Communication

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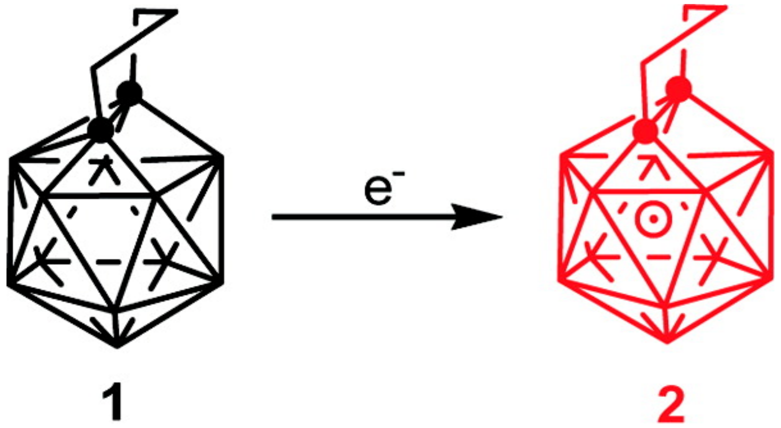

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Synthesis and Crystal Structure of a 13-Vertex Carborane Radical Anion with 2*n* + 3 Framework Electrons

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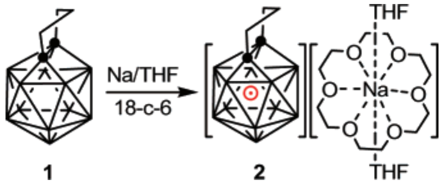
Boranes and carboranes with odd skeletal electron counts are rare. A few examples of $2n + 1$ clusters (n = the number of vertices), lying between the $2n + 2$ (*closo*) and $2n$ (*hypercloso*) structural types, have been reported, which include radical anions $[\cdot B_nX_n]^-$ (X = Cl, Br, I, $n = 6, 9$; X = Cl, $n = 8, 10$),[1] $[\cdot B_{12}R_{12}]^-$ (R = Me, $OCH_2C_6H_5$)[2] and neutral radical species $\cdot CB_{11}Me_{12}$,[3] with the latter two being crystallographically characterized. However, clusters with $2n + 3$ framework electrons, which fall between the two well-established and abundant closed $2n + 2$ (*closo*) and open $2n + 4$ (*nido*) structural systems,[4] have never been isolated, although they were detected by electrochemical techniques.[5] For example, two sequential and reversible one-electron reduction waves were observed in the electrochemical studies of 1,2-Ph_2-1,2-$C_2B_{10}H_{10}$ in DMSO/0.1 M NEt_4ClO_4 solution.[5] Treatment of biscarborane $(C_2B_{10}H_{11})_2$ with 2 equiv of Na metal resulted in the isolation of $[(C_2B_{10}H_{11})_2]^{2-}$ with a C═C double bond between two carborane polyhedra.[6] Reduction of 1,2-$(PhCH_2)_2$-1,2-$C_2B_{10}H_{10}$ with 1 equiv of K metal led to the deprotonated species $[(PhCH_2)(PhCH)C_2B_{10}H_{10}]^-$ in which a C═C double bond is observed between the cage and benzylidene unit.[7] No radical anions $[\cdot R_2C_2B_{10}H_{10}]^-$ have been isolated thus far in spite of many efforts and theoretical calculations suggesting that $[\cdot C_2B_{10}H_{12}]^-$ should have appreciable thermodynamic stability.[5d,8]

We discovered during the course of our studies that a dark-brown solution was generated when 13-vertex carborane 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ was treated with an excess amount of Na metal in THF, which was slowly turned to a pale yellow solution within 12 h. The final product was $[(CH_2)_3C_2B_{11}H_{11}][Na_2(THF)_4]$ as colorless crystals.[9] We wondered if the dark-brown solution contained long-sought carborane radical anion with a $2n + 3$ skeletal electron count. After many attempts, the first boron cluster with a $2n + 3$ system $[\cdot\{1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{11}H_{11}\}][Na(18\text{-crown-}6)(THF)_2]$ ([**2**][Na(18-crown-6)(THF)$_2$]) was isolated and fully characterized, which is reported in this communication.

Treatment of 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ (**1**)[9] with 1 equiv of finely cut Na metal in THF at room temperature gave, after recrystallization from a mixed THF/hexane solution of 18-crown-6, [**2**][Na(18-crown-6)(THF)$_2$] as brown crystals in 80% isolated yield (Scheme 1).[10] It is very air- and moisture-sensitive but remains stable for months at room temperature under an inert atmosphere. Traces of air immediately convert the intensively colored **2** to a pale yellow powder. The salt is soluble in THF and ether and insoluble in aromatic solvents and hexane.

Both THF solution and solid samples of [**2**][Na(18-crown-6)(THF)$_2$] exhibited an EPR signal as expected for a radical anion with $g = 1.994$ (line width = 23 G in solution and 5.5 G in solid state) at room temperature and no NMR signals, which is similar to those observed in $\cdot CB_{11}Me_{12}$[3] and $[\cdot B_{12}Me_{12}]^-$.[2] The UV−vis spectrum of [**2**][Na(18-crown-6)(THF)$_2$] in THF displayed a relatively intense absorption band centered at 360 nm.

Scheme 1. Preparation of [**2**][Na(18-crown-6)(THF)$_2$]



Cyclic voltammetry of **1** in MeCN/0.1 M Bu_4NPF_6 showed one reversible wave with $E_{1/2}(0/-1) = -1.28$ V for the one-electron process $\mathbf{1} + e^- \rightarrow \mathbf{2}$ and one quasi-reversible peak with $E_{1/2}(-1/-2) = -1.85$ V (vs ferrocene (Fc)) for another one-electron process $\mathbf{2} + e^- \rightarrow [(CH_2)_3C_2B_{11}H_{11}]^{2-}$ (Figure 1).

Single-crystal X-ray analyses revealed that [**2**][Na(18-crown-6)(THF)$_2$] consists of well-separated, alternating layers of discrete radical anions **2** and cations $[Na(18\text{-crown-}6)(THF)_2]^+$.[11] As shown in Figure 2, **2** bears two trapezoidal faces with the others being triangulated, giving one five- and one four-coordinate cage carbon atoms, respectively. This geometry is similar to that observed in 1,2-$(CH_2)_3$-3-Ph-1,2-$C_2B_{11}H_{10}$ (**3**)[9b] but is significantly different from that of $[(CH_2)_3C_2B_{11}H_{11}]^{2-}$ in $[(CH_2)_3C_2B_{11}H_{11}][Na_2(THF)_4]$.[9] Although the average B−B/B−C distances of 1.80(1)/1.71(1) Å are close to those found in **3** and other 13-vertex carboranes,[12] the C(1)···B(4)/B(3A) and C(1′A)···B(3)/B(2A) distances are longer than the corresponding values observed in **3**.

In conclusion, the carborane radical anion with $2n + 3$ framework electrons has been isolated and structurally characterized. It is an intermediate between the two well-established and abundant $2n + 2$ (*closo*) and $2n + 4$ (*nido*) systems. This result may imply that larger cages would enhance the thermodynamic stability of clusters with $2n + 3$ systems. The $(CH_2)_3$ linkage between the two cage carbons plays no obvious role in stabilizing the radical anion **2** since the corresponding 12-vertex radical anion $[\cdot(CH_2)_3C_2B_{10}H_{10}]^-$ cannot be prepared under the same reaction conditions. The next

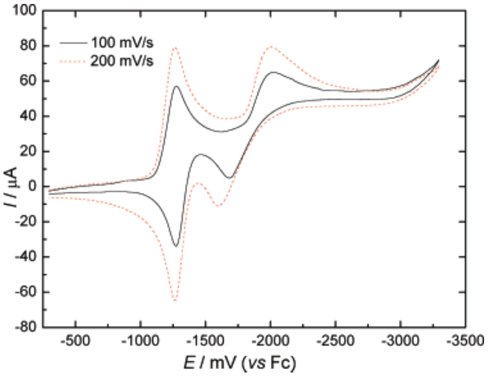


Figure 1. Cyclic voltammograms of **1** in MeCN/0.1 M Bu_4NPF_6 recorded at 100 mV/s (solid line in black) and 200 mV/s (dotted line in red).

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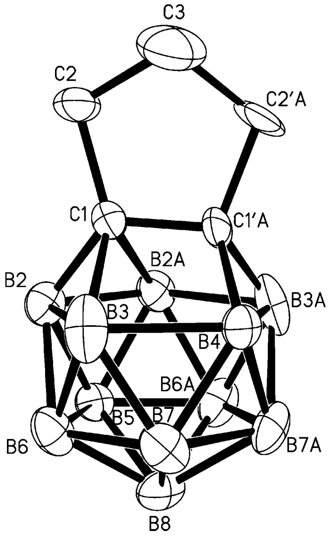

Figure 2. Molecular structure of **2** showing only one conformer. Selected bond lengths [Å]: C1−C1′A 1.45(1), C1−B2 1.49(1), C1−B3 1.91(1), C1−B2A 1.98(1), C1···B4 2.52 (1), C1···B3A 2.53 (1), C1′A···B3 2.37 (1) C1′A···B2A 2.17 (1), C1′A−B3A 1.49(1), C1′A−B4 1.67(1), C1−C2 1.56(1), C2−C3 1.52(1), C3−C2′A 1.47(1), C2′A−C1′A 1.51(1).

synthetic challenge in the preparation of clusters with odd skeletal electron counts will probably be carboranes with $2n + 5$ framework electrons.

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Supporting Information Available: Complete ref 1b, detailed experimental procedures, characterization data, and X-ray data in cif format for [**2**][Na(18-crown-6)(THF)$_2$]. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Detailed experimental procedures and complete characterization data including X-ray data are provided in the Supporting Information.

(11) Crystal data for [**2**][Na(18-crown-6)(THF)$_2$] ($C_{25}H_{57}B_{11}NaO_8$); fw = 627.61): monoclinic, space group $C2/m$, $a = 30.55(2)$ Å, $b = 11.514(8)$ Å, $c = 10.562(7)$ Å, $\beta = 97.58(1)°$, $V = 3683(4)$ Å^3, $T = 173$ K, $Z = 4$, $d_{\text{calcd}} = 1.132$ g/cm^3, $R1 = 0.088$ ($I > 2\sigma(I)$), $wR2(F^2) = 0.223$. Note that both C(1) and C(2) are disordered over two sets of positions with 0.50:0.50 occupancies.

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