

Supporting Information for:

**Diverse Reactions of N-heterocyclic Carbenes with an Alkynylborane and Isolation of a Reactive
Zwitterionic Borataallene**

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Experimental Section

General considerations: All manipulations were performed under an inert atmosphere of dry argon using either standard Schlenk-line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvent were distilled from appropriate drying agents.¹ Solvents were stored under argon over activated molecular sieves. Ethynylmagnesiumbromide,² Mes₂BF,³ IMe,⁴ IMes⁵ and IDip⁵ were prepared according to published procedures. NMR spectra were recorded on a Bruker DMX 600 (600.13 MHz for ¹H, 150.93 MHz for ¹³C{¹H}), Bruker Avance 500 NMR spectrometer (500.1 MHz for ¹H, 160.4 MHz for ¹¹B, 125.76 MHz for ¹³C{¹H}), Bruker Avance 400 NMR spectrometer (128.38 MHz for ¹¹B) or a Bruker DSX 400 Solid State NMR (128.38 MHz for ¹¹B, 100.63 MHz for ¹³C{¹H}). Chemical shifts (δ) are given in ppm and are referenced against external Me₄Si (¹H, ¹³C) and [BF₃·Et₂O] (¹¹B). Cq refers to quaternary carbon nuclei. Infrared data were acquired on a JASCO FT/IR-6200typeA apparatus. Melting points were measured with a Mettler Toledo DSC 823. Microanalyses were performed on an Elementar vario MICRO cube elemental analyzer. Elemental analyses were acquired on an Elementar Vario MICRO cube instrument or a CHNS-932 (Leco). UV-Vis spectra were measured with a JASCO-V660 UV-Vis spectrometer in a quartz glass cell (10 mm). All cyclic voltammetry experiments were conducted in an argon-filled glovebox, using a Gamry Instruments Reference 600 potentiostat. A standard three-electrode cell configuration was employed using a platinum disk working electrode, a platinum wire counter electrode, and a silver wire, separated by a Vycor tip, serving as the reference electrode. Formal redox potentials are reported versus the ferrocene/ferrocenium (Fc^{0/+}) redox couple obtained by using decamethylferrocene (Me₁₀Fc) as an internal standard and accounting for the difference in formal redox potentials in the respective solvent media ($E_{1/2} = E_{1/2}(\text{Fc}^{0/+}) - E_{1/2}(\text{Me}_{10}\text{Fc}^{0/+}) = +455 \text{ mV}$ in THF with 0.1 M nBu₄NPF₆ as the supporting electrolyte). Compensation for resistive losses (*iR* drop) was employed for all measurements.⁶

Synthesis of 1:

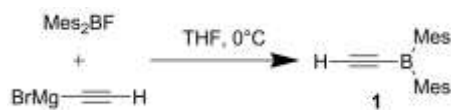


Figure S1. Synthesis of *1-dimesitylborylacetylene* (**1**).

Dimesitylfluoroborane (1.00 g, 3.73 mmol) was dissolved in a Schlenk tube in THF (20.0 mL). The reaction mixture was cooled to 0 °C and a solution of ethynylmagnesiumbromide in THF (436 mg, 3.73 mmol, *c* = 25.0 mg/mL) was added over 45 min with a syringe. The reaction mixture was stirred for 1 h at 0 °C. After removing all volatiles under high vacuum the oily residue was extracted with pentanes (3 x 20.0 mL). After removing the solvent under high vacuum, the residue was distilled with a Büchi oven (120 °C, $1 \cdot 10^{-3}$ bar). Compound **1** was isolated as a colourless solid (399 mg, 1.45 mmol, 39%). Single crystals suitable for X-ray diffraction were obtained by storing a hexane solution for 2 weeks at −30°C.

Melting point: 93.2 °C

Decomposition temperature: ~234 °C

^1H NMR (500.1 MHz, CDCl_3 , 296 K): δ = 6.81 (s, 4H, *m*- $\text{C}_{\text{Mes}}\text{H}$), 4.36 (s, 1H, $\text{C}\equiv\text{CH}$), 2.31 (s, 12H, *o*- $\text{C}_{\text{Mes}}\text{H}_3$), 2.28 (s, 6H, *p*- $\text{C}_{\text{Mes}}\text{H}_3$)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3 , 296 K): δ = 141.27 (s, C_{Mesq}), 140.18 (s, C_{Mesq}), 137.89 (s, C_{Mesq}), 128.80 (s, C_{MesH}), 114.6 (s, $\text{C}\equiv\text{CH}$), 23.24 (s, *o*- $\text{C}_{\text{Mes}}\text{H}_3$), 21.42 (s, *p*- $\text{C}_{\text{Mes}}\text{H}_3$)

$^{11}\text{B}\{^1\text{H}\}$ NMR (160.4 MHz, CDCl_3 , 296 K): δ = 64.0 (s)

IR (solid): 3246 cm^{-1} ($\equiv\text{C}-\text{H}$ stretch), 2041 cm^{-1} ($\text{C}\equiv\text{C}$ stretch)

Elemental analysis for $\text{C}_{20}\text{H}_{23}\text{B}$ [%]: calculated: C 87.60, H 8.45; found: C 87.67, H 8.55

Synthesis of 2:

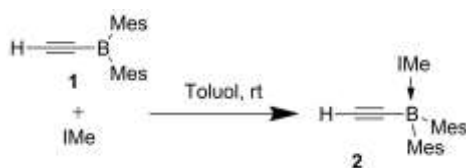


Figure S2. Synthesis of 2.

Dimesitylborylacetylene (**1**) (84.7 mg, 0.309 mmol) was dissolved in a Schlenk tube in toluene (5.00 mL). With stirring, a solution of IMe in toluene (2.85 mL, 0.309 mmol, $c = 10.0 \text{ mg/mL}$) was added by syringe. The orange reaction mixture was stirred for 10 min. After removing all volatiles under high vacuum, the residue was taken up with diethyl ether (2.00 mL) and filtered. After removing the solvent under high vacuum, the residue was washed with cold pentane (2 x 5.00 mL). A diethylether / pentane (2:1) solution of the residue was stored for one week at -60°C . After removing the supernatant solution by decantation the residue was dried under high vacuum. Compound **1** was isolated as a colourless solid (54.0 mg, 0.201 mmol, 65%). Single crystals suitable for X-ray diffraction were obtained by storing a THF / hexane (2:1) solution at -35°C for one week.

Decomposition temperature: $>197^\circ\text{C}$

^1H NMR (500.1 MHz, CDCl_3 , 296 K): $\delta = 6.89$ (d, 1H, $^3J_{\text{HH}} = 1.42 \text{ Hz}$, $\text{N}_{\text{NHC}}\text{CH}$), 6.74 (obscured, d, 1H, $^3J_{\text{HH}} = 1.42 \text{ Hz}$, $\text{N}_{\text{NHC}}\text{CH}$), 6.74 (bs, 4H, $\text{C}_{\text{Mes}}\text{H}$), 3.80 (s, 3H, NCH_3), 3.12 (s, 3H, NCH_3), 2.25 (s, 6H, $p\text{-C}_{\text{Mes}}\text{H}_3$), 2.17 (s, 1H, $\text{C}\equiv\text{CH}$), 2.06 (sb 12H, $o\text{-C}_{\text{Mes}}\text{H}_3$)

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CDCl_3 , 296 K): $\delta = 168.7$ (br m, $^1J_{\text{BC}} \sim 63 \text{ Hz}$, $\text{B}_{\text{NHC}}\text{Cq}$), 146.3 (br m, $^1J_{\text{BC}} \sim 48 \text{ Hz}$, Cq), 142.7 (br s, Cq), 133.73 (s, Cq), 127.92 (s, $\text{C}_{\text{Mes}}\text{H}$), 122.38 (s, $\text{C}_{\text{NHC}}\text{H}$), 122.06 (s, $\text{N}_{\text{NHC}}\text{CH}$), 105.3 (br m, $^1J_{\text{BC}} \sim 73 \text{ Hz}$, $\text{HC}\equiv\text{CB}$), 83.8 (s, $\text{C}\equiv\text{CH}$), 38.74 (s, $\text{C}_{\text{NHC}}\text{H}_3$), 37.23 (s, $\text{C}_{\text{NHC}}\text{H}_3$), 24.68 (s, $p\text{-C}_{\text{Mes}}\text{H}_3$), 20.85 (s, $o\text{-C}_{\text{Mes}}\text{H}_3$);

$^{11}\text{B}\{^1\text{H}\}$ NMR (160.4 MHz, CDCl_3 , 296 K): $\delta = -18.5$ (s)

IR (solid): 3238 cm^{-1} ($\equiv\text{C-H}$ stretch)

Elemental analysis for $\text{C}_{25}\text{H}_{33}\text{BN}_2$ [%]: calculated: C 81.06, H 8.44, N 7.56; found: C 81.09, H 8.60, N 7.43

128.43 (s, C10H), 127.27 (s, C5H), 127.19 (s, C7H), 124.4 (sb, C15H), 123.53 (s, C12H), 115.41 (s, C17H), 64.97 (s, C1H), 47.07 (s, C3H₂), 37.41 (s, C2H), 28.65 (s, C14H), 26.3-22.6 (br m, C13H₃), 22.26 (s, C8H₃), 22.18 (s, C4H₃), 21.74 (s, C11H₃), 21.30 (s, C6H₃), 20.49 (s, C9H₃)

¹¹B{¹H} NMR (160.4 MHz, C₆D₆, 296 K): δ = 81.4 (s)

¹⁵N-¹H HMBC NMR (50.69 MHz, C₆D₆, 296 K): δ = -271.6 (s)

IR (hexane): 1639 cm⁻¹ (C=C stretch), 1604 cm⁻¹ (C=C stretch)

UV/Vis (hexane): λ_{max} = 261.5 nm (ε = 15345 L mol⁻¹ cm⁻¹)

Elemental analysis for C₄₇H₅₉BN₂ [%]: calculated: C 85.17, H 8.79, N 4.23; found: C 84.70, H 9.04, N 4.13

Reaction of **1** with IDipp in hexane in order to isolate an intermediate

In a glovebox, **1** (20 mg, 0.073 mmol) and IDip (28.3 mg, 0.073 mmol) were added to a glass vial and hexane (1 mL) was added. The mixture was shaken by hand. After a short time a violet solid precipitated from the red/yellow solution. After filtration, the violet solid was dissolved in C₆H₅F, and the ¹¹B NMR spectrum of this solution showed a mixture of compounds including a major signal for **3** (δ 79.8), a signal presumably corresponding to a borataallene (δ ~27 ppm), and a sharp multiplet at δ 3.0). We were unable to confirm the existence of the presumed borataallene on spectroscopic grounds.

Synthesis of 4:

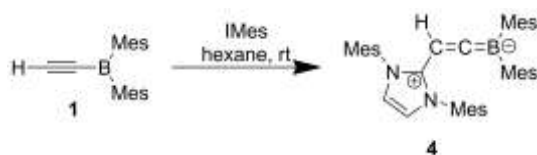


Figure S5. Synthesis of **4**.

Dimesitylborylacetylene (**1**) (200 mg, 0.729 mmol) and IMes (222 mg, 0.0729 mmol) were suspended in hexane (2.00 mL) in a vial in a glove box. The solid residue immediately turned red-violet (in one case orange). The solid was isolated by filtration and washed with hexane (5 x 1.00 mL). After removing all volatiles under high vacuum, **4** was isolated as a red violet (or orange) solid (317 mg, 0.548 mmol, 75 %). The red-violet and orange samples were found to be spectroscopically identical. Single crystals suitable for X-ray diffraction were obtained by storing a toluene / pentane solution at -35°C for two days.

Melting point: 130°C

^1H NMR (600.13 MHz, Tol- d_8 , 281 K): δ = 6.83 (s, 4H, $\text{C}_{\text{Mes}}\text{H}$), 6.77 (s, 1H, $\text{C}_{\text{vinyl}}\text{H}$), 6.53 (s, 4H, $\text{C}_{\text{Mes}}\text{H}$), 5.54 (s, 2H, $\text{N}_{\text{NHC}}\text{CH}$), 2.30 (s, 6H, $p\text{-C}_{\text{Mes}}\text{H}_3$), 2.26 (s, 12H, $o\text{-C}_{\text{Mes}}\text{H}_3$), 2.11 (sb, 12H, $o\text{-C}_{\text{Mes}}\text{H}_3$), 1.75 (s, 6H, $p\text{-C}_{\text{Mes}}\text{H}_3$)

$^{13}\text{C}\{^1\text{H}\}$ NMR (150.9 MHz, Tol- d_8 , 281 K): δ = 286.8 (bs, C_{NHCq}), 144.2 (bs, Cq), 142.90 (s, Cq), 140.88 (s, Cq), 139.44 (s, Cq), 137 (bs, $\text{B}=\text{C}=\text{C}$), 135.29 (s, Cq), 132.57 (s, Cq), 132.15 (s, Cq), 129.86 (s, $\text{C}_{\text{Mes}}\text{H}$), 127.54 (s, $\text{C}_{\text{Mes}}\text{H}$), 119.5 (s, $\text{N}_{\text{NHC}}\text{CH}$), 87.20 (s, $\text{B}=\text{C}=\text{CH}$), 24.93 (s, $p\text{-C}_{\text{Mes}}\text{H}_3$), 21.45 (s, $o\text{-C}_{\text{Mes}}\text{H}_3$), 21.12 (s, $o\text{-C}_{\text{Mes}}\text{H}_3$), 17.57 (s, $p\text{-C}_{\text{Mes}}\text{H}_3$)

$^{11}\text{B}\{^1\text{H}\}$ NMR (128.38 MHz, C_6D_6 , 296 K): δ = 22.3 (s)

^{13}C (VACP/MAS) NMR (150.63 MHz): δ = 276.1 (s, C_{NHCq}), 145.1 (s), 142.1 (s), 139.9 (s), 137.6 (s), 136.1 (s), 133.0 (s), 130.6 (s), 129.4 (s), 127.3 (s), 121.9 (s, $\text{N}_{\text{NHC}}\text{CH}$), 119.9 (s, $\text{N}_{\text{NHC}}\text{CH}$), 88.0 (s, $\text{C}=\text{CH}$), 25.7 (s, $\text{C}_{\text{Mes}}\text{H}_3$), 24.6 (s, $\text{C}_{\text{Mes}}\text{H}_3$), 22.7 (s, $\text{C}_{\text{Mes}}\text{H}_3$), 20.7 (s, $\text{C}_{\text{Mes}}\text{H}_3$), 19.4 (s, $\text{C}_{\text{Mes}}\text{H}_3$), 18.5 (s, $\text{C}_{\text{Mes}}\text{H}_3$), 17.2 (s, $\text{C}_{\text{Mes}}\text{H}_3$), 15.5 (s, $\text{C}_{\text{Mes}}\text{H}_3$)

^{11}B (VACP/MAS) NMR (128.38 MHz): δ = 20.5 (s)

IR (solid): 2919 cm^{-1} (C–H stretch), 2846 cm^{-1} (C–H stretch), 1606 cm^{-1} (C=C stretch), 1444 cm^{-1} (C=C stretch)

Elemental analysis for $\text{C}_{25}\text{H}_{33}\text{BN}_2$ [%]: calculated: C 85.10, H 8.19, N 4.84; found: C 84.80, H 8.24, N 4.70

Initial reaction of **1** with IMes in C₆D₆

Solid **1** (27 mg, 0.098 mmol) and IMes (30 mg, 0.099 mmol) were added to a sealable NMR tube in a glovebox, and were dissolved in C₆D₆. Directly after mixing the reagents the ¹¹B NMR spectrum of the mixture showed a major signal at δ 22.6 (**4**) along with a minor signal at ca. δ 73.5 which we assumed to be the boraindane compound analogous to **3**. After 3 d the ¹¹B NMR spectrum of the mixture showed that the signal for **4** had diminished while the signal at ca. δ 74 had grown. Nevertheless we were unable to isolate this compound.

UV/Vis Spectrum of 4

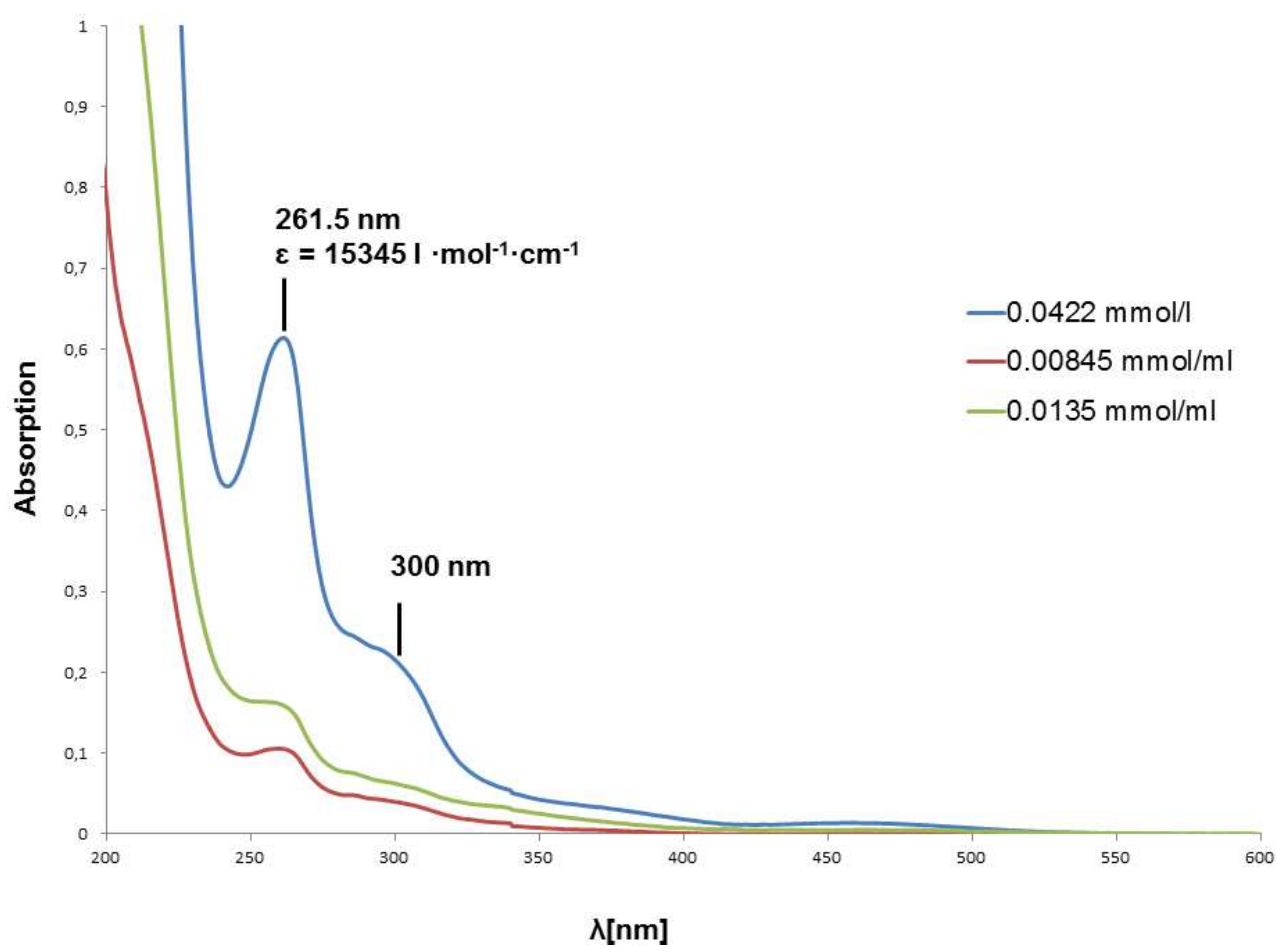


Figure S6. UV/Vis spectrum of **4**.

Cyclic voltammogram of **4**

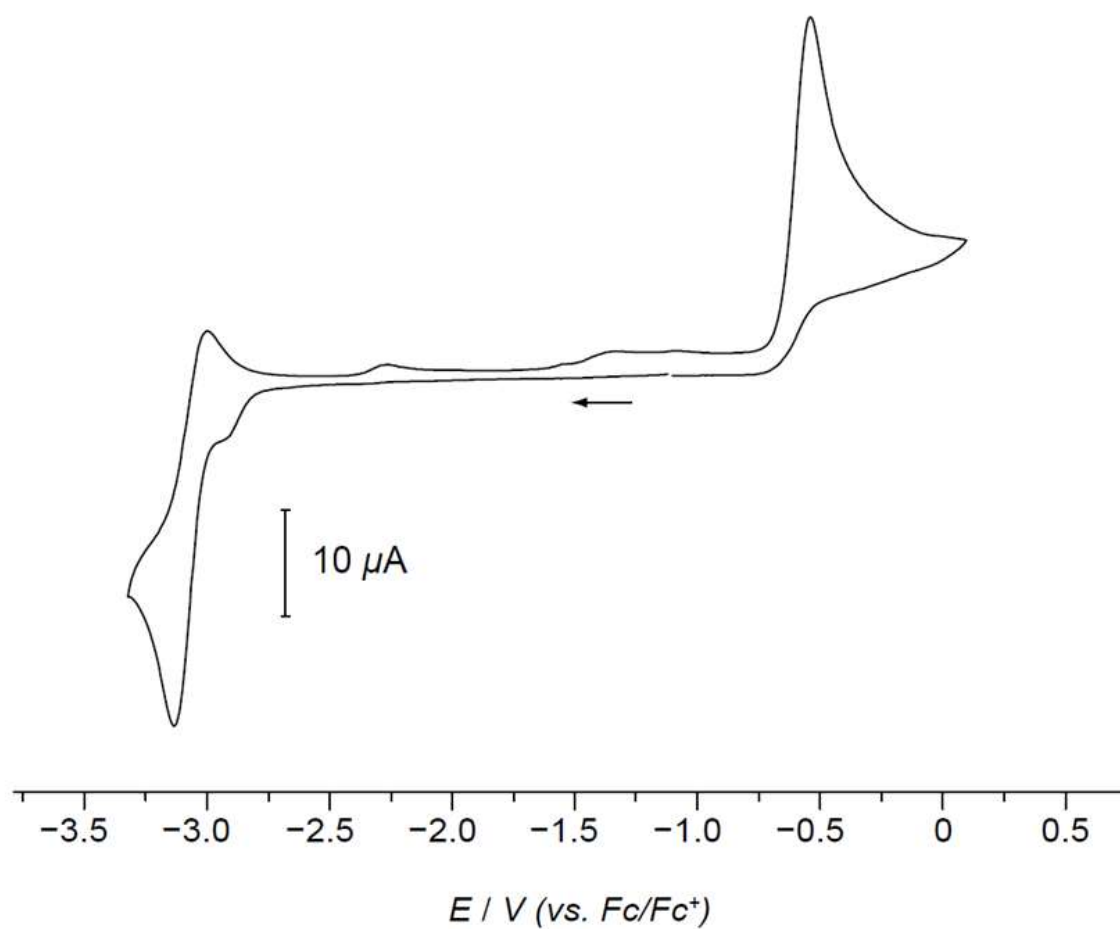


Figure S7. Cyclic voltammogram of **4**.

Crystal structure determination

The crystal data of **1-4** were collected on a Bruker SMART-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 package and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions.

Crystal data for **1**: C₂₀H₂₃B, $M_r = 274.19$, colourless block, 0.41×0.162×0.104 mm³, triclinic space group *P*-1, $a = 8.50(2)$ Å, $b = 12.77(5)$ Å, $c = 15.65(6)$ Å, $\alpha = 79.57(16)^\circ$, $\beta = 89.07(13)^\circ$, $\gamma = 88.20(12)^\circ$, $V = 1670(10)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.091$ g·cm⁻³, $\mu = 0.060$ mm⁻¹, $F(000) = 592$, $T = 100(2)$ K, $R_I = 0.0415$, $wR^2 = 0.0929$, 4890 independent reflections [$2\theta \leq 46.78^\circ$] and 399 parameters.

Crystal data for **2**: C₅₇H₇₀B₂N₄, $M_r = 832.79$, colourless block, 0.35×0.183×0.126 mm³, triclinic space group *P*-1, $a = 11.5165(8)$ Å, $b = 14.9171(12)$ Å, $c = 15.0308(11)$ Å, $\alpha = 93.716(4)^\circ$, $\beta = 107.248(3)^\circ$, $\gamma = 99.859(3)^\circ$, $V = 2411.2(3)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.147$ g·cm⁻³, $\mu = 0.066$ mm⁻¹, $F(000) = 900$, $T = 100(2)$ K, $R_I = 0.0575$, $wR^2 = 0.1111$, 10290 independent reflections [$2\theta \leq 53.72^\circ$] and 585 parameters.

Crystal data for **3**: C₄₇H₅₉BN₂, $M_r = 662.77$, red block, 0.489×0.344×0.156 mm³, monoclinic space group *P*2₁/*c*, $a = 19.927(9)$ Å, $b = 18.683(10)$ Å, $c = 11.255(6)$ Å, $\beta = 100.333(11)^\circ$, $V = 4122(4)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.068$ g·cm⁻³, $\mu = 0.060$ mm⁻¹, $F(000) = 1440$, $T = 100(2)$ K, $R_I = 0.1063$, $wR^2 = 0.1816$, 8769 independent reflections [$2\theta \leq 53.56^\circ$] and 487 parameters.

Crystal data for **4**: C₉₆H₁₀₈B₂N₄, $M_r = 1339.48$, yellow needle, 47.00×0.09×0.08 mm³, monoclinic space group *P*2₁/*c*, $a = 22.913(13)$ Å, $b = 14.472(9)$ Å, $c = 24.947(14)$ Å, $\beta = 104.380(12)^\circ$, $V = 8013(8)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.110$ g·cm⁻³, $\mu = 0.063$ mm⁻¹, $F(000) = 2888$, $T = 100(2)$ K, $R_I = 0.2090$, $wR^2 = 0.3028$, 17115 independent reflections [$2\theta \leq 53.66^\circ$] and 1042 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-948685 (**1**), CCDC-948686 (**2**), CCDC-948687 (**3**) and CCDC-948688 (**4**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

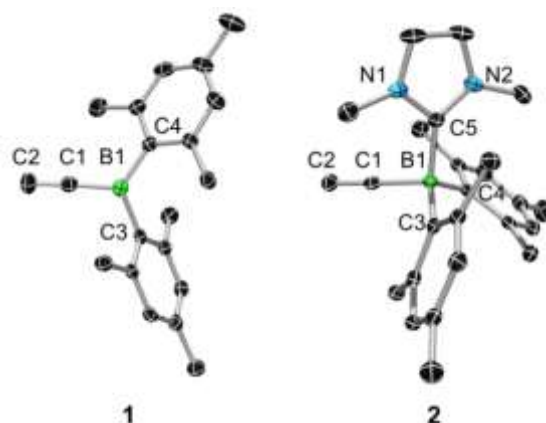


Figure S8. Molecular structure of **1** and **2** in the solid state. Thermal ellipsoids displayed at the 50% probability level. For clarity, only one of two molecules in the asymmetric units is displayed. Hydrogen atoms have been omitted. Relevant bond lengths [Å]: **1**: C1–C2: 1.194(5), B1–C1: 1.527(6), B1–C3: 1.565(5), B1–C4: 1.575(5); **2**: C1–C2: 1.197(2), B1–C1: 1.616(2), B1–C3: 1.660(2), B1–C4: 1.669(2), B1–C5: 1.641(5).

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