Electronic Supplementary Information

Synthesis of the Fluorohydridoborate Anions $[BHF_3]^-$ and $[1\text{-}HF_2B\text{-}9,12\text{-}X_2\text{-}\textit{closo}\text{-}1,2\text{-}C_2B_{10}H_9]^-$ (X = H, I): Deboronation of 1,2- and 1,7-dicarba-*closo*-dodecaboranes with anhydrous $[Me_4N]F$

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Experimental Section

Reactions involving air-sensitive compounds were performed either in 100 or 250 mL round bottom flasks or in 20 or 60 mL glass tubes equipped with valves with PTFE stems (Young, London) under argon using standard Schlenk line techniques. ^{1}H, ^{11}B, ^{19}F and ^{13}C NMR spectra were recorded at 25 °C either in CD_3CN on a Bruker Avance HD III 300, a Bruker Avance DPX 400 or a Bruker Avance 500 spectrometer. The NMR signals were referenced against TMS (^{1}H and ^{13}C), $BF_3{\cdot}OEt_2$ in $CDCl_3$ with $\Xi(^{11}B)$ = 32.083974 MHz and $CFCl_3$ with $\Xi(^{19}F)$ = 94.094011% as external standards.[1] ^{1}H and ^{13}C chemical shifts were calibrated against the residual solvent signal and the solvent signal, respectively ($\delta(^{1}H)$: CD_2HCN 1.94 ppm; $\delta(^{13}C)$: CD_3CN 118.26 and 1.32 ppm.[2] The assignment of the ^{11}B and ^{1}H signals is aided by $^{11}B\{^{1}H\}$-$^{1}H\{^{11}B\}$ 2D,[3] $^{11}B\{^{1}H\}$-$^{1}H\{^{11}B\}$ COSY[4] and $^{1}H\{^{11}B_{selective}\}$ experiments. ^{1}H-^{13}C HMBC and HSQC as well as $^{13}C\{^{11}B,^{1}H\}$ triple resonance experiments were performed to support the interpretation of the ^{13}C NMR spectroscopic data. The NMR spectroscopic data of the $[Me_4N]^+$ cations are omitted for clarity where applicable. IR spectra were measured in the attenuated total reflection (ATR) mode in the region of 4000–530 cm^{-1} with an apodized resolution of 1 cm^{-1} with a Bruker Alpha spectrometer equipped with a Bruker diamond single reflection ATR system. Raman spectra were measured using the 1064 nm excitation line of a Nd/YAG laser on crystalline samples contained in melting point capillaries in the region of 3500–80 cm^{-1} at room temperature on a Bruker IFS-120 spectrometer with an apodized resolution of 1 cm^{-1}. ESI mass spectra were acquired on a microTOF (Bruker Daltonics). Elemental analysis (C, H, N) were performed either with a Euro EA3000 instrument (HEKA-Tech, Germany).

Chemicals

All standard chemicals were obtained from commercial sources und used without further purification. Solvents were dried according to standard protocols[5] and stored in flasks equipped with valves with PTFE stems (Young, London) under an argon atmosphere. 1,2- and 1,7-dicarba-*closo*-dodecaborane and decaborane(14) were purchased from Katchem spol. s r. o. (Praha, Czech Republic). 1-R-*closo*-1,2-$C_2B_{10}H_{11}$ (R = Ph,[6] Me[7]), 9,12-I_2-*closo*-$C_2B_{10}H_{10}$[8] and $[Me_4N]F$[9] were synthesized according to known procedures.

Quantum Chemical Calculations

Density functional calculations (DFT)[10] were carried out using Becke's three-parameter hybrid functional and the Lee-Yang-Parr correlation functional (B3LYP)[11] using the Gaussian09 program suite (Table S1).[12] Geometries were optimized and energies were calculated with the 6-311++G(d,p) (SDD for iodine) basis sets. Diffuse functions were incorporated because improved energies are obtained for anions.[13] Structures represent true minima with no imaginary frequency on the respective hypersurface.

DFT-GIAO[14] NMR shielding constants $\sigma(^{11}B)$, $\sigma(^{13}C)$, $\sigma(^{15}N)$ and $\sigma(^{1}H)$ were calculated at the B3LYP/6-311++G(2d,p) level of theory using the geometries computed as described. The ^{11}B, ^{19}F and ^{1}H NMR shielding constants were calibrated to the respective chemical shift scale $\delta(^{11}B)$, $\delta(^{19}F)$ and $\delta(^{1}H)$ using predictions on diborane(6), $CFCl_3$ and Me_4Si with chemical shifts of 16.6 ppm for B_2H_6,[15] and 0 ppm for Me_4Si and $CFCl_3$.[16] Spin-spin coupling constants were calculated at the same level as the NMR shielding constants. Calculations of all NMR parameters were performed with the Gaussian09 program suite.[12]

Table S1. Thermochemical data calculated at the B3LYP/6-311++G(d,p) level of theory.

Anion	Symmetry	*H* (gas phase) [au]	*G* (gas phase) [au]	*H* (CH_3CN) [au]	*G* (CH_3CN) [au]
$[BH_4]^-$	T_d	-27.238209	-27.259706	-27.336957	-27.358429
$[BH_3F]^-$ (**1**)	C_{3v}	-126.577557	-126.603216	-126.674204	-126.699868
$[BH_2F_2]^-$	C_{2v}	-225.932952	-225.961465	-226.027959	-226.056487
$[BHF_3]^-$	C_{3v}	-325.297875	-325.328113	-325.391410	-325.422686
$[BF_4]^-$	T_d	-424.660619	-424.691356	-424.752170	-424.782901
$[1\text{-}HF_2B\text{-}closo\text{-}1,2\text{-}C_2B_{10}H_{11}]^-$ (**2**)	C_1	-556.792145	-556.840213	-556.859609	-556.907949
$[1\text{-}H_3B\text{-}closo\text{-}1,2\text{-}C_2B_{10}H_{11}]^-$	C_1	-358.098289	-358.142211	-358.165365	-358.209761
$[1\text{-}F_3B\text{-}closo\text{-}1,2\text{-}C_2B_{10}H_{11}]^-$	C_1	-656.149833	-656.199704	-656.218082	-656.267901

[b] The geometries were reoptimized using the C-PCM solvation model. MeCN: $\varepsilon = 35.688$.

$$[BH_2F_2]^- \xrightarrow[\Delta G(\text{gas phase}) = -36.9\ \text{kJ mol}^{-1}]{\Delta H(\text{gas phase}) = -43.2\ \text{kJ mol}^{-1}} 0.5\,[BF_4]^- + 0.5\,[BH_4]^- \qquad \Delta H(CH_3CN) = -43.6\ \text{kJ mol}^{-1},\ \Delta G(CH_3CN) = -37.2\ \text{kJ mol}^{-1}$$

$$[BH_3F]^- \xrightarrow[\Delta G(\text{gas phase}) = -37.8\ \text{kJ mol}^{-1}]{\Delta H(\text{gas phase}) = -42.6\ \text{kJ mol}^{-1}} 0.25\,[BF_4]^- + 0.75\,[BH_4]^- \qquad \Delta H(CH_3CN) = -43.5\ \text{kJ mol}^{-1},\ \Delta G(CH_3CN) = -38.5\ \text{kJ mol}^{-1}$$

Scheme S1 Calculated thermodynamic data for the dismutation reactions of $[BH_2F_2]^-$ and $[BHF_3]^-$ giving $[BH_4]^-$ and $[BF_4]^-$.

Crystal Structure Determination of $[Me_4N]$**1**, $[Me_4N]$**2** and $[Me_4N]$**3**

Colourless crystals of $[Me_4N][BHF_3]$ ($[Me_4N]$**1**), $[Me_4N][1\text{-}HF_2B\text{-}closo\text{-}1,2\text{-}C_2B_{10}H_{11}]$ ($[Me_4N]$**2**) and $[Me_4N][1\text{-}HF_2B\text{-}9,12\text{-}I_2\text{-}closo\text{-}1,2\text{-}C_2B_{10}H_9]$ ($[Me_4N]$**3**) were obtained from solutions in acetone by slow uptake of pentane vapour. Crystals were investigated with a Bruker X8-Apex II diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) in all cases. All structures were solved either by direct (SHELXS)[17] or by intrinsic phasing methods (SHELXT).[17a,18] Refinements are based on full-matrix least-squares calculations on F^2.[17a,19] $[Me_4N]$**1** and $[Me_4N]$**2** were refined as twins ($[Me_4N]$**1**: –1 0 0 0 0 1 0 –1 0; BASF 0.44; $[Me_4N]$**3**: –1 0 0 0 1 0 0 0 1; BASF 0.42). The anion $[BHF_3]^-$ in the crystal of $[Me_4N]$**1** is

located on a mirror plane. In the crystals of [Me_4N]**2** and [Me_4N]**3** two independent formula units are present. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were located from electron density difference maps. In the final steps of the refinement idealized bond lengths and angles were introduced. Both crystallographically independent anions in the crystal of [Me_4N]**2** and one of the independent anions in the crystal of [Me_4N]**3** reveal partially disordered BHF_2 groups. The H atom of the $[BHF_3]^-$ anion in [Me_4N]**1** and the H atom of the non-disordered crystallographically independent anion [1-HF_2B-9,12-I_2-*closo*-1,2-$C_2B_{10}H_9$]$^-$ in [Me_4N]**3** were refined without any restraints. Calculations were performed with the ShelXle graphical interface.[20] Molecular structure diagrams were drawn with the program Diamond 4.2.2.[21] Experimental details, crystal data, and the CCDC numbers are collected in Table S2. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Selected Crystal Data and Details of the Refinement of the Crystal Structures of [Me_4N][BHF_3] ([Me_4N]**1**), [Me_4N][1-HF_2B-*closo*-1,2-$C_2B_{10}H_{11}$] ([Me_4N]**2**) and [Me_4N][1-HF_2B-9,12-I_2-*closo*-1,2-$C_2B_{10}H_9$] ([Me_4N]**3**).

	[Me_4N]**1**	[Me_4N]**2**	[Me_4N]**3**
Formula	$C_4H_{13}BF_3N$	$C_6H_{24}B_{11}F_2N$	$C_6H_{22}B_{11}F_2I_2N$
M_W	142.96	267.17	518.95
T (K)	100	100	100
Crystal system	orthorhombic	monoclinic	triclinic
Space group	*Pbcm*	$P2_1$	*P*-1
a (Å)	5.5770(13)	10.452(3)	12.4538(7)
b (Å)	11.436(3)	13.828(3)	13.5015(8)
c (Å)	11.447(3)	10.773(2)	13.5440(8)
α			60.7590(10)
β		90.102(7)	72.300(2)
γ			86.331(2)
volume (Å^3)	730.1(3)	1557.1(6)	1883.28(19)
Z	4	4	4
d(calcd) (Mg m^{-3})	1.301	1.140	1.830
μ (mm^{-1})	0.129	0.072	3.343
F(000)	304	560	976
No. of collected reflections	5381	36594	19760
No. of unique reflections	883	6631	7950
R(int)	0.1394	0.0477	0.0202
No. of parameters / restraints	48 / 0	384 / 1	419 / 0
$R1$ ($I > 2\sigma(I)$)	0.0365	0.0688	0.0246
$wR2$ (all)	0.0954	0.1965	0.0555
GOF on F^2	1.074	1.097	1.058
Largest diff. peak / hole / e Å^{-3}	0.256 / –0.211	0.551 / –0.310	1.054 / –0.759
CCDC no.	1505729	1505730	1505731

Syntheses

Deboronation of *closo*-1,7-$C_2B_{10}H_{12}$ using [Me_4N]F. [Me_4N][BHF_3] ([Me_4N]**1**) and [Et_4N][*nido*-7,9-$C_2B_9H_{12}$]**.** A 100 mL glass tube equipped with a magnetic stirring bar was charged with 1,7-dicarba-*closo*-dodecaborane (0.430 g, 2.98 mmol), 4 equivalents of anhydrous [Me_4N]F (1.11 g, 11.93 mmol), and dry THF (50 mL) under argon. The suspension was stirred at 70 °C overnight. The reaction was complete when no 1,7-dicarba-*closo*-dodecaborane was detected by ^{11}B NMR spectroscopy in the reaction mixture. [Me_4N]**1** and [Me_4N]$_2$[*nido*-7,9-$C_2B_9H_{11}$] are both insoluble in THF. The colorless solid materials were isolated by filtration through a fine glass frit under argon and dried in a vacuum. The [Me_4N]**1** was extracted from the solid material with CH_3CN (3 x 50 mL) and the [Me_4N]$_2$[*nido*-7,9-$C_2B_9H_{11}$] remained as a solid. This solid was taken up into ice cold water and the residual CH_3CN was removed using a rotary evaporator. In some cases, a solid separated during removal of the CH_3CN that was redissolved by addition of a few drops of acetone to prevent co-precipitation of [Me_4N][*nido*-7,9-$C_2B_9H_{12}$] during the next step. An aqueous solution of [Et_4N]Cl (6.6 g, 23.8 mmol) was added and a colourless precipitate formed that was isolated by filtration and subsequently dried in a vacuum. Yield of [Et_4N][*nido*-7,9-$C_2B_9H_{12}$]: 0.472 g (1.79 mmol, 61%). The volume of the solution of [Me_4N][BHF_3] in acetonitrile was reduced to 75 mL and hexane (200 mL) was added. Colorless [Me_4N]**1** precipitated. The product was collected by filtration and dried in a vacuum overnight and contained 3% [Me_4N][BH_2F_2] as side product as assessed by NMR spectroscopy. Yield of [Me_4N]**1**: 0.090 g (0.63 mmol, 21%).

[Me_4N]**1**:

^{1}H NMR (500.13 MHz, CD_3CN): δ = 3.11 (t, 12-H, $^2J(^{14}N,^1H)$ = 0.6 Hz, $[N(CH_3)_4]^+$), 2.94 (qq, 1-H, $^1J(^{11}B,^1H)$ = 136.5 Hz, $^2J(^{19}F,^1H)$ = 92.7 Hz) ppm.

^{1}H{^{11}B} NMR (500.13 MHz, CD_3CN): δ = 3.11 (t, 12-H, $^2J(^{14}N,^1H)$ = 0.59 Hz, $[N(CH_3)_4]^+$, 2.94 (q, 1-H, $^2J(^{19}F,^1H)$ = 92.7 Hz) ppm.

^{1}H{^{19}F} NMR (400.13 MHz, CD_3CN): δ = 3.11 (t, 12-H, $^2J(^{14}N,^1H)$ = 0.59 Hz, $[N(CH_3)_4]^+$, 2.94 (q, 1-H, $^1J(^{11}B,^1H)$ = 136.5 Hz) ppm.

^{11}B NMR (160.46 MHz, CD_3CN): δ = 1.2 (dq, 1-B, $^1J(^{11}B,^1H)$ = 136.5 Hz, $^1J(^{19}F,^{11}B)$ = 69.3 Hz) ppm.

^{11}B{^{1}H} NMR (160.46 MHz, CD_3CN): δ = 1.2 (q, 1-B, $^1J(^{19}F,^{11}B)$ = 69.9 Hz) ppm.

^{19}F NMR (376.49 MHz, CD_3CN): δ = –136.89 (qd, 3-F, $^1J(^{19}F,^{11}B)$ = 69.9 Hz, $^2J(^{19}F,^1H)$ = 92.7 Hz) ppm.

^{19}F{^{1}H} NMR (376.75 MHz, CD_3CN): δ = –136.89 (q, 3-F, $^1J(^{19}F,^{11}B)$ = 69.9 Hz) ppm.

^{19}F{^{11}B} NMR (470.59 MHz, CD_3CN): δ = –136.89 (d, 3-F, $^2J(^{19}F,^1H)$ = 92.7 Hz) ppm.

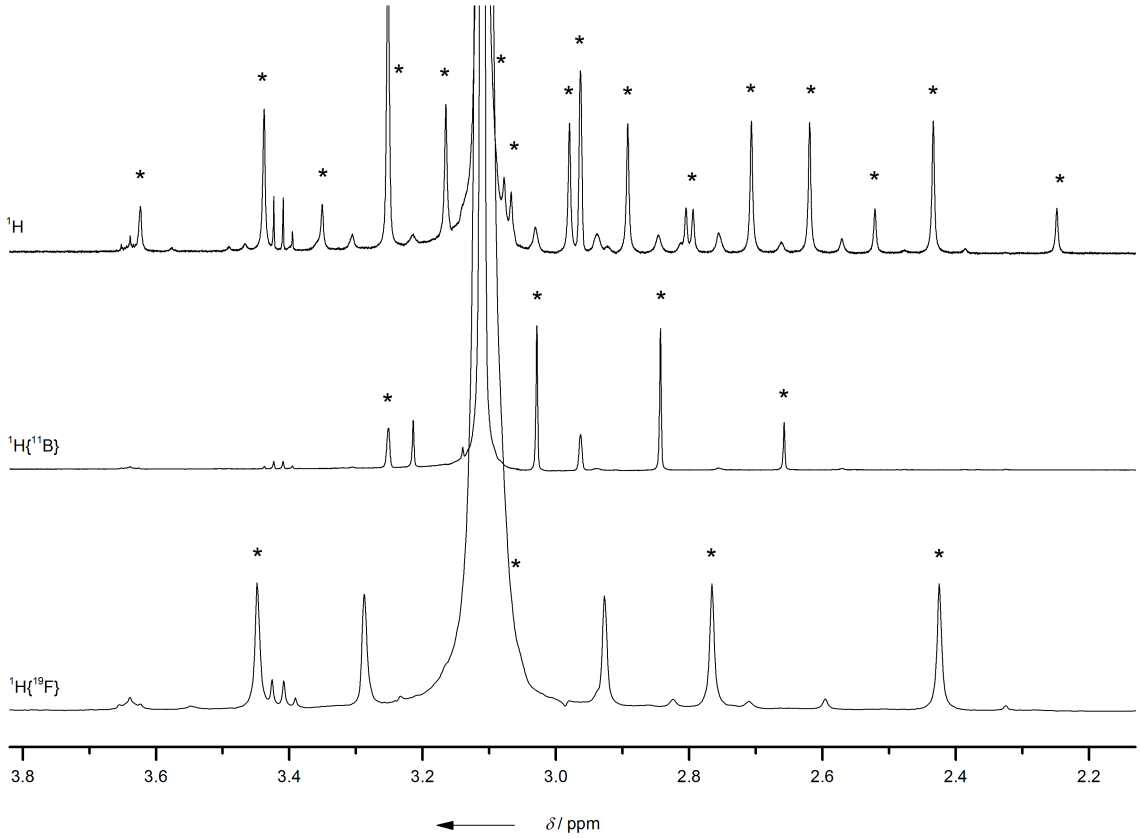

Figure S1. ^{1}H, ^{1}H{^{11}B} and ^{1}H{^{19}F} NMR spectra of [Me_4N]**1**.

IR (ATR): $\tilde{\nu}$ = 2375 (w, B−H), 2208 (w, B−H) cm^{-1}.

Raman: $\tilde{\nu}$ = 2375 (w, B−H), 2213 (w, B−H), 950 (m, sh, B−F) cm^{-1}.

ESI-MS *m/z* (isotopic abundance >10) calcd. for 1 $(HBF_3)^-$: 68 (25), 69 (100); found 68 (25), 69 (100).

Elemental analysis calcd (%) for $C_4H_{13}BF_3N$ (142.96): C 33.61, H 9.17, N 9.80; found C 34.04, H 9.87, N 10.12.

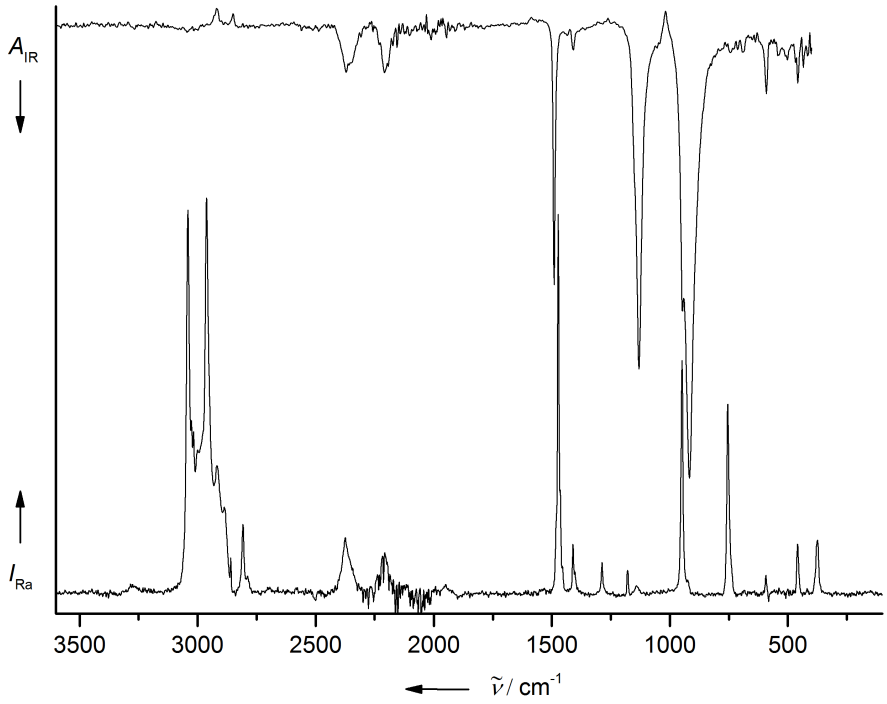

Figure S2. IR and Raman spectrum of $[Me_4N]$**1**.

$[Me_4N][BH_2F_2]$:

^{1}H NMR (500.13 MHz, CD_3CN): δ = 3.17 (qt, 2-H, $^{1}J(^{11}B,^{1}H)$ = 108.9 Hz, $^{2}J(^{19}F,^{1}H)$ = 55.3 Hz), 3.11 (t, 12-H, $^{2}J(^{14}N,^{1}H)$ = 0.59 Hz, $[N(CH_3)_4]^{+}$) ppm.

^{1}H{^{11}B} NMR (500.13 MHz, CD_3CN): δ = 3.17 (t, 2-H, $^{2}J(^{19}F,^{1}H)$ = 55.3 Hz), 3.11 (t, 1-H, $^{2}J(^{14}N,^{1}H)$ = 0.59 Hz, $[N(CH_3)_4]^{+}$) ppm.

^{11}B NMR (160.46 MHz, CD_3CN): δ = 5.1 (tt, 1-B, $^{1}J(^{11}B,^{1}H)$ = 108.9 Hz, $^{1}J(^{19}F,^{11}B)$ = 91.6 Hz) ppm.

^{11}B{^{1}H} NMR (160.46 MHz, CD_3CN): δ = 5.1 (t, 1-B, $^{1}J(^{19}F,^{11}B)$ = 91.6 Hz) ppm.

^{19}F NMR (376.49 MHz, CD_3CN): δ = –164.43 (qt, 2-F, $^{1}J(^{19}F,^{11}B)$ = 91.6 Hz, $^{2}J(^{19}F,^{1}H)$ = 55.3 Hz) ppm.

^{19}F{^{1}H} NMR (376.75 MHz, CD_3CN): δ = –164.43 (q, 2-F, $^{1}J(^{19}F,^{11}B)$ = 108.9 Hz) ppm.

^{19}F{^{11}B} NMR (470.59 MHz, CD_3CN): δ = –164.43 (t, 2-F, $^{2}J(^{19}F,^{1}H)$ = 55.3 Hz) ppm.

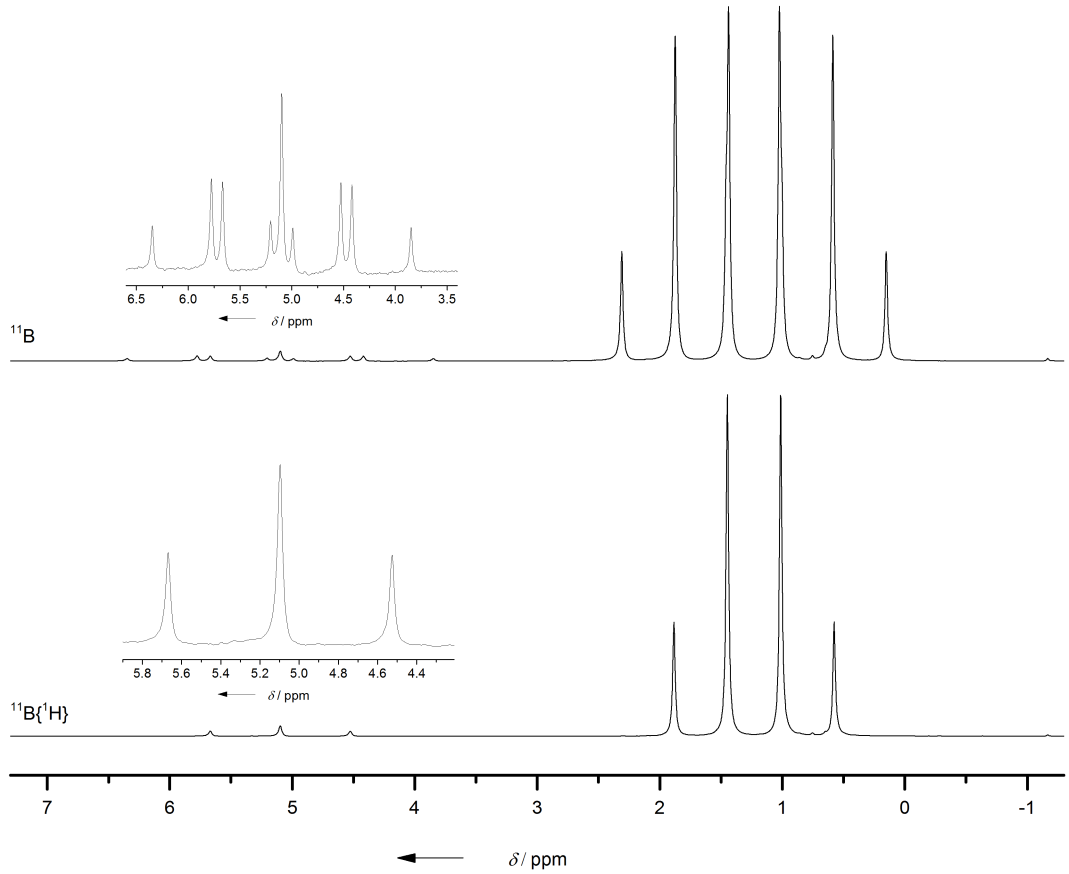

Figure S3. ^{11}B and $^{11}B\{^1H\}$ NMR spectra of $[Me_4N]$**1** with the side product $[Me_4N][BH_2F_2]$.

$[Et_4N][nido\text{-}7,9\text{-}C_2B_9H_{12}]$:

$^1H\{^{11}B\}$ NMR (500.13 MHz, CD_3CN): δ = 3.16 (q, 8-H, $^3J(^1H,^1H)$ = 7.4 Hz, $[NEt_4]^+$), 2.20 (s, 2-H, B2+5H), 2.01 (s, 1-H, B8H), 1.42 (dd, 2-H, $^2J(^1H,^1H_\mu)$ = 12.2 Hz, $^3J(^1H,^1H)$ = 3.5 Hz, B10+11H), 1.21 (tt, 12-H, $^3J(^{14}N,^1H)$ = 1.9 Hz, $^3J(^1H,^1H)$ = 7.4 Hz, $[NEt_4]^+$), 1.17 (s, 2-H, C7+9H), 1.08 (s, 2-H, B3+4H), 0.65 (s, 1-H, B1), 0.08 (s, 1-H, B6), –2.33 (t, 1-H, $^2J(^1H,^1H_\mu)$ = 12.2 Hz, BH_μ) ppm.

^{11}B NMR (160.46 MHz, CD_3CN): –4.7 (d, 2-B, $^1J(^{11}B,^1H)$ = 147.7 Hz, B2+5), –5.9 (d, 1-B, $^1J(^{11}B,^1H)$ = 134.4 Hz, B8), –21.6 (d, 2-B, $^1J(^{11}B,^1H)$ = 157.5 Hz, B3+4), –22.9 (dd, 2-B, $^1J(^{11}B,^1H)$ = 128.3 Hz, $^1J(^{11}B,^1H_\mu)$ = 49.6 Hz, B10+11), –34.4 (d, 1-B, $^1J(^{11}B,^1H)$ = overlapped, B1), –35.5 (d, 1-B, $^1J(^{11}B,^1H)$ = overlapped, B6) ppm.

$^{11}B\{^1H\}$ NMR (160.46 MHz, CD_3CN): δ = –4.7 (s, 2-B, B2+5), –5.9 (s, 1-B, B8), –21.6 (s, 2-B, B3+4), –22.9 (s, 2-B, B10+11), –34.4 (s, 1-B, B1), –35.5 (s, 1-B, B6) ppm.

$^{13}C\{^1H\}$ NMR (125.76 MHz, CD_3CN): δ = 53.08 (t, 4-C, $^1J(^{14}N,\ ^{13}C)$ = 3.1 Hz, $[Et_4N]^+$), 32.69 (brs, 2-C, C7+9), 7.68 (s, 4-C, $[Et_4N]^+$) ppm.

[Me_4N][1-HF_2B-*closo*-1,2-$C_2B_{10}H_{11}$] ([Me_4N]2). A 250 mL glass tube was charged with 1,2-dicarba-*closo*-dodecaborane (1 g, 6.9 mmol), 4 equivalents of anhydrous [Me_4N]F (5.18 g, 27.6 mmol), and dry THF (50 mL). The suspension was stirred at room temperature for 24 h. The resulting suspension was transferred by cannula onto a fine glass frit under argon. The filtrate contained the [Me_4N]**2** whereas [Me_4N]**1** and [Me_4N]$_2$[*nido*-7,8-$C_2B_9H_{11}$] are insoluble in THF. The solid material was worked up as described for the synthesis of [Me_4N]**1** and [Et_4N][*nido*-7,9-$C_2B_9H_{12}$] from 1,7-dicarba-*closo*-dodecaborane. Yield [Me_4N]**1**: 0.193 g (1.35 mmol, 20%); [Et_4N][*nido*-7,8-$C_2B_9H_{12}$]: 1.06 g (4.02 mmol, 58%). The solution of [Me_4N]**2** in THF was concentrated to approximately 10 mL using a rotary evaporator. Hexane (300 mL) was added to the solution. During the addition, a colourless precipitate formed that was isolated by filtration through a glass frit in air. Yield [Me_4N]**2**: 0.203 g (0.77 mmol, 22%).

[Me_4N]**2**:

^{1}H NMR (500.13 MHz, CD_3CN): δ = 3.65 (s, 1-C, C2H), 3.07 (t, 12-H, $^2J(^{14}N,^1H)$ = 0.6 Hz, $[N(CH_3)_4]^+$), 2.83 (qt, 1-H, $^1J(^{11}B,^1H)$ = 125.2 Hz, $^2J(^{19}F,^1H)$ = 63.2 Hz), 2.13 (s, 2-H, B3+6H or B7+11H), 2.00 (s, 8-H, B4+5/8+10/9/12/3+6 or 7+11H) ppm.

^{1}H{^{11}B} NMR (500.13 MHz, CD_3CN): δ = 3.65 (s, 1-C, C2H), 3.07 (t, 12-H, $^2J(^{14}N,^1H)$ = 0.6 Hz, $[N(CH_3)_4]^+$), 2.83 (t, 1-H, $^2J(^{19}F,^1H)$ = 63.2 Hz), 2.13 (s, 2-H, B3+6H or B7+11H), 2.00 (s, 8-H, B4+5/8+10/9/12/3+6 or 7+11H) ppm.

^{1}H{^{19}F} NMR (400.13 MHz, CD_3CN): δ = 3.65 (s, 1-C, C2H), 3.07 (t, 12-H, $^2J(^{14}N,^1H)$ = 0.6 Hz, $[N(CH_3)_4]^+$), 2.83 (q, 1-H, $^1J(^{11}B,^1H)$ = 125.2 Hz), 2.13 (s, 2-H, B3+6H or B7+11H), 2.00 (s, 8-H, B4+5/8+10/9/12/3+6 or 7+11H) ppm.

^{11}B NMR (160.46 MHz, CD_3CN) [DFT calculations]: δ = 3.0 [1.5] (dt, 1-B, $^1J(^{19}F,^{11}B)$ = 77.2 Hz, $^1J(^{11}B,^1H)$ = 126.2 Hz, HBF_2-Cluster), –3.6 [–5.8] (d, 1-B, $^1J(^{11}B,^1H)$ = 148.6 Hz, B9), –5.0 [–7.4] (d, 1-B, $^1J(^{11}B,^1H)$ = 143.9 Hz, B12), -9.2 [–11.1] (d, 2-B, $^1J(^{11}B,^1H)$ = 145.4 Hz, B8+10), –11.6 [–13.2] (d, 2-B, $^1J(^{11}B,^1H)$ = 158.6 Hz, B4+5), –13.4 [–15.8; –16.8] (d, 4-B, $^1J(^{11}B,^1H)$ = 148.6 Hz, B3+6/7+11) ppm.

^{11}B{^{1}H} NMR (160.46 MHz, CD_3CN) [DFT calculations]: δ = 3.0 [1.5] (t, 1-B, $^1J(^{19}F,^{11}B)$ = 77.2 Hz, HBF_2-Cluster), –3.6 [–5.8] (s, 1-B, B9), –5.0 [–7.4] (s, 1-B, B12), –9.2 [–11.1] (s, 2-B, B8+10), –11.6 [–13.2] (s, 2-B, B4+5), –13.4 [–15.8; –16.8] (s, 4-B, B3+6/7+11) ppm.

^{11}B{^{19}F} NMR (160.46 MHz, CD_3CN): 3.0 (d, 1-B, $^1J(^{11}B,^1H)$ = 126.2 Hz, HBF_2-Cluster), –3.6 (d, 1-B, $^1J(^{11}B,^1H)$ = 148.6 Hz, B9), –5.0 (d, 1-B, $^1J(^{11}B,^1H)$ = 143.9 Hz, B12), –9.2 (d, 2-B, $^1J(^{11}B,^1H)$ = 145.4 Hz, B8+10), –11.6 (d, 2-B, $^1J(^{11}B,^1H)$ = 158.6 Hz, B4+5), –13.4 (d, 4-B, $^1J(^{11}B,^1H)$ = 148.6 Hz, B3+6/7+11) ppm.

^{13}C{^{1}H} NMR (125.76 MHz, CD_3CN): δ = 81.4 (q, 1-C, $^1J(^{13}C,^{11}B)$ = 52.8 Hz, C1BHF_2), 60.48 (s, 1-C, C2), 56.18 (t, 4-C, $^2J(^{14}N,^{13}C)$ = 4.2 Hz, $[Me_4N]^+$) ppm.

^{13}C{^{1}H,^{11}B} NMR (75.48 MHz, CD_3CN): δ = 81.40 (t, 1-C, $^2J(^{19}F,^{13}C)$ = 37.1 Hz, C1BHF_2), 60.5 (t, 1-C, $^3J(^{19}F,^{13}C)$ = 2.77 Hz, C2), 56.18 (t, 4-C, $^2J(^{14}N,^{13}C)$ = 4.2 Hz, $[Me_4N]^+$) ppm.

^{19}F NMR (376.49 MHz, CD_3CN): δ = –154.87 (qd, 2-F, $^{1}J(^{19}F,^{11}B)$ = 76.7 Hz, $^{2}J(^{19}F,^{1}H)$ = 63.3 Hz) ppm.

$^{19}F\{^{1}H\}$ NMR (75.48 MHz, CD_3CN): δ = –154.87 (q, 2-F, $^{1}J(^{19}F,^{11}B)$ = 76.7 Hz) ppm.

$^{19}F\{^{11}B\}$ NMR (376.49 MHz, CD_3CN): δ = –154.87 (d, 2-F, $^{2}J(^{19}F,^{1}H)$ = 63.3 Hz) ppm.

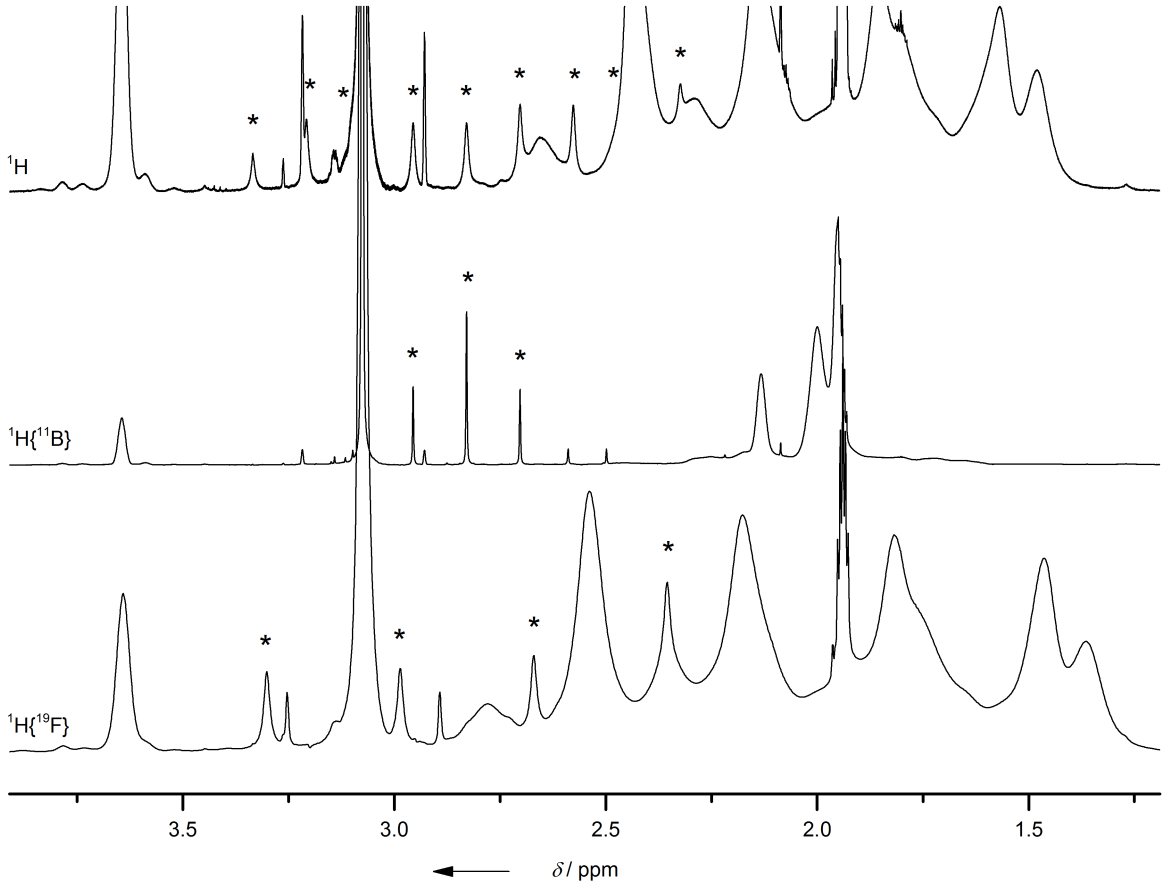

Figure S4. ^{1}H, $^{1}H\{^{11}B\}$ and $^{1}H\{^{19}F\}$ NMR spectra of $[Me_4N][1\text{-}HF_2B\text{-}closo\text{-}1,2\text{-}C_2B_{10}H_{11}]$ ($[Me_4N]$**2**); the signal of the BHF_2 unit is marked with asterisks.

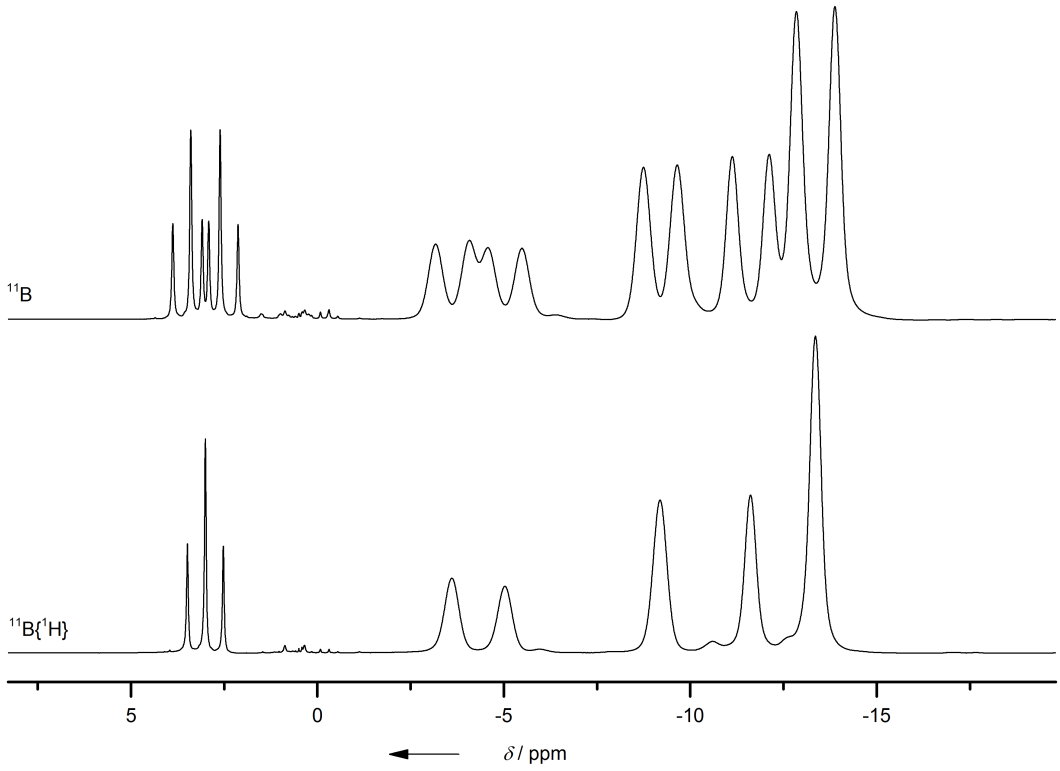

Figure S5. ^{11}B and ^{11}B{^{1}H} NMR spectra of [Me_4N][1-HF_2B-*closo*-1,2-$C_2B_{10}H_{11}$] ([Me_4N]**2**).

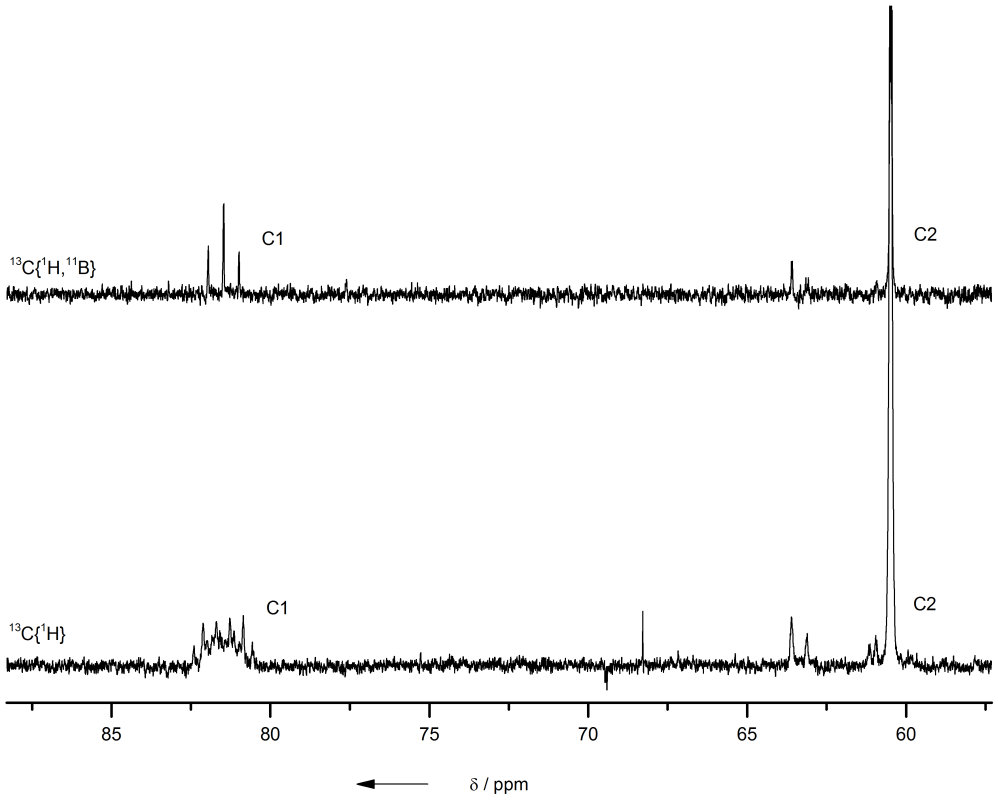

Figure S6. ^{13}C{^{1}H,^{11}B} and ^{13}C{^{1}H} NMR spectra of [Me_4N][1-HF_2B-*closo*-1,2-$C_2B_{10}H_{11}$] ([Me_4N]**2**).

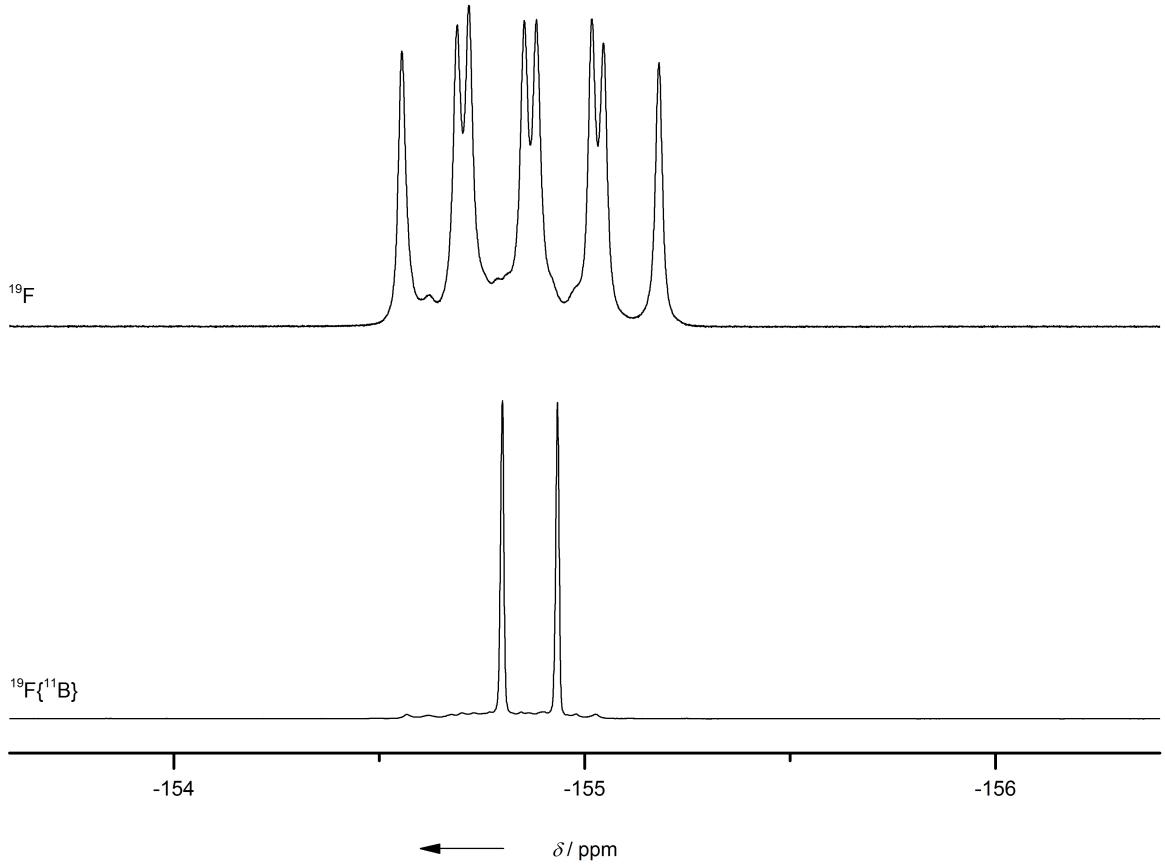

Figure S7. ^{19}F and $^{19}F\{^{11}B\}$ NMR spectra of $[Me_4N][1\text{-}HF_2B\text{-}closo\text{-}1,2\text{-}C_2B_{10}H_{11}]$ ($[Me_4N]$**2**).

IR (ATR): $\tilde{\nu}$ = 3081 (w, $C_{Cluster}$−H), 2633-2516 (m, B−H), 2341 (w, B−H), 2185 (w, B−H) cm^{-1}.
Raman: $\tilde{\nu}$ = 2683-2527 (s, B−H), 2342 (w, B−H), 2158 (w, B−H), 956 (m, sh, B−F) cm^{-1}.
ESI-MS *m/z* (isotopic abundance >10) calcd. for 2 $(C_2H_{12}B_{11}F_2)^-$: 190 (13), 191 (37), 192 (74), 193 (100), 194 (81), 195 (31); found 190 (13), 191 (37), 192 (73), 193 (100), 194 (83), 195 (31).
Elemental analysis calcd (%) for $C_6H_{24}B_{11}F_2N$ (267.18): C 26.97, H 9.05, N 5.24; found C 27.80, H 9.26, N 6.22.

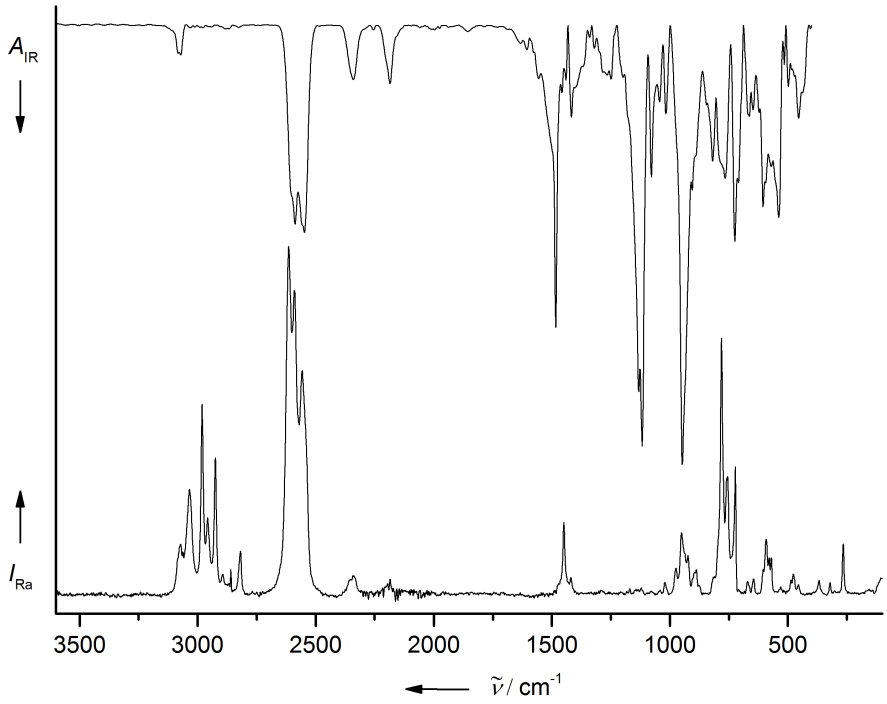

Figure S8. IR and Raman spectrum of $[Me_4N][1\text{-}HF_2B\text{-}closo\text{-}1,2\text{-}C_2B_{10}H_{11}]$ ($[Me_4N]$**2**).

$[Et_4N][nido\text{-}7,8\text{-}C_2B_9H_{12}]$:

$^1H\{^{11}B\}$ NMR (500.13 MHz, CD_3CN): δ = 3.16 (q, 8-H, $^3J(^1H,^1H)$ = 7.4 Hz, $[NEt_4]^+$), 1.86 (s, 2-H, B9+11H), 1.69 (s, 1-H, B3H), 1.21 (tt, 12-H, $^3J(^{14}N,^1H)$ = 1.9 Hz, $^3J(^1H,^1H)$ = 7.4 Hz, $[NEt_4]^+$), 1.14 (s, 4-H, B5+6/2+4H), 0.45 (s, 1-H, B1H), -0.01 (s, 1-H, B10H), –2.96 (m, 1-H, BH_μ) ppm.

^{11}B NMR (160.46 MHz, CD_3CN): δ = –11.1 (d, 2-B, $^1J(^{11}B,^1H)$ = 135.1 Hz, B9+11), –17.1 (d, 2-B, $^1J(^{11}B, ^1H)$ = overlapped, B5+6), –17.7 (d, 1-B, $^1J(^{11}B,^1H)$ = overlapped, B3), –22.3 (d, 2-B, $^1J(^{11}B, ^1H)$ = 149.2 Hz, B2+4), –33.5 (dd, 1-B, $^1J(^{11}B, ^1H)$ = 132.9 Hz, $^1J(^{11}B,^1H_\mu)$ = 35.3 Hz, B10), –38.1 (d, 1-B, $^1J(^{11}B,^1H)$ = 136.5 Hz, B1) ppm.

$^{13}C\{^1H\}$ NMR (125.76 MHz, CD_3CN): δ = 53.07 (t, 4-C, $^1J(^{14}N,^{13}C)$ = 3.1 Hz, $[Et_4N]^+$), 43.10 (brq, 2-C, $^1J(^{13}C,^{11}B)$ = 35.0 Hz, C7+8), 7.68 (s, 4-C, $[Et_4N]^+$) ppm.

$[Me_4N][1\text{-}HF_2B\text{-}9,12\text{-}I_2\text{-}closo\text{-}1,2\text{-}C_2B_{10}H_9]$ ($[Me_4N]$3). The reaction was performed as outlined for the preparation of $[Me_4N]$**2**. 9,12-diiodo-1,2-dicarba-*closo*-dodecaborane (0.42 g, 1.06 mmol), $[Me_4N]F$ (0.396 g, 4.24 mmol), and THF (20 mL) were employed as starting materials. Yield of $[Me_4N]$**3**: 0.066 g (0.13 mmol, 24%); $[Me_4N]$**1**: 0.030 g (0.21 mmol, 20%); and $[Et_4N][5,6\text{-}I_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_{10}]$: 0.306 g (0.594 mmol, 56%).

[Me_4N]**3**:

^{1}H NMR (500.13 MHz, CD_3CN): δ = 4.12 (s, 1-C, C2H), 3.07 (t, 12-H, $^{2}J(^{14}N,^{1}H)$ = 0.6 Hz, $[N(CH_3)_4]^+$), 2.79 (qt, 1-H, $^{1}J(^{11}B,^{1}H)$ = 128.8 Hz, $^{2}J(^{19}F,^{1}H)$ = 63.1 Hz), 2.66 (s, 2-H, B8+10H), 2.50 (s, 4-H, B4+5/7+11H), 2.26 (s, 2-H, B3+6H) ppm.

^{1}H{^{11}B} NMR (500.13 MHz, CD_3CN): δ = 4.12 (s, 1-C, C2H), 3.07 (t, 12-H, $^{2}J(^{14}N,^{1}H)$ = 0.6 Hz, $[N(CH_3)_4]^+$), 2.79 (t, 1-H, $^{2}J(^{19}F,^{1}H)$ = 63.1 Hz), 2.66 (s, 2-H, B8+10H), 2.50 (s, 4-H, B4+5/7+11H), 2.26 (s, 2-H, B3+6H) ppm.

^{1}H{^{19}F} NMR (400.13 MHz, CD_3CN): δ = 4.12 (s, 1-C, C2H), 3.07 (t, 12-H, $^{2}J(^{14}N,^{1}H)$ = 0.6 Hz, $[N(CH_3)_4]^+$), 2.79 (q, 1-H, $^{1}J(^{11}B,^{1}H)$ = 128.8 Hz), 2.66 (s, 2-H, B8+10H), 2.50 (s, 4-H, B4+5/7+11H), 2.26 (s, 2-H, B3+6H) ppm.

^{11}B NMR (160.46 MHz, CD_3CN) [DFT calculations]: δ = 3.1 [–0.4] (dt, 1-B, $^{1}J(^{19}F,^{11}B)$ = 76.9 Hz, $^{1}J(^{11}B,^{1}H)$ = 128.8 Hz, HBF_2-Cluster), –6.0 [–8.2] (d, 2-B, $^{1}J(^{11}B,^{1}H)$ = 153.7 Hz, B8+10), –11.1 [–16.4] (d, 2-B, $^{1}J(^{11}B,^{1}H)$ = 168.2Hz, B7+11), –12.7 [–12.8] (d, 2-B, $^{1}J(^{11}B,^{1}H)$ = overlapped, B4+5), –13.4 [–17.6] (d, 2-B, $^{1}J(^{11}B,^{1}H)$ = overlapped, B3+6), –14.8 [+2.2] (s, 1-B, B12), –16.7 [+4.5] (s, 1-B, B9) ppm.

^{11}B{^{1}H} NMR (160.46 MHz, CD_3CN): δ = 3.1 [–0.4] (t, 1-B, $^{1}J(^{19}F,^{11}B)$ = 76.9 Hz, HBF_2-Cluster), –6.0 [–8.2] (s, 2-B, B8+10), –11.1 [– 16.4] (s, 2-B, B7+11), –12.7 [–12.8] (s, 2-B, B4+5), –13.4 [–17.6] (s, 2-B, B3+6), –14.8 [+2.2] (s, 1-B, B12), –16.7 [+4.5] (s, 1-B, B9) ppm.

^{11}B{^{19}F} NMR (160.46 MHz, CD_3CN): δ = 3.1 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = 128.8 Hz, HBF_2-Cluster), –6.0 (d, 2-B, $^{1}J(^{11}B,^{1}H)$ = 153.7 Hz, B8+10), –11.1 (d, 2-B, $^{1}J(^{11}B,^{1}H)$ = 168.2 Hz, B7+11), –12.7 (d, 2-B, $^{1}J(^{11}B,^{1}H)$ = overlapped, B4+5), –13.4 (d, 2-B, $^{1}J(^{11}B,^{1}H)$ = overlapped, B3+6), –14.8 (s, 1-B, B12), –16.7 (s, 1-B, B9) ppm.

^{13}C{^{1}H} NMR (125.76 MHz, CD_3CN): δ = 76.97 (q, 1-C, $^{1}J(^{13}C,^{11}B)$ = 50.5 Hz, C1BHF_2), 57.9 (s, 1-C, C2), 56.20 (t, 4-C, $^{2}J(^{14}N,^{13}C)$ = 3.6 Hz, $[Me_4N]^+$) ppm.

^{13}C{^{1}H,^{11}B} NMR (75.48 MHz, CD_3CN): δ = 77.10 (t, 1-C, $^{2}J(^{19}F,^{13}C)$ = 37.9 Hz, C1BHF_2), 57.95 (s, 1-C, C2), 56.20 (t, 4-C, $^{2}J(^{14}N,^{13}C)$ = 3.6 Hz, $[Me_4N]^+$) ppm.

^{19}F NMR (376.49 MHz, CD_3CN): δ = –154.83 (qd, 2-F, $^{1}J(^{19}F,^{11}B)$ = 76.9 Hz, $^{2}J(^{19}F,^{1}H)$ = 63.1 Hz) ppm.

^{19}F{^{1}H} NMR (376.75 MHz, CD_3CN): δ = –154.83 (q, 2-F, $^{1}J(^{19}F,^{11}B)$ = 76.9 Hz) ppm.

^{19}F{^{11}B} NMR (376.49 MHz, CD_3CN): δ = –154.83 (d, 2-F, $^{2}J(^{19}F,^{1}H)$ = 63.1 Hz) ppm.

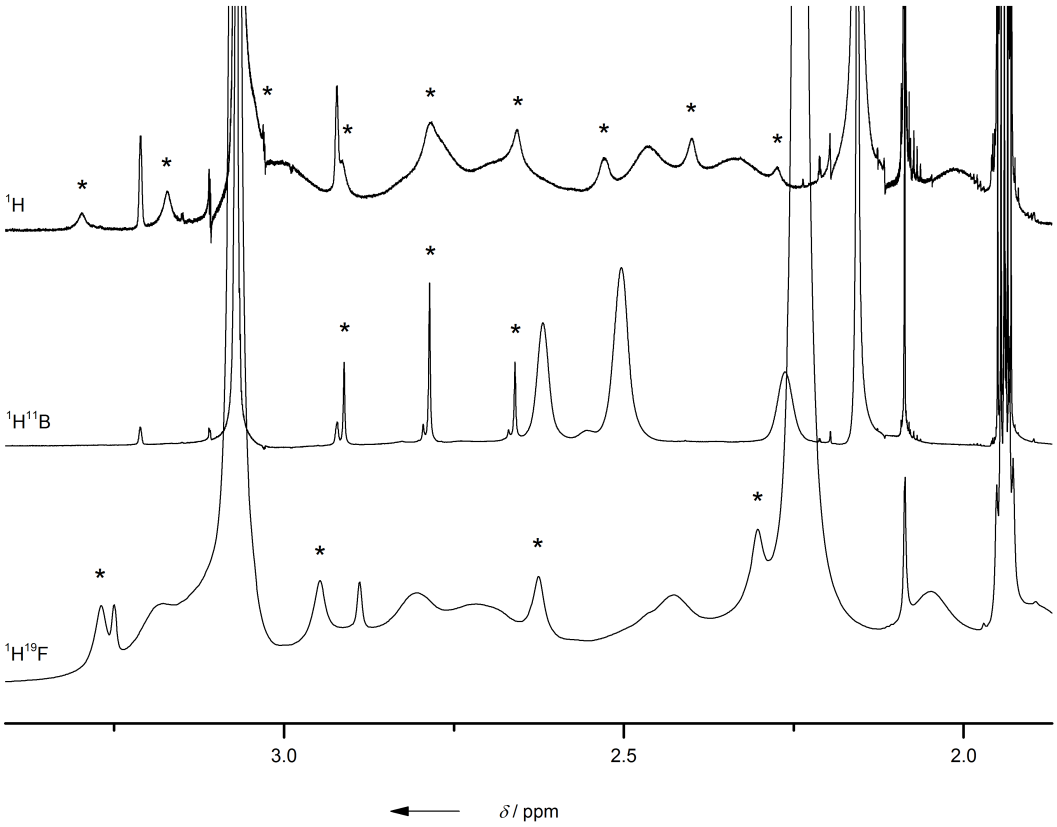

Figure S9. ^{1}H, ^{1}H{^{11}B} and ^{1}H{^{19}F} NMR spectra of [Me_4N][1-HF_2B-9,12-I_2-*closo*-1,2-$C_2B_{10}H_9$] ([Me_4N]**3**); the signal of the BHF_2 unit is marked with asterisks.

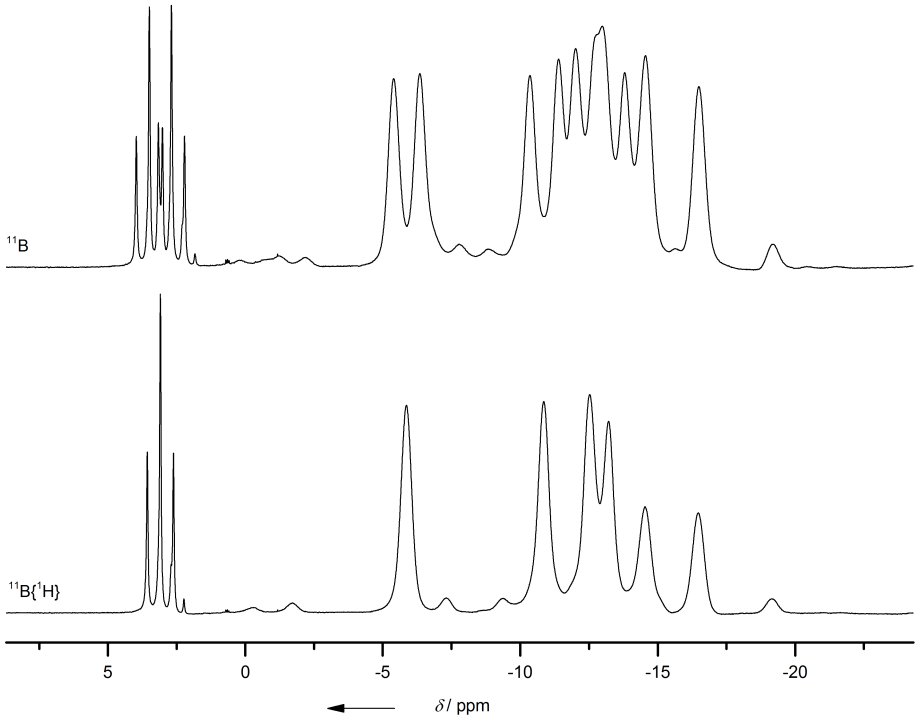

Figure S10. ^{11}B and ^{11}B{^{1}H} NMR spectra of [Me_4N][1-HF_2B-9,12-I_2-*closo*-1,2-$C_2B_{10}H_9$] ([Me_4N]**3**).

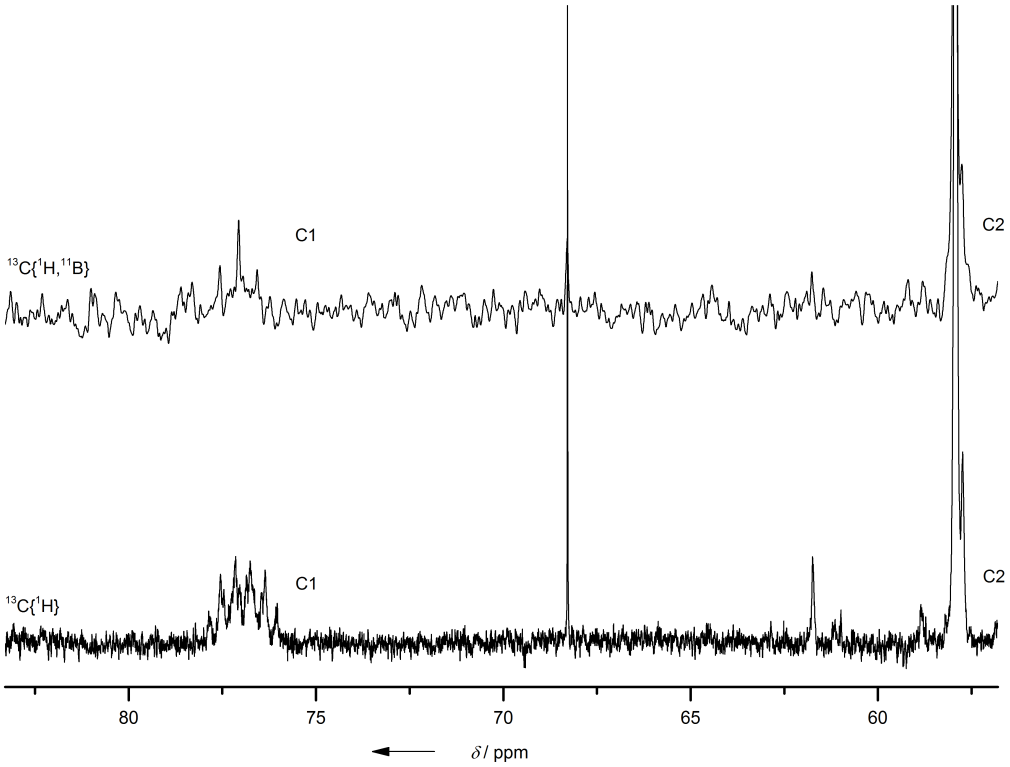

Figure S11. $^{13}C\{^{1}H,^{11}B\}$ and $^{13}C\{^{1}H\}$ NMR spectra of $[Me_4N][1\text{-}HF_2B\text{-}9,12\text{-}I_2\text{-}\textit{closo}\text{-}1,2\text{-}C_2B_{10}H_9]$ ($[Me_4N]$**3**).

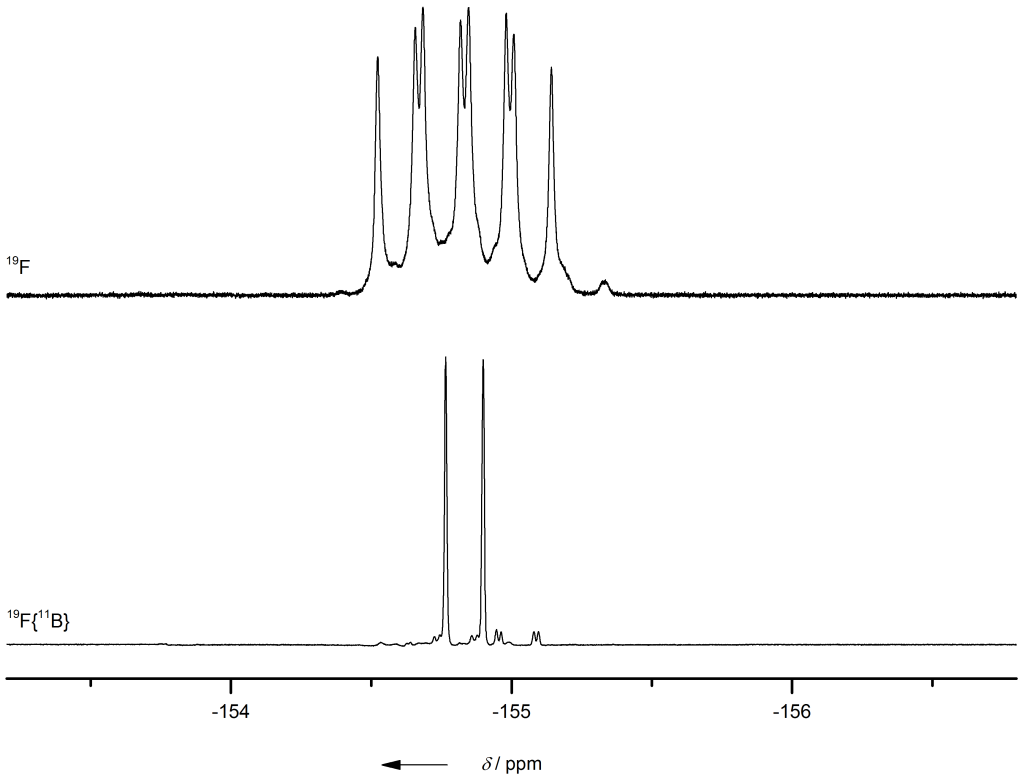

Figure S12. ^{19}F and $^{19}F\{^{1}H\}$ NMR spectra of $[Me_4N][1\text{-}HF_2B\text{-}9,12\text{-}I_2\text{-}\textit{closo}\text{-}1,2\text{-}C_2B_{10}H_9]$ ($[Me_4N]$**3**).

IR (ATR): $\tilde{\nu}$ = 3077 (w, $C_{Cluster}$−H), 3072 (vw, $C_{Cluster}$−H), 2644-2505 (m, B−H), 2340 (w, B−H), 2187 (w, B−H) cm^{-1}.

Raman: $\tilde{\nu}$ = 2675-2552 (s, B−H), 2350 (w, B−H), 2191 (w, B−H), 951 (m, sh, B−F), 220 (m, sh, B−I) cm^{-1}.

ESI-MS *m/z* (isotopic abundance >10) calcd. for 3 $(C_2H_{10}B_{11}F_2I_2)^-$: 442 (13), 443 (37), 444 (74), 445 (100), 446 (74), 447 (31); found 442 (13), 443 (38), 444 (73), 445 (100), 446 (80), 447 (29).

Elemental analysis calcd (%) for $C_6H_{22}B_{11}F_2I_2N$ (518.97): C 13.89, H 4.27, N 2.70; found C 14.04, H 4.35, N 3.23.

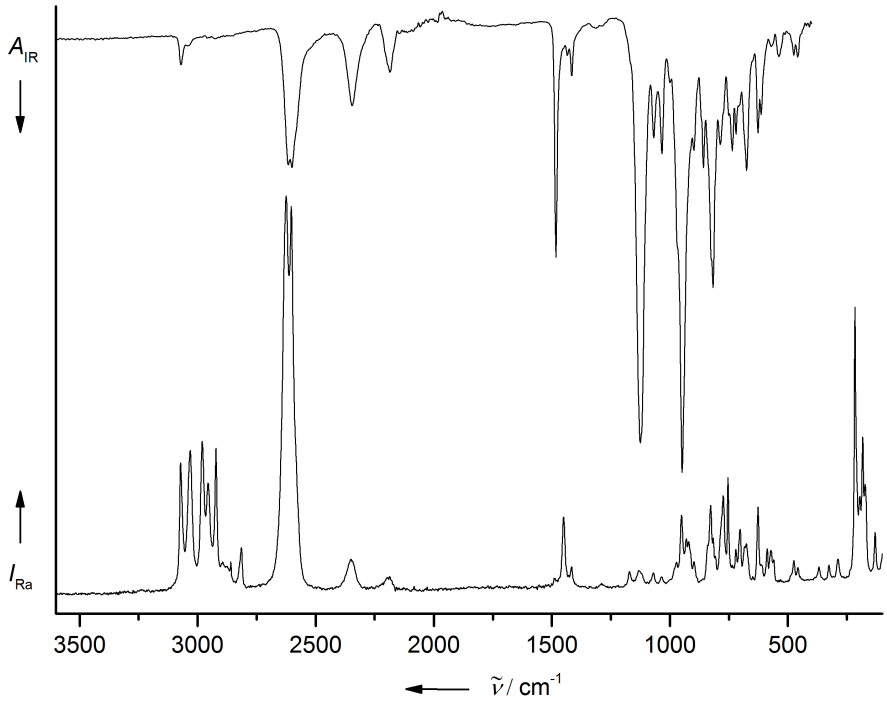

Figure S13. IR and Raman spectrum of $[Me_4N][1\text{-}HF_2B\text{-}9,12\text{-}I_2\text{-}closo\text{-}1,2\text{-}C_2B_{10}H_9]$ ($[Me_4N]$**3**).

$[Et_4N][5,6\text{-}I_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_{10}]$:

$^1H\{^{11}B\}$ NMR (500.13 MHz, CD_3CN): δ = 3.16 (q, 8-H, $^3J(^1H,^1H)$ = 7.4 Hz, $[NEt_4]^+$), 2.37 (s, 2-H, B9+11H), 2.18 (s, 2-H, C7+8H), 1.80 (s, 2-H, B2+4H**)**, 1.76 (s, 1-H, B3H), 1.22 (tt, 12-H, $^3J(^{14}N,^1H)$ = 1.9 Hz, $^3J(^1H,^1H)$ = 7.4 Hz, $[NEt_4]^+$), 0.96 (s, 1-H, B1H), 0.94 (d, 1-H**,** $^3J(^1H,^1H)$ = 7.4 Hz, B2H), 0.71 (s, 1 H, B10H), –2.13 (t, 1 H, $^2J(^1H,^1H_\mu)$ = 9.9 Hz, BH_μ) ppm.

^{11}B NMR (160.46 MHz, CD_3CN): δ = –9.4 (d, 2-B, $^1J(^{11}B,\ ^1H)$ = 141.9 Hz, B9+11), –16.9 (d, 1-B, $^1J(^{11}B,\ ^1H)$ = 167.3 Hz), –21.0 (d, 2-B, $^1J(^{11}B,^1H)$ = 157.1 Hz, B2+4), –24.3 (s, 2-B, B5+6), –27.9 (dd,

1-B, $^{1}J(^{11}B,^{1}H)$ = 132.4 Hz, $^{1}J(^{11}B,^{1}H_{\mu})$ = 39.3 Hz, B10), –33.7 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = 147.1 Hz, B1) ppm.

$^{13}C\{^{1}H\}$ NMR (125.76 MHz, CD_3CN): δ = 53.1 (t, 4-C, $^{1}J(^{14}N,^{13}C)$ = 3 Hz, $[NEt_4]^+$), 42.7 (brq, 2-C, $^{1}J(^{13}C,^{11}B)$ = 34.6 Hz C7+8,), 7.6 (s, 4-C, $[NEt_4]^+$) ppm.

$[Et_4N][7\text{-Me-}nido\text{-}7,8\text{-}C_2B_9H_{11}]$. A 100 mL glass tube equipped with a magnetic stirring bar was charged with 1-Me-1,2-dicarba-*closo*-dodecaborane (0.250 g, 1.58 mmol) 4 equivalents of anhydrous $[Me_4N]F$ (0.590 g, 6.32 mmol) and dry THF (15 mL) under an argon atmosphere. The suspension was stirred at room temperature for 24 h. The reaction mixture was taken up into ice-cold water and the residual THF was removed using a rotary evaporator. A solid separated during removal of the THF that was redissolved by addition of a few drops of acetone to prevent co-precipitation of $[Me_4N]^+$ salts during the next step. An aqueous solution of $[Et_4N]Cl$ (2.61 g, 15.80 mmol) was added to the clear solution and then a colourless precipitate was formed. The solid was isolated by filtration through a fine glass frit and dried in a vacuum overnight. Yield of 0.259 g $[Et_4N][7\text{-Me-}nido\text{-}7,8\text{-}C_2B_9H_{11}]$ (0.93 mmol, 59.1%).

$[Et_4N][7\text{-Me-}nido\text{-}7,8\text{-}C_2B_9H_{11}]$:

$^{1}H\{^{11}B\}$ NMR (500.13 MHz, CD_3CN): δ = 3.14 (q, 8-H, $^{3}J(^{1}H,^{1}H)$ = 7.3 Hz, $[Et_4N]^+$), 1.66 (s, 1-H, C8H), 1.88 (s, 1-H, B9H), 1.79 (s, 1-H, B11H), 1.61 (s, 1-H, B3H), 1.36 (s, 3-H, $C7CH_3$), 1.33 (s, 1-H, B2H or B6H), 1.21 (tt, 12-H, $^{3}J(^{14}N,^{1}H)$ = 1.9 Hz, $^{3}J(^{1}H,^{1}H)$ = 7.4 Hz, $[NEt_4]^+$), 1.11 (s, 2-H, B4H+B2H or B6H), 1.03 (s, 1-H, B5H), 0.43 (s, 1-H, B1H), -0.04 (s, 1-H, B10H), –2.72 (m, 1-H, BH_{μ}) ppm.

^{11}B NMR (160.46 MHz, CD_3CN): δ = –10.2 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = overlapped, B11), –11.1 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = overlapped, B9), –13.5 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = 156.1 Hz, B3), –18.0 (d, 2-B, $^{1}J(^{11}B,^{1}H)$ = overlapped, B2+B6), –18.9 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = overlapped, B5), –22.5 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = 147.5 Hz), –33.8 (dd, 1-B, $^{1}J(^{11}B,^{1}H)$ = 128.4 Hz, $^{1}J(^{11}B,^{1}H_{\mu})$ = 39.7 Hz, B10), –37.1 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = 137.7 Hz, B1) ppm.

$^{13}C\{^{1}H\}$ NMR (125.76 MHz, CD_3CN): δ = 54.97 (brq, 1-C, $^{1}J(^{13}C,^{11}B)$ = 34.8 Hz, $C7CH_3$), 53.08 (t, 4-C, $^{1}J(^{14}N,^{13}C)$ = 3.1 Hz, $[Et_4N]^+$), 49.55 (brq, 1-C, $^{1}J(^{13}C,^{11}B)$ = 34.8 Hz, C8H), 25.48 (s, 1-C, $C7CH_3$) 7.69 (s, 4-C, $[Et_4N]^+$) ppm.

$[Et_4N][7\text{-Ph-}nido\text{-}7,8\text{-}C_2B_9H_{11}]$. The reaction was performed as outlined for the preparation of $[Et_4N]$**4**. 1-Ph-1,2-dicarba-*closo*-dodecaborane (0.300 g, 1.36 mmol), $[Me_4N]F$ (0.509 g, 5.45 mmol), $[Et_4N]Cl$ (2.25 g, 13.60 mmol) and THF (20 mL) were employed as starting materials. Yield of 0.254 g $[Et_4N][1\text{-Ph-}nido\text{-}7,8\text{-}C_2B_9H_{11}]$ (0.75 mmol, 55.0%).

$[Et_4N][1\text{-Ph-}nido\text{-}7,8\text{-}C_2B_9H_{11}]$:

$^{1}H\{^{11}B\}$ NMR (500.13 MHz, CD_3CN): δ = 7.21 (m, 2-H, PhH), 7.13 (m, 2-H, PhH), 7.04 (m, 1-H, PhH), 3.14 (q, 8-H, $^{3}J(^{1}H,^{1}H)$ = 7.3 Hz, $[Et_4N]^+$), 2.28 (s, 1-H, C8H), 2.07 (s, 2-H, B9+11H), 1.77 (s,

1-H, B3H), 1.72 (s, 1-H, B2H), 1.23 (s, 3-H, B4+5+6H), 1.19 (tt, 12-H, $^{3}J(^{14}N,^{1}H)$ = 1.9 Hz, $^{3}J(^{1}H,^{1}H)$ = 7.4 Hz, $[NEt_4]^+$), 0.65 (s, 1-H, B1H), 0.15 (s, 1-H, B10H), –2.46 (s, 1-H, BH_μ) ppm.
^{11}B NMR (160.46 MHz, CD_3CN): δ = –8.8 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = 138.6 Hz, B11), –10.4 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = 136.7 Hz, B9), –13.7 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = 159.4 Hz, B3), –16.9 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = overlapped, B5), –18.1 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = overlapped, B6), –19.8 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = 148.9 Hz, B2), –22.7 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = 150.7 Hz, B4), –32.9 (dd, 1-B, $^{1}J(^{11}B,^{1}H)$ = 133.4 Hz, $^{1}J(^{11}B,^{1}H_\mu)$ = 39.4 Hz, B10), –36.1 (d, 1-B, $^{1}J(^{11}B,^{1}H)$ = 142.2 Hz, B1) ppm.
$^{13}C\{^{1}H\}$ NMR (125.76 MHz, CD_3CN): δ = 146.7 (s, 1-C, C_{Ph}), 128.45 (s, 2-C, C_{Ph}), 127.57 (s, 2-C, C_{Ph}), 125.65 (s, 1-C, C_{Ph}), 63.17 (brq, 1 C, $^{1}J(^{13}C,^{11}B)$ = 34.2 Hz, C7Ph), 53.07 (t, 4-C, $^{1}J(^{14}N,^{13}C)$ = 3.1 Hz, $[Et_4N]^+$), 46.32 (brq, 1-C, $^{1}J(^{13}C,^{11}B)$ = 34.2 Hz, C8H), 7.68 (s, 4-C, $[Et_4N]^+$) ppm.

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