Experimental Section

Materials: Iodine, from ABCR GmbH & Co. and 1,2-*closo*-$C_2B_{10}H_{12}$, 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$ and 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ from Katchem Ltd. (Prague) were used as purchased. 1,2-Me_2-1,2-*closo*-$C_2B_{10}H_{10}$[1] and 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$[2] were synthesized according to the literature or by slight variations of the procedures therein.

Instrumentation: Elemental analyses were performed using a Carlo Erba EA1108 microanalyser. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. ^1H and $^1H\{^{11}B\}$ NMR (300.13 MHz), $^{13}C\{^1H\}$ NMR (75.47 MHz) and ^{11}B and $^{11}B\{^1H\}$ NMR (96.29 MHz) spectra were recorded with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. Chemical shift values for ^{11}B and $^{11}B\{^1H\}$ NMR spectra were referenced to external $BF_3 \cdot OEt_2$ and those for ^1H, $^1H\{^{11}B\}$ and $^{13}C\{^1H\}$ NMR spectra were referenced to $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants in Hz. Negative-ion matrix-assisted laser desorption/ionization, time of flight, MALDI-TOF mass spectra were recorded on a N_2 laser source Bruker BIFLEX spectrometer. The electrospray-ionization mass espectra (ESI) were recorded on a Bruker Esquire 3000 spectrometer using a source of ionization and an ion trap analyzer.

Preparation of **1**:

<u>*Method A*</u>. A thick-walled Pyrex tube charged with 1,2-$C_2B_{10}H_{12}$ (98 mg, 0.68 mmol) and iodine (704 mg, 2.77 mmol) was put under vacuum, cooled down with liquid nitrogen and sealed. The tube was then placed in a furnace and the temperature gradually raised to 270 ºC, maintained for 24 h and allowed to drop slowly to room temperature. The mixture was then dissolved in ethanol (4 cm^3), excess iodine quenched by addition of 10% aqueous sodium metabisulphite (4 cm^3) and the resulting yellow suspension refluxed until complete dissolution of the solid. The white crystals formed upon cooling to room temperature were collected by filtration and washed with 1:1 ethanol/water mixture to give 8,9,10,12-I_4-1,2-$C_2B_{10}H_8$ **1**. A second crop of crystals, identified equally as pure **1** based on ^1H NMR spectroscopy, could be obtained by slow crystallization from the filtrate. (269 mg, 61%).

<u>*Method B*</u>. A thick-walled Pyrex tube charged with 1,2-$C_2B_{10}H_{12}$ (0.2 g, 1.39 mmol) and iodine (3.522 g, 13.9 mmol) was put under vacuum, cooled down with liquid nitrogen and sealed. The tube was then placed in a furnace and the temperature gradually raised

to 270 ºC during 15 minutes, maintained for 4 h and allowed to drop slowly to room temperature. Excess iodine was effectively separated by sublimation from the reaction mixture at 50 ºC under reduced pressure. The resulting solid was recrystallized from 1:1 ethanol/water mixture to yield 8,9,10,12-I_4-1,2-$C_2B_{10}H_8$ **1**. A second crop of crystals, identified equally as pure **1** based on ^1H NMR spectroscopy, could be obtained by slow crystallization from the filtrate. (0.680 g, 76%). ^1H NMR (CD_3COCD_3): δ 5.57 (2 H, br s, CH). $^1H\{^{11}B\}$ NMR (CD_3COCD_3): δ 3.02 (4 H, br s, BH), 3.38 (2 H, br s, BH) and 5.57 (2 H, br s, CH). ^{11}B NMR (CD_3COCD_3): δ -16.3 (2 B, s, B(8,10)), -13.2 (2 B, d, ^1J(B,H) = 188, B(3,6)), -9.5 (4 B, d, ^1J(B,H) = 177, B(4,5,7,11)) and -7.1 (2 B, s, B(9,12)). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ 57.1 ($C_{cluster}$-H). FTIR (KBr), ν (cm^{-1}): 3024 (s, C_c-H), 2621 (s, B-H). MALDI-TOF MS: *m/z* 647 (M – H^+, 14%), 637 (7), 521 (12) and 127 (I^-, 100).

Compounds **2**-**5** were prepared as white crystalline solids by the method B in more than 75% yield.

Spectroscopic data for **2**: The resulting solid was recrystallized from 3:2 ethanol/water mixture to yield pure compound **2**. Found: C, 5.73; H, 1.49. $C_3H_{10}B_{10}I_4$ requires C, 5.44; H, 1.52%). ^1H NMR (CD_3COCD_3): δ 2.22 (3 H, s, CH_3) and 5.73 (1 H, br s, $C_{cluster}$-H). $^1H\{^{11}B\}$ NMR (CD_3COCD_3): δ 2.22 (3 H, s, CH_3), 3.05 (2 H, br s, BH), 3.12 (2 H, br s, BH), 3.40 (2 H, br s, BH) and 5.73 (1 H, br s, $C_{cluster}$-H). ^{11}B NMR (CD_3COCD_3): δ -16.2 (2 B, s, BI), -8.9 [broad shoulder at -9.7] (5 B, br m, 4 x BH and 1 x BI) and -6.5 (3 B, br m, 2 x BH and 1 x BI). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ 24.8 (CH_3), 63.5 ($C_{cluster}$-H) and 73.0 ($C_{cluster}$-CH_3). FTIR (KBr), ν (cm^{-1}): 3026 (s, $C_{cluster}$-H), 2922 (w, CH_3), 2853 (w, CH_3), 2633 (s, BH), 2613 (w, BH) and 2602 (w, BH). MALDI-TOF MS: *m/z* 661 (M – H^+, 81%) and 127 (I^-, 100).

Spectroscopic data for **3**: The resulting solid was recrystallized from 5:2 ethanol/water mixture to yield pure compound **3**. Found: C, 13.42; H, 1.58. $C_8H_{12}B_{10}I_4$ requires C, 13.27; H, 1.67%. ^1H NMR (CD_3COCD_3): δ 6.21 (1 H, br s, $C_{cluster}$-H), 7.50 (2 H, br t, aromatic *meta*-CH), 7.59 (1 H, t, ^3J(H,H) = 7.4, aromatic *para*-CH) and 7.75 (2 H, d, ^3J(H,H) = 7.7, aromatic *ortho*-CH). $^1H\{^{11}B\}$ NMR (CD_3COCD_3): δ 3.17 (2 H, br s, BH), 3.41 (2 H, br s, BH), 3.63 (2 H, br s, BH), 6.21 (1 H, br s, $C_{cluster}$-H), 7.50 (2 H, br t, aromatic *meta*-CH), 7.59 (1 H, t, ^3J(H,H) = 7.4, aromatic *para*-CH) and 7.75 (2 H, d,

^3J(H,H) = 7.7, aromatic *ortho*-CH). ^{11}B NMR (CD_3COCD_3): δ -15.8 (2 B, s, BI), -6.8 [large broad shoulders at -8.7 and -9.7] (8 B, br m). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ 62.0 ($C_{cluster}$-H), 78.4 ($C_{cluster}$-Ph), 128.6, 130.3, 131.5 and 132.0 (Ph). FTIR (KBr), ν (cm^{-1}): 3055 (w, aromatic CH), 3036 (w, aromatic CH), 3026 (s, $C_{cluster}$-H), 2653 (w, BH), 2635 (w, BH) and 2608 (s, BH). MALDI-TOF MS: *m/z* 723 (M – H^+, 29%) and 586 ($[M – BI]^-$, 100).

Spectroscopic data for **4**: The resulting solid was recrystallized from 1:1 ethylacetate/hexane mixture to yield pure compound **4**. ^{1}H NMR (CD_3COCD_3): δ 2.24 (6 H, s, CH_3). $^1H\{^{11}B\}$ NMR (CD_3COCD_3): 2.24 (6 H, s, CH_3), 3.17 (4 H, br s, BH), 3.25 (2 H, br s, BH). ^{11}B NMR (CD_3COCD_3): δ -17.1 (2 B, s, BI), -8.5 (2 B, s, BI), -5.7 [broad shoulder at -6.7] (6 B, br m, BH). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ 22.7 (CH_3), 76.3 ($C_{cluster}$-Me). FTIR (KBr), ν (cm^{-1}): 2962 (w, CH_3), 2931 (w, CH_3), 2646 (w, BH) and 2608 (s, BH). ESI MS: *m/z* 698.8 (M + Na^+, 100%).

Spectroscopic data for **5**: The resulting solid was recrystallized from 1:1 ethylacetate/hexane mixture to yield pure compound **5**. ^{1}H NMR (CD_3COCD_3): δ 7.34 (2 H, br t, aromatic *meta*-CH), 7.46 (1 H, t, ^3J(H,H) = 7.4, aromatic *para*-CH) and 7.71 (2 H, d, ^3J(H,H) = 7.7, aromatic *ortho*-CH). $^1H\{^{11}B\}$ NMR (CD_3COCD_3): δ 3.41 (4 H, br s, BH), 4.38 (2 H, br s, BH), 7.34 (2 H, br t, aromatic *meta*-CH), 7.46 (1 H, t, ^3J(H,H) = 7.4, aromatic *para*-CH) and 7.71 (2 H, d, ^3J(H,H) = 7.7, aromatic *ortho*-CH). ^{11}B NMR (CD_3COCD_3): δ -17.2 (2 B, s, BI), -9.5 (2 B, d, ^1J(B,H) = 185, BH), -5.8 (6 B, br m, 4 x BH and 2 x BI). $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ 87.6 ($C_{cluster}$-Ph), 130.1, 131.9 and 132.8 (Ph). FTIR (KBr), ν (cm^{-1}): 3101 (w, aromatic CH), 3055 (w, aromatic CH), 2662 (w, BH) and 2608 (s, BH). ESI MS: *m/z* 822.8 (M + Na^+, 100%).

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[1] T. L. Heying, J. W. Ager Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, J. W. Szymanski, *Inorg. Chem.*, 1963, **2**, 1089.

[2] M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, M. S. Cohen, *Inorg. Chem.*, 1963, **2**, 1111.