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Experimental Section

Elemental analyses were performed using a Carlo Erba EA1108 microanalyser. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. ^{1}H and $^{1}H\{^{11}B\}$ NMR (300.13 MHz), $^{13}C\{^{1}H\}$ NMR (75.47 MHz) and ^{11}B 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 NMR spectra were referenced to external $BF_3{\leftarrow}OEt_2$ and those for ^{1}H, $^{1}H\{^{11}B\}$ and $^{13}C\{^{1}H\}$ 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. The mass spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF-MS [N_2 laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)].

3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ (**3**), 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2$ (**4**), 3,4,5,7,8,9,10,11,12-I_9-1,2-*closo*-$C_2B_{10}H_3$ (**1**) and 4,5,7,8,9,10,11,12-I_8-1,2-*closo*-$C_2B_{10}H_4$ were synthesized according to the literature.[1] 1,2-*closo*-$C_2B_{10}H_{10}$ was supplied by Katchem Ltd. (Prague) and used as received.

Synthesis of $[HN(CH_3)_3]_2$[1,2,3,4,5,6,9,10,11-I_9-7,8-*nido*-$C_2B_9H_2$], alternatively $[HN(CH_3)_3]_2$[7,8-H_2-7,8-*nido*-$C_2B_9I_9$], $[HN(CH_3)_3]_2$[2].

To a solution of KOH (100mg, 1.78 mmol) in degassed EtOH (50 mL) 3,4,5,6,7,8,9,10,11,12-I_{10}-1,2-*closo*-$C_2B_{10}H_2$ (500 mg, 0.35 mmol) was added. The solution was refluxed for 3 h. After cooled to room temperature, the solvent was eliminated and the solid was dissolved in 20 mL of water. The solution was neutralized with HCl 1M. Afterwards, a $[HNMe_3]Cl$ water solution was added dropwise to precipitate the compound. The white solid was rinsed with water and diethyl ether obtaining $[HN(CH_3)_3]_2$[*nido*-1a] (415 mg, yield 86 %). Crystals were successfully

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isolated in crystalline form suitable for X-ray diffraction from acetone solution. Elemental analysis calcd. (%) for $C_8B_9I_9H_{22}N_2$ (1385.72): C 6.93, H 1.60; found C 6.89, H 1.65. ^{1}H NMR (CD_3COCD_3): δ= 3.18 (s, $[HN(CH_3)_3]$). $^{13}C\{^1H\}$ NMR: δ= 45.4 (s, $[HN(CH_3)_3]$), 40.4 (m, $C_{cluster}$). ^{11}B NMR: δ= -15.9 (s, 2B), -19.3 (s, 3B), -24.9 (s, 2B), -26.7 (s, 1B), -38.9 (s, 1B). MALDI-TOF-MS: *m/z* =1266.8 (M+1), 1139.9 (M-I+1), 1013.9(M-2I+1).

Synthesis of $[HN(CH_3)_3]_2$[7,8-H_2-7,8-*nido*-$C_2B_9I_9$] ($[HN(CH_3)_3]_2$[2]) and $[HN(CH_3)_3]_2$[3,7,8-H_3-7,8-*nido*-$C_2B_9I_8$] ($[HN(CH_3)_3]_2$[3]).

In an analogous manner, from 3,4,5,7,8,9,10,11,12-I_9-1,2-*closo*-$C_2B_{10}H_3$ (500 mg, 0.39 mmol) was added to a solution of KOH (110 mg, 1.95 mmol) in degassed EtOH (50 mL). The solution was refluxed for 3 h. After, it was cooled to room temperature, the solvent was eliminates and the solid residue was dissolved in 20 mL of water. The solution was neutralized with HCl 1M. Afterwards, $[HNMe_3]Cl$ in water was added dropwise to the solution to precipitate the compound. The white solid was rinsed with water and diethyl ether obtaining a (1:1) mixture of ($[HN(CH_3)_3]_2$[**2**]. and $[HN(CH_3)_3]_2$[**3**]). After recrystallization with acetone $[HN(CH_3)_3]_2$[3,7,8-H_3-7,8-*nido*-$C_2B_9I_8$], ($[HN(CH_3)_3]_2$[**3**]) was isolated. ^{1}H NMR: CD_3COCD_3**,** δ= 3.22 (s, 9H; $[HN(CH_3)_3]$), 1.95 (br s, 2H, $C_{cluster}$-H). $^1H\{^{11}B\}$ NMR: CD_3COCD_3**,** δ= 3.22 (s, 9H; $[HN(CH_3)_3]$), 3.00 (br t, J(H,H)= 6.4, 1H, B(3)-H), 1.95 (d, J(H,H)= 6.4, 2H, $C_{cluster}$-H). $^{13}C\{^1H\}$ NMR: δ= 45.4 (s, $[HN(CH_3)_3]$), 41.3 (m, $C_{cluster}$). ^{11}B NMR: δ= -16.1 (s, 2B), -19.1 (s, 4B), -27.0 (s, 2B), -41.0 (s, 1B). MALDI-TOF-MS: *m/z* =1140.7 (M+1), 1013.7 (M-I+1).

Synthesis of $[HN(CH_3)_3]$[1,2,4,5,6,9,10,11-I_8-7,8-*nido*-$C_2B_9H_3$], alternatively $[HN(CH_3)_3]_2$[3,7,8-H_3-7,8-*nido*-$C_2B_9I_8$] ($[HN(CH_3)_3]_2$[3])..

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In an analogous manner, from 4,5,7,8,9,10,11,12-I_8-1,2-*closo*-$C_2B_{10}H_4$ (449 mg, 0.39 mmol) was added to a solution of KOH (110 mg, 1.95 mmol) in degassed EtOH (50 mL). The solution was refluxed for 5 h. After, it was cooled to room temperature, the solvent was eliminates and the solid residue was dissolved in 20 mL of water. The solution was neutralized with HCl 1M. Afterwards, $[HNMe_3]Cl$ in water was added dropwise to the solution to precipitate the compound. ^1H NMR: CD_3COCD_3, δ= 3.22 (s, 9H; $[HN(CH_3)_3]$), 1.95 (br s, 2H, $C_{cluster}$-H). $^1H\{^{11}B\}$ NMR: CD_3COCD_3, δ= 3.22 (s, 9H; $[HN(CH_3)_3]$), 3.00 (br t, J(H,H)= 6.4, 1H, B(3)-H), 1.95 (d, J(H,H)= 6.4, 2H, $C_{cluster}$-H). $^{13}C\{^1H\}$ NMR: δ= 45.4 (s, $[HN(CH_3)_3]$), 41.3 (m, $C_{cluster}$). ^{11}B NMR: δ= -16.1 (s, 2B), -19.1 (s, 4B), -27.0 (s, 2B), -41.0 (s, 1B). MALDI-TOF-MS: *m/z* =1140.7 (M+1), 1013.7 (M-I+1).

Synthesis of $[HNMe_3][3\text{-}I\text{-}7,8\text{-}nido\text{-}C_2B_9H_{11}]$.

In an analogous manner, from 3,6-I_2-1,2-*closo*-$C_2B_{10}H_{10}$ (154 mg, 0.39 mmol) was added to a solution of KOH (110 mg, 1.95 mmol) in degassed EtOH (50 mL). The solution was refluxed for 3 h. After, it was cooled to room temperature, the solvent was eliminates and the solid residue was dissolved in 20 mL of water. The solution was neutralized with HCl 1M. Afterwards, $[HNMe_3]Cl$ in water was added dropwise to the solution to precipitate the compound. $^1H\{^{11}B\}$ NMR: CD_3COCD_3, δ= 3.22 (s, 9H, $[HN(CH_3)_3]$), 3.00-0.00 (br m, 8H, B-$H_{terminal}$), 1.95 (br s, 2H, $C_{cluster}$-H), -2.67 (br m, 1H, B-H_{bridge}). $^{13}C\{^1H\}$ NMR: CD_3COCD_3, δ= 48.0 ($C_{cluster}$), 45.2 (s, $HN(CH_3)_3$). ^{11}B NMR: CD_3COCD_3, δ= -9.3 (d, ^1J(B,H)= 139, 2B, B(9,11)), -15.5 (d, ^1J(B,H)= 136, 2B, B(5,6)), -19.8 (d, ^1J(B,H)= 153, 2B, B(2,4)), -28.8 (s, 1B, B(3)), -34.1 (dd, $^1J(B,H_{terminal})$= 138, $^1J(B,H_{bridge})$= 55, 1B, B(10)), -35.8 (d, ^1J(B,H)= 154, 1B, B(1)). MALDI-TOF-MS: *m/z* = 260.39 (M+1), 127.05 (M-I+1).

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[1] (a) Teixidor, F.; Barberà, G.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Inorg.* Chem., 2006, **45**, 3496. (b) Barbera, G.; Teixidor, F.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Eur. J. Inorg. Chem.*, 2003, 1511.(c) R. R Srivastava, D. K. Hamlin, D. S. Wilbur. *J. Org. Chem*. 1996, **61**, 9041.