Inorganica Chimica Acta, 221 (1994) 5–7

Inorganica
Chimica Acta
Preliminary Communication

Ten-vertex polyhedral dicarbaborane chemistry: new positional isomers of cluster constituents in the ten-vertex *arachno* dicarbaborane family: the parent [*arachno*-5,10-$C_2B_8H_{13}$]$^-$ anion and the isomeric ligand derivatives *exo*-9-L-arachno-5,6-$C_2B_8H_{12}$ and *exo*-6-L-*arachno*-5,10-$C_2B_8H_{12}$*

Josef Holub, Bohumil Štíbr** and Zbyněk Janoušek
Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Řež (Czech Republic)

John D. Kennedy and Mark Thornton-Pett
School of Chemistry, University of Leeds, Leeds LS2 9JT (UK)

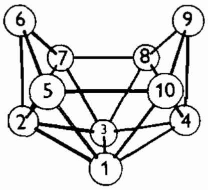
(Received January 14, 1994)

Abstract

Ammonia and primary amines (L = NH_3 and NH_2Pr^n) react with *nido*-5,6-$C_2B_8H_{12}$ in dichloromethane at ambient temperature to give the ligand derivatives *exo*-9-L-arachno-5,6-$C_2B_8H_{12}$, whereas tertiary amines (L = NEt_3 and $NBu^n{}_3$) afford the isomeric compounds *exo*-6-L-*arachno*-5,10-$C_2B_8H_{12}$; parent anion [*arachno*-5,10-$C_2B_8H_{13}$]$^-$ is prepared from the reaction between *exo*-6-(NEt_3)-*arachno*-5,10-$C_2B_8H_{12}$ and sodium metal in thf.

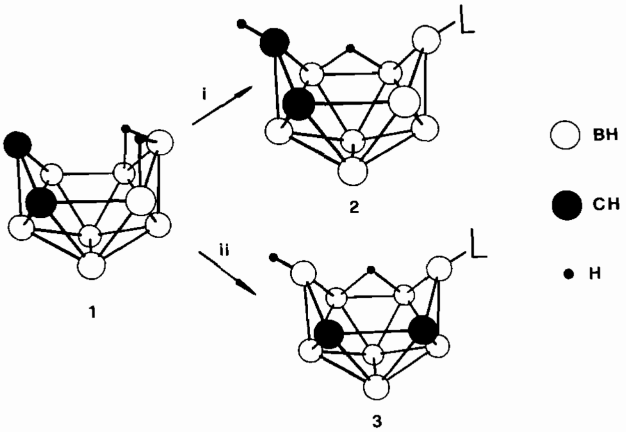
Key words: Crystal structures; Boron complexes; Dicarbaborane complexes

Our two groups have been interested for a long time in ten-vertex dicarbaboranes [1] and in their metalated analogues [2]. In the {C_2B_8} class we have reported on fundamental cluster types such as [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$ [3], *nido*-5,6-$C_2B_8H_{12}$ [4], *arachno*-6,9-$C_2B_8H_{14}$ [5] and some MC_2B_8 [6]. In this area *arachno*-6,9-$C_2B_8H_{14}$ and its substituted derivatives [7] constitute the only previously reported ten-vertex *arachno* family of dicarbaboranes, and, surprisingly, other arrangements of the two carbons are unknown in this system. However, the stability of the dicarbaplatinaborane [9,9-$(PPh_3)_2$-5,6,9-$C_2PtB_7H_{11}$] [8] suggested to us that arrangements of the cluster carbon atoms other than {6,9-C_2} would also be feasible in non-metalated parent compounds, and in accord with this we now report preliminary results on the isolation of members of the new {5,6-C_2} and {5,10-C_2} families of the ten-vertex *arachno* dicarbadecaboranes (numbering as in structure I).



Structure I.

Reactions between *nido*-5,6-$C_2B_8H_{12}$ [4] (**1**) and an equivalent amount of ammonia and n-propylamine in dichloromethane (reaction scale 5 mmol) over a period of 24 h at ambient temperature, followed by chromatographic purification on a silica gel column in dichloromethane, give white solid compounds, identified as the ligand derivatives *exo*-9-L-*arachno*-5,6-$C_2B_8H_{12}$ (structure **2**, where L = NH_3 (**2a**), NH_2Pr^n (**2b**); path i in Scheme 1) in yields 50 and 68%, respectively. By contrast, under similar conditions tertiary amines such as triethylamine and n-tributylamine give compounds of the alternative {5,10-C_2} constitution, viz. *exo*-6-L-*arachno*-5,10-$C_2B_8H_{12}$ (structure **3**; where L = NEt_3 (**3a**) and $NBu^n{}_3$ (**3b**); path ii in Scheme 1; yields 32 and 58%, respectively).



Scheme 1.

---

*Contribution No. 37 from the Řež–Leeds Anglo–Czech Polyhedral Collaboration (A.C.P.C.).

**Author to whom correspondence should be addressed.

0020-1693/94/$07.00 © 1994 Elsevier Science S.A. All rights reserved
SSDI 0020-1693(94)03972-Q

The parent (i.e. unsubstituted) [*arachno*-5,10-$C_2B_8H_{13}]^-$ anion (compound **3c**; structure **3**; $L = H^-$) was obtained from the reaction of the NEt_3 compound **3a** with sodium naphthalene in thf at room temperature for 2.5 h: hydrolysis and precipitation of the aqueous solution by $[PPh_4]Cl$ thence gave the $[PPh_4]^+$ salt in 31% yield. Anion **3c** can also be obtained in 22% yield from a similar reaction between the *nido* dicarbaborane **1** and sodium metal in thf, or, alternatively, from an interesting desulfurization reaction between *nido*-7,8,10-$C_2SB_8H_{10}$ [9] and activated sodium metal under comparable conditions (yield 19%).

All these new compounds of types **2** and **3** were identified by NMR spectroscopy[*] and mass spectrometry[**], with the general type being additionally confirmed by a single crystal X-ray diffraction study[†] on **3a** (Fig. 1). A diagnostic difference between the NMR spectra of the {5,6-C_2} species of type **2** and the {5,10-C_2} species of type **3** lies in the presence of the two typical $CH_2(6)$ *exo* and *endo* proton resonances at δ (^{1}H) *c*. 0.0 ppm (see ref. 5, for example) for compounds of structure **2**, whereas an ^{11}B NMR spectrum of a compound of type **3** exhibits a triplet for the $^{11}B(9)H_2$ resonance. This triplet is of relative intensity 2B for the unsubstituted parent anion **3c**, in which it arises from the degenerate $^{11}B(6,9)H_2$ resonance. Each of the ^{1}H NMR spectra of all compounds of types **2** and **3** also shows a high-field broad resonance attributable to the μH(7,8) bridging proton.

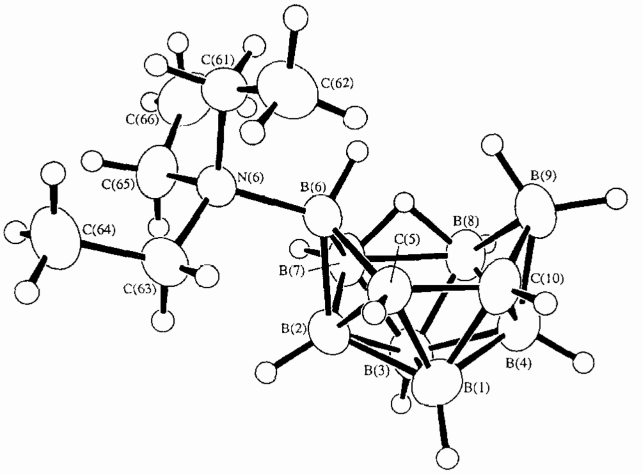


Fig. 1. ORTEP drawing of *exo*-6-(NEt_3)-*arachno*-5,10-$C_2B_8H_{12}$ (**3a**). Selected bond distances (in Å): C(5)–B(6) 1.623(3), B(6)–B(7) 1.997(3), B(6)–N(6) 1.623(3), B(7)–B(8) 1.844(4), B(8)–B(9) 1.959(4), B(9)–B(10) 1.648(4), C(5)–C(10).

We are currently working to extend this chemistry to other Lewis bases, to the chemistry of individual enantiomers via chiral HPLC separations [12], and to the use of these compounds for new metalladicarbaborane syntheses.

Supplementary material

All supplementary data including fractional atomic coordinates, thermal parameters and complete lists of

---

[*] NMR parameters for compounds of type **2** and **3** ($CDCl_3$ solution at 294 K) {ordered as assignment, $\delta(^{11}B)$ (ppm) ∓ 0.5 [$^1J(^{11}B-^1H)$ (Hz) ∓ 8 in square brackets], $\delta(^1H)$ (ppm) ∓ 0.05} (assignments by [$^{11}B-^{11}B$]-COSY and $^1H-\{^{11}B(\text{selective})\}$ experiments): **2a**, BH(4), −3.3 [128], +2.02; BH(2), −8.7 [174], +2.47; BH(10), −14.9 [131], +1.88; BH(7), −16.2 [135], +2.21; BH(8), −23.5 [134/38], +1.39; BH(9) (*endo*), −25.5 [133], −0.22; BH(1), −37.0 [153], +0.85; BH(3), −49.5 [147], +0.07; C*H*(5), +1.88; C*H*(6) (*exo*), +0.61; C*H*(6) (*endo*), −0.45; μH(7,8), −3.54; **2b**, BH(4), −3.6 [125], +2.01; BH(2), −8.4 [159], +2.52; BH(10), −15.8 [*c*. 131], +2.25; BH(7), −15.8 [*c*. 131], +1.86; BH(9), −22.3 [*c*.116], −0.35; BH(8), −24.0 [135], +1.39; BH(1), −36.9 [152], +0.90; BH(3), −49.5 [147], +0.11; C*H*(5), +1.90; C*H*(6) (*exo*), +0.61; C*H*(6) (*endo*), −0.49; μH(7,8), −3.60; **3a**, BH(8), −4.1 [130], +2.83; BH(1), −5.5 [*c*. 118], +2.47, BH(2), −10.9, [134], +2.17; BH(4), −12.8 [136], +2.04; BH(6) (*endo*), −16.8 [137], +0.24; BH(7), −22.9 [166], +2.22; BH(9), −32.9 (t) [116/119], +0.52(*exo*), −0.39(*endo*); BH(3), −56.0 [148], −0.36; C*H*(5,10), +1.78; μH(7,8), −3.43; **3b** BH(8), −4.2, [158], +2.76; BH(1), −5.3 [165], +2.44; BH(2), −10.8 [153], +2.14; BH(4), −12.7 [149], +2.01; BH(6) (*endo*), +16.1 [140], +0.24; BH(7), −22.9 [168], +2.20; BH(9), −32.8 (t) [125/125], +0.49(*exo*), −0.42(*endo*); BH(3), −56.0 [147], −0.39; C*H*(5,10), +1.78; μH(7,8), +3.48; **3c** BH(7,8), −7.6 [134], +2.17; BH(2,4), −9.4 [146], +1.94; BH(1), −23.4 [159], +1.98; BH(6,9), −33.5 (t) [116/119], +0.26(*exo*), −0.45(*endo*); BH(3), −55.3 [140], −0.63; C*H*(5,10), +2.35; μH(7,8), −3.44.

[**] Mass spectra for compounds of type **2** and **3** [70 eV (*c*. 1.12×10^{-17} J), electron impact]: high-mass cut-off (found): **2a** *m/z* 141 (M^+); **2b** *m/z* 183 (M^+); **3a** *m/z* 225 (M^+); **3b** *m/z* 309 (M^+).

[†] Crystal data for **3a**: $C_8H_{27}B_8N$, $M = 223.79$, orthorhombic, space group $Pna2_1$; $a = 14.8766(6)$, $b = 13.5419(8)$, $c = 7.3505(8)$ Å; $U = 1480.8(2)$ Å^3; $Z = 4$; $D_x = 1.004$ g cm^{-3}, $\mu = 0.335$ mm^{-1}, crystal dimensions $0.69 \times 0.22 \times 0.17$ mm. All measurements were carried out at room temperature on a Stoe STADI4 diffractometer operating in the ω/θ scan mode using Cu Kα radiation ($\lambda = 1.54184$ Å). 5293 reflections were collected in the range $4.0 < 2\theta < 130°$, 2402 were unique and 2000 had $F_o > 4.0\sigma(F_o)$. The structure was solved by direct methods using SHELXS-86 [10] and refined by full-matrix least-squares (based on F^2) using SHELXL-93 [11] which uses all data in refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters. All ethyl hydrogen atoms were constrained to predicted positions (C–H = 0.96 and 0.97 Å for tertiary and secondary hydrogens, respectively) with a fixed isotropic thermal parameter of $n(U_{eq})$ of the parent carbon atom, where $n = 1.5$ and 1.2 for methyl and methylene groups respectively. All cage associated atoms were freely refined with isotropic thermal parameters. The polar axis direction could not be unambiguously determined. The weighting scheme was $w = [\sigma^2(F_o^2) + (0.0809P)^2 + 0.1184P]^{-1}$, where $P = (F_0^2 + 2F_c^2)/3$. Final R values were $R_w^2 = 0.1226$ and $R^1 = 0.0569$, where $R_w^2 = (\Sigma[w(F_o^2 - 2F_c^2)^2]/\Sigma[wF_o^4])^{1/2}$ and $R^1 = \Sigma(||F_o| - |F_c||/|F_o|)$. The latter is given for comparison with refinements based on F and uses reflections with $F_o > 4.0\sigma(F_o)$.

bond lengths and angles have been deposited at the Cambridge Crystallographic Centre.

Acknowledgements

The authors thank Dr J. Fusek and F. Mareš for NMR measurements, Dr J. Plešek for helpful discussions, and Dr Z. Plzák for the mass spectra. We also thank the Royal Society, Borax Research Limited, the SERC, and the Academy of Sciences of the Czech Republic (Grant Nos. 432 03 and 432 402) for support, and Dr T.S. Griffin, Dr R.A. Walker and Dr D.M. Wagnerová for their helpful cooperation.

References

1 B. Štíbr, *Chem. Rev., 92* (1992) 225, and refs. therein.
2 M. Bown, T. Jelínek, B. Štíbr, S. Heřmánek, X.L.R. Fontaine, N.N. Greenwood, J.D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.,* (1988) 974.
3 B. Štíbr, J. Plešek and S. Heřmánek, *Collect. Czech. Chem. Commun., 38* (1973) 338.
4 J. Plešek and S. Heřmánek, *Chem. Ind. (London),* (1971) 1267; *Collect. Czech. Chem. Commun., 34* (1974) 821.
5 B. Štíbr, J. Plešek and S. Heřmánek, *Chem. Ind. (London),* (1972) 649; *Collect. Czech. Chem. Commun., 39* (1974) 1805.
6 J.D. Kennedy, B. Štíbr, T. Jelínek, X.L.R. Fontaine and M. Thornton-Pett, *Collect. Czech. Chem. Commun., 58* (1993) 2090, and refs. therein.
7 B. Štíbr, Z. Janoušek, J. Plešek, T. Jelínek and S. Heřmánek, *J. Chem. Soc., Chem. Commun.,* (1985) 1365; Z. Janoušek, J. Plešek, S. Heřmánek and B. Štíbr, *Polyhedron, 4* (1985) 1797; B. Štíbr, Z. Janoušek, J. Plešek, T. Jelínek and S. Heřmánek, *Collect. Czech. Chem. Commun., 52* (1987) 103; B. Štíbr, J. Plešek, T. Jelínek, S. Heřmánek, K.A. Solntsev and N.T. Kuznetsov, *Collect. Czech. Chem. Commun., 52* (1987) 957; I.Yu. Kuznetsov, K.A. Solntsev, L.A. Butman, N.T. Kuznetsov, B. Štíbr, J. Plešek and T. Jelínek, *Koord. Khim., 15* (1989) 458.
8 B. Štíbr, S. Heřmánek, J. Plešek, K. Baše and I.A. Zakharova, *Chem. Ind. (London),* (1980) 468; B. Štíbr, K. Baše, T. Jelínek, X.L.R. Fontaine, J.D. Kennedy and M. Thornton-Pett, *Collect. Czech. Chem. Commun., 56* (1991) 646.
9 V.A. Brattsev, S.P. Knyazev, G.N. Danilova and V.I. Stanko, *Zh. Obsch. Khim., 45* (1975) 1393.
10 G.M. Sheldrick, *Acta Crystallogr., Sect. A, 46* (1990) 467.
11 G.M. Sheldrick, *J. Appl. Crystallogr.,* (1993) in preparation.
12 J. Plešek, B. Grüner and P. Maloň, *J. Chromatogr., 633* (1993) 197; J. Plešek, B. Grüner, T. Vaněk and H. Votavová, *J. Chromatogr., 633* (1993) 197; B. Grüner and J. Plešek, in G.W. Kabalka (ed.), *Current Topics in the Boron Chemistry,* Royal Society of Chemistry, London, 1993, in press.