

SYNTHESIS AND REACTIONS OF 1,2-DICARBA-*closo*-DODECABORANE-1-YL TETRAHYDROBORATE(1-)

Jaromír PLEŠEK, Tomáš JELÍNEK, Stanislav HEŘMÁNEK and Bohumil ŠTÍBR

Institute of Inorganic Chemistry,

Czechoslovak Academy of Sciences, 250 68 Prague — Řež

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Preparation of the $[1\text{-H}_3\text{B-1,2-C}_2\text{B}_{10}\text{H}_{11}]^-$ anion in various ways is reported. The species is a substituted derivative of the $[\text{BH}_4]^-$ anion and can be employed for obtaining a family of the $1\text{-L-H}_2\text{B-1,2-C}_2\text{B}_{10}\text{H}_{11}$ ($\text{L} = (\text{CH}_3)_2\text{S}, \text{C}_5\text{H}_5\text{N}, (\text{CH}_3)_3\text{N},$ and $(\text{C}_2\text{H}_5)_3\text{N}$) base adducts. Constitution of all compounds isolated was established primarily on the basis of their ^1H , ^{11}B , and ^{13}C NMR spectra.

We have recently^{1,2} reported the reaction of triethylamine borane with compounds of the general formula $7\text{-L-7-CB}_{10}\text{H}_{12}$ ($\text{L} = \text{H}_3\text{N}, (\text{CH}_3)_3\text{N},$ and $(\text{CH}_3)_2\text{S}$). The reaction proceeded with the insertion of one more boron atom into the open pentagonal face of the monocarbollide cage to isolate a series of *closo*-1-L-1-CB₁₁H₁₁ species. We wish to report herein the results of an analogous insertion reaction with the isoelectronic $[7,8\text{-C}_2\text{B}_9\text{H}_{12}]^-$ dicarborane system along with some chemistry of the isolated products.

Prolonged heating of the $[7,8\text{-C}_2\text{B}_9\text{H}_{12}]^- \text{Cs}^+$ salt^{3,4} (*Ia*) with triethylamine borane at 200°C resulted in the consumption of two moles of the latter compound under the formation of a $[\text{C}_2\text{B}_{11}\text{H}_{14}]^- \text{Cs}^+$ salt (*Iia*) and two equivalents of hydrogen. The *Iia* salt is moderately soluble in ether and very soluble in water, tetrahydrofuran, acetone, and dimethyl sulphide. The water insoluble tetramethylammonium salt *Iib*, obtained by precipitation of aqueous *Iia* with tetramethylammonium chloride, is readily soluble in acetone and tetrahydrofuran and moderately soluble in ethanol.

^{11}B NMR spectra of *Iia* and *Iib* (Fig. 1) are analogous to that of $1\text{-CH}_3\text{-1,2-C}_2\text{B}_{10}\text{H}_{11}$ (Table I). The presence of an additional high-field BH_3 quartet and absence of a B singlet are unambiguously consistent with the proposed structure for compound *II* (Fig. 2). The observed antipodal effects⁵ of the BH_3 (-4.39 ppm) and CH_3 (-4.30 ppm) groups on the $\text{B}_{(12)}$ atom of the $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ cage are essentially identical, which is indicative of a similar hyperconjugation effect of both groups within the carborane system.

The ^1H NMR spectrum of *Iia* (Table II) clearly shows the presence of a broad quartet of the $1\text{-H}_3\text{B}$ group and a singlet due to the skeletal CH proton. In the ^1H

NMR spectrum of *Ib*, only the $[(\text{CH}_3)_4\text{N}]^+$ singlet can be reliably identified, other signals are superimposed. The ^{13}C NMR spectrum of *Ib*, however, clearly shows the desired CH skeletal doublet and a sharp quartet due to the $[(\text{CH}_3)_4\text{N}]^+$ carbons as well as a broader quartet. The third signal is evidently split due to the ^{13}C - ^{11}B coupling and can be assigned to the $\text{C}_{(1)}$ atom bearing the BH_3 group. The above data can be hardly interpreted otherwise than as those corresponding to the tetrahydroborate(1-) ion substituted by the 1-(1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$) group.

Chemical properties of anion *II* are also in agreement with the proposed constitution. Surprisingly, ^{11}B NMR measurements of the acetone solution of *II* indicated only a minimum change in one-week period, thus showing a distinct stability of *II* towards acetone. This decrease in reactivity, in comparison with the parent $[\text{BH}_4]^-$ anion, is likely a result of a strong electron withdrawing force of the 1-(1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$) substituent.

On acidification of *II*, three moles of hydrogen are evolved and 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ (*III*) can be almost quantitatively isolated from the resulting solution after heating

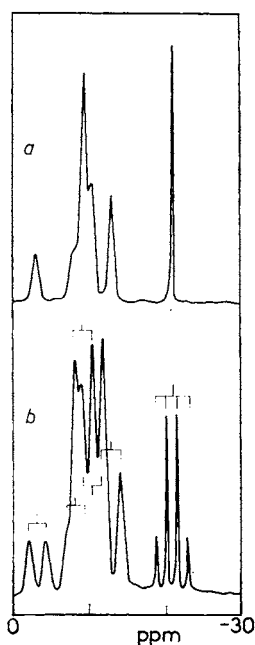


FIG. 1
 ^{11}B NMR spectrum of $[1\text{-H}_3\text{B-1,2-C}_2\text{B}_{10}\text{.H}_{11}]^-[(\text{CH}_3)_4\text{N}]^+$ in hexadeuterioacetone
a) ^1H decoupled *b*) undecoupled

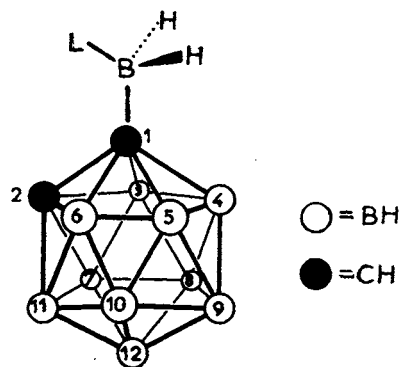


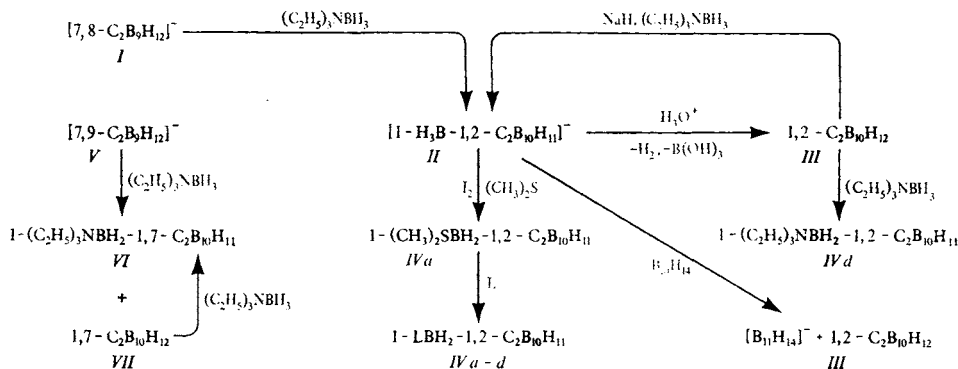
FIG. 2
Proposed structure of 1-L-BH₂-1,2- $\text{C}_2\text{B}_{10}\text{.H}_{11}$ compounds

TABLE I
Assignment of the ^{11}B NMR signals ($\delta_{\text{B}} \pm 0.05$ ppm, hexadeuterioacetone, all doublets) for 1-X-1,2-C₂B₁₀H₁₁ derivatives

X	Compound	B ₍₉₎	B _(1,2)	B _(8,10)	B _(7,11)	B _(4,5)	B _(3,6)	exoskel. B
H	III	-3.52		-10.25	-14.67		-15.80	-
CH ₃	-	-2.73(146) ^a 0.67 ^b	-7.71(150) -4.30	-10.10(150) 0.15	-13.66(165) 1.01	-11.59(160) 3.08	-11.22(169) 3.58	-
BH ₃ ⁻	II	-3.01(146) 0.42	-7.80(151) -4.39	-9.15(155) 1.10	-12.86(154) 1.81	-9.15(155) 5.52	-10.31(174) 5.49	-20.43(88) ^c -
(CH ₃) ₂ SBH ₂	IV _a	-2.18 1.23	-2.49 0.92	-8.43(147) 1.82	-12.92 2.88	-12.01(150) ^d 2.66	-12.92(168) 2.88	-11.00 ^d
C ₅ H ₅ NBH ₂	IV _b	-2.63 0.78	-4.95(149) -1.84	-8.83(146) 1.42	-12.60 2.07	-11.00 3.67	-12.60 3.20	-3.54 ^e (110)
(CH ₃) ₃ NBH ₂	IV _c	-2.64(154) 0.78	-3.85(148) -0.44	-8.57(153) 1.68	-12.17(154) 1.96	-11.00 3.67	-11.00 4.80	-2.19 ^e (107)
(C ₂ H ₅) ₃ NBH ₂	IV _d	-2.73(146) 0.68	-3.95(146) -0.54	-8.61(144) 1.64	-12.75(160) 1.92	-10.75(160) 3.72	-10.95(156) 4.85	-8.29 ^e (110)

^a $\delta_{\text{B}}(J_{11\text{B}-1\text{H}}$ in Hz); ^b $\Delta\delta_{\text{B}}$ value (δ_{B} for 1-X-1,2-C₂B₁₀H₁₁ - δ_{B} for 1,2-C₂B₁₀H₁₂), positive values denote a downfield shift; ^c quartet; ^d estimated; ^e triplet.

it briefly to 80°C. Reaction of *Ila* with one equivalent of iodine in dimethyl sulphide yields 1-(CH₃)₂SBH₂-1,2-C₂B₁₀H₁₁ (*IVa*) in essentially quantitative yield to evolve



SCHEME 1

Formation and reactions of 1-LBH₂-1,2-C₂B₁₀H₁₂ (*II*, L = H⁻; *IVa*, L = (CH₃)₂S; *IVb*, L = C₅H₅N; *IVc*, L = (CH₃)₃N; *IVd*, L = (C₂H₅)₃N) and 1-(C₂H₅)₃NBH₂-1,7-C₂B₁₀H₁₁ (*VI*)

one equivalent of hydrogen. Displacement of dimethyl sulphide from *IVa* either by pyridine or trimethylamine afforded 1-C₅H₅NBH₂-1,2-C₂B₁₀H₁₁ (*IVb*) and 1-(CH₃)₃NBH₂-1,2-C₂B₁₀H₁₁ (*IVc*), respectively, the latter compound being prob-

TABLE II

Some properties of the 1-L-BH₂-1,2-C₂B₁₀H₁₁ compounds

L	Compound	<i>R_F</i> ^a	<i>m/z</i>	¹ H NMR ^b		M.p., °C
				skeletal CH	other	
H ⁻	<i>Ila</i>	0·30 ^c	—	3·444	1·67 ^d	—
H ⁻	<i>Ilb</i>	0·30 ^c	—	—	3·44 ^e	—
(CH ₃) ₂ S	<i>IVa</i>	0·54	316 ^f	4·252	2·05 ^g	120—123
C ₅ H ₅ N	<i>IVb</i>	0·24	237	4·015	7·93—8·65	220 ^h
(CH ₃) ₃ N	<i>IVc</i>	0·49	217	3·866	2·746 ^g	210—215
(C ₂ H ₅) ₃ N	<i>IVd</i>	0·60	259	3·854	1·169 ⁱ 2·967 ^j	113—115

^a In benzene; ^b in hexadeuterioacetone; ^c in acetonitrile-chloroform (1 : 2); ^d 1-H₃B quartet; ^e (CH₃)₃N⁺ protons; ^f corresponding to [(H₂BC₂B₁₀H₁₁)₂]⁺; ^g CH₃ singlet; ^h decomposition; ⁱ CH₃ triplet; ^j CH₂ quartet.

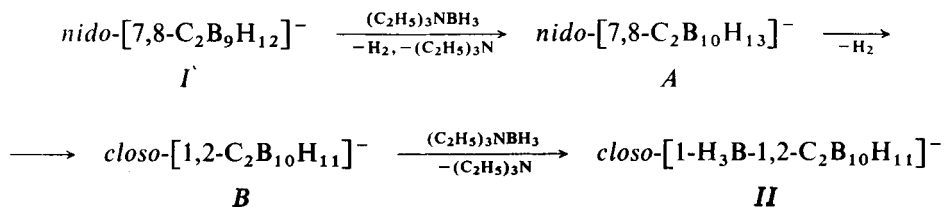
ably identical with that obtained by Hawthorne and coworkers^{6,7} in another way. The triethylamine analogue, 1-(C₂H₅)₃NBH₂-1,2-C₂B₁₀H₁₁ (*IVd*) was prepared either by displacement of dimethyl sulphide from *IVa* or directly from carborane *III* by prolonged heating with triethylamine borane at 190°C.

¹¹B NMR spectra of compounds *IVa-d* (Table I) show 1 : 1 : 2 : 2 : 2 : 2 patterns of doublets, which are typical for 1-substituted derivatives of *III*, along with one triplet assigned to the LBH₂ group. The corresponding ¹H NMR spectra of *IVa-d*, consisting of one singlet of the skeletal CH group and the signals of ligands, are also in agreement with the proposed structure. The missing BH₂ quartet cannot be reliably identified among the signals of terminal BH groups.

Mass spectra of compounds *IVb-d* exhibit the expected cut-offs corresponding to the [LBH₂C₂B₁₀H₁₁]⁺ molecular ion. On the other hand, the spectrum of *IVa* clearly indicates its fragmentation to dimethyl sulphide (*m/s* 62) and H₂BC₂B₁₀H₁₁ (*m/s* 158) under the conditions of the mass spectral experiment. The relevant spectrum shows a cut-off at *m/z* 316 corresponding to a (H₂BC₂B₁₀H₁₁)₂ substituted diborane.

As we have found, anion *II* can also be prepared directly from carborane *III* by treatment with sodium hydride and triethylamine-borane in refluxing diethylene glycol dimethyl ether. The product was isolated as the tetramethylammonium salt *IIB*, however, in only c. 40% yield, apparently due to unpleasant properties of the solvent and material losses during the work up procedure. It is noteworthy that carborane *III* itself does not react with sodium hydride in the solvent to any measurable extent due to a very low acidity of the carborane CH protons. For the same reason has failed an attempted synthesis of *II* in the reaction of carborane *III* with sodium tetrahydroborate in refluxing diethylene glycol dimethyl ether.

It is reasonable to postulate that the formation of anion *II* can be explained in terms of the following three step sequence of reactions:



Intermediate *A* should be third isomer of the *nido*-12-vertex family of carboranes⁶⁻⁹ two members of which have already been isolated. Upon dehydrogenation, intermediate *A* affords anion *B* with a lone electron pair on the carbon atom and, at the final stage, anion *B* displaces triethylamine from the second molecule of triethylamine-borane to yield anion *II*. Since the species *B* is a known compound, obtainable *e.g.*

by lithiation¹⁰ of carborane *III*, hydroborate *II* should be also available by the reaction of 1-Li-1,2-C₂B₁₀H₁₁ with diborane.

Anion *II* can be used as a source of the BH₃ group, as demonstrated by the insertion reaction of *Ila* with decarborane in boiling dioxane to give high yield of the [B₁₁H₁₄]⁻ anion¹¹ along with 1,2-C₂B₁₀H₁₂ and hydrogen.

In contrast to anion *I*, the isomeric [7,9-C₂B₉H₁₂]⁻ compound³ does not form an analogous [1-H₃B-1,7-C₂B₁₀H₁₁]⁻ isomer of *II* on heating with triethylamine-borane at 200°C. Instead of the anticipated compound, 1-(C₂H₅)₃NBH₂-1,7-C₂B₁₀H₁₁ (*VI*) along with 1,7-C₂B₁₀H₁₂ (*VII*) were isolated in low yield. Limited amounts of compound *VI* were also isolated on prolonged heating of carborane *VII* with triethylamine borane at 200°C.

EXPERIMENTAL

¹H (200 MHz), ¹³C (50.31 MHz), and ¹¹B (64.18 MHz) NMR spectra were recorded on a Varian XL-200 equipment. Chemical shifts are given in δ (ppm related to tetramethylsilane (¹H and ¹³C) and BF₃·O(C₂H₅)₃, positive values downfield). IR spectra were obtained in Nujol mulls using a Perkin-Elmer 684 instrument. Mass spectra were collected on a GC/MS HP-5985 spectrometer at 70 eV. Melting points were determined in sealed capillaries and are uncorrected. Purity of individual compounds was monitored by TLC on Silufol (silica gel on aluminium foil, starch as binder, producer Kavalier, Czechoslovakia, detection by iodine vapours followed by AgNO₃ spray). Starting [7,8-C₂B₉H₁₂]⁻Cs⁺ and [7,8-C₂B₉H₁₂]⁻Cs⁺ salts were prepared according to the literature^{3,4}. Solvents for measurements were spectral grade, other solvents were dried and distilled by standard procedures prior to use. All evaporations of solvents were performed *in vacuo* on a standard rotatory evaporator and all syntheses were carried out under nitrogen, unless otherwise stated. Properties of all compounds isolated are summarized in Tables I and II.

Cesium 1,2-Dicarba-*closo*-dodecaborane-1-yl Tetrahydroborate(1-) (*Ila*)

A suspension of [7,8-C₂B₉H₁₂]⁻Cs⁺ (13.3 g; 0.05 mol) in triethylamine borane (22.5 ml; 17.1 g; 0.125 mol) was heated to 200°C for 4 h. The triethylamine evolved was collected by condensing and the hydrogen evolution was checked using a bubbler filled with toluene. At the end of the reaction, the hydrogen evolution slowed down to c. 1 ml/min and crude triethylamine (9.8 g; 97%) was collected. The mixture was cooled down to ambient temperature and the last traces of triethylamine were removed *in vacuo*. Benzene (150 ml) was added, the mixture was shaken for 30 min and then put aside for 3 h. The suspension was sucked off, the insoluble portion was washed with three 20 ml doses of benzene and dissolved in tetrahydrofuran (50 ml). The solution was filtered to toluene (150 ml), the tetrahydrofuran was removed, the separated crystalline substance was sucked off and dried at 25°C/1.3 Pa for 4 h to obtain 12.7 g (88%) of [1-H₃B-1,2-C₂B₁₀H₁₁]⁻Cs⁺ (*Ila*), the purity of which exceeded 95%, according to the hydrolysable hydrogen and isolable 1,2-C₂B₁₀H₁₂.

Tetramethylammonium salt I Ib: A solution of the salt *Ila* (2.9 g; 10 mmol) in water (30 ml) was added to 1 mol l⁻¹ tetramethylammonium chloride (15 ml). The suspension was heated to 80°C and enough ethanol was added to obtain clear solution. After allowing it to stand overnight, leaflets of the product were separated. Pure [1-H₃B-1,2-C₂B₁₀H₁₁]⁻ [N(CH₃)₄]⁺ (*I Ib*) (2.0 g; 85%) was obtained after sucking it off, washing with two 25 ml portions of water and drying in air. ¹³C NMR spectrum (hexadeuterioacetone): δ_c 86.18 (1 C, q, J_{13C-11B} 39 Hz,

$C_{(1)}$, 66.63 (1 C, d, J_{13C-1H} 190 Hz, $C_{(2)}$), 55.87 (4 C, q, J_{13C-1H} 104 Hz, $[(CH_3)_4N]^+$). IR spectrum (cm^{-1}): 3 060 ($\nu_{as}(C-H$ skel.)), 3 030 ($\nu_{as}((CH_3)_4N)^+$), 2 580, 2 550 ($\nu(B-H$ terminal)), 2 290 ($\nu_{as}(B-H, BH_3$ group)), 2 230 ($\nu_{sym}(B-H, BH_3$ group)), 1 485 ($\delta_{as}((CH_3)_4N)^+$), 1 420 ($\delta_{sym}((CH_3)_4N)^+$), 1 290, 1 140, 1 080, 1 020, 950 (rocking $((CH_3)_4N)^+$), 935, 885, 543, 488, 455, 258, 245.

Tetramethylammonium salt IIb from 1,2-C₂B₁₀H₁₂: To a solution of 1,2-C₂B₁₀H₁₂ (4.3 g; 0.03 mol) and triethylamine borane (6.0 ml; 0.04 mol) in diglyme (40 ml) was added sodium hydride (0.85 g; 0.035 mol) and the mixture was refluxed for 4 h. After cooling to room temperature, it was carefully decomposed with water (5 ml) and stripped off to a volume of c. 20 ml. After adding water (50 ml), the mixture was filtered and precipitated with 1 mol l⁻¹ tetramethylammonium chloride (30 ml). The precipitate was sucked off, washed with benzene (20 ml), water (20 ml) and again with benzene (20 ml). After recrystallization from 50% ethanol, the first crop (1.1 g) of the product was isolated. Further product was obtained after evaporating gradually ethanol from the mother liquors. Total yield of 2.6 g (37%) of $[1-H_3B-C_2B_{10}H_{11}]^- [(CH_3)_4N]^+$, which was identified by its ¹¹B NMR spectrum, was attained.

Analytical Hydrolysis of $[1-H_3B-1,2-C_2B_{10}H_{11}]^- Cs^+$

Solution of compound *Ila* (1.406 g; 4.847 mmol) in water (30 ml) was acidified with 1 mol l⁻¹ hydrochloric acid (10 ml) to evolve 14.1 mmol (96.9%) of hydrogen, measured in a gasometer. The resulting turbid solution was heated to 80°C for 30 min and the formed suspension was extracted twice with hexane (20 ml). The combined hexane extracts were evaporated and the residue was sublimed at 80°C (bath) (1.3 Pa) to isolate 0.667 g (95.4%) of 1,2-C₂B₁₀H₁₂, which was identified by its ¹¹B NMR spectrum.

Dimethyl Sulphide 1,2-Dicarba-*closo*-dodecaborane-1-yl Borane (*IVa*)

Under stirring, to a solution of the salt *Ila* (2.9 g; 0.01 mol) in dimethyl sulphide (30 ml) was added dropwise a solution of iodine (1.28 g; 5 mmol) in benzene (50 ml) during 10 min to evolve hydrogen and to separate a slurry of cesium iodide (exothermic reaction). After fading out the brown colour, water (20 ml) was added followed by benzene (30 ml). The organic layer was evaporated, the crystalline residue was suspended in hexane (20 ml) and sucked off to yield 2.1 g (95.0%) of (CH₃)₂SBH₂-1,2-C₂B₁₀H₁₁ (*IVa*) as white crystals after drying at 29°C/1.3 Pa for 4 h.

Amine Adducts of 1,2-Dicarba-*closo*-dodecaborane-1-yl Borane, 1-LBH₂-1,2-C₂B₁₀H₁₁ (*IVb*, L = C₅H₅N; *IVc*, L = (CH₃)₃N; and *IVd*, L = (C₂H₅)₃N)

The compounds were generally obtained by treatment of a benzene solution of compound *IVa* with excess pyridine, trimethylamine and triethylamine for c. 1 h at ambient temperature. The progress of the ligand exchange was monitored by TLC in benzene, checking a slower spot of compounds *IVb-d* which, in contrast to the *IVa* species, do not reduce the Ag⁺ ion. After the starting compound had disappeared, the solution was evaporated and the residue was recrystallized from cyclohexane to give 85–95% of compounds *IVb-d*. IR spectrum of *IVa* (cm^{-1}): 3 065 ($\nu_{as}(C-H$ skel.)), 2 610, 2 560 ($\nu(B-H$ terminal)), 2 430 ($\nu_{as}(B-H, BH_2$ group)), 2 403 ($\nu_{sym}(B-H, BH_2$ group)), 1 430, 1 415 ($\delta_{as}CH_3$), 1 335, 1 295 ($\delta_{sym}CH_3$), 1 184, 1 155, 1 135, 1 093, 1 075, 1 048, 1 036, 1 020, 1 003, 975 (asym. rocking CH₃), 960, 690 ($\nu_{sym}CSC$), 575, 550, 530, 505, 470, 275 (δCSC), 230. IR spectrum of *IVc* (cm^{-1}): 3 063 ($\nu_{as}(CH$ skel.)), 2 640, 2 600, 2 540, 2 400 ($\nu(B-H$ terminal)), 2 365 ($\nu_{as}(B-H, BH_2$ group)), 2 300 ($\nu_{sym}(B-H, BH_2$ group)), 1 483, 1 410 ($\delta_{sym}CH_3$), 1 245, 1 186, 1 168, 1 130, 1 105, 1 078, 1 045, 1 022, 1 010, 978 (asym. rocking CH₃), 850, 690, 580, 483, 465, 410, 336, 290.

Triethylamine 1,2-Dicarba-*closo*-dodecaborane-1-yl Borane (*IVd*)
from 1,2-Dicarba-*closo*-dodecaborane(12) (*III*)

A suspension of 1,2-C₂B₁₀H₁₂ (14.4 g; 0.1 mol) in triethylamine-borane (15 ml; 0.1 mol) was heated at 200°C over 10 h to evolve hydrogen. The volatiles were removed *in vacuo* and the residue was sublimed at 90°C/1.3 Pa to produce a mixture of recovered compound *III* and triethylamine borane. The sublimate was decomposed with a boiling mixture of ethanol (100 ml) and concentrated hydrochloric acid (10 ml) during 3 h to recover 8.4 g (58%) of carborane *III*. The viscous residue remaining after removing the crude sublimate was digested with water (30 ml) and benzene (30 ml), the benzene layer was filtered and evaporated. The residue was recrystallized from cyclohexane (50 ml) to give 9.1 g (35%) of *IVd*.

Reaction of [1-H₃B-1,2-C₂B₁₀H₁₁]⁻Cs⁺ with Decaborane(14)

Compound *Ila* (1.6 g; 5.5 mmol) and decaborane(14) (0.8 g; 6.5 mmol) were dissolved in dioxane (15 ml) and the mixture was refluxed for 5 h. The formed crystalline precipitate was then sucked off, washed with dioxane (15 ml) and dried at 25°C/1.3 Pa. After dissolving in water (50 ml), it was precipitated with 1 mol l⁻¹ tetramethylammonium chloride (10 ml) and the resulting precipitate was recrystallized from aqueous acetone to yield 0.95 g (83%) of [B₁₁H₁₄]⁻[(CH₃)₄N]⁺, which was identified by its ¹¹B NMR spectrum (hexadeuterioacetone): δ_B -16.26 (140 Hz). The dioxane filtrate was evaporated and the residue was dried at 25°C/1.3 Pa and extracted with benzene. The benzene was removed and the residue was sublimed at 90°C/1.3 Pa to yield 0.65 g (90%) of carborane *III*.

Triethylamine-1,7-Dicarba-*closo*-dodecaborane-1-yl Borane(*VI*)

a) From [7,9-C₂B₉H₁₂]⁻Cs⁺ (*V*): Compound *V* (1.0 g; 0.045 mol) was heated with triethylamine borane (29 ml; 0.19 mol) at 200°C for 8 h. The volatiles were collected by condensation and the hydrogen evolution was checked in a bubbler. After cooling down to ambient temperature, the residue was extracted with three 50 ml portions of benzene. The extract was evaporated with silica gel (10 g) and the solid was placed atop a column (2.5 × 35 cm) of silica gel. Elution with benzene-hexane (1 : 2) developed two major bands of *R_f* 0.57 and 0.23. Pure fractions were combined and evaporated to give 1.8 g (28%, based on compound *V* used) of 1,7-C₂B₁₀H₁₂ (*VII*) (identified by its ¹¹B NMR spectrum) and 0.8 g (7%) of 1-(C₂H₅)₃NBH₂-1,7-C₂B₁₀H₁₁ (*VI*). ¹H NMR spectrum (hexadeuterioacetone): δ 3.07 (1 H, s, CH skel.), 2.997 (6 H, q, CH₂), 1.187 (9 H, t, CH₃); ¹¹B NMR spectrum (hexadeuterioacetone): δ_B -6.36 (3 B, m, B_(5,12), exoskeletal BH₂), -10.06 (2 B, d, B_(9,10)), -12.28 (2 B, d, B_(4,7)), -12.70 (2 B, d, B_(8,11)), -14.75 (2 B, d, B_(2,3)). The solid residue remaining after extraction of the original reaction mixture with benzene was extracted with tetrahydrofuran (2 × 50 ml) and the starting compound *V* (6.1 g; 51%) was isolated on evaporating the tetrahydrofuran and drying the residue at 25°C/1.3 Pa.

b) From 1,7-Dicarba-*closo*-dodecaborane(12) (*VII*): A suspension of carborane *VII* (14.4 g; 0.1 mol) in triethylamine borane (15 ml; 0.1 mol) was heated at 190–210°C for 19 h. Further work up of the mixture as in the preceding experiment resulted in the recovery of 10.2 g (71%) of 1,7-C₂B₁₀H₁₂ and isolation of 2.7 g (10%) of 1-(C₂H₅)₃NBH₂-1,7-C₂B₁₀H₁₁ (*VI*).

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