DALTON

Ten-vertex monocarbaborane chemistry. Synthesis of carbon-substituted ligand derivatives 1-L-*closo*-1-CB_9H_9 and crystal and molecular structure of 1-(Me_3N)-*closo*-1-CB_9H_9

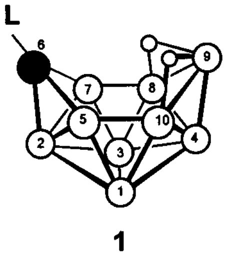
Tomáš Jelínek,[a] Bohumil Štíbr,[a] Jaromír Plešek,[a] Mark Thornton-Pett[b] and John D. Kennedy[b]

[a] *Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Řež, the Czech Republic*
[b] *School of Chemistry, University of Leeds, Leeds, UK LS6 9JT*

The monocarbaborane ligand derivative (1-(H_3N)-*closo*-1-CB_9H_9 has been isolated in 75% yield from the reaction between 6-(H_3N)-*nido*-6-CB_9H_{11} and $Et_3N{\cdot}BH_3$ in tetrahydrofuran in the presence of $NaBH_4$. Further reactions involving the exoskeletal H_3N group have led to the isolation of the series of related derivatives 1-L-*closo*-1-CB_9H_9, where L = Me_2S, $[H_2N]^-$, Me_3NH, or Me_3N. Boron-11 and ^1H NMR measurements were consistent with the proposed structure of all the compounds, with the structure of the NMe_3 derivative 1-(Me_3N)-*closo*-1-CB_9H_9 additionally determined by an X-ray diffraction analysis.

Dicarbaborane chemistry dominates heteroborane chemistry.[1] By contrast, monocarbaborane,[1,2] tricarbaborane,[3] and polycarbaborane[3b,4] chemistries are less developed, although there is currently an increasing interest and activity in these areas. We have been interested for some time in the chemistry of monocarbaboranes,[1,2] of which the ten-vertex *closo* family, as represented by the parent [*closo*-1-$CB_9H_{10}]^-$ anion,[5] constitutes a fundamental but not well explored set of compounds. This parent (*i.e.* unsubstituted) anion was first reported by Knoth[5b] as a product from the thermal comproportionation of the [*nido*-7-$CB_{10}H_{13}]^-$ anion (which also gives the twelve-vertex [*closo*-1-$CB_{11}H_{11}]^-$ anion), and it can also be obtained as a product in low yield from the reductive deamination of 6-(Me_3N)-*nido*-6-CB_9H_{11} with sodium metal.[5b] As we have reported elsewhere, the best yield of the [*closo*-1-$CB_9H_{10}]^-$ anion (70%) is now achieved from the reaction between 6-(Me_3N)-*nido*-6-CB_9H_{11} and piperidine at 70 °C.[5c] The only C-substituted compound of the ligand-substituted 1-L-*closo*-1-CB_9H_9 family previously reported is 1-(Me_3N)-*closo*-1-CB_9H_9, prepared in a low yield *via* thermal decomposition of the cobaltamonocarbaborane [1-(η^5-C_5H_5)-2-(Me_3N)-*closo*-1,2-$CoCB_9H_9$].[6] The only other ten-vertex *closo* monocarbaborane in this general area is the B-substituted compound 6-(Me_2PhP)-*closo*-1-CB_9H_9 formed by thermal decomposition of the platinamonocarbaborane [8,8-(Me_2PhP)-*nido*-8,7-$PtCB_9H_{11}$].[7] These ligand-substituted *closo* compounds are sometimes regarded as zwitterionic because of the quaternization of the amine nitrogen atom and the anionic nature of the $[CB_9H_{10}]^-$ parent species.

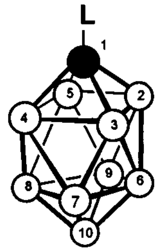
We now report a general preparative method for the synthesis of members of this family of compounds 1-L-*closo*-1-CB_9H_9, specifically where L = H_3N, $[H_2N]^-$, Me_2NH, Me_3N, or Me_2S, which are thereby now available in good yields for further work. The route uses 6-(H_3N)-*nido*-6-CB_9H_{11} as the starting material.[8] This is prepared from $B_{10}H_{14}$ and NaCN followed by acidification with HCl. General structures and numbering systems for the ten-vertex *nido*, the ten-vertex *closo*, and the twelve-vertex *closo* compounds encountered in this work are in structures **1**, **2**, and **3** respectively.



1

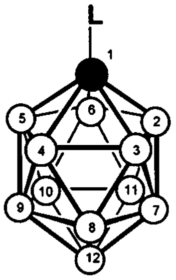
L	
H_3N	**1a**
Me_3N	**1b**

○ BH
● C
o H



2

L	
H^-	**2a$^-$**
H_3N	**2b**
Me_3N	**2c**
Me_2NH	**2d**
Me_2S	**2e**
N_2	**2f**



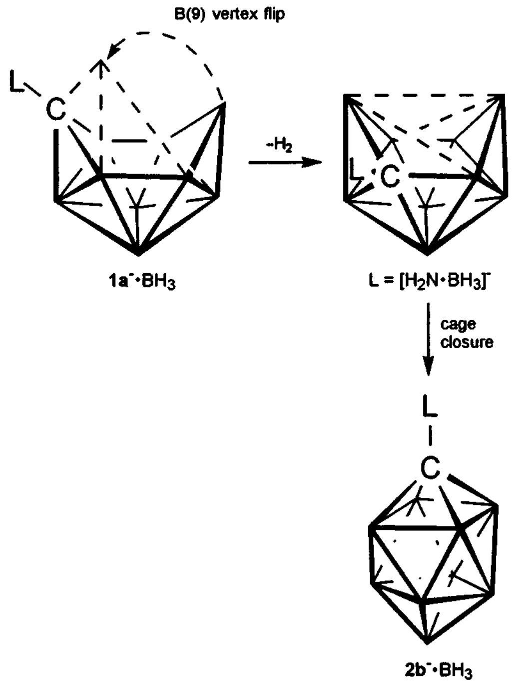
3

L	
H_3N	**3a**
Me_2NH	**3b**

Results and Discussion

Syntheses

Treatment of a solution of 6-(H_3N)-*nido*-6-CB_9H_{11} **1a**[8b] in tetrahydrofuran (thf) with a slight excess of $NaBH_4$ at ambient temperature, followed by the addition of $Et_3N{\cdot}BH_3$, evaporation of the thf, heating of the resulting mixture to *ca.* 200 °C, decomposition with a mixture of methanol and hydrochloric acid, and alkalization of the product resulted in the formation of the [1-(H_2N)-*closo*-1-$CB_9H_9]^-$ anion **2b**$^-$. A by-product is the previously reported[9] twelve-vertex [1-(H_2N)-*closo*-1-$CB_{11}H_{11}]^-$ anion **3a**$^-$. Acidification of the anion **2b**$^-$ led ultimately to the isolation of ten-vertex neutral 1-(H_3N)-*closo*-1-CB_9H_9 **2b** in an



Scheme 1

overall yield of 75%. The main reaction mode of this rather complex process, the formation of the anion **2b**$^-$, is not inconsistent with equations (1)–(4); alkalization of compound **2b** from equation (4) would yield the anion **2b**$^-$.

$$\underset{\mathbf{1a}}{6\text{-}(H_3N)\text{-}\mathit{nido}\text{-}6\text{-}CB_9H_{11}} + BH_4^- \longrightarrow \underset{\mathbf{1a}^-\cdot BH_3}{[6\text{-}(H_3B\cdot H_2N)\text{-}\mathit{nido}\text{-}6\text{-}CB_9H_{11}]^-} + H_2 \quad (1)$$

$$\underset{\mathbf{1a}^-\cdot BH_3}{[6\text{-}(H_3B\cdot H_2N)\text{-}\mathit{nido}\text{-}6\text{-}CB_9H_{11}]^-} \xrightarrow{\approx 200\,^\circ C} \underset{\mathbf{2b}^-\cdot BH_3}{[1\text{-}H_3B\cdot H_2N]\text{-}\mathit{closo}\text{-}1\text{-}CB_9H_9]^-} + H_2 \quad (2)$$

$$\underset{\mathbf{2b}^-\cdot BH_3}{[1\text{-}(H_3B\cdot H_2N)\text{-}\mathit{closo}\text{-}1\text{-}CB_9H_9]^-} + 3\,MeOH \longrightarrow B(OMe)_3 + \underset{\mathbf{2b}^-}{[1\text{-}(H_2N)\text{-}\mathit{closo}\text{-}1\text{-}CB_9H_9]^-} + 3\,H_2 \quad (3)$$

$$\underset{\mathbf{2b}^-}{[1\text{-}(H_2N)\text{-}\mathit{closo}\text{-}1\text{-}CB_9H_9]^-} + H_3O^+ \longrightarrow \underset{\mathbf{2b}}{1\text{-}(H_3N)\text{-}\mathit{closo}\text{-}1\text{-}CB_9H_9} \quad (4)$$

According to this scheme the $Et_3N\cdot BH_3$ used as one of the reaction components does not appear to participate directly in the main reaction mode. Nevertheless, the reaction does not proceed without its addition and the same reaction in refluxing diglyme (2,5,8-trioxanonane) but without $Et_3N\cdot BH_3$ did not lead to the expected product **2b**. A significant role of the $Et_3N\cdot BH_3$ may therefore be to catalyse the dehydrogenation step (2). This step is also probably associated with the rearrangement of the substituted carbon atom in the *nido* (6) position in the **1a**$^-\cdot BH_3$ anion into the higher-connectivity *nido* (5) position prior to skeletal closure. This would be in agreement with the previously formulated *nido* ten-vertex vertex-flip mechanism,[5c,10] as outlined for this particular case in Scheme 1.

The side formation of the twelve-vertex anion **3a**$^-$, as a major by-product in about 25% yield, is consistent with the insertion of two {BH} vertices into the open hexagonal face of the *nido* anion **1a**$^-\cdot BH_3$ *via* reaction with $Et_3N\cdot BH_3$. Interestingly, this two-boron insertion mode is much more evident in the reaction between 6-(Me_3N)-*nido*-6-CB_9H_{11} **1b** and $Et_3N\cdot BH_3$ at 200–210 °C for 8 h, in which it predominates. Thus, from this last system, the previously reported[11] 1-(Me_2NH)-*closo*-$CB_{11}H_{11}$ **3b** was isolated in 61% yield as a single product upon reductive monodemethylation of the trimethylamine ligand [equation (5)].

$$\underset{\mathbf{1b}}{Me_3N\cdot CB_9H_{11}} + 2\,Et_3N\cdot BH_3 \longrightarrow \underset{\mathbf{3b}}{Me_2NH\cdot CB_{11}H_{11}} + CH_4 + 2\,Et_3N + 2\,H_2 \quad (5)$$

The simple H_3N derivative **2b** can be employed as a source of other ligand derivatives of type **2**. Thus, methylation of **2b** by means of Me_2SO_4 in an alkaline solution afforded the trimethylamine derivative 1-(Me_3N)-*closo*-1-CB_9H_9 **2c** in a 77% isolated yield. Treatment of **2c** with a solution of elemental sodium in liquid ammonia resulted in the monodemethylation[9,11] of the Me_3N functionality and the formation of the dimethylamine derivative 1-(Me_2NH)-*closo*-1-CB_9H_9 **2d** (yield 47%). This last reaction is also accompanied by a complete deamination that results in the formation of a similar amount (50%) of the parent[5] anion **2a**$^-$. In a different approach to derivative formation, the H_3N group in compound **2b** was replaced by Me_2S in the reaction between **2b** and sodium nitrite in the presence of SMe_2 in an acidic solution, equation (6). This procedure gave 1-(Me_2S)-*closo*-1-CB_9H_9 **2e** in 68% yield as a final product. This reaction might be supposed to proceed *via* a transient diazo derivative $N_2CB_9H_9$ **2f**, which was not isolated.

$$\underset{\mathbf{2b}}{H_3N\cdot CB_9H_9} \xrightarrow[-2\,H_2O]{+HNO_2} \underset{\mathbf{2f}}{N_2CB_9N_9} \xrightarrow[-N_2]{+Me_2S} \underset{\mathbf{2e}}{Me_2S\cdot CB_9H_9} \quad (6)$$

Structural studies

The structure of the neutral trimethylamine derivative **2c** was determined unambiguously by a single-crystal X-ray diffraction analysis. As shown in Fig. 1, the study reveals a classical *closo* ten-vertex bicapped Archimedean square-antiprismatic structure, with the carbon atom occupying the low-connectivity axial 1 position. The Me_3N ligand is attached to this axial cluster carbon, thus confirming the previously proposed 'zwitterionic' constitution.[6] Selected interatomic distances and angles for compound **2c** are in Table 1. In general, the cluster interatomic separations in **2c** are typical of *closo* ten-vertex boron-containing cluster species. Thus the following mean distances B(10)–B (belt) 169.7(4), B–B (lower belt) 184.2(4) B–B (interbelt) 180.2(4), B–B (upper belt) 184.8(4), and C(1)–B (belt) 160.8 pm are very similar to those of the parent anionic analogue **2a**$^-$, which has corresponding mean distances of 165.2(25), 185.9(30), 180.5(23), 182.0(26) and 155.5(29) pm.[5c]

The series consisting of the substituted derivatives of type **2** was also examined by NMR spectroscopy. The observed NMR data (Table 2), together with the results of mass spectrometry, are in excellent agreement with their formal descriptions as zwitterionic C-ligand-substituted compounds based on the *closo* ten-vertex 1-monocarbadecaborate(1−) constitution. All the cluster ^{11}B and ^{1}H resonances were interrelated by [^{11}B–^{11}B] correlation spectroscopy (COSY)[13] and/or ^{1}H-{^{11}B(selective)}[14] experiments, which permitted complete assignments and thence comparisons with the parent anion **2a**$^-$.[5] The interrelation of the ^{11}B and ^{1}H chemical shifts for all C-substituted derivatives

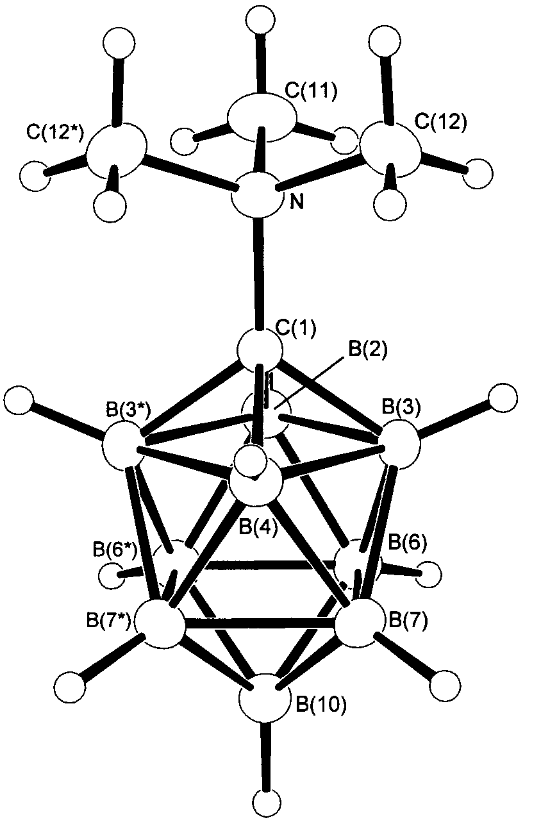


Fig. 1 An ORTEP-type[12] diagram of the crystal and molecular structure of 1-(Me_3N)-*closo*-1-CB_9H_9 **2c**. Ellipses are shown at the 40% probability level. In the interests of clarity hydrogen atoms are drawn as circles with an arbitrarily small radius

of type **2** thus far isolated is demonstrated graphically in Fig. 2.

The comparison reveals a straightforward similarity of the corresponding resonances to those that have been previously established[5c] for the parent anion **2a**$^-$. Of the chemical-shift differences observed among the members of the family, the most marked are the α and γ (antipodal)[15] shifts in δ(^{11}B) arising from the variation of ligands on the axial position C(1). As seen in Fig. 2 (bottom traces), the antipodal $^{11}B(10)$ shielding increases in the order $[H_2N]^- > H_3N > Me_2NH > Me_3N > Me_2S$ with the differences being much less pronounced among the set of amine-substituted compounds than between the amines and the sulfide. This is in accord with known antipodal shielding effects.[15] Conversely, the presence of the ligands leads to the deshielding of the nuclei of the boron atoms adjacent (α) to the carbon vertex, but this effect is much less marked than the antipodal shielding increases.

Conclusion

The results reported here show that a simple ligand derivative of type **2**, namely the H_3N derivative **2b**, is now readily available in good yield in two reaction steps from decaborane(14). The work also demonstrates the principle that the $\{(H_3N)C\}$ functionality in **2b** can be easily modified, also in good yield, both by substitution on nitrogen and by ligand-exchange reactions at the cluster carbon centre, to generate a range of carbon-substituted compounds that are formally based on the ten-vertex *closo*-1-monocarbadecaborate(1−) skeleton. As mentioned in the introduction, there is a developing interest and activity in monocarbaborane chemistry, and these and similar derivatives have good potential use for designed syntheses in monocarbaborane chemistry to parallel the versatility of *closo* species such as $C_2B_{10}H_{12}$ and the $[B_{10}H_{10}]^{2-}$ dianion, and their derivatives, in dicarbaborane chemistry and in borane chemistry itself.

Table 1 Selected interatomic distances (pm) and angles (°) for 1-(Me_3N)-*closo*-1-CB_9H_9 **2c**

C(1)–N	149.8(3)	B(6)–B(2)	180.5(4)
B(3)–C(1)	160.9(4)	B(4)–B(3)	185.3(4)
B(3)–B(2)	184.3(4)	B(7)–B(3)	180.2(4)
B(6)–B(3)	180.2(4)	B(7)–B(4)	179.7(4)
B(10)–B(6)	169.5(4)	B(7)–B(6)	184.2(4)
B(6)–B(6*)	182.9(5)	B(10)–B(7)	169.9(4)
B(2)–C(1)	161.2(4)	B(7)–B(7*)	185.4(5)
B(4)–C(1)	160.3(4)		
B(2)–C(1)–N	127.2(2)	B(3)–C(1)–N	125.6(2)
B(3)–C(1)–B(2)	69.8(2)	B(3)–C(1)–B(3*)	108.7(2)
B(4)–C(1)–N	124.1(2)	B(4)–C(1)–B(2)	108.7(2)
B(4)–C(1)–B(3)	70.5(2)		
B(2)–B(2)–C(1)	55.0(2)	B(3)–B(2)–B(3*)	90.4(2)
B(6)–B(2)–C(1)	108.0(2)	B(6)–B(2)–B(3)	59.2(2)
B(6)–B(2)–B(3*)	101.9(2)	B(6)–B(2)–B(6*)	60.9(2)
B(2)–B(3)–C(1)	55.2(2)	B(4)–B(3)–C(1)	54.6(2)
B(4)–B(3)–B(2)	89.9(2)	B(6)–B(3)–C(1)	108.3(2)
B(6)–B(3)–B(2)	59.4(2)	B(6)–B(3)–B(4)	101.7(2)
B(7)–B(3)–C(1)	107.9(2)	B(7)–B(3)–B(2)	102.5(2)
B(7)–B(3)–B(4)	58.9(2)	B(7)–B(3)–B(6)	61.5(2)
B(3)–B(4)–C(1)	54.9(2)	B(7)–B(4)–B(3*)	89.8(2)
B(7)–B(4)–C(1)	108.4(2)	B(7)–B(4)–B(3)	59.1(2)
B(7)–B(4)–B(3*)	102.4(2)	B(7)–B(4)–B(7*)	62.1(2)
B(3)–B(6)–B(2)	61.4(2)	B(6*)–B(6)–B(2)	59.6(2)
B(6*)–B(6)–B(3)	102.6(2)	B(7)–B(6)–B(2)	102.4(2)
B(7)–B(6)–B(3)	59.3(2)	B(7)–B(6)–B(6*)	90.4(2)
B(10)–B(6)–B(2)	112.2(2)	B(10)–B(6)–B(3)	112.0(2)
B(10)–B(6)–B(6*)	57.4(2)	B(10)–B(6)–B(7)	57.2(2)
B(4)–B(7)–B(3)	62.0(2)	B(6)–B(7)–B(3)	59.3(2)
B(6)–B(7)–B(4)	102.3(2)	B(7*)–B(7)–B(3)	102.2(2)
B(7*)–B(7)–B(4)	59.0(2)	B(7*)–B(7)–B(6)	89.6(2)
B(10)–B(7)–B(3)	111.8(2)	B(10)–B(7)–B(4)	111.5(2)
B(10)–B(7)–B(6)	57.1(2)	B(10)–B(7)–B(7*)	56.9(2)
B(6)–B(10)–B(6*)	65.3(2)	B(7)–B(10)–B(6)	65.7(2)
B(7)–B(10)–B(6*)	100.2(2)	B(7)–B(10)–B(7*)	66.1(2)

Atoms marked * are related to their unmarked reference atoms at x, y, z by the symmetry $x, 0.5 - y, z$.

Experimental

General

All reactions were carried out under anaerobic conditions, although some operations, such as column chromatography and crystallizations, were performed in air. Tetrahydrofuran was distilled from sodium diphenylketyl, dichloromethane from CaH_2, and methanol and dimethyl sulfide from KOH, prior to use. Gaseous ammonia was passed through solid KOH and liquefied by condensation at −78 °C (solid CO_2 bath). The starting amine derivative **1a** was prepared from $B_{10}H_{14}$ and NaCN followed by acidification with HCl according to the literature.[8b] Other starting materials were of reagent or analytical grade and were used as purchased. Analytical TLC was performed on silica gel G sheets (Silufol, producer Kavalier; detection by diiodine vapour followed by spray with 2% aqueous $AgNO_3$) and column (2.5 × 30 cm) chromatography on silica gel (Aldrich, 200–400 mesh).

Physical measurements

Low-resolution mass spectra [70 eV, *ca.* 1.12×10^{-17} J; electron impact (EI) ionisation] were obtained using a Finnigan MAT MAGNUM ion-trap quadrupole mass spectrometer equipped with a heated-inlet option, as developed by Spectronex AG, Basle, Switzerland. Proton (^1H) and boron (^{11}B) NMR spectroscopy was performed at 9.4 and 11.75 T on Bruker AM 400 and Varian XL-500 instruments, respectively. The [^{11}B–^{11}B]-COSY[13] and ^1H-{^{11}B(selective)}[14] NMR experiments were performed essentially as described previously.[16] Chemical shifts are given in ppm to high frequency (low field) of $\Xi = 32.083\,971$ MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for ^{11}B (quoted ± 0.5

Table 2 The NMR data for 1-L-*closo*-1-CB_9H_9 compounds **2**

L	Nucleus	δ (multiplicity, assignment, J_{BH}/Hz)
H_3N, **2b**	$^{11}B^{a}$	29.2 [B(10), 158], −16.8 [B(2–5), 150], −25.8 [d, B(6–9), 143]
	$^{11}B–^{11}B^{b}$	Cross-peaks: B(10)–B(6–9); B(2–5)–B(6–9)
	$^{1}H^{c}$	10.15 (H_3N, 3 H), 5.53 [H(10)], 2.34 [H(2–5)], 0.81 [H(6–9)]
$[H_2N]^-$, **2b**$^-$	$^{11}B^{a}$	26.0 [B(10), 154], −17.2 [B(2–5), 147], −25.8 [d, B(6–9), 139]
	$^{11}B–^{11}B^{b}$	Cross-peaks: B(10)–B(6–9); B(2–5)–B(6–9)
	$^{1}H^{c}$	8.52 (H_2N, 2 H), 5.40 [H(10)], 1.69 [H(2–5)], 0.91 [H(6–9)]
Me_3N, **2c**	$^{11}B^{a}$	31.4 [B(10), 161], −17.3 [B(2–5), 154], −25.9 [d, B(6–9), 144]
	$^{11}B–^{11}B^{b}$	Cross-peaks: B(10)–B(6–9); B(2–5)–B(6–9)
	$^{1}H^{c}$	5.92 [H(10)], 3.96 (Me_3N, 9 H), 1.90 [H(2–5)], 0.90 [H(6–9)]
Me_2NH, **2d**	$^{11}B^{a}$	30.8 [B(10), 156], −17.6 [B(2–5), 154], −25.9 [d, B(6–9), 143]
	$^{11}B–^{11}B^{b}$	Cross-peaks: B(10)–B(6–9); B(2–5)–B(6–9)
	$^{1}H^{c}$	10.94 (Me_2N*H*), 5.73 [H(10)], 3.79 (*Me*$_2$NH, 6H), 1.92 [H(2–5)], 0.77 [H(6–9)]
Me_2S, **2e**	$^{11}B^{a}$	38.3 [B(10), 152], −15.4 [B(2–5), 154], −23.9 [d, B(6–9), 144]
	$^{11}B–^{11}B^{b}$	Cross-peaks: B(10)–B(6–9); B(2–5)–B(6–9)
	$^{1}H^{c}$	6.07 [H(10)], 3.64 (Me_2S, 6 H), 1.85 [H(2–5)], 0.85 [H(6–9)]

[a] $\delta(^{11}B)$ values in CD_3CN (determined by ^{11}B-{^1H(broad band)} measurements with assignments by [$^{11}B–^{11}B$]-COSY NMR spectroscopy); all signals are doublets. [b] Measured under the conditions of {^1H(broad band)} decoupling. [c] Assignments by ^1H-{^{11}B(broad band)} and ^1H-{^{11}B(selective)} NMR spectroscopy; unless stated otherwise, all signals are singlets of relative intensity 1 in the ^1H-{^{11}B(broad band)} spectrum.

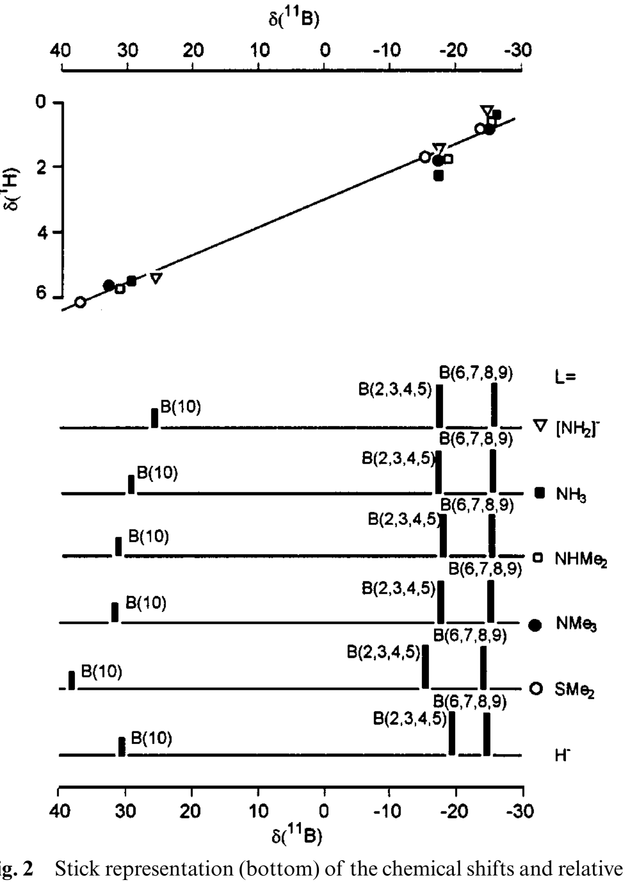


Fig. 2 Stick representation (bottom) of the chemical shifts and relative intensities in the ^{11}B NMR spectra of the set of compounds of 1-L-*closo*-1-CB_9H_9 **2** (L = Me_2S **2e**, Me_3N **2c**, Me_2NH **2d**, H_3N **2b**, and $[H_2N]^-$ **2b**$^-$) together with those of the parent anion [*closo*-1-CB_9H_{10}]$^-$ **2a**$^-$ [data from ref. 5(*c*)] for comparison. The upper diagram is a plot of ^1H *versus* ^{11}B chemical shifts for the individual {BH(*exo*)} units for this series of compounds

ppm) and Ξ = 100 MHz ($SiMe_4$) for ^1H (quoted ± 0.05 ppm), Ξ being defined as in ref. 17. Solvent resonances were used as internal secondary standards. Coupling constants $^1J(^{11}B–^1H)$ were taken from resolution-enhanced ^{11}B spectra with digital resolution ±8 Hz and are given in Hz.

Syntheses

1-(H_3N)-*closo*-1-CB_9H_9 2b and [$NHEt_3$]$^+$ [1-(H_2N)-*closo*-1-CB_9H_9]$^-$ 2b$^-$. A solution of compound **1a** (6.5 g, 47 mmol) in thf (40 cm^3) was treated with $NaBH_4$ (2.5 g, 66 mmol) and this mixture was allowed to stand at ambient temperature for 12 h (dihydrogen solution). It was then treated with $Et_3N{\cdot}BH_3$ (10.5 cm^3, 70 mmol) and heated progressively over *ca.* 8 h with simultaneous removal of the thf until a bath temperature of 200 °C was reached. Upon cooling to room temperature, the mixture was carefully decomposed by adding methanol (40 cm^3, portionwise) and, after the violent reaction had ceased, by carefully adding concentrated aqueous hydrochloric acid (20 cm^3). The mixture thus obtained was heated at reflux for 5 h and the acidic aqueous layer was then separated and discarded. The residual viscous material was successively treated with two 350 cm^3 portions of 10% aqueous NaOH at reflux (1 h each), and the resulting alkaline solutions were combined and extracted twice with diethyl ether (2 × 40 cm^3). Water (100 cm^3) was added, the ether was evaporated, and the remaining aqueous solution (solution A) acidified with concentrated aqueous hydrochloric acid to pH 3. This solution was then carefully evaporated with gentle heating until the first crystals started to appear at a solution temperature of *ca.* 50 °C. At this point the solution was left standing at room temperature to crystallize. The crystals were filtered off, vacuum dried and identified by integrated ^{11}B NMR spectroscopy as a 3 : 1 mixture of the anions **2b**$^-$ and **3a**$^-$ as their Na^+ salts. The mother-liquors were then evaporated to dryness, vacuum dried, and washed with CH_2Cl_2 (50 cm^3) to yield 4.8 g (75%) of 1-(H_3N)-*closo*-1-CB_9H_9 **2b**, which was identified by NMR spectroscopy (Found: C, 8.41; H, 8.53. $CH_{12}B_9N$ requires C, 8.86; H, 8.87%). Mass spectrum; *m*/*z* 137; [$^{12}C^1H_{12}{}^{11}B_9{}^{14}N$]$^+$ requires *m*/*z*$_{max}$ 137.

The solution A was treated with an aqueous solution of [$NHEt_3$]Cl (1 M, 50 cm^3) to precipitate a white crystalline material. This was filtered off, and repeated crystallization from ethanol then gave a white crystalline compound which was identified by NMR spectroscopy as the [$NHEt_3$]$^+$ salt of the anion [1-(H_2N)-*closo*-1-CB_9H_9]$^-$ **2b**$^-$ (5.5 g, 49%) (Found: C, 34.13; H, 10.87. $C_4H_{27}B_9N_2$ requires C, 35.52; H, 11.50%).

1-(Me_3N)-*closo*-1-CB_9H_9 2c. A solution of compound **2b** (1.2 g, 8.8 mmol) in 5% aqueous NaOH (50 cm^3) was treated dropwise with Me_2SO_4 (3.3 cm^3, 35 mmol) while stirring and cooling with an ice-bath. The stirring was continued for an additional hour at ambient temperature, and the mixture was then treated with 20% aqueous NH_3 (5 cm^3) for 30 min. The resulting white precipitate was filtered off, washed with two 10 cm^3 portions of water and 50% aqueous ethanol, and then vacuum dried to obtain 1-(Me_3N)-*closo*-1-CB_9H_9 **2c** as a white solid (1.2 g, 77%), identified by NMR spectroscopy (Found: C, 26.48; H, 9.84. $C_4H_{18}B_9N$ requires C, 27.05; H, 10.22%). Mass spectrum: *m*/*z* 179; [$^{12}C_4{}^1H_{18}{}^{11}B_9{}^{14}N$]$^+$ requires *m*/*z*$_{max}$ 179.

1-(Me_2NH)-*closo*-1-CB_9H_9 2d and [*closo*-1-CB_9H_{10}]$^-$ 2a$^-$. Liquid ammonia (80 cm^3) was condensed onto a solid sample of compound **2c** (0.7 g, 3.91 mmol) and the resulting solution treated with several portions of sodium metal (total 300 mg; 13 mmol). The mixture was left to stand for 3 h under reflux and the resulting blue solution was then decomposed carefully with methanol (20 cm^3). The ammonia and excess of methanol were removed by evaporation and the resulting mixture treated with water (30 cm^3). The solution thus formed was filtered, and then acidified with concentrated aqueous hydrochloric acid (5 cm^3) to precipitate a white crystalline compound. This was filtered off, dried *in vacuo* at 50 °C for 6 h, and identified as 1-(Me_2NH)-*closo*-1-CB_9H_9 **2d** (300 mg, 47%) by NMR spectroscopy (Found: C, 21.48; H, 9.50. $C_3H_{16}B_9N$ requires C, 22.01; H, 9.85%). Mass spectrum: *m*/*z* 165; [$^{12}C_3{}^1H_{16}{}^{11}B_9{}^{14}N$]$^+$ requires m/z_{max} 165. The filtrate was diluted with water (20 cm^3) and precipitated with [$NHMe_3$]Cl (1 g). The white precipitate thus formed was filtered off and dried *in vacuo* at ambient temperature to give the [Me_3NH]$^+$ salt of the anion **2a**$^-$ (350 mg, 50%), which was identified by NMR spectroscopy.

1-(Me_2S)-*closo*-1-CB_9H_9 2e. A stirred solution of compound **2b** (500 mg, 3.7 mmol) in dilute (1 : 3, v/v) aqueous hydrochloric acid (20 cm^3) was treated with SMe_2 (20 cm^3), and then cooled in an ice-bath while $NaNO_2$ (3.0 g) was added in small portions over 1 h. After the initial exothermic reaction (accompanied by a red coloration) ceased, the stirring was continued for 3 h, during which the mixture turned colourless. The SMe_2 layer was separated and evaporated to leave a semisolid residue. This residue was purified by column chromatography, using CH_2Cl_2 as the liquid phase, to collect the main fraction which had R_F 0.35 by analytical TLC (CH_2Cl_2 solvent). This was filtered, reduced in volume by evaporation and the resulting solution overlayered with a two-fold volume of hexane. After standing for 2 d the crystals deposited were filtered off and dried *in vacuo* to give white crystals which were identified as 1-(Me_2S)-*closo*-1-CB_9H_9 **2e** (450 mg, 68%) by NMR spectroscopy (Found: C, 18.64; H, 8.11. $C_3H_{15}B_9S$ requires C, 19.95; H, 8.37%). Mass spectrum: *m*/*z* 182; [$^{12}C_3{}^1H_{15}{}^{11}B_9{}^{32}S$]$^+$ requires m/z_{max} 182.

1-(Me_2NH)-*closo*-1-$CB_{11}H_{11}$ 3b. A mixture of compound **1b** (4.0 g, 22 mmol) and $Et_3N\cdot BH_3$ (5.3 cm^3, 35 mmol) was heated at 200–210 °C for 8 h (dihydrogen evolution). It was then cooled to ambient temperature, and decomposed carefully with methanol (25 cm^3). After the exothermic reaction had ceased the decomposition was completed by adding concentrated aqueous hydrochloric acid (25 cm^3), followed by heating at reflux for 12 h. The methanol was removed *in vacuo* and the aqueous solution separated from the viscous residue. This latter pasty material was heated successively with two portions of 10% aqueous NaOH (2 × 30 cm^3). The combined aqueous layers were filtered with charcoal, extracted with diethyl ether (2 × 30 cm^3), the combined ether extracts treated with water (40 cm^3), and the ether evaporated. The resulting aqueous solution was then acidified with concentrated aqueous hydrochloric acid (5 cm^3) to precipitate a white solid. This was filtered off, washed with water, and then vacuum dried to give 1-(Me_2NH)-*closo*-1-$CB_{11}H_{11}$ **3b** (2.5 g, 61%), identified by NMR spectroscopy as reported previously.[11]

X-Ray crystallography

All crystallographic measurements on compound **2c** were carried out at 200 K on a Stoe STADI4 four-circle diffractometer operating in the ω–θ scan mode using graphite-monochromated Cu-Kα radiation (λ = 1.541 84 Å). The data set was corrected for absorption using azimuthal *y* scans (maximum and minimum transmission factors 0.926 and 1.000 respectively). The structure was solved by direct methods using SHELXS 86[18] and refined by full-matrix least squares (on all F^2 values) using SHELXL 93.[19] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located on a Fourier-difference map and freely refined with isotropic displacement parameters. The weighting scheme $w = 1/[\sigma^2(F_o^2) + 0.0617P^2 + 0.259P]$, where $P = (F_o^2 + 2F_c^2)/3$, was used. The final Fourier-difference map was flat and showed no features of chemical significance (maximum and minimum residual densities 0.161 and −0.180 e Å^{-3} respectively).

Crystal data. $C_4H_{18}B_9N$, $M = 177.48$, orthorhombic, space group *Pnma*, $a = 13.6247(6)$, $b = 9.8769(5)$, $c = 8.3571(3)$ Å, $U = 1124.61(9)$ Å^3, $Z = 4$, $D_c = 1.048$ Mg m^{-3}, $F(000) = 376$, $\mu = 0.326$ mm^{-1}, crystal size 0.52 × 0.32 × 0.32 mm.

Data collection. $6.21 \leqslant \theta \leqslant 64.57°$, scan widths 1.05° + α-doublet splitting, scan speeds 1.5–8.0° min^{-1} (subject to a fast pre-scan). Total number of data collected = 1116, number of unique data = 990.

Structure refinement. $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}} = 0.1130$ for all data, conventional R [on F values of 928 reflections with $F_o^2 > 2\sigma(F_o^2)$] = 0.0377, goodness of fit $S = 1.138$ on all F^2 for 114 parameters. Maximum $\Delta/\sigma = 0.001$, mean $\Delta/\sigma = 0.000$.

CCDC reference number 186/692.

Acknowledgements

Contribution no. 70 from Anglo-Czech Polyhedral Collaboration (ACPC). We thank the Grant Agency of the Czech Republic (Grant No. 203/97/0060), the Academy of Sciences of the Czech Republic, the EPSRC (United Kingdom) and the Royal Society (London) for support, and Dr Z. Plzák for mass spectra.

References

1 See, for example, T. Onak, in *Boron Hydride Chemistry*, ed. E. L. Muetterties, Academic Press, New York, 1973, pp. 349–382; B. Štíbr, *Chem. Rev.*, 1992, **92**, 225.

2 For review see, for example, B. Štíbr, J. Plešek, T. Jelínek, K. Baše, Z. Janoušek and S. Heřmánek, in *Boron Chemistry*, *Proceedings of the Sixth International Meeting on Boron Chemistry*, Bechyně, 22–26 June, 1987, S. Heřmánek, World Scientific Publishing Co. PTE, Singapore, 1987, pp. 175–206; B. Štíbr, J. Plešek and S. Heřmánek, in *Molecular Structure and Energetics*, *Advances in Boron and the Boranes*, eds. J. F. Liebman, A. Greenberg and R. E. Williams, VCH, New York, 1988, vol. 5, ch. 3, pp. 35–70.

3 See, for example, (*a*) B. Štíbr, J. Holub, I. Císařová, F. Teixidor, C. Viñas, J. Fusek and Z. Plzák, *Inorg. Chem.*, 1996, **35**, 3635; (*b*) M. A. Fox, R. Greatrex and A. Nikrahi, *Chem. Commun.*, 1996, 175; (*c*) B. A. Barnum, P. J. Carroll and L. G. Sneddon, *Inorg. Chem.*, 1997, **36**, 1327.

4 See, for example, R. J. Astheimer and L. G. Sneddon, *Inorg. Chem.*, 1983, **22**, 1928; B. Štíbr, T. Jelínek, E. Drdáková, S. Heřmánek and J. Plešek, *Polyhedron*, 1988, **7**, 669; J. W. Bausch, R. C. Rizzo, L. G. Sneddon, A. E. Wille and R. E. Williams, *Inorg. Chem.*, 1996, **35**, 131.

5 (*a*) H. Knoth, *J. Am. Chem. Soc.*, 1967, **89**, 1274; (*b*) W. H. Knoth, *Inorg. Chem.*, 1971, **10**, 598; (*c*) K. Nestor, B. Štíbr, J. D. Kennedy, M. Thornton-Pett and T. Jelínek, *Collect. Czech. Chem. Commun.*, 1992, **57**, 1262.

6 R. V. Schultz, J. C. Huffman and L. J. Todd, *Inorg. Chem.*, 1979, **18**, 2883.

7 J. H. Jones, B. Štíbr, J. D. Kennedy and M. Thornton-Pett, *Collect. Czech. Chem. Commun.*, 1993, **58**, 2924.

8 (*a*) F. R. Scholer and L. J. Todd, *J. Organomet. Chem.*, 1968, **14**, 261; (*b*) K. Baše, B. Štíbr, J. Dolanský and J. Duben, *Collect. Czech. Chem. Commun.*, 1981, **46**, 2345; (*c*) T. Jelínek, B. Štíbr, J. Plešek and S. Heřmánek, *J. Organomet. Chem.*, 1986, **307**, C13.

9 T. Jelínek J. Plešek, S. Heřmánek and B. Štíbr, *Collect. Czech. Chem. Commun.*, 1986, **51**, 819.

10 B. Štíbr, J. Plešek and A. Zobáčová, *Polyhedron*, 1982, **1**, 824; J. H. Jones, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, M. Thornton-Pett, B. Štíbr and H. Langhoff, *J. Organomet. Chem.*, 1993, **445**, C15.

11 J. Plešek, T. Jelínek, E. Drdáková, S. Heřmánek and B. Štíbr, *Collect. Czech. Chem. Commun.*, 1984, **49**, 1559.

12 P. McArdle, *J. Appl. Crystallogr.*, 1995, **28**, 65.

13 See, for example, J. D. Kennedy, in *Multinuclear N. M. R.*, ed. J. Mason, Plenum, New York, 1987, p. 221; W. C. Hutton, T. L. Venable and R. N. Grimes, *J. Am. Chem. Soc.*, 1984, **106**, 29; J. Schraml and J. M. Bellama, *Two-Dimensional NMR Spectroscopy*, Wiley, New York, 1982.

14 R. Fontaine and J. D. Kennedy, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 1573.

15 S. Heřmánek, *Chem. Rev.*, 1992, **92**, 325 and refs. therein.

16 J. Plešek, B. Štíbr, X. L. R. Fontaine, J. D. Kennedy, S. Heřmánek and T. Jelínek, *Collect. Czech. Chem. Commun.*, 1991, **56**, 1618.

17 W. McFarlane, *Proc. R. Soc. London*, *Ser. A*, 1986, **306**, 185.

18 G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.

19 G. M. Sheldrick, SHELXL 93, Program for refinement of crystal structures, University of Göttingen, 1993.

Received 20*th May* 1997; *Paper* 7/03469E