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Monocarbaborane chemistry. Preparation and characterisation of $[4\text{-}CB_8H_9]^-$, the 'missing' *closo*-carbaborane anion†‡

Tomáš Jelínek,[a] Bohumil Štíbr,[b] Josef Holub,[c] Mario Bakardjiev,[c] Drahomír Hnyk,[c] Daniel L. Ormsby,[d] Colin A. Kilner,[a] Mark Thornton-Pett,[a] Hans-Jörg Schanz,[b] Bernd Wrackmeyer[b] and John D. Kennedy*[a]

[a] *School of Chemistry of the University of Leeds, West Yorkshire, UK LS2 9JT*
[b] *Laboratorium für Anorganische Chemie der Universität Bayreuth, Postfach 101251, Bayreuth, Bayern D-95440, Germany*
[c] *Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic, 25068, Řež-by Prague, The Czech Republic*
[d] *Department of Chemistry of the Imperial College of Science, Technology and Medicine, Exhibition Road, London, UK SW7 2AY*

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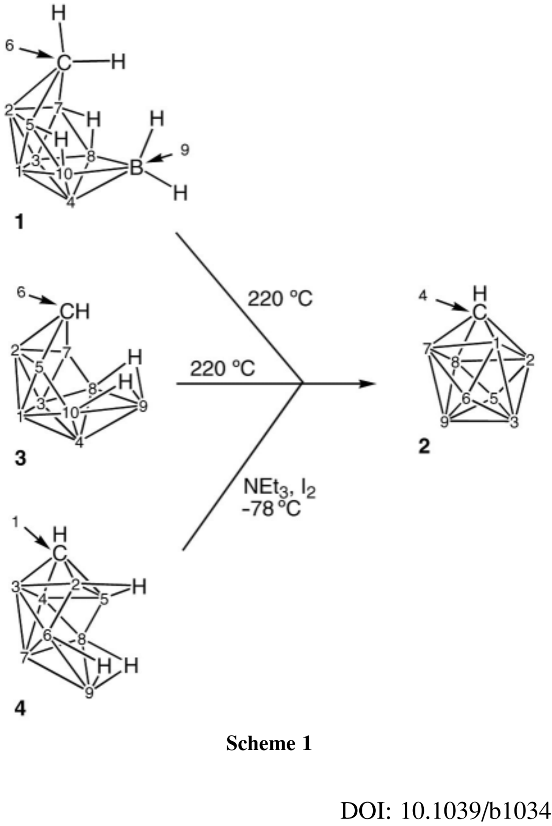
Thermolysis in the solid state of $Cs^+[arachno\text{-}CB_9H_{14}]^-$, or of $Cs^+[nido\text{-}CB_9H_{12}]^-$, or the oxidation of *nido*-1-CB_8H_{12} with I_2 in THF at −78 °C in the presence of NEt_3, gives the first nine-vertex *closo* monocarbaborane, the stable [*closo*-4-CB_8H_9]$^-$ anion, in yields of 56, 61 and 75%, respectively.

Although carbaborane chemistry is the most investigated area of polyhedral boron-containing cluster chemistry,[1,2] it is dominated by dicarbaborane chemistry. Monocarbaborane chemistry, by contrast, is sparsely represented,[1] and many of the fundamental cluster types are unreported. Of the classically *closo* $[CB_nH_{n+1}]^-$ monocarbaborane anions, $[CB_5H_6]^-$ (known only as its conjugate acid CB_5H_7), together with the $[CB_9H_{10}]^-$, $[CB_{10}H_{11}]^-$ and $[CB_{11}H_{12}]^-$ anions, have been recognised for some 30 years.[3] Of these, the $[CB_9H_{10}]^-$ and $[CB_{10}H_{11}]^-$ species and their derivatives attract much current attention.[4,5] More recently, the $[CB_7H_8]^-$ species has been reported,[6] but $[CB_6H_7]^-$ and $[CB_8H_9]^-$ have remained elusive. We now report three routes for the preparation of one of these last two missing species, *viz.* the nine-vertex $[CB_8H_9]^-$ anion, in good yields. The first two routes are simple solid-state thermolyses, of Cs^+[*arachno*-6-CB_9H_{14}]$^-$ and of Cs^+[*nido*-6-CB_9H_{12}]$^-$,[7] and the third is the straightforward oxidation of the neutral monocarbaborane *nido*-1-CB_8H_{12}[8,9] with I_2 in the presence of NEt_3. The geometries and numbering systems for the ten-vertex *nido* and *arachno* cages, and for the nine-vertex *closo* and *nido* cages, are shown in Scheme 1: unlettered vertices represent BH(*exo*) units.

In the first method a sample of Cs^+[*arachno*-CB_9H_{14}]$^-$ (compound **1** in Scheme 1)[7] is heated at 220 °C for 3 h, followed by dissolution of the product in $(Me)_2CO$, and filtration. Examination of the solution by NMR spectroscopy showed the [*closo*-4-CB_8H_9]$^-$ anion (compound **2**; *ca.* 60%), and smaller quantities of the [*nido*-CB_9H_{12}]$^-$ and [*closo*-CB_9H_{10}]$^-$ anions (*ca.* 5 and 35% respectively); no starting anion **1** remained. Chromatographic separation on a silica column (30 cm × 2.5 cm) using MeCN–CH_2Cl_2 5:95 as the eluting phase, followed by precipitation with $[PMePh_3]^+Cl^-$, thence resulted in crystalline $[PMePh_3]^+[CB_8H_9]^-$ (56% isolated). The second method consists of a similar heating of Cs^+[*nido*-CB_9H_{12}]$^-$ (compound **3**)[7] at 220 °C for 3 h, again followed by dissolution of the product in $(Me)_2CO$ and filtration. Examination by NMR spectroscopy§ again showed the [*closo*-CB_8H_9]$^-$ anion (*ca.* 61% after purification as above), but now with smaller quantities of [*nido*-$CB_{10}H_{13}$]$^-$ (20%) and [*closo*-CB_9H_{10}]$^-$ (*ca.* 3%); no starting anion **3** remained. The by-products of the formation of $[CB_9H_{10}]^-$ by these two variants suggest a series of competing reactions. Thus, $[CB_9H_{14}]^-$ may lose H_2 to give $[CB_9H_{12}]^-$, and $[CB_9H_{12}]^-$ may lose H_2 to give $[CB_9H_{10}]^-$. Alternatively, $[CB_9H_{14}]^-$ may lose $\{BH_3\}$ to give $[CB_8H_{11}]^-$ which would be unstable to H_2 loss to give $[CB_8H_9]^-$, and $[CB_9H_{12}]^-$ may lose $\{BH_3\}$ to give $[CB_8H_9]^-$ directly. $[CB_9H_{12}]^-$ may add transient $\{BH_3\}$ to give $[CB_{10}H_{12}]^-$ *via* elimination of H_2, whereas relatively hydrogen-rich $[CB_9H_{14}]^-$ would not add $\{BH_3\}$ so readily. These considerations suggest that the thermolysis conditions may be tailorable to favour between $[CB_8H_9]^-$ or $[CB_9H_{10}]^-$ formation. We currently devise experiments to examine for this possibility.

The other, efficient and fast, route for the preparation of the [*closo*-4-CB_8H_9]$^-$ anion **2** is based on the oxidation of *nido*-1-CB_8H_{12} (compound **4**).[8,9] Treatment of neutral **4** with NEt_3 (3 mol equiv.) and I_2 (1 mol equiv.) in THF solution at −78 °C for



Scheme 1

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† Electronic supplementary information (ESI) available: NMR spectroscopy and calculated coordinates for the B3LYP/6-31G* symmetry-locked structure for $[CB_8H_9]^-$. See http://www.rsc.org/suppdata/cc/b1/b103408c/

‡ Systematic IUPAC nomenclature: the *closo*-4-carbanonaborate(1−) anion; characterised crystallographically as its methyltriphenylphosphonium salt.

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1 h, followed by stirring at room temperature for a further hour, resulted in the formation of the $[NHEt_3]^+$ salt of the [*closo*-4-$CB_8H_9]^-$ anion **2**. The reaction is consistent with the stoichiometry as in eqn. (1).

$$1\text{-}CB_8H_{12}\ \mathbf{4} + 3NEt_3 + I_2 \rightarrow 3[NHEt_3]^+ + [4\text{-}CB_8H_9]^-\ \mathbf{2} + 2I^- \quad (1)$$

The $[NHEt_3]I$ by-product was removed by filtration, the filtrate evaporated to dryness, and then treated with aqueous KOH, followed by aqueous $[PBu^n_4]Br$. Extraction with CH_2Cl_2 and chromatographic separation of the CH_2Cl_2 extract on a silica column (25 cm × 2.5 cm) using MeCN–CH_2Cl_2 5 : 95 as eluting phase, thence gave crystalline $[PBu^n_4]^+$[*closo*-4-$CB_8H_9]^-$ (75%). Mechanistically, the formation of anion **2** as in eqn. (1) seems to agree with a deprotonation of CB_8H_{12} **4** by NEt_3 and thence oxidation of the transient [*nido*-1-$CB_8H_{11}]^-$ anion with I_2. Closure of the nine-vertex *nido* cage by joining the B(9) vertex of **4** with the B(2) and B(5) vertices (Scheme 1), would yield the product configuration of **2**.

The structure of the [*closo*-4-$CB_8H_9]^-$ anion **2** was confirmed by a single-crystal X-ray diffraction analysis of the $[PMePh_3]^+$ salt (Fig. 1).¶ It has the classical tricapped trigonal prismatic structure of $[B_9H_9]^{2-}$, but with a carbon atom in a four-connectivity 4-position. As with the $[B_9H_9]^{2-}$ anion,[10] the edges of the central trigonal prism, at 191.4(4)–200.4(4) pm, are at the longer end of typical interboron cluster bonding distances. NMR spectroscopy on a bulk sample was consistent with the structure derived from the single-crystal work.§¶ Like the $[CB_7H_8]^-$ anion,[6] the new compound is a stronger reducing agent than the $[CB_9H_{10}]^-$ and $[CB_{11}H_{12}]^-$ congeners. It is similarly iodinated at the sites distal from carbon; thus monoiodination with elemental I_2 in CH_2Cl_2 solution gives [3-I-*closo*-4-$CB_8H_8]^-$ and [5-I-*closo*-4-$CB_8H_8]^-$.

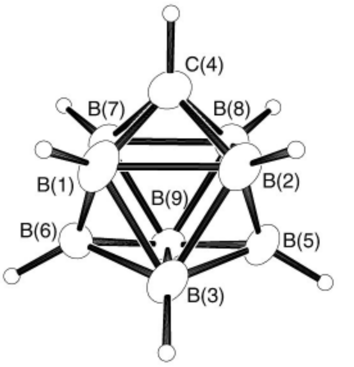

Fig. 1 Crystallographically determined molecular structure of the [*closo*-4-$CB_8H_9]^-$ anion in its $[PMePh_3]^+$ salt. The crystal had two independent $[PMePh_3]^+[CB_8H_9]^-$ units per unit cell. One anion was disordered, the other not. The anion shown here is the undisordered one. Distances (in pm throughout) from C(4) to its adjacent B atoms are in the range 162.8(5)–164.6(5), and the corresponding distances from B(5) and B(6) 'caps' are in the range 165.4(5)–177.4(5). The triangular faces of the internal trigonal prism are longer at 191.4(4)–200.4(4) than the trigonal prism edge distances at 177 6.8(5)–180.0(5); correspondingly, the angles (in degrees throughout) subtended at C(4) fall into two sets: 65.2(2)–66.2(2), and 71.9(2)–75.8(2). Similarly, angles subtended at B(5) and B(6) are in two sets: 63.3(2)–65.0(2) and 67.9(2)–72.5(2).

These results, allied with efficient routes from $B_{10}H_{14}$ to the starting monocarboranes **1**, **3** and **4**,[7,9,11] mean that the [*closo*-4-$CB_8H_9]^-$ anion is now one of the most readily accessible *closo*-carboranes. Long the missing link between eight- and ten-vertex $[1\text{-}CB_7H_8]^-$ and $[1\text{-}CB_9H_{10}]^-$, its chemistry should now contribute substantially to the development of carborane science. For example, the anion could act as a 'weakly coordinating anion' to complement $[CB_9H_{10}]^-$ and $[CB_{10}H_{11}]^-$, and their derivatives:[4] it is also likely to be amenable to substitution and metallacarborane chemistries. We currently work on the optimisation of its synthesis and on the development of other nine-vertex monocarborane chemistry.

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Notes and references

§ *NMR data*, 294–297 K, ordered as: assignment $\delta(^{11}B)$/ppm, [$\delta(^{1}H)$, {$\delta(^{13}C)$/ppm where appropriate}], observed splitting from $^1J(^{11}B^1H)$/Hz (relative intensity in parentheses): for $[PMePh_3]^+[CB_8H_9]^-$ (CD_3CN solution): BH(5,6) +12.85, [+4.35], 145, (2BH); BH(1,2,7,8), −14.40, [+1.46], 150, (4BH); BH(3,9), −20.3, [+0.60], 135, (2BH); and CH(4), —, [+4.10], —, (1CH). For $[PBu_4]^+[CB_8H_9]^-$ ($CDCl_3$ solution): BH(5,6) +12.80, [+4.37], 145, (2BH); BH(1,2,7,8) −14.30, [+1.42], 148, (4BH); BH(3,9) −20.3, [+0.64], 136, (2BH); and CH(4), —, [+4.13, {+44.5 $J(^{13}C\text{–}^{1}H)$} 182 Hz], —, (1CH).

¶ *Crystal data* for $[PMePh_3][CB_8H_9]$ (colourless, from EtOH/Et_2O at 290 K, 0.46 × 0.22 × 0.11 mm): $C_{20}H_{27}B_8P$, M = 384.87, monoclinic, space group $P2_1/a$, a = 14.7338(2), b = 14.1571(3), c = 22.7377(4) Å, β = 107.7840(10)°, U = 4516.17(14) Å^3, Z = 8, Mo-Kα radiation, λ = 0.71073 Å, μ = 0.126 mm^{-1}, T = 150(2) K, $R1$ = 0.0549 for 6775 reflections with $I > 2\sigma(I)$, $wR2$ = 0.1491 for all 8821 independent data; methods and programs were standard and from the SHELX suite.[12]

CCDC 159456. See http://www.rsc.org/suppdata/cc/b1/b103408c/ for crystallographic data in CIF or other electronic format.

1 B. Štíbr, *Chem. Rev.*, 1992, **92**, 225.
2 V. I . Bregadze, *Chem. Rev.*, 1992, **92**, 209.
3 T. Onak, R. P. Drake and G. B. Dunks, *J. Am. Chem. Soc.*, 1965, **87**, 2505; S. R. Prince and R. Schaeffer, *Chem. Commun.*, 1968, 451; T. Onak, P. Matschei and E. Groszek, *J. Chem. Soc. A*, 1969, 1990; W. H. Knoth, *J. Am. Chem. Soc.*, 1967, **89**, 1274; W. H. Knoth, *Inorg. Chem.*, 1971, **10**, 598; W. H. Knoth, *Inorg. Chem.*, 1973, **12**, 785.
4 C. Reed, *Acc. Chem. Res.*, 1998, **31**, 133; S. Strauss, *Chem. Rev.*, 1993, **93**, 927.
5 P. Kaszynski, *Collect. Czech. Chem. Commun.*, 1999, **64**, 895; and references cited therein.
6 J. Plešek, T. Jelínek, B. Štíbr and S. Heřmánek, *J. Chem. Soc., Chem. Commun.*, 1988, 348; T. Jelínek, B. Štíbr, J. Plešek, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1995, 431.
7 B. Brellochs, *Contemporary Boron Chemistry*, ed. M. G. Davidson, A. K. Hughes, T. B. Marder and K. Wade, Royal Society of Chemistry, Cambridge, UK, 2000, pp. 212–214.
8 K. Baše, S. Heřmánek and B. Štíbr, *Chem. Ind. (London)*, 1977, 951; K. Baše, B. Štíbr, J. Dolanský and J. Duben, *Collect. Czech.Chem. Commun.*, 1981, **46**, 2345.
9 T. Jelínek, I. Kanerová, J. Holub, B. Štíbr, O. Tok and B. Wrackmeyer, in preparation.
10 J. Guggenberger, *Inorg. Chem.*, 1968, **7**, 2260; M. E. O'Neill and K. Wade, *Polyhedron*, 1983, **2**, 963.
11 $B_{10}H_{14}$ (12.4 g, 100 mmol) in hexane (200 cm^3) was treated with 15% aqueous NaOH (500 cm^3) with vigorous stirring at room temperature and cooled to 0 °C. 37% aqueous HCHO (containing 36.5 g HCHO, molar ratio $B_{10}H_{14}$: HCHO = 1 : 4.5) was added together with H_2O (30 cm^3) over 1 h. The aqueous layer was separated and extracted with Et_2O (3 × 100 cm^3). Addition of saturated aqueous CsCl (100 mmol) to the combined Et_2O extracts followed by evaporation of the Et_2O, filtration, and recrystallisation of the precipitate from hot H_2O gave $Cs[CB_9H_{14}]$ (44%), as used in the thermolysis. For the CB_8H_{12} route, H_2O (100 cm^3) was added, and the Et_2O removed by rotary evaporation, resulting in an aqueous solution of $Na[CB_9H_{14}]$ [at this stage, precipitation with $[NEt_4]Cl$ can be used to give $[NEt_4][CB_9H_{14}]$ (48%)], which was added dropwise to a stirred mixture of aqueous HCl (*ca.* 4.5 M; 350 cm^3), $FeCl_3{\cdot}6H_2O$ (65 g) and hexane (200 cm^3), and stirred for 3 h. The hexane layer was separated and evaporated, and the resulting white solid sublimed to give CB_8H_{14} (5.4 g; 47%); which was converted to CB_8H_{12} by dehydrogenation at 350 °C as in ref. 8.
12 G. M. Sheldrick, University of Göttingen, Germany, 1997G. M. Sheldrick, Bruker AXS Inc., Madison, WI, 1994 and 1998.