

Supplementary Material

for the paper

Lewis-Base Adducts of 9,10-Dihydro-9,10-diboraanthracene: Ditopic Hydroboration Reagents and a B-N Analogue of Triptycene

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1. Syntheses and NMR spectroscopic characterisations of **3**, **5**, **6**, Li[7], and hydroboration of *t*BuCCH with **3** and **5**

All reactions were carried out under an atmosphere of dry nitrogen using Schlenk techniques. (Deutero)benzene, diethyl ether, dimethyl sulphide, hexane and (*d*₈-)THF were dried over Na/benzophenone and freshly distilled prior to use. NMR: Bruker AM250, Avance300 and Avance400; all NMR spectra were measured at 20 °C. Chemical shifts are referenced to residual solvent peaks (¹H, ¹³C{¹H}) or external BF₃·Et₂O (¹¹B, ¹¹B{¹H}) and Si(CH₃)₄ (²⁹Si INEPT). Abbreviations: s = singlet, d = doublet, m = multiplet, br = broad, n. o. = not observed, bpdz = benzo[*d*]pyridazine, pdz = pyridazine, pz = 4-trimethylsilylpyrazolide.

Synthesis of 3. A clear solution of **1** (525 mg, 2.99 mmol) in dimethyl sulphide (35 cm³) was cooled to -78 °C to yield colourless crystals of **3** suitable for X-ray crystallography. The crystals were collected on a frit and dried under dynamic vacuum for 30 min (392 mg, 44%).

¹H NMR: δ_H(300.0 MHz; C₆D₆) 1.16 (12 H, s, SCH₃), 5.48 (2 H, br s, *h*_{1/2} = 200 Hz, BH), 7.38 (4 H, m, C₆H₄), 8.00 (4 H, m, C₆H₄); ¹¹B NMR: δ_B(96.3 MHz; C₆D₆) 28.1 (br s, *h*_{1/2} = 370 Hz), δ_B(96.3 MHz; DMS) 1.9 (br d, *J*_{BH} ≈ 60 Hz); ¹³C{¹H} NMR: δ_C(75.5 MHz; C₆D₆) 18.5 (SCH₃), 129.3 (C₆H₄), 138.5 (C₆H₄), n. o. (BC). *Note:* All chemical shifts are strongly influenced by the amount of dimethyl sulphide present in the sample.

Hydroboration of *t*BuCCH with 3. Neat *t*BuCCH (30 mg, 0.37 mmol) was added via syringe to **3** (22.1 mg, 0.0736 mmol) in benzene (4 cm³) at r. t. The mixture was stirred for 30 min and then freeze-dried for 2 h in a dynamic vacuum. All NMR spectroscopic data of the resulting colourless microcrystalline residue were in agreement with literature values of **4**. No ¹H NMR signal for SME₂ (free or coordinated) was detectable; combustion analysis of the sample gave a relative sulphur content of 0%.

Synthesis of 5. A vigorously stirred solution of **3** (47.3 mg, 0.158 mmol) in benzene (8 cm³) was treated at r. t. with pyridazine (12.7 mg, 0.159 mmol) whereupon a voluminous yellow solid formed. After 1 h, the precipitate was isolated by centrifugation and dried in vacuum. **5**·0.25 C₆H₆ (34 mg, 78%) was obtained as a yellow microcrystalline solid (*note:* The amount of benzene was estimated by ¹H NMR spectroscopy). Reprecipitation of **5**·0.25 C₆H₆ from a THF solution into hexane yielded benzene-free samples.

¹H NMR: δ_H(400.1 MHz; *d*₈-THF) 4.47 (2 H, br s, *h*_{1/2} = 240 Hz, BH), 6.72 (4 H, m, C₆H₄), 7.39 (4 H, m, C₆H₄), 8.08 (2 H, m, pdzH-4,5), 9.63 (2 H, m, pdzH-3,6); ¹¹B NMR: δ_B(128.4 MHz; *d*₈-THF) 5.3 (br s, *h*_{1/2} = 230 Hz); ¹³C{¹H} NMR: δ_C(62.9 MHz; *d*₈-THF) 124.4 (C₆H₄), 131.0 (C₆H₄), 135.1

(pdzC-4,5), 149.8 (pdzC-3,6), n. o. (BC). Found: C, 74.8; H, 5.5; N, 10.7. $C_{16}H_{14}B_2N_2$ requires C, 75.1; H, 5.5; N, 11.0.

Hydroboration of *t*BuCCH with **5.** A solution of **5**·0.25 C_6H_6 (1 mg, 0.004 mmol) in d_8 -THF (0.5 cm^3) was transferred to an NMR tube and treated with excess *t*BuCCH (10 mg, 0.1 mmol). The NMR tube was flame-sealed and kept at 20 °C for 2 h. 1H NMR spectroscopy revealed approximately 50% conversion (Fig. S1). Therefore, the sample was stored at 40 °C for further 30 min to achieve quantitative conversion (Fig. S1).

1H NMR: δ_H (300.0 MHz; d_8 -THF) 1.33 (18 H, s, CH_3), 6.45 (2 H, d, $J_{HH} = 18.6$ Hz, C(H)=C(H)), 6.67 (2 H, d, $J_{HH} = 18.6$ Hz, C(H)=C(H)), 6.78 (4 H, m, C_6H_4), 7.54 (4 H, m, C_6H_4), 7.99 (2 H, br s, pdzH-4,5), 9.77 (2 H, br s, pdzH-3,6); $^{11}B\{^1H\}$ NMR: δ_B (96.3 MHz; d_8 -THF) 4.6 (br s, $h_{1/2} = 700$ Hz).

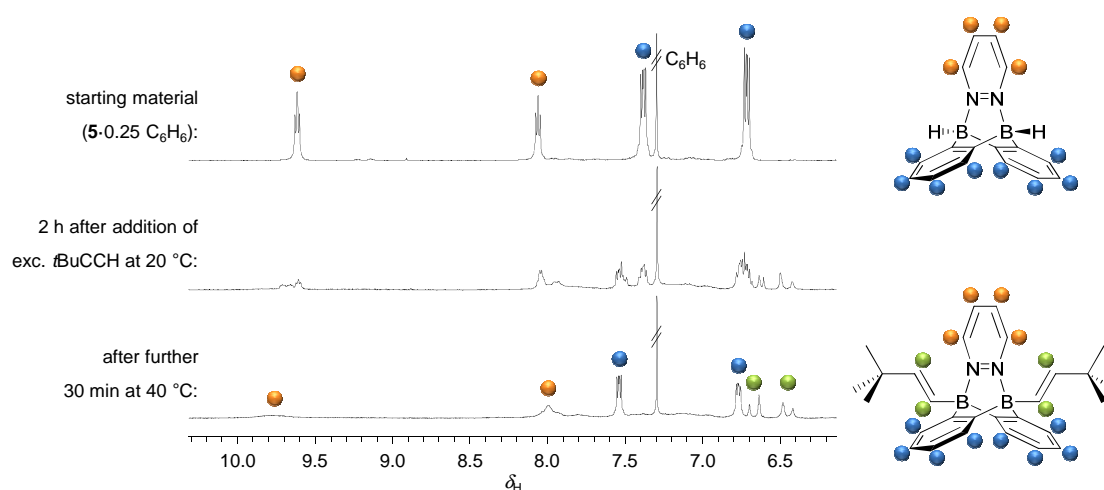


Fig. S1 Hydroboration of *t*BuCCH with **5**·0.25 C_6H_6 in d_8 -THF.

Note: The hydroboration of *t*BuCCH with Li[**7**] is also possible under similar conditions, however, it requires higher reaction temperatures of 60 °C.

Synthesis of **6.** Benzo[*d*]pyridazine (13 mg, 0.10 mmol) in benzene (1 cm^3) was added dropwise at r. t. to a stirred solution of **3** (25.5 mg, 0.0850 mmol) in benzene (3 cm^3), whereupon a pale yellow solid precipitated. Stirring was continued for 30 min and afterwards all volatiles were removed in vacuum. Yellow X-ray quality crystals of **6**·THF were grown by vapour diffusion of diethyl ether into a THF (4 cm^3) solution of the crude product (4 mg, 12% based on isolated single crystalline material).

1H NMR: δ_H (400.1 MHz; d_8 -THF) 4.52 (2 H, br s, $h_{1/2} = 170$ Hz, BH), 6.74 (4 H, m, C_6H_4), 7.42 (4 H, m, C_6H_4), 8.20 (2 H, m, bpdzH), 8.36 (2 H, m, bpdzH), 10.21 (2 H, s, bpdzH-1,4); ^{11}B NMR: δ_B (96.3 MHz; d_8 -THF) 4.4 (br s, $h_{1/2} = 390$ Hz); $^{13}C\{^1H\}$ NMR: δ_C (62.9 MHz; d_8 -THF) 124.4 (C_6H_4), 129.4 (bpdzC-4a,8a), 129.6 (bpdzC), 131.0 (C_6H_4), 137.2 (bpdzC), 150.7 (bpdzC-1,4), n. o. (BC).

Synthesis of Li[7]. Lithium 4-trimethylsilylpyrazolide (24.7 mg, 0.169 mmol; prepared from 4-trimethylsilylpyrazole and *n*-butyllithium in hexane) was dissolved in a mixture of benzene (5 cm³) and THF (0.03 cm³) and added at r. t. via syringe to a stirred solution of **3** (49.1 mg, 0.164 mmol) in benzene (6 cm³). After 1 h, all volatiles were removed from the clear solution in vacuum and the residue was redissolved in THF (5 cm³). The resulting clear solution was concentrated to saturation under reduced pressure and stored at -40 °C for 15 h to yield colourless X-ray quality crystals of Li(thf)₄[7]·THF (46 mg, 41% based on isolated single crystalline material).

¹H NMR: δ_H(300.0 MHz; C₆D₆) -0.01 (9 H, s, SiCH₃), 4.79 (2 H, br s, *h*_{1/2} = 190 Hz, BH), 7.04 (4 H, m, C₆H₄), 7.71 (2 H, s, pzH-3,5), 7.97 (4 H, m, C₆H₄); ¹¹B NMR: δ_B(96.3 MHz; C₆D₆) -5.8 (br s, *h*_{1/2} = 350 Hz); ¹³C{¹H} NMR: δ_C(75.5 MHz; C₆D₆) -0.3 (SiCH₃), 112.4 (pzC-4), 124.5 (C₆H₄), 131.8 (C₆H₄), 136.2 (pzC-3,5), n. o. (BC); ²⁹Si NMR (INEPT): δ_{Si}(59.6 MHz; C₆D₆) -11.4; ESI-MS: *m/z* 315.2 ([7]⁻, 100%). Found: C, 66.4; H, 8.8; N, 4.4. C₃₄H₅₃B₂LiN₂O₄Si requires C, 66.9; H, 8.75; N, 4.6.

2. Single crystal X-ray structure analyses of **3**, **6**·THF, Li(thf)₄[7]·THF

Crystal data of 3. C₁₆H₂₂B₂S₂, *M* = 300.08 g mol⁻¹, monoclinic, *a* = 14.0791(11) Å, *b* = 7.3214(5) Å, *c* = 16.6356(14) Å, β = 102.414(6)°, *V* = 1674.7(2) Å³, *T* = 173(2) K, space group *P*2₁/*n*, *Z* = 4, μ(Mo-K_α) = 0.305 mm⁻¹, 18440 reflections measured, 3128 unique (*R*_{int} = 0.0764) which were used in all calculations. The final *wR*(*F*²) was 0.0947 (all data).

Crystal data of 6·THF. C₂₄H₂₄B₂N₂O, *M* = 378.07 g mol⁻¹, triclinic, *a* = 10.6419(7) Å, *b* = 13.8641(8) Å, *c* = 13.8898(9) Å, α = 91.748(5)°, β = 95.552(5)°, γ = 92.350(5)°, *V* = 2036.8(2) Å³, *T* = 173(2) K, space group *P*1, *Z* = 4, μ(Mo-K_α) = 0.074 mm⁻¹, 34216 reflections measured, 7626 unique (*R*_{int} = 0.0887) which were used in all calculations. The final *wR*(*F*²) was 0.2108 (all data).

The compound crystallises together with one equivalent of THF molecules, which are disordered. The asymmetric unit contains two crystallographically independent molecules, **6**·THF_A and **6**·THF_B. Since most structure parameters of **6**·THF_A and **6**·THF_B are the same within the experimental error margins, only the plot and selected data of **6**·THF_A are shown in Fig. S2.

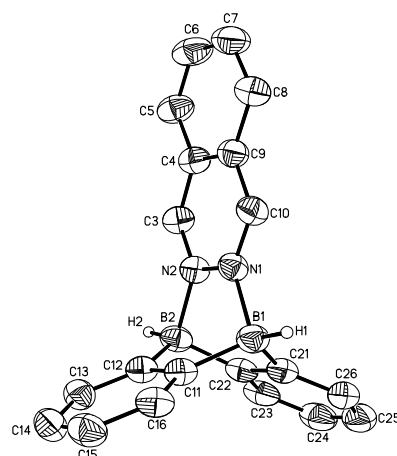


Fig. S2 Molecular structure and numbering scheme of compound **6**·THF_A; displacement ellipsoids are drawn at the 50% probability level; protons attached to carbon atoms and the THF molecule are omitted for clarity. Selected bond lengths [Å], atom···atom distances [Å], bond angles [°] and dihedral angles [°]: B(1)–C(11) = 1.617(4), B(1)–C(21) = 1.602(4), B(2)–C(12) = 1.614(4), B(2)–C(22) = 1.609(4), B(1)–N(1) = 1.641(3), B(2)–N(2) = 1.639(3), B(1)–H(1) = 1.12(3), B(2)–H(2) = 1.17(3), B···B = 2.730(4); C(11)–B(1)–C(21) = 108.7(2), C(12)–B(2)–C(22) = 108.9(2), C(11)–B(1)–N(1) = 102.2(2), C(21)–B(1)–N(1) = 102.3(2), C(12)–B(2)–N(2) = 101.9(2), C(22)–B(2)–N(2) = 102.6(2), B(1)–N(1)–N(2) = 114.5(2), B(2)–N(2)–N(1) = 114.1(2); Ar(C(11))//Ar(C(21)) = 126.9, B(1)C(11)C(21)/B(2)C(12)C(22) = 88.7.

Crystal data of Li(thf)₄[7]·THF. C₃₈H₆₁B₂LiN₂O₅Si, *M* = 682.54 g mol⁻¹, monoclinic, *a* = 10.0824(12) Å, *b* = 17.4274(15) Å, *c* = 12.4327(16) Å, β = 110.322(9)°, *V* = 2048.6(4) Å³, *T* = 173(2) K, space group *P*2₁, *Z* = 2, μ(Mo-K_α) = 0.098 mm⁻¹, 12751 reflections measured, 7065 unique (*R*_{int} = 0.0377) which were used in all calculations. The final *wR*(*F*²) was 0.1822 (all data). Flack *x*-parameter = -0.04(19).

CCDC reference numbers: 762845 (**3**), 762846 (**6**·THF), 762847 (Li(thf)₄[7]·THF).