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Synthesis and Structural Characterization of the First Seven-Vertex *nido*-Carborane Anion: *nido*-3,4-$Et_2C_2B_5H_6^-$

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Summary: The reaction of *closo*-2,3-$Et_2C_2B_5H_5$ with Li(BEt_3)H in the presence of $(CH_3)_4NCl$ has been found to result in the formation of the first seven-vertex *nido*-carborane anion *nido*-3,4-$Et_2C_2B_5H_6^-$. A single-crystal X-ray study has demonstrated that the anion adopts an open-cage geometry based on a dodecahedron missing one five-connected vertex. Crystal data: space group $P2_12_12_1$, $Z = 4$, $a = 9.257$ (1) Å, $b = 9.359$ (3) Å, $c = 17.803$ (2) Å. The structure was refined by full-matrix least squares to a final R of 0.055 and R_w of 0.064 for the 1128 unique reflections having $F_o^2 > 3\sigma(F_o^2)$.

Seven-vertex nido cage systems are rare in polyhedral boron chemistry.[1] There are, in fact, no previous reports of either a neutral or anionic borane or carborane which belongs to this class.[1,2] Known examples of seven-vertex nido cage systems are found among boranes and carboranes containing metal or metalloid heteroatoms and include, for example, $(\eta^5\text{-}C_5Me_5)_2Co_2B_5H_9$,[3] $[(Me_3Si)(Me)C_2B_4H_4]SiH_2$,[4] and 6-$AlHNEt_3$-3,4-$Et_2C_2B_4H_4$;[5] however, none of these compounds have been structurally characterized.[6] We report herein both the synthesis of the first seven-vertex *nido*-carborane anion, *nido*-3,4-$Et_2C_2B_5H_6^-$, and the results of a single-crystal X-ray determination of the compound which provides the first structural details concerning this class of nido polyhedral boron clusters.

In a previous communication[7] we have reported that the small carborane *closo*-2,3-$Et_2C_2B_5H_5$ can be prepared in the simple capping reaction shown in eq 1.

$$\textit{nido}\text{-2,3-}Et_2C_2B_4H_6 + Et_3NBH_3 \xrightarrow{140\ °C} \textit{closo}\text{-2,3-}Et_2C_2B_5H_5 + Et_3N + 2H_2 \quad (1)$$

This selective route to *closo*-2,3-$Et_2C_2B_5H_5$ has now allowed initial studies of the chemical properties of this carborane. Of particular interest was the possibility of effecting cage opening of the closo framework to produce a nido precursor to larger cage carborane systems.

The use of metal hydrides to effect cage opening of a *closo*-carborane has been previously reported by Onak.[8] It was shown, for example, that the small *closo*-carborane 1,6-$C_2B_4H_6$ slowly reacts with NaH or LiH to produce *nido*-2,4-$C_2B_4H_7^-$. Similarily, we have now found that reaction of *closo*-2,3-$Et_2C_2B_5H_5$ with a slight molar excess of Li(BEt_3)H and 1 equiv of $(CH_3)_4NCl$ results in the formation of $(CH_3)_4N^+[\textit{nido}\text{-3,4-}Et_2C_2B_5H_6]^-$ consistent with eq 2.[9]

$$\textit{closo}\text{-2,3-}Et_2C_2B_5H_5 + Li(BEt_3)H + (CH_3)_4NCl \xrightarrow[\text{room temp}]{THF} (CH_3)_4N^+[\textit{nido}\text{-3,4-}Et_2C_2B_5H_6]^- + LiCl + BEt_3 \quad (2)$$

The salt is isolated as an air-stable powdery white solid,[10] mp >300 °C, which is soluble in polar solvents including methylene chloride and dry acetone but decomposes in water.

The 64.2-MHz ^{11}B NMR spectra (Figure 1) of the anion show four resonances in a 1:1:2:1 area ratio consistent with the existence of a molecular mirror plane. Furthermore, the peak at 19.3 ppm appears as a triplet, indicating that the addition of hydride has produced a $-BH_2$ group rather than a more commonly observed B–H–B bridging-hydrogen structure. It should also be noted that the peak assigned to B1 shows quartet coupling ($J_{BB} = 26$ Hz) resulting from strong interaction with another boron (B2) in the cage. A single-crystal X-ray structural determination[11] of the compound has confirmed these structural

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[1] Several review articles have discussed nido seven-vertex cage systems. See, for example: (a) Kennedy, J. D. *Prog. Inorg. Chem.* **1984**, *32*, 519–679. (b) Greenwood, N. N. *Chem. Soc. Rev.* **1984**, *13*, 353–374. (c) Greenwood, N. N. *Pure Appl. Chem.* **1983**, *55*, 1415–1430. (d) Grimes, R. N. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds., Pergamon: Oxford, 1982; Vol. 1, Chapter 5.5. (e) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1987; Chapters 3,4.

[2] Seven-vertex nido-cage systems are known for several borazine and boracycle transition-metal complexes as well as for isoelectronic π-arene systems. These species exhibit structures based on a hexagonal pyramid missing one six-connected vertex. See, for example: (a) $(\eta^6\text{-}B_3N_3Et_6)Cr(CO)_3$: Werner, H.; Prinz, R.; Deckelman, E. *Chem. Ber.* **1969**, *102*, 95–103. Huttner, G.; Krieg, B. *Chem. Ber.* **1972**, *105*, 3437–3444. (b) $(\eta^6\text{-}C_5H_5BPh)Mn(CO)_3$: Herberich, G. E.; Becker, H. J. *Angew, Chem., Int. Ed. Engl.* **1973**, *12*, 764–765. Huttner, G.; Gartzke, W. *Chem. Ber.* **1974**, *107*, 3786–3799. (c) Herberich, G. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 1, Chapter 5.3. (d) $(\eta^6\text{-}C_6H_6)Cr(CO)_3$: Fischer, E. O. *Angew. Chem.* **1957**, *69*, 715. Fischer, E. O.; Öfele, K. *Chem. Ber.* **1957**, *90*, 2532–2535. Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1314–1319.

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[6] Several formally closo seven-vertex heteroatom boranes and carboranes are known to exhibit distorted closo structures which approximate the corresponding open-faced geometry of a dodecahedron missing one vertex. See, for example: (a) $(Ph_3P)_2(CO)\overline{Os(PhMe_2P)(ClH}PtB_5H_7)$: Bould J.; Crook, J. E.; Greenwood, N. N.; Kennedy, J. D. *J. Chem. Soc., Chem. Commun.* **1983**, 951–952. (b) 1,2,3-$(Et_3P)_2PtMe_2C_2B_4H_4$: Barker, G. K.; Green, M.; Onak, T. P.; Stone, F. G. A.; Ungermann, C. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1978**, 169–171. (c) 1-Sn-2-$[Si(CH_3)_3]$-2,3-$C_2B_4H_5$ and 1-$Sn[C_{10}H_8N_2]$-2,3-$[Si(CH_3)_3]_2$-2,3-$C_2B_4H_4$: Hosmane, N. S.; Sirmokadam, N. N.; Herber, R. H. *Organometallics* **1984**, *3*, 1665–1669. Hosmane, N. S.; de Meester, P.; Maldar, N. N.; Potts, S. B.; Chu, S. S. C.; Herber, R. H. *Organometallics* **1986**, *5*, 727–778.

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[9] In a typical reaction, 171 mg (1.21 mmol) of *closo*-2,3-$Et_2C_2B_5H_5$, ~1.4 mmol of Li(BEt_3)H (1.4 mL of a 1 M THF solution), and 136 mg (1.24 mmol) of $(CH_3)_4NCl$ were combined in 5 mL of THF in vacuo. The reaction mixture was warmed slowly to room temperature and allowed to stir for 24 h. The resulting solution was then filtered under a blanket of argon and LiCl removed. Solvent and Et_3B were evaporated from the filtrate under high vacuum to give a white powdery solid. Recrystallization from methylene chloride/octane at −10 °C afforded 143 mg (0.66 mmol) (54.6%) of pure $(CH_3)_4N^+[\textit{nido}\text{-3,4-}Et_2C_2B_5H_6]^-$. Anal. Calcd for $C_{10}N_1B_5H_{28}$: C, 55.51; H, 13.04; N, 6.47. Found: C, 55.15; H, 13.09; N, 6.09.

[10] Spectroscopic data for $(CH_3)_4N^+[\textit{nido}\text{-3,4-}Et_2C_2B_5H_6]^-$: ^{11}B NMR (64.2 MHz, ppm, acetone-d_6) 24.1 (d, B2, $J_{BH} = 139$ Hz), 19.3 (t, B6, $J_{BH} = 110$ Hz), 4.8 (d, B5,7, $J_{BH} = 128$ Hz), −21.3 (d of q, $J_{BH} = 155$ Hz, $J_{BB} = 26$ Hz); ^1H NMR (200.1 MHz, δ, methylene-d_2 chloride) 3.27 (s, $(CH_3)_4N^+$), 2.31 ((m, CH_2(cage Et)), $J_{HH} = 7.5$ Hz), 1.11 (t, CH_3, (cage Et)), $J_{HH} = 7.5$ Hz); ^1H NMR (^{11}B spin-decoupled) δ 4.6 (s, BH), 2.7 (s, BH), 2.3 (s, 2BH), −0.3 (s, BH); IR (KBr pellet) 3020 (m), 2960 (s), 2930 (m), 2900 (w), 2870 (m), 2530 (s, BH), 2520 (s, BH), 2500 (m, BH), 2460 (s, BH), 2440 (s, BH), 2360 (m, BH), 2310 (s, BH), 1485 (s), 1455 (m), 1445 (w), 1420 (w), 1370 (w), 1360 (w), 1310 (w), 1285 (w), 1180 (m), 1150 (w), 1060 (w), 1030 (w), 1000 (w), 980 (w), 950 (s), 920 (w), 880 (w), 850 (w), 810 (w), 750 (w), 710 (w) cm^{-1}.

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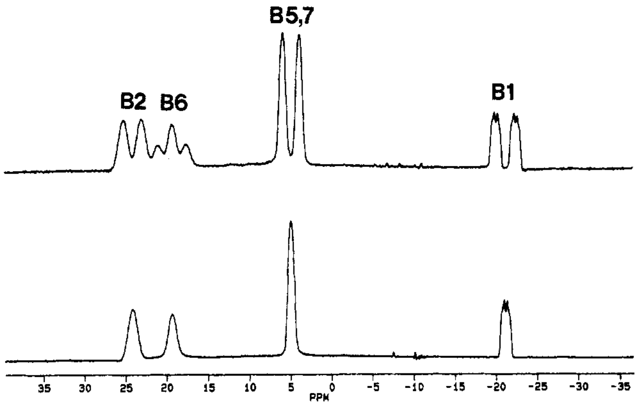

Figure 1. The 64.2-MHz ^{11}B NMR spectra of *nido*-3,4-$Et_2C_2B_5H_6^-$. The bottom spectrum is proton-spin decoupled. Two-dimensional ^{11}B–^{11}B NMR established the following connectivities: B1–B2; B1–B5,7; B2–B5,7; B2–B6; B6–B5,7.

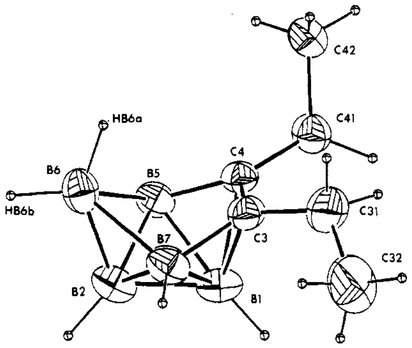

Figure 2. ORTEP drawing of the molecular structure of the *nido*-3,4-$Et_2C_2B_5H_6^-$ anion. Selected bond lengths (Å) and angles (deg): B1–B2, 1.677 (8); B1–C3, 1.739 (7); B1–C4, 1.728 (7); B1–B5, 1.835 (7); B1–B7, 1.838 (8); B2–B5, 1.712 (7); B2–B6, 1.695 (8); B2–B7, 1.704 (8); C3–C4, 1.432 (6); C3–B7, 1.534 (7); C4–B5, 1.538 (7); B5–B6, 1.972 (8); B6–B7, 1.966 (8); B6–HB6a, 1.18 (5), B6–HB6b, 1.11 (5); B2–B6–HB6a, 145 (2); B2–B6–HB6b, 107 (3); B5–B6–HB6a, 101 (2); B5–B6–HB6b, 131 (3); B7–B6–HB6a, 100 (2); B7–B6–HB6b 129 (3); HB6a–B6–HB6b, 108 (3).

features and demonstrated that the anion adopts a nido geometry consistent with its 18 skeletal-electron count.

Thus, as shown in the ORTEP drawing in Figure 2, the structure of the anion is based on a dodecahedron missing one five-connected vertex and is the first seven-vertex *nido*-boron cluster for which this geometry has been conclusively demonstrated. All boron-connected hydrogens were located and refined, and a $-BH_2$ group, consistent both with the NMR data and with the formation of the anion from *closo*-2,3-$Et_2C_2B_5H_5$, is found at B6. The distances and angles within the cage are in the normal ranges observed in polyhedral carboranes,[12] except for the unusually short B1–B2 distance of 1.677 (8) Å. This distance is again consistent with the NMR results showing strong coupling between these two atoms.

The susceptibility of *closo*-2,3-$Et_2C_2B_5H_5$ to attack by hydride is interesting in view of the fact that the nonadjacent carbon isomers, *closo*-2,4-$R_2C_2B_5H_5$ (R = H or Et), are unreactive toward nucleophilic attack by reagents such as Me_3N[13] or $Li(BEt_3)H$.[14] Molecular orbital calculations indicate,[15] however, that *closo*-2,3-$C_2B_5H_7$ has a significantly higher dipole moment than the closo-2,4-isomer, suggesting that it should be particularly reactive toward polar reagents. The X-ray results for *nido*-3,4-$Et_2C_2B_5H_6^-$, which confirm that the cage carbons remain adjacent, in conjunction with the mild reaction conditions leading to the formation of the anion, support a cage-opening process involving no major rearrangement of the *closo*-2,3-$Et_2C_2B_5H_5$ skeletal framework. Such a process resulting in the formation of the five-membered open face requires that hydride add exclusively at one of the apical (B1,7) positions and be accompanied by the opening of a triangular C–B–C face. These conclusions are also consistent with calculations[15,16] of the ground-state charges in *closo*-2,3-$C_2B_5H_7$ which indicate that the apical borons are the only positively charged borons in the molecule and would, therefore, be the sites of nucleophilic attack.

The isolation of $(CH_3)_4N^+$[*nido*-3,4-$Et_2C_2B_5H_6]^-$ suggests that an isoelectronic neutral carborane of the general formula *nido*-$R_2C_2B_5H_7$ may exist. Studies now in progress are aimed at the production of a neutral analogue of *nido*-3,4-$Et_2C_2B_5H_6^-$ as well as exploring the reactivity of the anion toward borane expansion reagents and transition-metal complexes.

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Supplementary Material Available: Listings of positional parameters, general temperature factor expressions, bond distances, bond angles, and molecular planes (10 pages); a listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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(11) $(CH_3)_4N^+$[*nido*-3,4-$Et_2C_2B_5H_6]^-$ crystallized in the orthorhombic space group $P2_12_12_1$ with a = 9.257 (1) Å, b = 9.359 (3) Å, c = 17.803 (2) Å, V = 1542.4 (6) Å^3, and ρ_{calcd} = 0.932 g/cm^3 for Z = 4. The crystal dimensions were 0.25 × 0.35 × 0.20 mm. Diffraction data: Enraf-Nonius CAD4 diffractometer; Cu radiation (Kα, 1.54184 Å); range $6.0 \leq 2\theta \leq 120°$; ($+h,+k,\pm l$), 10,10,±20; 1344 unique data, 1128 observed $F_o^2 > 3.0\sigma(F_o^2)$; corrected for anomalous dispersion, Lorentz, and polarization effects. The structure was solved by direct methods (MULTAN 11/82) and difference Fourier syntheses. Final refinements included anisotropic thermal parameters for non-hydrogen atoms and fixed thermal parameters (6.0 Å^2) for the cage hydrogens and the methyl hydrogens of the $(CH_3)_4N^+$ cation. Hydrogen atom positions for the ethyl hydrogens were calculated and included (but not refined) in the structure factor calculations. Final agreement factors were R = 0.055 and R_w = 0.064. The final difference Fourier map was featureless with the largest peak being 0.218 e/Å^3.

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