Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

for

Dihaloborenium cations stabilized by a four-membered N-heterocyclic carbene: Electron deficiency compensation by asymmetric structural changes

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General Procedures and Physical Measurements

All manipulations were carried out using standard Schlenk techniques and a dry-box. Toluene and hexane were distilled over sodium while DCM-d_2 and fluorobenzene were distilled over CaH_2. All solvents were stored over 4 Å molecular sieves. Iminium salt **1** was prepared according to the reported method[S1] while all other reagents were obtained from commercial sources and used without further purification. The NMR spectra were recorded on an Jeol 400 MHz (^{1}H NMR at 400 MHz; ^{13}C NMR at 100 MHz, ^{11}B NMR at 128 MHz, ^{27}Al NMR at 104 MHz and ^{31}P NMR at 162 MHz) instrument. Tetramethysilane was used as reference for ^{1}H and ^{13}C NMR, while ^{11}B and ^{27}Al NMR spectra were recorded with respect to $Et_2O{\cdot}BF_3$ and $AlCl_3/D_2O$, respectively. ^{31}P NMR spectra were recorded with respect to H_3PO_4. Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using the electro spray ionization (ESI) mode.

Crystallographic Methods

Single crystals were mounted on quartz fiber and the X-ray intensity data were collected at 103(2) K on a Bruker X8 APEX system, using Mo Kα radiation, with the SMART suite of programs.[S2] Data were processed and corrected for Lorentz and polarization effects with SAINT[S3] and for absorption effects with SADABS.[S4] Structural solution and refinement were carried out with the SHELXTL suite of programs.[S5] The structure was solved by direct method and refined for all data by full-matrix least-squares methods on F^2. All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters. Selected crystal data, data collection and refinement parameters for **2a**, **3a** and **3b** are included in Table S1.

Table S1.

	2a	**3a**	**3b**
Formula	$C_{31}H_{48}BCl_3N_3P$ $\cdot 0.32(C_6H_{14})\cdot 0.18(C_7H_8)$	$C_{31}H_{48}AlBCl_6N_3P$	$C_{31}H_{48}AlBBr_6N_3P$
CCDC	986261	986260	986262
Formula weight	657.52	744.18	1010.94
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a /Å	10.314(4)	14.972(1)	14.823(1)
b /Å	18.60(1)	14.162(1)	14.827(1)
c /Å	19.16(1)	18.753(1)	19.120(1)
β /°	99.54(2)	99.050(5)	103.137(2)
V / Å^3	3624(3)	3926.8(5)	4092.3(5)
Z	4	4	4
D_c/ g cm^{-3}	1.205	1.259	1.641
F(000)	1410	1560	1992
Crystal size/ mm	0.40 x 0.20 x 0.20	0.18 x 0.24 x 0.30	0.20 x 0.18 x 0.12
θ range/°	1.54-28.01	1.38-29.22	2.09 to 29.16
No. of reflns collected	41400	50162	31555
No. of indep reflns	8489	10588	11018
$R1$ [$I > 2\sigma(I)$]	0.0797	0.0430	0.0609
wR_2 (all data)	0.2370	0.1364	0.1848
Peak and hole/e Å^{-3}	0.626 and -1.051	0.910 and -0.619	1.065 and -1.238

Syntheses

Preparation of the neutral precursors **2a** and **2b**.

A 30 mL of toluene solution containing iminium salt **1** was cooled down to 0°C using an ice bath. After 1.1 equiv of $K[N(SiMe_3)_2]$ was added the ice bath was removed. 10 mL of hexane was then introduced into the reaction mixture after 10 min followed by filtration. 0.57 equiv of BX_3 (X = Cl or Br) was added to the filtrate resulting in an immediate formation of a white solid. The solid was isolated by filtration and dried under reduced pressure.

2a: 1.2 g (2.43 mmol) of **1**, 0.52 g (2.61 mmol) of $K[N(SiMe_3)_2]$ and 1.4 mL (1.4 mmol) of a 1.0 M BCl_3 solution in hexane. Yield: 0.54 g, (63% - with respect to added BCl_3). Crystals suitable for X-ray diffraction were obtained by layering a toluene sample with hexane. ^{1}H NMR (CD_2Cl_2): δ 1.16 (d, $^3J_{H,H}$ = 5.5 Hz, 6H, CH_3), 1.25 (d, $^3J_{H,H}$ = 6.0 Hz, 6H, CH_3), 1.36 (d, $^3J_{H,H}$ = 6.0 Hz, 6H, CH_3), 1.38 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, CH_3), 1.44 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, CH_3), 3.17 (m, 2H, CH), 3.45 (m, 3H, CH), 4.00 (br, 1H, CH), 7.25 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, H_{arom}), 7.29 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, H_{arom}), 7.41 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, H_{arom}). ^{13}C{H} NMR (CD_2Cl_2): δ 23.1 (br, CH_3), 23.8 (s, CH_3), 25.6 (s, CH_3), 26.8 (s, CH_3), 27.4 (d, $^3J_{PC}$ = 14 Hz, CH_3), 28.5 (s, CH_3), 30.2 (d, $^3J_{PC}$ = 13 Hz, CH_3), 46.3 (d, $^2J_{CP}$ = 30 Hz, CH), 51.9 (d, $^2J_{CP}$ = 8 Hz, CH), 124.4 (s, C_{arom}), 124.8 (s, C_{arom}), 128.9 (s, C_{arom}), 131.9 (s, C_{arom}), 146.1 (s, C_{arom}), 147.1 (s, C_{arom}). ^{11}B{H} NMR (CD_2Cl_2): δ - 0.2. ^{31}P {H} NMR (CD_2Cl_2): δ 126.5. MS (ES$^+$): *m/z* calcd for $C_{31}H_{48}BN_3PCl_2$ ($[M-Cl]^+$) 574.3056; found 574.3045.

2b: 0.5 g (0.78 mmol) of **1**, 0.17 g (0.86 mmol) of $K[N(SiMe_3)_2]$ and 0.45 mL (0.45 mmol) of a 1.0 M BBr_3 solution in hexane. Yield: 0.14 g, (42% - with respect to added BBr_3). ^{1}H NMR (CD_2Cl_2): δ 1.14 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, CH_3), 1.21 (d, $^3J_{H,H}$ = 6.4 Hz, 6H, CH_3), 1.27 (d, $^3J_{H,H}$ = 6.9 Hz, 6H, CH_3), 1.33 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, CH_3), 1.42 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, CH_3), 1.44 (d, $^3J_{H,H}$ = 6.4 Hz, 6H, CH_3), 3.13 (m, 2H, CH), 3.48 (m, 3H, CH), 4.00 (br, 1H, CH), 7.21 (d, $^3J_{H,H}$ = 7.7 Hz, 2H, H_{arom}), 7.25 (d, $^3J_{H,H}$ = 7.7 Hz, 2H, H_{arom}), 7.39 (t, $^3J_{H,H}$ = 7.7 Hz, 2H, H_{arom}). ^{13}C{H} NMR (CD_2Cl_2): δ 23.1 (br, CH_3), 23.8 (s, CH_3), 25.8 (s, CH_3), 27.3 (s, CH_3), 27.5 (d, $^3J_{PC}$ = 6 Hz, CH_3), 28.5 (s, CH_3), 30.3 (d, $^3J_{PC}$ = 15 Hz, CH_3), 46.3 (d, $^2J_{CP}$ = 34 Hz, CH), 52.1 (br, CH), 124.6 (s, C_{arom}), 124.9 (s, C_{arom}), 129.0 (s, C_{arom}), 132.3 (s, C_{arom}), 146.2 (s, C_{arom}), 147.5 (s, C_{arom}). ^{11}B{H} NMR (CD_2Cl_2): δ - 17.5. ^{31}P{H} NMR (CD_2Cl_2): δ 128.3. MS (ES$^+$): *m/z* calcd for $C_{31}H_{48}BN_3PBr_2$ ($[M-Br]^+$) 664.2025; found 664.2027.

Preparation of borenium cations **3a** and **3b**.

After dissolving the neutral precursor in 5 mL of DCM 1.0 equiv of AlX_3 (X = Cl or Br) was added. The reaction mixture was left to stir overnight and it was layered with 5 mL of hexane. After 2 days it was possible to collect a pale yellow crystalline material by filtration.

3a: 0.030g (0.049 mmol) of **2a** and 0.007 g (0.049 mmol) of $AlCl_3$. Yield: 0.028 g (76%). ^{1}H NMR (CD_2Cl_2): δ 1.15 (d, $^3J_{H,H}$ = 6.4 Hz, 6H, CH_3), 1.32 (m, 12H, CH_3), 1.39 (m, 12H, CH_3), 1.45 (d, $^3J_{H,H}$ = 6.8 Hz, 6H, CH_3), 3.00 (m, 2H, CH), 3.15 (m, 2H, CH), 3.75 (m, 2H, CH), 7.39 (second order triplet, 4H, H_{arom}), 7.55 (t, $^3J_{H,H}$ = 7.8 Hz, 2H, H_{arom}). ^{13}C{H} NMR (CD_2Cl_2): δ 22.0 (s, CH_3), 23.1 (s, CH_3), 24.2 (s, CH_3), 25.0 (s, CH_3), 26.3 (s, CH_3), 27.6 (d, $^3J_{PC}$ = 13 Hz, CH_3), 29.2 (s, CH_3), 30.0 (d, $^3J_{PC}$ = 15 Hz, CH_3), 48.4 (d, $^2J_{CP}$ = 28 Hz, CH), 54.8 (d, $^2J_{CP}$ = 9 Hz, CH), 125.5 (s, C_{arom}), 125.8 (s, C_{arom}), 129.3 (s, C_{arom}), 131.5 (s, C_{arom}), 144.2 (s, C_{arom}), 145.1 (s, C_{arom}). ^{11}B{H} NMR (CD_2Cl_2): δ 48.4. ^{27}Al{H} NMR (CD_2Cl_2): δ 106.3. ^{31}P{H} NMR (CD_2Cl_2): δ 135.5. MS (ES$^+$): *m/z* calcd for $C_{31}H_{48}BN_3PCl_2$ ($[M-AlCl_4]^+$) 574.3056; found 574.3067.

3b: 0.030g (0.040 mmol) of **2b** and 0.011 g (0.040 mmol) of $AlBr_3$. Yield: 0.029 g (71%). ^1H NMR (CD_2Cl_2): δ 1.12 (d, $^3J_{H,H}$ = 6.0 Hz, 6H, CH_3), 1.30 (m, 12H, CH_3), 1.37 (m, 12H, CH_3), 1.42 (d, $^3J_{H,H}$ = 7.2 Hz, 3H, CH_3), 1.48 (d, $^3J_{H,H}$ = 6.8 Hz, 3H, CH_3), 3.97 (m, 2H, CH), 3.13 (m, 2H, CH), 3.68 (m, 1H, CH), 3.76 (m, 1H, CH) 7.37 (second order triplet, 4H, H_{arom}), 7.53 (t, $^3J_{H,H}$ = 7.8 Hz, 2H, H_{arom}). $^{13}C\{H\}$ NMR (CD_2Cl_2): δ 22.0 (s, CH_3), 23.1 (s, CH_3), 24.2 (s, CH_3), 25.0 (s, CH_3), 26.3 (d, $^3J_{PC}$ = 6 Hz, CH_3), 27.6 (d, $^3J_{PC}$ = 13 Hz, CH_3), 29.2 (s, CH_3), 30.0 (d, $^3J_{PC}$ = 11 Hz, CH_3), 48.4 (d, $^2J_{CP}$ = 29 Hz, CH), 54.7 (d, $^2J_{CP}$ = 11 Hz, CH), 125.5 (s, C_{arom}), 125.8 (s, C_{arom}), 129.3 (s, C_{arom}), 131.5 (s, C_{arom}), 144.2 (s, C_{arom}), 145.1 (s, C_{arom}). $^{11}B\{H\}$ NMR (CD_2Cl_2): δ 48.0. $^{27}Al\{H\}$ NMR (CD_2Cl_2): δ 84.0. $^{31}P\{H\}$ NMR (CD_2Cl_2): δ 136.1. Numerous attempts to detect the cation by ES-MS were unsuccessful.

Computation details

All calculations were performed with the Gaussian 09 package.[S6] The geometry of the free ligand, **2a** and **3a** fully optimized by B3LYP[S7] method with 6-31G(d,p) basis set using atom coordinates from the solid state analysis. Harmonic frequency calculation is performed to validate the optimized geometry is local minimum on the potential energy surface by yielding zero imaginary vibrational frequency. We have also taken the ligand coordinates from the free ligand, **2a** and **3a** for energy-only calculations in order to measure the change in the HOMO-LUMO gap of the ligand moiety.

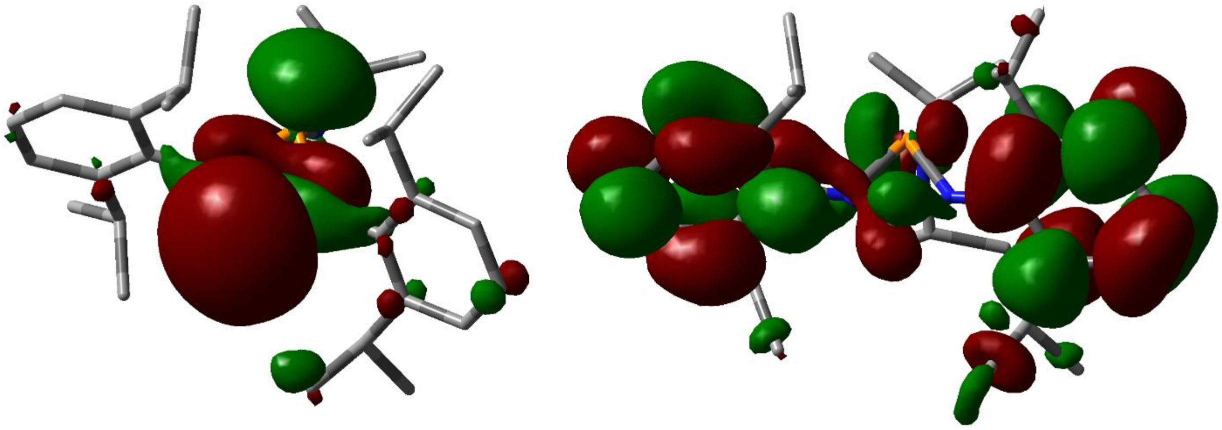

Figure S1. HOMO (left) and LUMO (right) of the free ligand.

References

S1 E. Despagnet-Ayoub and R. H. Grubbs, *J. Am. Chem. Soc.*, 2004, **126**, 10198-10199.

S2 SMART version 5.628; Bruker AXS Inc.: Madison, WI, 2001.

S3 SAINT+ version 6.22a; Bruker AXS Inc.: Madison, WI, 2001.

S4 Sheldrick, G. M. SADABS; 1996.

S5 SHELXTL version 5.1; Bruker AXS Inc.: Madison, WI, 1997.

S6 Gaussian 09, Revision B.01, 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, Inc., Wallingford CT, 2010.

S7 a) A. D. J. Becke, *Chem. Phys.* 1993, **98**, 5648-5652. b) J. P. Perdew, In *Electronic Structure of Solids '91* (Eds: P. Ziesche, H. Eschrig) Akademie Verlag: Berlin, 1991, pp 11-20. c) J. P. Perdew, K. Burke, Y. Wang, *Phys. Re*V. *B: Condens. Matter* 1996, **54**, 16533-16539. d) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Re*V. *B: Condens. Matter* 1992, **46**, 6671-6687. e) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Re*V. *B: Condens. Matter* 1993, **48**, 4987.