Supplementary Information

New Polycyclic Borazine Species

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Compound 3: To a solution of **2** (0.107 g, 0.46 mmol) in thf (20 cm^3) cooled to -78°C, Bu^{n}Li (1.6M, 1.15 cm^3, 1.8 mmol) was added dropwise and the resulting pale yellow coloured solution was allowed to warm to room temperature with stirring. After 30 minutes, the reaction mixture was brought briefly to reflux and then left to stir for 5 h at room temperature. A solution of $B_2Cl_2(NMe_2)_2$[9] (0.167 g, 0.92 mmol) in Et_2O (5 cm^3) was then added and the mixture stirred for a further 16 h. After this time, all volatiles were removed under reduced pressure and the residue extracted into toluene (3 × 5 cm^3) and the extracts combined. After storage for 6 h at 5 °C, compound **3** was isolated (0.089 g, 43 %) as colourless crystals, one of which was used for X-ray crystallography and shown to be a toluene solvate (**3.toluene**). All solvent of crystallisation present was removed under vacuum (10^{-2} torr, 30 minutes). **Spectroscopic data for 3:** ^{11}B-{^{1}H} NMR (96 MHz, $CDCl_3$) δ = 36.9 (br. s, only one resonance observed for both B environments); ^{1}H NMR (300 MHz, $CDCl_3$) 7.22 (m, 4H, C_6H_4), 6.98 (m, 4H, C_6H_4), 3.07 (s, 12H, Me), 2.89 (s, 12H, Me); ^{13}C-{^{1}H} (100 MHz, $CDCl_3$) δ = 143.0 (s, C_6H_4), 119.3 (s, C_6H_4), 116.7 (s, C_6H_4), 43.7 (s, Me), 40.9 (s, Me). Anal. Calc. for $C_{20}H_{32}B_6N_8$, C, 53.45; H, 7.20; N, 24.95; found C, 53.55; H, 7.10; N, 24.90 %.

Compound 4: 1,8-Diaminonaphthalene (0.718 g, 4.54 mmol) and $B_2(NMe_2)_4$[9b,12] (0.427 g, 2.16 mmol, 0.5 cm^3) were dissolved in toluene (15 cm^3) and the solution was heated under reflux for 5 h and then allowed to cool to room temperature affording a white precipitate. The solvent was removed by syringe and the solid washed with hexane (3 × 5 cm^3) and then dried under reduced pressure affording crude **4** (0.525 g, 73 %). Colourless crystals of **4** were obtained by dissolving the crude solid in a minimum of hot DMF followed by slow cooling to room temperature. One of these crystals was used for X-ray crystallography and shown to be a bis-DMF solvate (**4.2DMF**). All solvent of crystallisation present was removed under vacuum (10^{-2} torr, 60 minutes). **Spectroscopic data for 4:** ^{11}B-{^{1}H} NMR (96 MHz, thf) δ = 29.3 (br. s); ^{1}H NMR (300 MHz, dmso-d_6) δ = 8.12 (s, 4H, NH), 7.08 (t, J_{HH} = 9 Hz, 4H, $C_{10}H_6$), 6.89 (d, J_{HH} = 9 Hz, 4H, $C_{10}H_6$), 6.34 (d, J_{HH} = 9 Hz, 4H, $C_{10}H_6$); ^{13}C-{^{1}H} (100

MHz, dmso-d_6) δ = 142.2 (s, $C_{10}H_6$), 136.8 (s, $C_{10}H_6$), 128.4 (s, $C_{10}H_6$), 121.1 (s, $C_{10}H_6$),116.7 (s, $C_{10}H_6$), 105.3 (s, $C_{10}H_6$). Anal. Calc. for $C_{20}H_{16}B_2N_4$, C, 71.90; H, 4.85; N, 16.80; found C, 72.40; H, 5.20; N, 16.60 %.

Compound 5: To a solution of **4** **(**0.154 g, 0.46 mmol) in thf (20 cm^3), a solution of Bu^nLi (1.6M, 1.15 cm^3, 1.8 mmol) was added dropwise at -78 °C and the resulting pale yellow coloured solution was allowed to warm to room temperature with stirring. After 30 minutes, the reaction mixture was brought briefly to reflux and then left to stir for a further 5 h at room temperature. A solution of $B_2Cl_2(NMe_2)_2$[9] (0.167 g, 0.92 mmol) in Et_2O (5 cm^3) was added by syringe and the reaction mixture was stirred for 16 h. After this time, the solvent was removed under reduced pressure and the residue extracted into toluene (3 × 5 cm^3) and the extracts were combined. After storage for 16 h at 5 °C, compound **5** was isolated as colourless crystals (0.119 g, 47 %) one of which was used for X-ray crystallography and shown to be a bis-toluene solvate (**5.2toluene**). A further recrystallisation of the mother liquor yielded a secind crop of crystals (0.026 g, 10 %). All solvent of crystallisation present was removed under vacuum (10^{-2} torr, 30 minutes). **Spectroscopic data for 5:** $^{11}B\text{-}\{^1H\}$ NMR (96 MHz, $CDCl_3$) δ = 39.5 (br. s, only one resonance observed for both B environments); ^1H NMR (300 MHz, $CDCl_3$) δ = 7.18 (t, J_{HH} = 9 Hz, 4H, $C_{10}H_6$), 7.07 (d, J_{HH} = 9 Hz, 4H, $C_{10}H_6$), 6.39 (d, J_{HH} = 9 Hz, 4H, $C_{10}H_6$), 3.07 (s, 12H, CH_3), 2.50 (s, 12H, CH_3); $^{13}C\text{-}\{^1H\}$ (100 MHz, $CDCl_3$) δ = 140.5 (s, $C_{10}H_6$), 136.4 (s, $C_{10}H_6$), 126.7 (s, $C_{10}H_6$), 122.8 (s, $C_{10}H_6$), 117.8 (s, $C_{10}H_6$), 110.2 (s, $C_{10}H_6$), 43.1 (s, Me), 40.3 (s, Me). Anal. Calc. for $C_{28}H_{36}B_6N_8$, C, 61.20; H, 6.60; N, 20.30; found C, 61.10; H, 6.55; N, 19.90 %.

Compound **6** was prepared using a similar method to that described for the synthesis of **3**, replacing compound **1** with $B_2\{NHPh\}_4$[7] (0.180g, 0.46mmol) which afforded colourless crystals of **6** (0.123 g, 44 %). $^{11}B\text{-}\{^1H\}$ NMR (96 MHz, $CDCl_3$) δ 45.5 (br. s), 38.8 (br. s); ^1H NMR (300 MHz, $CDCl_3$) 7.06 (m, 8H, Ph), 6.95 (m, 4H, Ph), 6.65 (m, 8H, Ph), 3.09-1.91 (br. s, 24H, Me); $^{13}C\text{-}\{^1H\}$ (100 MHz, $CDCl_3$) δ 149.1 (s, Ph), 127.9 (s, Ph), 126.6 (s, Ph), 122.3 (s, Ph), 44.1 (s, Me), 40.8 (s, Me). Anal. Calc. for $C_{32}H_{44}B_6N_8$: C, 63.45; H, 7.30; N, 18.50; found C, 63.40; H, 7.28; N, 18.48 %.

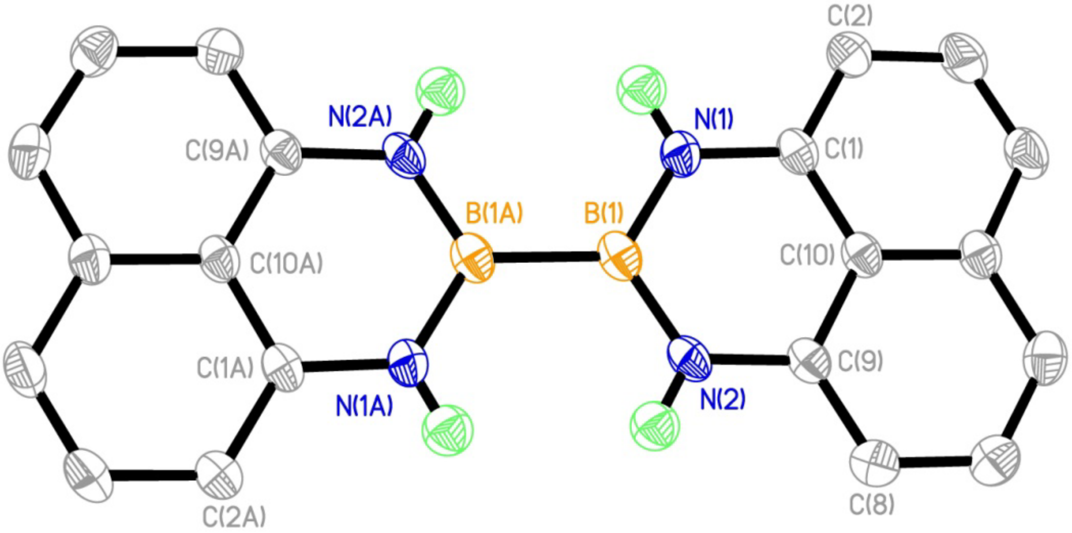

Figure S1 A view of the molecular structure of compound **4**. Thermal ellipsoids are set at the 50% probability level. All CH hydrogen atoms and the solvent of crystallisation (two molecules of DMF) have been omitted for clarity. Selected bond distances (Å) and angles (°) include: B(1)-B(1A) 1.690(5), B(1)-N(1) 1.420(3), B(1)-N(2) 1.421(3), B(1A)-B(1)-N(1) 122.6(2), B(1A)-B(1)-N(2) 122.1(2), N(1)-B(1)-N(2) 115.2(2), B(1)-N(1)-C(1) 124.0(2), B(1)-N(2)-C(9) 123.9(2), N(2A)-B(1A)-B(1)-N(1) 0.5(3). Symmetry transformations used to generate equivalent atoms labelled “A” 1-*x*, -*y*, 1-*z*.