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Electronic Supplementary Information

Direct Functionalization at the Boron Center of Antiaromatic Chloroborole

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1) Experimental details on the crystal structure determinations of compounds 5−7:

The crystal data of **5−7** were collected at a Bruker X8APEX diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structures were solved using direct methods, refined with the SHELX software package (G. Sheldrick, University of Göttingen 1997) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factor calculations.

Crystal data for **5**: $C_{34}H_{27}BClN$, $M_r = 495.83$, yellow plate, 0.26×0.09×0.03 mm^3, Triclinic space group $P\bar{1}$, $a = 10.1102(7)$Å, $b = 10.2560(8)$Å, $c = 14.1830(10)$Å, $\alpha = 75.426(4)°$, $\beta = 83.792(4)°$, $\gamma = 65.424(3)°$, $V = 1294.37(16)$Å^3, $Z = 2$, $\rho_{calcd} = 1.272$ g·cm^{-3}, $\mu = 0.172$ mm^{-1},

$F(000) = 520$, $T = 99(2)$ K, $R_1 = 0.0576$, $wR^2 = 0.1088$, 5117 independent reflections [$2\theta \leq 52.14°$] and 335 parameters.

Crystal data for **6**: $C_{72}H_{46}B_2F_{24}N_2$, $M_r = 1416.73$, yellow plate, 0.26×0.24×0.02 mm^3, Monoclinic space group $P2/n$, $a = 19.4229(8)$Å, $b = 9.4370(4)$Å, $c = 22.0877(9)$Å, $\beta = 115.149(2)°$, $V = 3664.8(3)$Å^3, $Z = 2$, $\rho_{calcd} = 1.284$ g·cm^{-3}, $\mu = 0.117$ mm^{-1}, $F(000) = 1436$, $T = 100(2)$ K, $R_1 = 0.0663$, $wR^2 = 0.1376$, 7220 independent reflections [$2\theta \leq 52.08°$] and 453 parameters. There is a void of considerable size (129 Å^3) in the crystal structure, containing disordered CH_2Cl_2 solvent molecules, which could not be refined reasonably. Hence, the PLATON/SQUEEZE tool was applied, whereby relevant data are given without any disordered solvent.

Crystal data for **7**: $C_{34}H_{38}BNSi_2$, $M_r = 527.64$, red plate, 0.20×0.10×0.02 mm^3, Monoclinic space group $P2_1/n$, $a = 12.5821(6)$ Å, $b = 11.4550(6)$ Å, $c = 22.2650(11)$ Å, $\beta = 102.334(2)°$, $V = 3134.9(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.118$ g·cm^{-3}, $\mu = 0.135$ mm^{-1}, $F(000) = 1128$, $T = 100(2)$ K, $R_1 = 0.0542$, $wR^2 = 0.0897$, 6144 independent reflections [$2\theta \leq 52.04°$] and 343 parameters.

Crystallographic data are also deposited with Cambridge Crystallographic Data Centre. Copies of the data [**5**–**7**: CCDC 685645−685647] can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB 1EZ, UK; fax +44 1223 336033.

Crystal Structure of $[Ph_4C_4B{\cdot}(NC_5H_4Me)_2][BAr^f_4]$ (6):

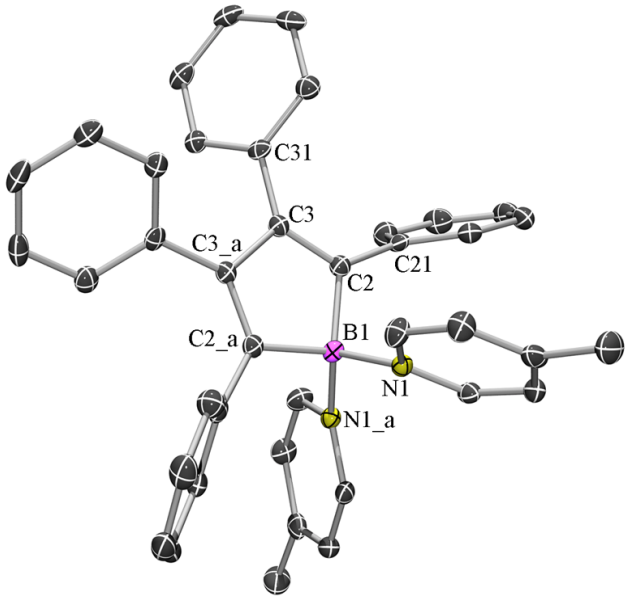

Fig. 1 Molecular structure of $[Ph_4C_4B{\cdot}(NC_5H_4Me)_2][BAr^f_4]$ (**6**) in the solid-state. The $[BAr^f_4]^-$ anion is omitted for clarity. Symmetry-related atom positions are labeled with _a (x+1/2, y, z+3/2). Selected bond lengths [Å] and angles [°]: B1−N1 1.5972(18), B1−C2 1.6177(20), C2−C3 1.3508(21), C3−C3_a 1.5087(25), C2−B1−C2_a 101.81(16), C2−B1−N1 109.35(7), C2−B1−N1_a 112.79(7), N1−B1−N1_a 110.53(17), B1−C2−C3 107.32(12), C2−C3−C3_a 111.77(8).

The central 5-membered ring is planar [rms deviation: 0.0135 Å] and best described as an isolated diene system [B1−C2: 1.6177(20) Å; C2−C3: 1.3508(21) Å; C3−C3_a: 1.5087(25) Å]. Due to the steric requirements of the two 4-Me-C_5H_4N moieties at the boron atom and the adjacent C_6H_5 substituents, the latter are tilted much stronger to the BC_4 plane than in **5**, which is reflected by a larger value for the corresponding torsion angle B1−C2−C21−C22 = −68.03(19)° [*cf.* **5**: B1−C2−C21−C22 = 35.61(21)°]. Contrary, the torsion angle C2−C3−C31−C22 = −52.9(2)° strongly resembles those observed for **5** [*cf.* **5**: C2−C3−C31−C32 = 49.53(25)°; C5−C4−C41−C46 = 46.4(3)°].

2) Experimental section:

General remarks: All manipulations were performed under an inert atmosphere of dry argon using standard Schlenk techniques or in a glovebox. Solvents were dried according to standard procedures, freshly distilled prior to use, degassed and stored under argon over activated molecular sieves. CD_2Cl_2 was distilled from CaH_2, C_6D_6 from potassium over a glass bridge and subjected to several *freeze-pump-thaw* cycles. $Me_2SnC_4Ph_4$[1], $Na[BAr^f_4]$[2] were prepared according to known methods. BCl_3 was used as a solution in toluene (80 mg/mL). The NMR spectra were recorded on a Bruker AV 500 (^{1}H: 500.13 MHz; ^{13}C: 125.76 MHz, ^{11}B: 160.46 MHz) FT-NMR spectrometer at 293 K (unless stated otherwise). ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external TMS *via* the residual protons of the solvent (^{1}H) or the solvent itself (^{13}C). ^{11}B{^{1}H} NMR spectra were referenced to $BF_3{\cdot}OEt_2$. Microanalyses for C, H and N were performed on a Leco CHNS-932 Elemental Analyzer. UV-Vis spectra were recorded on a Shimadzu UV Mini 1240 UV-Vis-photometer.

$ClBC_4Ph_4$ (4): A solution of $Me_2SnC_4Ph_4$ (**3**) (1.00 g, 1.98 mmol) in CH_2Cl_2 (15 mL) was cooled to −30 °C and treated with BCl_3 (4.35 mL, 2.97 mmol) resulting in an instantaneous color change from yellow to deep blue. The reaction mixture was stirred for 2 h and subsequently allowed to warm to 0 °C. All volatiles were removed in *vacuo* and the residue was triturated with hexanes (2×5 mL) at −30 °C. The side-product Me_2SnCl_2 (0.43 g, 1.98 mmol) was removed quantitatively by sublimation at 50 °C and 10^{-3} mbar within 30 min and the blue residue was recrystallized from toluene (10 mL) at −60 °C. $ClBC_4Ph_4$ (**4**) (0.69 g, 1.72 mmol, 87%) was isolated as a deep blue solid after washing with cold pentane (3×3 mL).

^{1}H-NMR (500 MHz, CD_2Cl_2, 233 K): δ = 6.77−6.79 (d, 4H, C_6H_5), 7.05−7.10 (m, 8H, C_6H_5), 7.15−7.20 (m, 8H, C_6H_5); ^{11}B-NMR (160 MHz, CD_2Cl_2, 233 K): δ = 66.4; ^{13}C-NMR (126 MHz, CD_2Cl_2, 233 K): δ = 126.22, 127.35, 127.72, 127.82, 129.00, 129.24 (C_6H_5), 134.97, 135.83 (*ipso*-C_6H_5), 162.87 (B−C=*C*) (the signals of the carbons bound to boron are not observed due to the quadrupolar moment of the boron nucleus); UV-Vis: λ_{max} (CH_2Cl_2)/nm 553 nm (ε/dm^3 mol^{-1} cm^{-1} 556); Elemental analysis (%): Found: C, 83.88; H, 4.79. Calcd. for $C_{28}H_{20}BCl$ (402.72): C, 83.51; H, 5.01.

Ph_4C_4BCl·(NC_5H_4Me) (5): A solution of $ClBC_4Ph_4$ (**4**) (0.11 g, 0.27 mmol) in benzene (5 mL) was treated with 4-Me-C_5H_4N (25.4 mg, 0.27 mmol) at RT resulting in an instantaneous color change from deep blue to pale yellow. Removal of all volatiles in *vacuo* and recrystallization of the residue from heptane (5 mL) at −60 °C afforded Ph_4C_4BCl·(NC_5H_4Me) (**5**) (0.13 g, 0.25 mmol, 93%) as a pale yellow solid, which was washed with pentane (2×2 mL) and dried in *vacuo*.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 2.50 (s, 3H, NC_5H_4*Me*), 6.84−6.87 (m, 4H, C_6H_5), 6.91−7.00 (m, 10H, C_6H_5), 7.04−7.08 (m, 6H, C_6H_5), 7.42 (m, 2H, NC_5H_4Me), 8.81 (m, 2H, NC_5H_4Me); ^{11}B-NMR (160 MHz, CD_2Cl_2): δ = 5.6; ^{13}C-NMR (126 MHz, CD_2Cl_2): δ = 21.72 (NC_5H_4*Me*), 125.19 (N*C*$_5H_4$Me), 126.13, 127.11, 127.56, 127.66, 128.94, 130.23 (C_6H_5), 139.11, 140.83 (*ipso*-C_6H_5), 143.83 (N*C*$_5H_4$Me), 150.52, 155.58 (B−*C*=*C*); UV-Vis: λ_{max} (CH_2Cl_2)/nm 373 nm (ε/dm^3 mol^{-1} cm^{-1} 3520); Elemental analysis (%): Found C, 81.97; H, 5.45; N, 2.97. Calcd. for $C_{34}H_{27}BClN$ (495.85): C, 82.36; H, 5.49; N 2.82.

$[Ph_4C_4B{\cdot}(NC_5H_4Me)_2][BAr^f_4]$ (6): A resealable Schlenk tube equipped with a *J. Young* teflon-valve was charged with $Ph_4C_4BCl{\cdot}(NC_5H_4Me)$ (**5**) (0.12 g, 0.24 mmol), $Na[BAr^f_4]$ (0.21 g, 0.24 mmol), 4-Me-C_5H_4N (22.5 mg, 0.24 mmol) and CH_2Cl_2 (5 mL) and was heated to 80 °C over a period of 2 h resulting in a gradual color change from yellow to orange and the formation of a white NaCl precipitate. All volatiles were removed in *vacuo*. The residue was extracted with CH_2Cl_2 (10 mL) and filtered over a pad of celite. The filtrate was reduced to 2 mL in volume and layered with hexanes (2 mL). Crystallization at −35 °C yielded $[Ph_4C_4B{\cdot}(NC_5H_4Me)_2][BAr^f_4]$ (**5**) (0.26 g, 0.19 mmol, 77%) as a golden, crystalline solid, which was washed with pentane (3×3 mL) and dried in *vacuo*.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 2.53 (s, 6H, $NC_5H_4\mathit{Me}$), 6.56−6.59 (m, 4H, $C_6\mathit{H}_5$), 6.93−6.95 (m, 4H, $C_6\mathit{H}_5$), 7.00−7.04 (m, 6H, $C_6\mathit{H}_5$), 7.05−7.12 (m, 6H, $C_6\mathit{H}_5$), 7.53 (m, 4H, $NC_5\mathit{H}_4Me$), 7.58 (m, 4H, BAr^f), 7.76 (m, 4H, BAr^f), 8.43 (m, 4H, $NC_5\mathit{H}_4Me$); ^{11}B-NMR (160 MHz, CD_2Cl_2): δ = −7.5, 7.2; ^{13}C-NMR (126 MHz, CD_2Cl_2): δ = 21.09 ($NC_5H_4\mathit{Me}$), 117.80 (BAr^f), 124.88 (q, $^1J_{C,F}$ = 272.9 Hz, $\mathit{C}F_3$), 126.71, 127.20, 127.80 (C_6H_5), 128.46 (NC_5H_4Me), 128.57, 128.70 (C_6H_5), 129.01 (q, $^2J_{C,F}$ = 32.0 Hz, BAr^f), 130.02 (C_6H_5), 135.10 (BAr^f), 137.32, 139.40 (*ipso*-C_6H_5), 143.77 (NC_5H_4Me), 155.91, 159.32 (B−*C*=*C*), 162.06 (q, $^1J_{C,B}$ = 49.8 Hz, BAr^f); UV-Vis: λ_{max} (CH_2Cl_2)/nm 425 nm (ε/dm^3 mol^{-1} cm^{-1} 2145); Elemental analysis (%): Found C, 61.44; H, 3.31; N, 2.24. Calcd. for $C_{72}H_{46}B_2F_{24}N_2$ (1416.73): C, 61.04; H, 3.27; N, 1.98.

$Ph_4C_4BN(SiMe_3)_2$ (7): A solution of $ClBC_4Ph_4$ (**4**) (0.15 g, 0.37 mmol) in benzene (8 mL) was treated with solid $K[N(SiMe_3)_2]$ (74.3 mg, 0.37 mmol) at RT resulting in a gradual color change

from deep blue to red within 1 h and the formation of a white KCl precipitate. All volatiles were removed in *vacuo* and the residue extracted with heptane (5 mL). After filtration over a pad of celite, the filtrate was reduced to 3 mL in volume and stored at −35 °C. $Ph_4C_4BN(SiMe_3)_2$ (**7**) (0.16 g, 0.31 mmol, 84%) was isolated as a red solid after washing with cold pentane (2×2 mL) and drying in *vacuo*.

^{1}H-NMR (500 MHz, C_6D_6): δ = 0.11 (s, 18H, Si*Me*$_3$), 6.80−6.82 (m, 6H, C_6H_5), 6.87−6.88 (m, 4H, C_6H_5), 6.97−7.01 (m, 2H, C_6H_5), 7.10−7.13 (m, 4H, C_6H_5), 7.20−7.21 (m, 4H, C_6H_5); ^{11}B-NMR (160 MHz, C_6D_6): δ = 59.5; ^{13}C-NMR (126 MHz, C_6D_6): δ = 3.48 (Si*Me*$_3$), 125.79, 127.04, 127.48, 128.15, 128.76, 130.14 (C_6H_5), 136.80, 140.31 (*ipso*-C_6H_5), 138.50 (B−*C*=C), 161.35 (B−C=*C*); UV-Vis: λ_{max} (CH_2Cl_2)/nm 478 nm (ε/dm^3 mol^{-1} cm^{-1} 1635); Elemental analysis (%): Found C, 76.94; H, 7.21; N, 2.44. Calcd. for $C_{34}H_{38}BNSi_2$ (527.65): C, 77.39; H, 7.26; N, 2.65.

3) Solution UV-visible spectra of 4−7 in CH_2Cl_2:

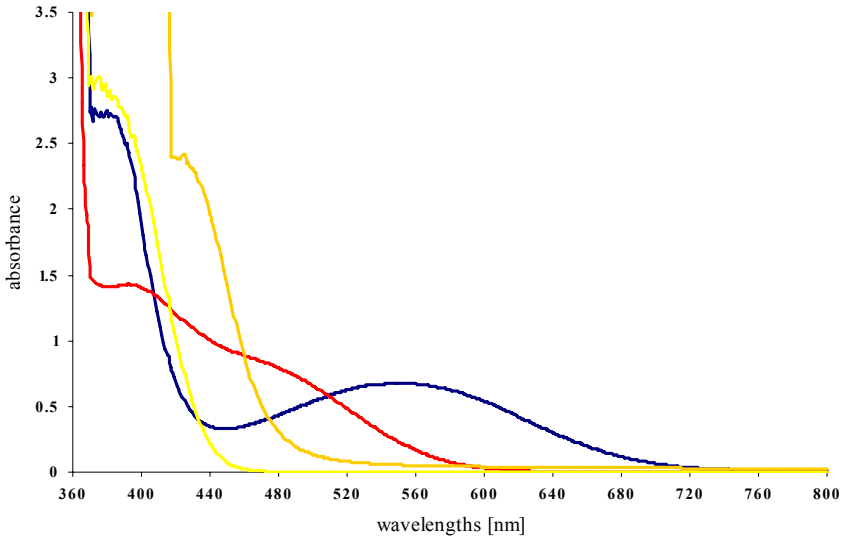

Figure S1. UV-visible spectra of compounds **4** (blue), **5** (yellow), **6**(gold) and **7** (red) in CH_2Cl_2 at concentrations of 1 mmol L^{-1}.

[1] J. J. Eisch, J. E. Galle, S. Kozima, *J. Am. Chem. Soc*. **1986**, *108*, 379−385.

[2] N, A, Yakelis, R. G. Bergman, *Organometallics* **2005**, *24*, 3579−3581.