100	2.64689600	-0.76254600
C	2.76438500	0.58272200	0.17615800
C	3.52956500	-0.54492900	0.12054100
C	2.93268300	-1.80883400	-0.09725600
C	1.57227400	-1.89178400	-0.25354400
C	0.78866200	-0.72859200	-0.20112300
H	3.16080700	1.57316400	0.35119300
H	4.60062900	-0.45214100	0.25222700
H	3.54718500	-2.70067000	-0.13468800
H	1.07701900	-2.84258600	-0.41380400
N	1.40577100	0.49905100	0.01701100
H	1.86270900	3.18243500	1.08224600
H	1.12357800	3.66628400	-0.66162600
H	-0.15927000	3.66191100	0.81916000
B	0.83218900	3.08625400	0.47653300
B	-2.88632500	-1.61521400	1.74285800
H	-2.37740800	-2.69681200	1.65125600
H	-2.25740800	-0.69590400	2.17609100
H	-4.08018200	-1.54310000	1.67855700

Table S8. C=B DB; E_{tot} = -570.516807:

Atom	x	y	z
C	2.97217900	-1.47766600	-0.14469000
C	3.35919800	-0.13653300	-0.37520300
C	2.43118900	0.87300500	-0.49424800
C	1.06055200	0.55048400	-0.38576400
C	0.68355100	-0.79758200	-0.16099900
C	1.64234100	-1.81672200	-0.03598100

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Atom	x	y	z
H	3.73553800	-2.24279900	-0.05213400
H	4.41593700	0.09776000	-0.45604800
H	2.73466800	1.89991600	-0.66509100
H	1.34378500	-2.84522700	0.14213700
C	-0.10925600	1.37128100	-0.48328700
C	-2.51197200	0.76438200	-0.30393100
C	-3.43363300	-0.22480900	-0.11221000
C	-3.01419700	-1.55745000	0.09041000
C	-1.67181300	-1.84739100	0.09268600
C	-0.73904800	-0.82048200	-0.10799300
H	-2.76407100	1.80373600	-0.46041900
H	-4.48564900	0.03225400	-0.11719300
H	-3.74780700	-2.34052200	0.24349800
H	-1.30819000	-2.85655700	0.24744100
N	-1.17945500	0.47310500	-0.30631300
H	-1.28445500	3.39523000	-0.81285900
H	0.77615300	3.48104800	-0.84900400
B	-0.22585900	2.83710200	-0.72654000
B	1.21416700	0.94946700	2.36102400
H	1.53325700	2.09655400	2.25411300
H	0.05710900	0.66519700	2.47936200
H	2.04752700	0.09989700	2.46953800
H	-2.21527200	2.64063000	2.18539800
H	-1.53843700	2.54519400	1.89028500

Table S9. TS1; E_{tot} = -570.50271:

Atom	x	y	z
C	-3.05395100	-1.54737000	-0.01225100
C	-3.44075900	-0.19463800	-0.00661800
C	-2.50864900	0.82824300	-0.00752200
C	-1.15512800	0.49037000	-0.01750000
C	-0.77273900	-0.85830800	-0.01998000
C	-1.71606000	-1.89176300	-0.01686600
H	-3.81333600	-2.32150000	-0.01030200
H	-4.49823200	0.04986300	0.00141200
H	-2.80957700	1.86926800	0.00393500
H	-1.40846300	-2.93287900	-0.01748600
C	0.03402800	1.35188200	0.01569700
H	0.40329700	2.65689700	-0.18075900
C	2.43566200	0.68265800	-0.01708100
C	3.36602000	-0.32795700	-0.01559800
C	2.93405600	-1.66227900	-0.01184500
C	1.58425700	-1.95078200	-0.01093600
C	0.66685100	-0.89864900	-0.01975000

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H	2.68344900	1.73534100	0.00264600
H	4.41938400	-0.07939800	-0.00973000
H	3.66225000	-2.46556200	-0.00581100
H	1.21999700	-2.97080700	-0.00231600
N	1.12278500	0.38278000	-0.02698400
H	1.16357600	2.81817200	1.50879100
H	-0.85272900	2.87420600	1.60737400
H	0.16708100	1.29082100	2.40342500
B	0.12746600	2.15977300	1.56097700
B	0.09424000	2.37489700	-1.43259800
H	0.57219000	3.44479700	-0.95315000
H	0.90559700	1.92682500	-2.19012200
H	-1.02404300	2.62269700	-1.76941100

Table S10. B; E_{tot} = -570.575620:

| Atom	x	y	z
C	2.78286000	-1.99530700	-0.00031600
C	3.32816200	-0.69465000	0.00161200
C	2.52597300	0.42999000	0.00245800
C	1.13581300	0.25728600	0.00127200
C	0.59796400	-1.04182200	-0.00040900
C	1.41585700	-2.18030300	-0.00124300
H	3.44731600	-2.85273600	-0.00092000
H	4.40743200	-0.57733900	0.00255400
H	2.95122900	1.42742400	0.00445100
H	0.98725700	-3.17784600	-0.00257200
C	0.06943200	1.24071300	0.00176300
C	-2.39780500	0.88032200	0.00081400
C	-3.43874800	-0.01332300	-0.00022900
C	-3.17446800	-1.39296300	-0.00159100
C	-1.87028000	-1.83795200	-0.00186100
C	-0.82979900	-0.90443100	-0.00074500
H	-2.52201200	1.95432700	0.00201500
H	-4.45398800	0.36275700	0.00007000
H	-3.99351800	-2.10331700	-0.00235300
H	-1.63015700	-2.89437400	-0.00287600
N	-1.12196500	0.43195600	0.00056400
H	-0.93139200	2.76390500	-1.53593600
H	0.06932700	3.52535900	0.00306300
H	1.13467200	2.75887200	-1.50232200
B	0.09387800	2.57348700	-0.93525100
H	-0.93217000	2.76183500	1.54061900
H	1.13463100	2.75775100	1.50685800
B	0.09382500	2.57181200	0.94097800

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| H | 3.54936600 | 4.10128200 | 0.02655800 |
| H | 2.82748200 | 3.95654900 | -0.08093200 |

5.2 Aromaticity analysis

Nucleus-independent chemical shifts (NICS)[9] were obtained from B3LYP NMR calculations based on the GIAO formalism[10] using the B3LYP/6-311+G(d,p) basis set. The empirical dispersion correction was omitted since it has no effect on the computation of electronic properties. NICS(0) indices were calculated at the ring critical points of the corresponding arene rings, and at distances of 1 Å above and below the plane defined by the carbon atom bound to boron and the two neighbouring carbon nuclei of the corresponding phenyl fragment, to give NICS(1) and NICS(-1) parameters.[11]

5.3 Analysis for chemical bondings.

Wiberg bond indices (WBI)[12] and Adaptive Natural Density Partitioning (AdNDP),[13] are based on the natural bonding orbital (NBO) method.[14] The AdNDP method recovers multicentre Lewis bondings (3c–2e bonds). The density matrix at the basis of the natural atomic orbitals, as well as the transformation matrix between atomic orbital and natural atomic orbital basis sets were generated at the B3LYP/6-31G(d) level with the NBO v. 3.1. Visualised AdNDP models were generated using Multiwfn[15] program.
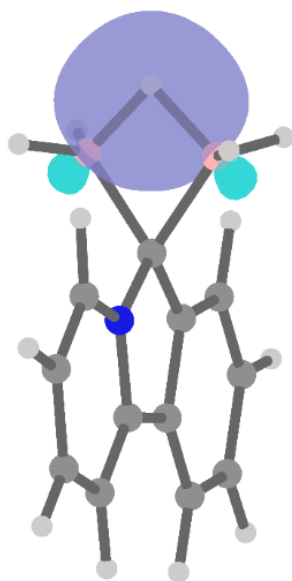
Figure S9. Visualised AdNDP model for the 3c–2e B–H–B orbital (ON = 1.9916 |e|).

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