Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION of SYNTHESES, STRUCTURES, AND COMPUTATIONS

1,3,2-Diazaborole-Derived Carbene Complexes of Boron

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SUPPORTING INFORMATIONS of SYNTHESES

Materials and Methods

General.

The syntheses of air-sensitive compounds were performed under purified argon using Schlenk techniques and an inert atmosphere drybox (M-Braun LabMaster SP). Chemicals were purchased from Aldrich and Strem and used as received. The solvents were dried and distilled under argon from Na/benzophenone prior to use. ^{1}H NMR, ^{13}C{^{1}H} NMR, and ^{11}B NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer and a Varian Unity Inova 500 MHz spectrometer. X-ray intensity data for **2**, **3**, and **4** were collected at room temperature on a Bruker D8 Quest PHOTON 100 CMOS X-ray diffractometer system with Incoatec Microfocus Source (IμS) monochromated Mo Kα radiation (λ = 0.71073 Å, sealed tube) using phi and omega-scan technique. Elemental analyses were performed by Complete Analytical Laboratories, Inc. (Highland Park, NJ).

Compound **2**: 8.9 mL of 1.0 M BBr_3 (in hexanes, 8.90 mmol) solution was added to a Schlenk flask containing **1** (1.037 g, 2.22 mmol) in 25 mL of hexane at room temperature. The mixture was then stirred overnight, giving **2** in a quantitative yield with excess BBr_3 (in terms of the ^{1}H NMR data). X-ray quality crystals of **2** were observed after crystallization of **2** in the concentrated parent solution at -20 °C overnight. Mp: gradually decomposed (>144°C). ^{1}H NMR (400.14 MHz, CD_2Cl_2): δ 1.25-1.27 [multiple d, J = 4.0 Hz, 12H, CH(CH_3)$_2$], 1.34 [d, J = 4.0 Hz, 6H, CH(CH_3)$_2$], 1.41 [d, J = 4.0 Hz, 6H, CH(CH_3)$_2$], 2.69 [m, J = 8.0 Hz, 2H, CH(CH$_3$)$_2$], 2.83 [m, J = 8.0 Hz, 2H, CH(CH$_3$)$_2$], 5.82 [s, 2H, N-CH_2], 7.28-7.32 [multiple d, J = 8.0 Hz, 4H, Ar-H], 7.44 [t, J = 8.0 Hz, 1H, Ar-H], 7.51 [t, J = 8.0Hz, 1H, Ar-H]. ^{13}C{^{1}H} NMR (100.63 MHz, CD_2Cl_2): δ 24.22, 24.64, 24.93, 24.99 [CH(*C*H$_3$)$_2$], 29.69, 30.30 [*C*H(CH$_3$)$_2$], 69.88 [NC*C*H$_2$], 124.88, 125.17, 130.32, 131.19, 132.85, 133.91, 143.35, 145.79 [Ar-*C*], 132.61 [N*C*CH$_2$]. ^{11}B NMR (C_6D_6, 160.35 MHz): δ For **2**, +30.28 (NBN), -14.42 (CBBr$_3$); For **1**, +20.10 (NBN); For free BBr_3, +37.14. Anal. (CALI, Highland Park, NJ) Calcd (found) for **2**: C 43.50 (43.48); H 5.06 (5.19); N 3.90 (3.82).

Compound **3**: 25 mL of hexane was added to a Schlenk flask containing **1** (1.000 g, 2.14 mmol) and BI_3 (0.922 g, 2.35 mmol) at room temperature. The resulting mixture was stirred overnight, giving **3** in a quantitative yield with excess BI_3 (in terms of the ^{1}H NMR data). X-ray quality yellow crystals of **3** were observed after recrystallization of **3** in 1,2-difluorobenzene at -20 °C overnight. Mp: 148.2°C. ^{1}H NMR (400.14 MHz, CD_2Cl_2): δ 1.22-1.26 [multiple d, J = 8.0 Hz, 12H, CH(CH_3)$_2$], 1.31 [d, J = 8.0 Hz, 6H, CH(CH_3)$_2$], 1.45 [d, J = 8.0 Hz, 6H, CH(CH_3)$_2$], 2.72 [m, J = 8.0 Hz, 2H, CH(CH$_3$)$_2$],

2.88 [m, J = 8.0 Hz, 2H, CH(CH_3)$_2$], 6.42 [s, 2H, N-CH_2], 7.27-7.30 [multiple d, J = 8.0 Hz, 4H, Ar-H], 7.42 [t, J = 8.0 Hz, 1H, Ar-H], 7.51 [t, J = 8.0 Hz, 1H, Ar-H]. $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2): δ 24.16, 24.66, 24.74, 24.76 [CH(CH_3)$_2$], 29.60, 30.16 [CH(CH_3)$_2$], 71.42 [NCCH_2], 125.00, 125.01, 130.12, 131.30, 133.69, 144.24, 145.83 [Ar-C], 132.52 [NCCH_2]. ^{11}B NMR (C_6D_6, 160.35 MHz): δ For **3**, +30.42 (NBN), -69.52 [CBI_3]; For free BI_3, -8.07; For **1**, +20.21 (NBN); For the unknown species, +25.26, -45.60. Anal. (CALI, Highland Park, NJ) Calcd (found) for **3**: C 36.36 (35.80); H 4.23 (4.25); N 3.26 (3.07).

SUPPORTING INFORMATIONS of COMPUTATIONS

All computations employed the Gaussian09 programs:
For Gaussian 09: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09*, revision D.01; Gaussian, Inc., Wallingford CT, 2013.

Table S1. Coordinates of the B3LYP/6-311G** optimized geometry of **2-Me**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	2.442683	0.273251	-0.010674
2	5	0	-1.442053	-0.016639	-0.007940
3	35	0	4.192891	-0.515245	-0.007055
4	35	0	-1.834886	-1.213335	-1.613118
5	35	0	-1.818714	-0.923223	1.792698
6	35	0	-2.534205	1.699781	-0.147301
7	7	0	1.162639	-0.503284	-0.000372
8	7	0	2.108349	1.615066	-0.024540
9	6	0	0.135209	0.323441	-0.014482
10	6	0	0.657872	1.727460	-0.032018
11	1	0	0.268938	2.274820	0.835093
12	1	0	0.278336	2.247592	-0.919682
13	6	0	2.932841	2.811668	-0.036160
14	1	0	3.983600	2.526119	-0.031638
15	1	0	2.734892	3.409096	-0.930934
16	1	0	2.732419	3.427837	0.845218
17	6	0	1.070128	-1.971035	0.009370
18	1	0	0.248408	-2.280902	0.650316
19	1	0	0.887567	-2.328469	-1.004089
20	1	0	2.011467	-2.370079	0.380064

Table S2. Coordinates of the B3LYP/6-311G** optimized geometry of **3-Me**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	-2.935026	-0.382629	-0.043086
2	5	0	0.937885	0.004844	-0.011654
3	35	0	-4.709946	0.349665	-0.026256
4	7	0	-1.680426	0.431001	-0.006363
5	7	0	-2.562241	-1.712679	-0.092349
6	6	0	-0.622218	-0.364117	-0.038075
7	6	0	-1.110309	-1.783216	-0.098318
8	1	0	-0.710372	-2.347170	0.752883
9	1	0	-0.717208	-2.267767	-1.000159
10	6	0	-3.349953	-2.932816	-0.142166
11	1	0	-4.408813	-2.679190	-0.133846
12	1	0	-3.130844	-3.497631	-1.053057
13	1	0	-3.133764	-3.567979	0.721811
14	6	0	-1.649206	1.898151	0.046583
15	1	0	-0.863078	2.226946	0.722820
16	1	0	-1.450400	2.294337	-0.949637
17	1	0	-2.616838	2.247409	0.398982
18	53	0	1.380963	1.399046	-1.761993
19	53	0	1.318750	0.939367	2.049812
20	53	0	2.242814	-1.860952	-0.215824

SUPPORTING INFORMATIONS of X-RAY

Compound 2

Table S3. Sample and crystal data for 2.

Identification code	**2**	
Chemical formula	$C_{26}H_{36}B_2Br_4N_2$	
Formula weight	717.82 g/mol	
Temperature	297(2) K	
Wavelength	0.71073 Å	
Crystal size	0.250 x 0.260 x 0.450 mm	
Crystal system	orthorhombic	
Space group	Pbca (No. 61)	
Unit cell dimensions	a = 19.6037(12) Å	α = 90°
	b = 17.1792(11) Å	β = 90°
	c = 37.549(2) Å	γ = 90°
Volume	12645.5(14) $Å^3$	
Z	16	
Density (calculated)	1.508 g/cm^3	
Absorption coefficient	5.108 mm^{-1}	
F(000)	5696	

Table S4. Data collection and structure refinement for 2.

Theta range for data collection	2.08 to 25.25°	
Index ranges	-22<=h<=23, -18<=k<=20, -45<=l<=45	
Reflections collected	107342	
Independent reflections	11448 [R(int) = 0.1521]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7454 and 0.1543	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	11448 / 4 / 625	
Goodness-of-fit on F^2	1.010	
Δ/σ_{max}	0.001	
Final R indices	5934 data; I>2σ(I)	R1 = 0.0734, wR2 = 0.1574
	all data	R1 = 0.1618, wR2 = 0.1941
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0744P)^2+51.2858P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.955 and -1.494 eÅ^{-3}	
R.M.S. deviation from mean	0.102 eÅ^{-3}	

Table S5. Bond lengths (Å) for 2.

B1-N2	1.359(10)	B1-N1	1.492(10)
B1-Br1	1.888(9)	B2-C1	1.579(11)
B2-Br4	1.963(10)	B2-Br2	2.006(10)
B2-Br3	2.063(10)	N1-C1	1.325(9)
N1-C15	1.466(9)	N2-C3	1.448(9)
N2-C2	1.445(9)	C1-C2	1.493(10)
C2-H2A	0.98(2)	C2-H2B	0.99(2)
C3-C8	1.385(11)	C3-C4	1.403(11)
C4-C5	1.392(12)	C4-C12	1.497(12)
C5-C6	1.364(13)	C6-C7	1.352(13)
C7-C8	1.388(11)	C8-C9	1.505(11)
C9-C11	1.501(12)	C9-C10	1.529(12)
C12-C14	1.501(16)	C12-C13	1.544(15)
C15-C20	1.391(12)	C15-C16	1.394(12)
C16-C17	1.385(12)	C16-C24	1.489(12)
C17-C18	1.372(14)	C18-C19	1.359(15)
C19-C20	1.396(12)	C20-C21	1.497(13)
C21-C23	1.530(15)	C21-C22	1.524(14)
C24-C26	1.498(15)	C24-C25	1.508(15)
B3-N4	1.343(10)	B3-N3	1.488(11)
B3-Br5	1.894(9)	B4-C27	1.600(12)
B4-Br6	1.987(11)	B4-Br8	1.995(11)
B4-Br7	2.058(14)	N3-C27	1.305(9)
N3-C41	1.464(9)	N4-C29	1.452(9)
N4-C28	1.462(9)	C27-C28	1.483(11)
C28-H28B	0.98(2)	C28-H28A	0.99(2)
C29-C30	1.373(11)	C29-C34	1.405(12)
C30-C31	1.381(12)	C30-C38	1.492(12)
C31-C32	1.367(15)	C32-C33	1.348(15)
C33-C34	1.385(12)	C34-C35	1.501(13)
C35-C36	1.515(14)	C35-C37	1.522(16)
C38-C40	1.524(14)	C38-C39	1.534(13)
C41-C46	1.378(12)	C41-C42	1.381(11)
C42-C43	1.395(12)	C42-C50	1.501(13)

C43-C44	1.360(15)	C44-C45	1.352(15)
C45-C46	1.385(13)	C46-C47	1.520(14)
C47-C49	1.538(16)	C47-C48	1.532(14)
C50-C51	1.535(14)	C50-C52	1.531(14)

Table S6. Bond angles (°) for 2.

N2-B1-N1	106.9(7)	N2-B1-Br1	128.9(6)
N1-B1-Br1	124.1(6)	C1-B2-Br4	119.7(6)
C1-B2-Br2	108.7(6)	Br4-B2-Br2	110.4(5)
C1-B2-Br3	99.8(6)	Br4-B2-Br3	109.0(4)
Br2-B2-Br3	108.5(5)	C1-N1-C15	126.2(6)
C1-N1-B1	110.4(6)	C15-N1-B1	123.3(6)
B1-N2-C3	131.5(6)	B1-N2-C2	109.1(6)
C3-N2-C2	119.3(6)	N1-C1-C2	107.1(6)
N1-C1-B2	131.7(7)	C2-C1-B2	121.1(7)
H2A-C2-H2B	101(6)	H2A-C2-N2	113(4)
H2B-C2-N2	115(4)	H2A-C2-C1	111(4)
H2B-C2-C1	112(4)	N2-C2-C1	106.3(6)
C8-C3-C4	123.3(7)	C8-C3-N2	118.6(7)
C4-C3-N2	118.1(7)	C5-C4-C3	115.5(8)
C5-C4-C12	121.9(9)	C3-C4-C12	122.5(7)
C6-C5-C4	122.6(9)	C7-C6-C5	119.5(9)
C6-C7-C8	122.3(9)	C7-C8-C3	116.8(8)
C7-C8-C9	120.5(8)	C3-C8-C9	122.7(7)
C11-C9-C8	112.9(8)	C11-C9-C10	111.3(9)
C8-C9-C10	112.9(7)	C14-C12-C4	111.7(9)
C14-C12-C13	111.2(11)	C4-C12-C13	110.8(10)
C20-C15-C16	124.7(7)	C20-C15-N1	118.5(7)
C16-C15-N1	116.6(7)	C17-C16-C15	115.7(9)
C17-C16-C24	120.1(9)	C15-C16-C24	124.2(7)
C18-C17-C16	121.4(9)	C19-C18-C17	121.2(9)
C18-C19-C20	121.0(10)	C19-C20-C15	116.0(9)
C19-C20-C21	119.9(9)	C15-C20-C21	124.1(8)
C20-C21-C23	111.7(10)	C20-C21-C22	112.9(9)
C23-C21-C22	108.8(9)	C16-C24-C26	113.4(9)
C16-C24-C25	113.5(9)	C26-C24-C25	107.6(10)
N4-B3-N3	108.1(7)	N4-B3-Br5	128.8(7)
N3-B3-Br5	123.2(6)	C27-B4-Br6	117.8(7)
C27-B4-Br8	108.7(7)	Br6-B4-Br8	109.8(6)

C27-B4-Br7	100.7(7)	Br6-B4-Br7	110.8(6)
Br8-B4-Br7	108.5(5)	C27-N3-C41	126.8(6)
C27-N3-B3	109.6(6)	C41-N3-B3	123.3(6)
B3-N4-C29	132.0(6)	B3-N4-C28	108.3(6)
C29-N4-C28	119.4(6)	N3-C27-C28	108.4(6)
N3-C27-B4	132.2(7)	C28-C27-B4	119.3(7)
H28B-C28-H28A	104(6)	H28B-C28-N4	106(4)
H28A-C28-N4	114(4)	H28B-C28-C27	112(4)
H28A-C28-C27	116.(4)	N4-C28-C27	105.4(6)
C30-C29-C34	123.3(8)	C30-C29-N4	119.2(8)
C34-C29-N4	117.4(7)	C31-C30-C29	117.1(9)
C31-C30-C38	120.6(9)	C29-C30-C38	122.3(8)
C30-C31-C32	121.1(10)	C33-C32-C31	120.8(9)
C32-C33-C34	121.5(10)	C33-C34-C29	116.1(9)
C33-C34-C35	120.4(9)	C29-C34-C35	123.5(8)
C34-C35-C36	111.2(9)	C34-C35-C37	113.1(9)
C36-C35-C37	109.9(11)	C30-C38-C40	112.0(9)
C30-C38-C39	112.2(8)	C40-C38-C39	108.7(9)
C46-C41-C42	123.1(8)	C46-C41-N3	115.7(8)
C42-C41-N3	120.9(8)	C43-C42-C41	117.3(9)
C43-C42-C50	120.1(9)	C41-C42-C50	122.7(8)
C44-C43-C42	120.3(10)	C45-C44-C43	121.1(10)
C44-C45-C46	121.3(11)	C45-C46-C41	116.9(10)
C45-C46-C47	120.0(10)	C41-C46-C47	123.0(8)
C46-C47-C49	111.6(9)	C46-C47-C48	113.2(11)
C49-C47-C48	112.0(11)	C42-C50-C51	110.5(9)
C42-C50-C52	112.7(9)	C51-C50-C52	110.1(9)

Compound 3

Table S7. Sample and crystal data for 3.

Identification code	**3**	
Chemical formula	$C_{26}H_{36}B_2BrI_3N_2$	
Formula weight	858.80 g/mol	
Temperature	297(2) K	
Wavelength	0.71073 Å	
Crystal size	0.150 x 0.210 x 0.400 mm	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$ (No. 19)	
Unit cell dimensions	a = 12.2369(6) Å	α = 90°
	b = 14.6825(7) Å	β = 90°
	c = 18.0610(8) Å	γ = 90°
Volume	3245.0(3) $Å^3$	
Z	4	
Density (calculated)	1.758 g/cm^3	
Absorption coefficient	4.137 mm^{-1}	
F(000)	1640	

Table S8. Data collection and structure refinement for 3.

Theta range for data collection	2.01 to 27.88°
Index ranges	-16<=h<=16, -19<=k<=19, -23<=l<=23
Reflections collected	104369
Independent reflections	7743 [R(int) = 0.0503]
Max. and min. transmission	0.7457 and 0.2577
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7743 / 0 / 308
Goodness-of-fit on F^2	1.072
Δ/σ_{max}	0.001
Final R indices	6716 data; $I>2\sigma(I)$ R1 = 0.0378, wR2 = 0.0925
	all data R1 = 0.0471, wR2 = 0.0982
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0485P)^2+3.1668P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.052(17)
Largest diff. peak and hole	0.851 and -1.603 eÅ^{-3}
R.M.S. deviation from mean	0.142 eÅ^{-3}

Table S9. Bond lengths (Å) for 3.

B1-N2	1.342(8)	B1-N1	1.503(7)
B1-Br1	1.899(6)	B2-C1	1.615(9)
B2-I1	2.200(8)	B2-I2	2.229(8)
B2-I3	2.265(8)	N1-C1	1.311(8)
N1-C15	1.446(7)	N2-C3	1.443(7)
N2-C2	1.461(8)	C1-C2	1.491(8)
C3-C8	1.382(9)	C3-C4	1.406(10)
C4-C5	1.373(10)	C4-C12	1.536(11)
C5-C6	1.359(12)	C6-C7	1.369(12)
C7-C8	1.391(8)	C8-C9	1.513(10)
C9-C11	1.524(13)	C9-C10	1.493(13)
C12-C13	1.503(15)	C12-C14	1.526(14)
C15-C16	1.395(8)	C15-C20	1.404(8)
C16-C17	1.387(10)	C16-C24	1.512(11)
C17-C18	1.378(13)	C18-C19	1.358(12)
C19-C20	1.372(10)	C20-C21	1.519(10)
C21-C22	1.509(13)	C21-C23	1.532(13)
C24-C26	1.522(17)	C24-C25	1.56(2)

Table S10. Bond angles (°) for 3.

N2-B1-N1	107.7(5)	N2-B1-Br1	128.7(4)
N1-B1-Br1	123.6(4)	C1-B2-I1	120.7(5)
C1-B2-I2	105.1(5)	I1-B2-I2	108.5(3)
C1-B2-I3	103.4(4)	I1-B2-I3	108.2(3)
I2-B2-I3	110.7(3)	C1-N1-C15	128.3(5)
C1-N1-B1	109.4(5)	C15-N1-B1	122.2(5)
B1-N2-C3	131.8(5)	B1-N2-C2	109.0(5)
C3-N2-C2	119.2(5)	N1-C1-C2	108.4(5)
N1-C1-B2	131.7(5)	C2-C1-B2	119.9(5)
N2-C2-C1	105.3(5)	C8-C3-C4	122.4(5)
C8-C3-N2	119.1(5)	C4-C3-N2	118.5(5)
C5-C4-C3	117.2(6)	C5-C4-C12	121.0(7)
C3-C4-C12	121.8(6)	C6-C5-C4	121.9(7)
C5-C6-C7	119.8(7)	C8-C7-C6	121.7(7)
C3-C8-C7	116.9(6)	C3-C8-C9	123.8(5)
C7-C8-C9	119.3(6)	C8-C9-C11	111.2(6)
C8-C9-C10	112.7(7)	C11-C9-C10	109.0(9)
C4-C12-C13	110.6(7)	C4-C12-C14	111.2(8)
C13-C12-C14	112.6(10)	C16-C15-C20	123.5(6)
C16-C15-N1	118.2(5)	C20-C15-N1	118.1(5)
C17-C16-C15	116.4(6)	C17-C16-C24	120.7(7)
C15-C16-C24	122.9(6)	C18-C17-C16	121.1(7)
C19-C18-C17	120.4(7)	C20-C19-C18	122.3(7)
C19-C20-C15	116.2(6)	C19-C20-C21	121.2(6)
C15-C20-C21	122.5(6)	C22-C21-C20	113.3(8)
C22-C21-C23	109.7(8)	C20-C21-C23	110.3(6)
C16-C24-C26	111.0(9)	C16-C24-C25	108.1(11)
C26-C24-C25	111.2(10)		

Compound 4

Table S11. Sample and crystal data for 4.

Identification code	**4**	
Chemical formula	$C_{26}H_{37}B_2Br_5N_2$	
Formula weight	798.74 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.180 x 0.300 x 0.400 mm	
Crystal system	monoclinic	
Space group	$P2_1/c$ (No. 14)	
Unit cell dimensions	a = 12.317(2) Å	α = 90°
	b = 22.811(5) Å	β = 109.718(6)°
	c = 14.606(3) Å	γ = 90°
Volume	3863.3(13) $Å^3$	
Z	4	
Density (calculated)	1.373 g/cm^3	
Absorption coefficient	5.216 mm^{-1}	
F(000)	1568	

Table S12. Data collection and structure refinement for 4.

Theta range for data collection	2.08 to 26.02°	
Index ranges	-15<=h<=15, -28<=k<=28, -18<=l<=18	
Reflections collected	118311	
Independent reflections	7600 [R(int) = 0.0999]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7454 and 0.2455	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7600 / 3 / 329	
Goodness-of-fit on F^2	1.023	
Δ/σ_{max}	0.001	
Final R indices	6114 data; $I>2\sigma(I)$	R1 = 0.0390, wR2 = 0.0836
	all data	R1 = 0.0534, wR2 = 0.0884
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0332P)^2+7.0875P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.960 and -0.950 eÅ^{-3}	
R.M.S. deviation from mean	0.089 eÅ^{-3}	

Table S13. Bond lengths (Å) for 4.

B1-N1	1.403(5)	B1-N2	1.475(5)
B1-Br1	1.882(4)	B2-Br5	2.003(4)
B2-Br4	2.017(4)	B2-Br3	2.007(4)
B2-Br2	2.024(4)	N1-C1	1.419(4)
N1-C15	1.450(4)	N2-C2	1.344(4)
N2-C3	1.460(4)	C1-H1A	0.974(19)
C1-H1B	0.996(19)	C1-C2	1.470(5)
C2-H2	0.946(19)	C3-C4	1.393(5)
C3-C8	1.400(5)	C4-C5	1.399(5)
C4-C12	1.510(6)	C5-C6	1.369(6)
C6-C7	1.384(6)	C7-C8	1.389(5)
C8-C9	1.520(6)	C9-C10	1.523(5)
C9-C11	1.534(6)	C12-C14	1.540(6)
C12-C13	1.526(6)	C15-C16	1.406(5)
C15-C20	1.392(5)	C16-C17	1.385(6)
C16-C24	1.536(6)	C17-C18	1.368(6)
C18-C19	1.377(6)	C19-C20	1.396(5)
C20-C21	1.511(5)	C21-C23	1.519(6)
C21-C22	1.545(6)	C24-C26	1.531(7)
C24-C25	1.540(8)		

Table S14. Bond angles (°) for 4.

N1-B1-N2	106.0(3)	N1-B1-Br1	128.0(3)
N2-B1-Br1	126.0(3)	Br5-B2-Br4	110.1(2)
Br5-B2-Br3	110.75(19)	Br4-B2-Br3	109.3(2)
Br5-B2-Br2	107.95(19)	Br4-B2-Br2	109.23(19)
Br3-B2-Br2	109.4(2)	B1-N1-C1	110.1(3)
B1-N1-C15	129.1(3)	C1-N1-C15	120.8(3)
C2-N2-C3	123.3(3)	C2-N2-B1	108.8(3)
C3-N2-B1	127.9(3)	H1A-C1-H1B	89(4)
H1A-C1-N1	121(3)	H1B-C1-N1	114(3)
H1A-C1-C2	115(3)	H1B-C1-C2	111(3)
N1-C1-C2	105.4(3)	H2-C2-N2	117(3)
H2-C2-C1	133.(3)	N2-C2-C1	109.5(3)
C4-C3-C8	124.3(3)	C4-C3-N2	117.9(3)
C8-C3-N2	117.8(3)	C5-C4-C3	116.6(4)
C5-C4-C12	120.2(4)	C3-C4-C12	123.3(3)
C6-C5-C4	120.7(4)	C5-C6-C7	121.1(4)
C6-C7-C8	121.1(4)	C3-C8-C7	116.2(4)
C3-C8-C9	122.9(3)	C7-C8-C9	120.9(4)
C10-C9-C8	112.9(3)	C10-C9-C11	110.2(4)
C8-C9-C11	110.8(3)	C14-C12-C4	110.4(4)
C14-C12-C13	110.3(3)	C4-C12-C13	111.5(3)
C16-C15-C20	123.1(3)	C16-C15-N1	118.4(3)
C20-C15-N1	118.5(3)	C15-C16-C17	117.1(4)
C15-C16-C24	122.4(3)	C17-C16-C24	120.4(4)
C18-C17-C16	121.3(4)	C17-C18-C19	120.5(4)
C20-C19-C18	121.3(4)	C19-C20-C15	116.7(3)
C19-C20-C21	120.1(3)	C15-C20-C21	123.2(3)
C23-C21-C20	111.7(4)	C23-C21-C22	111.0(3)
C20-C21-C22	110.3(3)	C16-C24-C26	110.2(4)
C16-C24-C25	110.7(4)	C26-C24-C25	111.3(4)