Electronic Supplementary Material (ESI) for Chemical Communications.

Synthetic procedures

General synthetic considerations: All manipulations were conducted either under an atmosphere of dry argon or under vacuum using standard Schlenk line or glovebox techniques. Solvents (pentane, toluene) were purified according standard procedures and storage under dry argon over molecular sieves (4 Å). C_6D_6 and toluene-d_8 were degassed by three freeze−pump−thaw cycles and stored over molecular sieves (4 Å). NMR spectra were acquired on a Bruker Avance 400 (^{1}H: 400.1 MHz, ^{11}B: 128.3 MHz, ^{13}C: 100.6 MHz) FT−NMR spectrometer. NMR spectra were referenced to external TMS (^{1}H, ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B), Cl_3CF (^{19}F) and 85% H_3PO_4 (^{31}P). Microanalyses (C, H, N) were performed on either a LecoCHNS-932 or a Carlo Erba Model 1106 instrument. The diboranes(4) $Dur_2B_2F_2$ and $Mes_2B_2F_2$ (**1**) were synthesized based on a literature procedure.[1]

Synthesis of $B_2F_2Dur_2$: As we were unable to obtain crystallographic-quality single crystals of **1**, the analogous diborane(4) $B_2F_2Dur_2$ was prepared for structural reference (Figure S1). $B_2F_2Dur_2$ was synthesized based on a literature procedure.[1] Colorless single crystals of $B_2F_2Dur_2$ suitable for X-ray diffraction were obtained by slow evaporation of pentane solution at −25 °C.

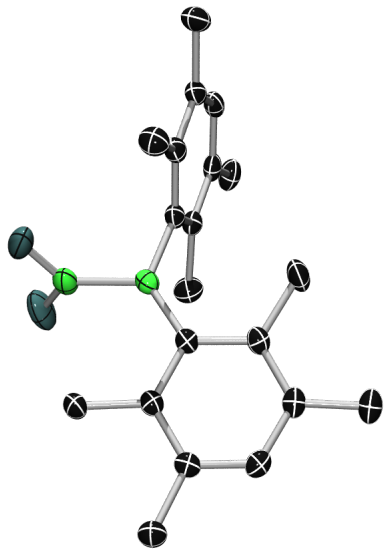

Figure S1. Crystallographically-derived structure of $F_2B_2Dur_2$, with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are removed for clarity.

Synthesis of $B_2F_2Mes_2{\cdot}PMe_3$ (2a): An excess of PMe_3 (147.0 mg, 0.2 mL, 1.93 mmol, 5.8 equiv.) was added to a solution of **1** (100.0 mg, 0.336 mmol) in pentane (1.5 mL) at room temperature. The mixture was stirred for 10 minutes before all volatiles were removed under

vacuum. The residue was collected in pentane and the mixture was stored at −35 °C. **2a** was obtained as a colorless powder (19.6 mg, 0.052 mmol, 16%). Colorless single crystals of **2a** suitable for X−ray diffraction were obtained by slow evaporation of benzene solution at room temperature. **^{1}H NMR** (500.1 MHz, C_6D_6): δ = 6.81 (s, 4 H, aryl-*H*), 2.21 (s, 6 H, *para*-CH_3), 2.18 (s, 12 H, *ortho*-CH_3), 0.72 (d, $^{2}J_{PH}$ = 9 Hz, 9 H, P(CH_3)$_3$). **^{13}C{^{1}H} NMR** (125.8 MHz, C_6D_6): δ = 141.82 (br s, *ipso*-C_q), 133.90 (s, *para*-C_q), 129.81 (s, aryl-*C*H), 129.31 (d, J = 13.8 Hz, aryl-*C*H), 26.19 (s, *ortho*-*C*H$_3$), 20.93 (s, *para*-*C*H$_3$), 14.23 (d, $^{2}J_{CP}$ = 31.18 Hz, P(*C*H$_3$)$_3$). **^{11}B{^{1}H} NMR** (160.5 MHz, C_6D_6): δ = 35.9 (br s, *B*F$_2$), –12.7 (br s, *B*Mes$_2$). **^{19}F{^{1}H} NMR** (470.6 MHz, C_6D_6): δ = –45.1 (s, B*F*$_2$). **^{31}P{^{1}H} NMR** (202.5 MHz, C_6D_6): δ = –16.4 (s, *P*Me$_3$). **Elemental analysis (%):** calcd for $C_{21}H_{31}B_2F_2P$ (374.06 g·mol^{-1}) C: 67.43, H: 8.35; found: C: 67.41, H: 8.53.

Synthesis of $B_2F_2Mes_2$·P(OMe)$_3$ (2b): A solution of P(OMe)$_3$ (31.3 mg, 0.411 mmol, 2.5 equiv.) in pentane (1.0 mL) was added to a solution of **1** (49.0 mg, 0.164 mmol) in pentane (1.0 mL) at room temperature. The mixture was stirred for 1.5 hours before all volatiles were removed under vacuum. The residue was collected in pentane and the mixture was stored at room temperature. **2b** was obtained as a colorless single crystals suitable for X−ray diffraction (10 mg, 0.027 mmol, 16%). Compound **2b** is not stable in solution, wherein dissociation of the adduct and formation of the diborane(4) and phosphine in a ratio of 1:1 was observed. **Elemental analysis (%):** calcd for $C_{21}H_{31}B_2F_2O_3P$ (422.07 g·mol^{-1}) C: 59.76, H: 7.40; found: C: 59.09, H: 7.10.

Synthesis of $B_2F_2Mes_2$·(DMAP)$_2$ (3): A solution of DMAP (42 mg, 0.34 mmol, 2.0 equiv.) in toluene (1.0 mL) was added to a solution of **1** (50 mg, 0.17 mmol, 1.0 eq) in toluene at −78 °C. The mixture was stirred for 1 h −35 °C. All volatiles were removed under vacuum. The residue was extracted with pentane and the mixture was stored at −35 °C, providing **3** as a colorless powder (10 mg, 0.02 mmol, 27%). Single crystals of **3** suitable for X−ray diffraction were obtained by slow evaporation of a DCM/pentane (2:1) solution at −35 °C. **^{1}H NMR** (400.1 MHz, toluene-d_8): δ = 7.99 (d, $^{3}J_{HH}$ = 7.2 Hz, 4 H, NC$_5$*H*$_4$-4-NMe$_2$), 6.94 (s, 4 H, aryl-C*H*), 5.39 (d, 4 H, $^{3}J_{HH}$ = 7.4 Hz, NC$_5$*H*$_4$-4-NMe$_2$), 2.68 (s, 12 H, *ortho*-CH_3), 2.30 (s, 6 H, *para*-CH_3), 1.92 (s, 12 H, NC$_5$H$_4$-4-N(CH_3)$_2$). **^{13}C{^{1}H} NMR** (100.6 MHz, toluene-d_8): δ = 143.4 (*C*H, N*C*$_5$H$_4$-4-NMe$_2$), 129.5 (aryl-*C*H), 105.8 (*C*H, N*C*$_5$H$_4$-4-NMe$_2$), 38.2 (*C*H$_3$, NC$_5$H$_4$-4-N(*C*H$_3$)$_2$), 23.8 (*ortho*-*C*H$_3$), 21.2 (*para*-*C*H$_3$). The C_q atoms of the Mes groups were not detected. **^{11}B{^{1}H} NMR** (128.4 MHz, toluene-d_8): δ = 6.8. **^{19}F{^{1}H} NMR** (376.5 MHz, toluene-d_8): δ = –139.8 (br s, B*F*$_2$) ppm. **Elemental analysis (%):** calcd for $C_{32}H_{42}B_2F_2N_4$ (542.33 g·mol^{-1}) C: 70.87, H: 7.81, N: 10.33; found: C: 71.01, H: 7.74, N: 10.57.

Crystallographic details

The crystal data of **2a** and **3** were collected on a Bruker D8-Quest diffractometer with a CMOS area detector and those of $B_2F_2Dur_2$ and **2b** on a Bruker X8-APEX II diffractometer with a CCD area detector. Both systems were equipped with a multi-layer mirror monochromated $Mo_{K\alpha}$ radiation source (ImS micro-source tube and FR-591 rotation anode, respectively). The structure were solved using the intrinsic phasing method (ShelXT),[2] refined with the ShelXL program[3] 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 idealised geometric positions.

Crystal data for **$F_2B_2Dur_2$**:

$C_{20}H_{26}B_2F_2$, M_r = 326.03, colourless block, 1.00×0.75×0.50 mm^3, monoclinic space group $P2_1/n$, a = 9.024(3) Å, b = 15.783(8) Å, c = 12.907(5) Å, β = 96.65(2)°, V = 1826.0(13) Å^3, Z = 4, ρ_{calcd} = 1.182 g·cm^{-3}, μ = 0.079 mm^{-1}, F(000) = 696, T = 100(2) K, R_1 = 0.0558, wR^2 = 0.1082, 3722 independent reflections [2θ≤52.744°] and 225 parameters.

Crystal data for **2a**:

The BF_2 groups were rotationally disordered. The displacement parameters of disordered atoms were restrained to the same value with similarity restraint SIMU and 'rigid bond' restraint DELU.

$C_{21}H_{31}B_2F_2P$, M_r = 374.05, colourless block, 0.17×0.064×0.03 mm^3, orthorhombic space group $Pbca$, a = 8.463(2) Å, b = 14.865(2) Å, c = 32.625(11) Å, V = 4104.4(18) Å^3, Z = 8, ρ_{calcd} = 1.211 g·cm^{-3}, μ = 0.153 mm^{-1}, F(000) = 1600, T = 100(2) K, R_1 = 0.0594, wR^2 = 0.1059, 4198 independent reflections [2θ≤52.742°] and 263 parameters.

Crystal data for **2b**:

The BF_2 groups were rotationally disordered. The geometry of both residues was restrained to be planar (FLAT) with the same interatomic distances (SAME). The displacement parameters of disordered atoms were restrained to the same value with similarity restraint SIMU and 'enhanced rigid bond' restraint RIGU. The U_{ij} elements of the ADP matrix were restrained with the ISOR keyword to approximate isotropic behavior.

$C_{21}H_{31}B_2F_2O_3P$, M_r = 422.05, colourless plate, 0.509×0.332×0.124 mm^3, monoclinic space group $P21/c$, a = 10.300(6) Å, b = 14.375(10) Å, c = 15.204(9) Å, β = 104.850(14)°,

V = 2176(2) Å^3, Z = 4, ρ_{calcd} = 1.288 g·cm^{-3}, μ = 0.163 mm^{-1}, F(000) = 896, T = 296(2) K, R_1 = 0.0758, wR^2 = 0.1455, 5394 independent reflections [2θ≤56.65°] and 299 parameters.

Crystal data for **3**:

The crystal was a pseudo-merohedral twin with a second domain described by the [0 –1 0][–1 0 0][0 0 –1] matrix. The BASF parameter was refined to 18%.

$C_{16.50}H_{22}BClFN_2$, M_r = 313.62, colourless block, 0.16×0.39×0.48 mm^3, triclinic space group $P\ \bar{1}$, a = 11.043(2) Å, b = 11.083(4) Å, c = 14.473(3) Å, α = 92.267(9)°, β = 92.359(10)°, γ = 113.535(10)°, V = 1619.5(7) Å^3, Z = 4, ρ_{calcd} = 1.286 g·cm^{-3}, μ = 0.242 mm^{-1}, F(000) = 664, T = 100(2) K, R_1 = 0.0666, wR^2 = 0.1768, 7433 independent reflections [2θ≤55.086°] and 399 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-1452951 ($F_2B_2Dur_2$), -1452952 (**2a**), -1452953 (**2b**), -1452954 (**3**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Computational details

Energy minimization calculations were conducted within the Kohn-Sham Density Functional Theory (DFT) at the B3LYP/6-311G*[4-11] level using the Gaussian09[12] program. To obtain the singlet state, spin-restricted calculations were performed constraining the projection of the total electronic spin along a reference axis to zero. Frequency calculations were conducted to determine if each stationary point corresponds to a minimum. The Wiberg bond indices (WBI)[13] and so-called natural charges were determined in Natural Bond Orbital (NBO)[14-15] basis. The Jmol[16] program was used for visualisation purposes.

	Type G L = PMe_3 R = Mes X = F	**Type G L = PMe_3 R = Mes X = Cl**	**Type G L = PMe_3 R = Mes X = Br**	**Type C L = PMe_3 R = Mes X = F**	**Type C L = PMe_3 R = Mes X = Cl**	**Type C L = PMe_3 R = Mes X = Br**
q(B_X)	1.14	0.41	0.24	0.71	-0.14	-0.28
q(B_{Mes})	-0.19	-0.07	-0.06	0.60	0.68	0.67
q(X_1)	-0.53	-0.18	-0.10	-0.56	-0.28	-0.21
q(X_2)	-0.51	-0.23	-0.14	-0.55	-0.28	-0.21
q(C_{Mes1})	-0.29	-0.35	-0.35	-0.47	-0.48	-0.48
q(C_{Mes2})	-0.31	-0.31	-0.31	-0.39	-0.41	-0.41
q(P)	1.30	1.28	1.28	1.09	1.27	1.28
d(BB) (Å)	1.71	1.72	1.72	1.75	1.76	1.76
d(BX_1) (Å)	1.36	1.79	1.96	1.41	1.91	2.09
d(BX_2) (Å)	1.34	1.81	1.99	1.41	1.92	2.10
d(BC_{Mes1}) (Å)	1.66	1.64	1.64	1.58	1.58	1.59
d(BC_{Mes2}) (Å)	1.65	1.66	1.66	1.58	1.59	1.59
d(BP) (Å)	2.13	2.21	2.23	2.23	2.04	2.03

Table S1. Calculated structural parameters and natural charges of isomers of type **G** and **C** with R = Mes, X = F, Cl, Br and L = PMe_3.

	Type G L = DMAP R = Mes X = F	Type G L = DMAP R = Mes X = Cl	Type C L = DMAP R = Mes X = F	Type C L = DMAP R = Mes X = Cl
$q(B_X)$	1.16	0.43	0.86	0.23
$q(B_{Mes})$	0.16	0.23	0.67	0.77
$q(X_1)$	-0.53	-0.23	-0.55	-0.28
$q(X_2)$	-0.52	-0.18	-0.55	-0.29
$q(C_{Mes1})$	-0.30	-0.32	-0.46	-0.47
$q(C_{Mes2})$	-0.29	-0.30	-0.42	-0.45
$q(N_{DMAP})$	-0.48	-0.49	-0.51	-0.55
d(BB) (Å)	1.73	1.78	1.76	1.76
$d(BX_1)$ (Å)	1.36	1.82	1.41	1.88
$d(BX_2)$ (Å)	1.34	1.78	1.42	1.92
$d(BC_{Mes1})$ (Å)	1.66	1.67	1.59	1.60
$d(BC_{Mes2})$ (Å)	1.66	1.67	1.59	1.60
$d(BN_{DMAP})$ (Å)	1.70	1.68	1.66	1.62

Table S2. Calculated structural parameters and natural charges of isomers of type **G** and **C** with R = Mes, X = F, Cl, Br and L = DMAP.

	Type F L = DMAP R = Mes X = F	**Type F L = DMAP R = Mes X = Cl**	**Type F L = DMAP R = Mes X = Br**	**Type C' L = DMAP R = Mes X = F**	**Type C' L = DMAP R = Mes X = Cl**	**Type C' L = DMAP R = Mes X = Br**
$q(B_{X1})$	0.70	0.45	0.43	N/A	0.40	0.29
$q(B_{Mes})$	0.70	0.45	0.43	N/A	0.37	0.37
$q(X_1)$	-0.58	-0.35	-0.32	N/A	-0.33	-0.26
$q(X_2)$	-0.58	-0.35	-0.32	N/A	-0.30	-0.23
$q(C_{Mes1})$	-0.36	-0.41	-0.43	N/A	-0.34	-0.34
$q(C_{Mes2})$	-0.36	-0.41	-0.43	N/A	-0.32	-0.32
$q(N_{DMAP1})$	-0.50	-0.54	-0.56	N/A	-0.50	-0.50
$q(N_{DMAP2})$	-0.50	-0.54	-0.56	N/A	-0.56	-0.58
d(BB) (Å)	1.80	1.83	1.82	N/A	1.87	1.88
$d(BX_1)$ (Å)	1.45	1.99	2.23	N/A	1.93	2.13
$d(BX_2)$ (Å)	1.45	1.99	2.23	N/A	1.91	2.10
$d(BC_{Mes1})$ (Å)	1.65	1.66	1.65	N/A	1.68	1.68
$d(BC_{Mes2})$ (Å)	1.65	1.66	1.65	N/A	1.68	1.68
$d(BN_{DMAP1})$ (Å)	1.68	1.66	1.65	N/A	1.72	1.72
$d(BN_{DMAP2})$ (Å)	1.68	1.66	1.65	N/A	1.67	1.66

Table S3. Calculated structural parameters and natural charges of isomers of type **F** and **C'** with R = Mes, X = F, Cl, Br and L = DMAP. Structure **C'** is similar to **C** but with an additional L unit on the R_2B boron atom.

	Type C'' L = DMAP R = Me X = F	Type C'' L = DMAP R = Me X = Cl	Type C'' L = DMAP R = Me X = Br
$q(B_X)$	0.97	0.40	0.30
$q(B_{Me})$	0.27	0.32	0.31
$q(X_1)$	-0.57	-0.33	-0.27
$q(X_2)$	-0.56	-0.31	-0.24
$q(C_{Me1})$	-0.89	-0.89	-0.89
$q(C_{Me2})$	-0.85	-0.88	-0.88
$q(N_{DMAP1})$	-0.46	-0.48	-0.48
$q(N_{DMAP2})$	-0.49	-0.54	-0.56
d(BB) (Å)	1.76	1.77	1.77
$d(BX_1)$ (Å)	1.43	1.92	2.11
$d(BX_2)$ (Å)	1.41	1.90	2.08
$d(BC_{Me1})$ (Å)	1.63	1.63	1.63
$d(BC_{Me2})$ (Å)	1.64	1.63	1.63
$d(BN_{DMAP1})$ (Å)	1.65	1.66	1.66
$d(BN_{DMAP2})$ (Å)	1.68	1.62	1.61

Table S4. Calculated structural parameters and natural charges of isomers of type **C''** with R = Me, X = F, Cl, Br and L = DMAP. Type **C''** is similar to **C** but with the Mes groups replaced by Me groups.

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