

# The first full-sandwich potassacarborane and a novel 'carbons-adjacent' $R_2C_2B_{10}H_{11}^-$ monoanion

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By taking advantage of a cage carbon-linked *o*-carborane, the full-sandwich potassacarborane and a novel carborane monoanion have been prepared and structurally characterized for the first time, in which the cage carbon atom adjacency of the precursor is maintained.

It has been well documented that *o*- $R_2C_2B_{10}H_{10}$  ( $R = H$ , alkyl, aryl) can be readily reduced by alkali metals to form the  $[nido-R_2C_2B_{10}H_{10}]^{2-}$  dianion in which the cage carbon atoms are in *meta* positions.<sup>1</sup> The cage C–C bond is completely broken during this two-electron reductive process.<sup>1</sup> The structures of its alkali metal salts have recently been reported.<sup>2</sup> These salts are very useful versatile synthons for the production of numerous metallocarboranes of s-, p-, d-, and f-block elements.<sup>1</sup> Protonation of  $[nido-R_2C_2B_{10}H_{10}]^{2-}$  affords two isomers, the kinetic one **A** and the thermodynamic product **B**, as shown in Scheme 1.<sup>3</sup> Isomer **B** is more stable than **A** by 6.7 kcal mol<sup>-1</sup> according to the computational results.<sup>4</sup> We have found that the two cage carbon atoms remain adjacent in *ortho* positions during the two-electron reductive process if they are linked by a short bridge, which leads to the isolation and structural characterization of the first full-sandwich potassacarborane and the novel isomer of the  $[R_2C_2B_{10}H_{11}]^-$  monoanion. These new findings are reported in this communication.

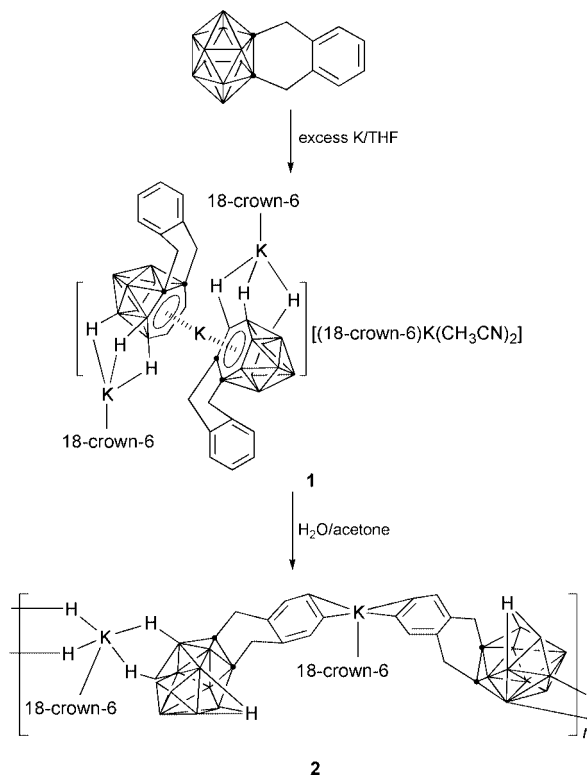
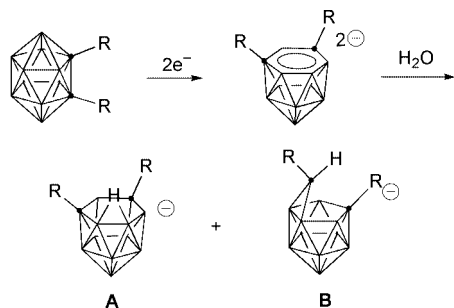
Treatment of  $\mu$ -1,2- $[o-C_6H_4(CH_2)_2]$ -1,2- $C_2B_{10}H_{10}$ <sup>5</sup> with excess finely cut potassium metal in THF at room temperature gives, after recrystallization from a THF/CH<sub>3</sub>CN solution of 18-crown-6, the first full-sandwich potassacarborane  $[closo-exo-\{\mu$ -1,2- $[o-C_6H_4(CH_2)_2]$ -1,2- $C_2B_{10}H_{10}\}_2K_3(18-crown-6)_2][(18-crown-6)K(CH_3CN)_2]$  (**1**) as yellow crystals in 74% yield.<sup>†</sup> **1** is extremely air- and moisture-sensitive but remains stable for months at room temperature under an inert atmosphere. Protonation of **1** generates a novel carborane monoanion  $[\{\mu$ -1,2- $[o-C_6H_4(CH_2)_2]$ -1,2- $C_2B_{10}H_{11}\}K(18-crown-6)]_n$  (**2**) as colorless crystals.<sup>†</sup> These transformations are summarized in Scheme 2. Both **1** and **2** have been fully characterized by various spectroscopic, elemental and X-ray analyses.

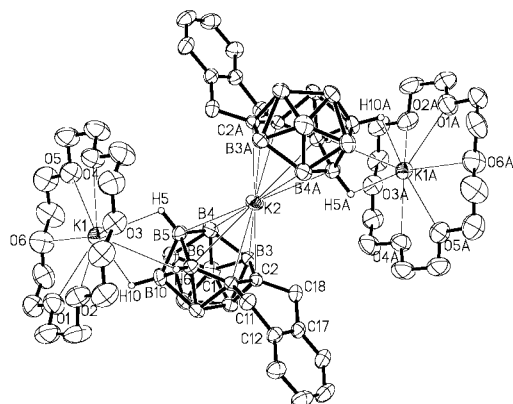
The <sup>1</sup>H NMR spectra show that methylene protons on the carborane cage in both **1** and **2** are non-equivalent in solution, and support the ratios of 1.5 18-crown-6 and one acetonitrile molecule per carboranyl ligand for **1**, and one 18-crown-6 molecule per ligand for **2**, respectively. The <sup>13</sup>C NMR spectra are consistent with the results derived from their <sup>1</sup>H NMR

spectra. The <sup>11</sup>B NMR spectra exhibit 2:2:1:2:1:1:1 and 1:4:3:1:1 splitting patterns for **1** and **2**, respectively. Their solid-state IR spectra display both a characteristic doublet centered around 2450 cm<sup>-1</sup> and a shoulder at about 2360 cm<sup>-1</sup> attributable to a K–H–B stretching mode.<sup>6</sup>

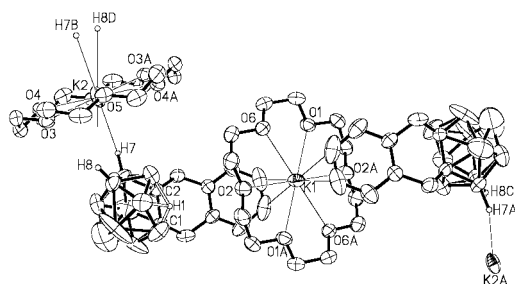
An X-ray analysis<sup>‡</sup> reveals that **1** is a centrosymmetric molecule consisting of well-separated, alternating layers of discrete cations  $[(18-crown-6)K(CH_3CN)_2]^+$  and complex anions  $[closo-exo-\{\mu$ -1,2- $[o-C_6H_4(CH_2)_2]$ -1,2- $C_2B_{10}H_{10}\}_2K_3(18-crown-6)_2]^-$ . In the anion, the K2 atom sits at an inversion center and bonds to two *nido*-carboranyl ligands in a  $\eta^6$  fashion to form a fully sandwiched metallocarborane, shown in Fig. 1. It is interesting to note that the cage carbon atom adjacency of the precursor is maintained in the product due to the presence of the short bridge between the two cage carbon atoms. The six atoms of the hexagonal  $C_2B_4$  bonding face are coplanar compared with the staggered arrangement of the two carbon atoms of the hexagonal face in the 'carbons-apart' dianionic species  $[nido-R_2C_2B_{10}H_{10}]^{2-}$ .<sup>3</sup> The average K2–cage atom distance of 3.064(4) Å is close to the corresponding value of 3.174(2) Å observed in  $[closo-exo-\{(C_6H_5CH_2)_2C_2B_{10}H_{10}\}K_2(THF)_2(O_2C_4H_8)_{0.5}]_n$ .<sup>2</sup>

In contrast to **1**, **2** adopts a polymeric structure in which the carboranyl and potassium ions serve as alternating bridging groups to give a zigzag carborane–K–carborane–K chain that is maintained in one-dimension throughout the lattice (Fig. 2). The





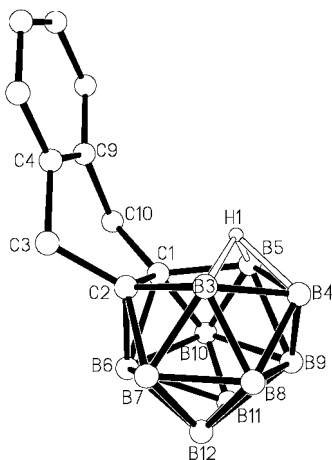
**Fig. 1** ORTEP illustration of  $[\text{closo-exo-}\{\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}_2\text{K}_3(18\text{-crown-}6)_2\text{-}]^-$  in **1** with thermal ellipsoids drawn at the 35% probability level.



**Fig. 2** ORTEP illustrations of **2** showing a portion of the infinite polymeric chain (thermal ellipsoids drawn at the 35% probability level).

most significant part of this structure is the arrangement of the cage atoms: 5-coordinate carbon and boron (C1, C2 and B11), 6-coordinate boron (B3–B5, B7, B8, B10 and B12), and 7-coordinate boron (B9 and B6), shown in Fig. 3. There are two pentagonal belts, one (B6B7B8B9B10) is capped by two boron atoms (B11 and B12) and the other (C1C2B3B4B5) is partially capped by one  $\mu_3\text{-H}$  atom. This is a brand new isomer of the  $[\text{R}_2\text{C}_2\text{B}_{10}\text{H}_{11}]^-$  monoanion which has never been observed before. Since **2** is prepared in a hot acetone solution, it is reasonable to suggest that **2** is the thermodynamic ('stable') product, which is also supported by  $^{11}\text{B}$  NMR data. It is very obvious that the presence of a short bridge plays a significant role in the generation of the novel carborane monoanion in **2**.

In summary, the 'carbons-adjacent' carborane dianion and monoanion of the  $\text{C}_2\text{B}_{10}$  system can be readily produced by introducing a short bridge between two cage carbon atoms of an *o*-carborane. This study implies that these anions may exhibit a different chemistry from the corresponding 'carbons-apart' species.



**Fig. 3** Closer view of  $[\mu\text{-}1,2\text{-}\{o\text{-C}_6\text{H}_4(\text{CH}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{11}\}]^-$  in **2**.

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## Notes and references

† **Preparation of 1:** To a THF (25 mL) solution of  $\mu\text{-}1,2\text{-}[o\text{-C}_6\text{H}_4(\text{CH}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}]$  (0.246 g, 1.00 mmol) was added finely cut K metal (0.25 g, 6.39 mmol), and the mixture was stirred at room temperature for a week. After removal of excess K, the clear orange solution was concentrated to about 10 mL to which was added a  $\text{CH}_3\text{CN}$  solution (10 mL) of 18-crown-6 (0.53 g, 2.00 mmol). **1** was isolated as yellow crystals after this solution stood at room temperature for a week (0.56 g, 74%).  $^1\text{H}$  NMR (pyridine- $d_5$ ):  $\delta$  7.22 (m, 2H, aryl H), 7.10 (m, 2H, aryl H), 4.29 (d,  $J = 15.0$  Hz, 2H,  $\text{C}_6\text{H}_4(\text{CH}_2)_2$ ), 4.15 (d,  $J = 15.0$  Hz, 2H,  $\text{C}_6\text{H}_4(\text{CH}_2)_2$ ), 3.47 (s, 36H,  $\text{C}_{12}\text{H}_{24}\text{O}_6$ ), 1.87 (s, 3H,  $\text{CH}_3\text{CN}$ );  $^{13}\text{C}$  NMR (pyridine- $d_5$ ):  $\delta$  141.28, 125.99, 124.73 ( $\text{C}_6\text{H}_4(\text{CH}_2)_2$ ), 117.60 ( $\text{CH}_3\text{CN}$ ), 69.54 ( $\text{C}_{12}\text{H}_{24}\text{O}_6$ ), 48.54 ( $\text{C}_6\text{H}_4(\text{CH}_2)_2$ ), 0.35 ( $\text{CH}_3\text{CN}$ ), the cage carbon atoms were not observed;  $^{11}\text{B}$  NMR (pyridine- $d_5$ ):  $\delta$  3.23 (2B),  $-3.25$  (2B),  $-5.83$  (1B),  $-11.59$  (2B),  $-18.06$  (1B),  $-22.28$  (1B),  $-24.16$  (1B); IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{BH}}$  2456 (vs), 2398 (s), 2351 (s). Anal. Calc. for  $\text{C}_{60}\text{H}_{114}\text{B}_{20}\text{K}_4\text{N}_2\text{O}_{18}$ : C, 47.28; H, 7.54; N, 1.84. Found: C, 46.92; H, 7.53; N, 1.94%.

**2:** To a THF (25 mL) solution of **1** (0.38 g, 0.25 mmol) was added degassed  $\text{H}_2\text{O}$  (2 mL), and the mixture was stirred at room temperature for 0.5 h. After removal of the solvent, the residue was extracted with hot acetone ( $2 \times 10$  mL). The clear colorless solution was concentrated to about 4 mL. **2** was isolated as colorless crystals after this solution stood at room temperature for a week (0.24 g, 87%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.10–6.96 (m, 4H, aryl H), 3.92 (d,  $J = 9.0$  Hz, 1H,  $\text{C}_6\text{H}_4(\text{CH}_2)_2$ ), 3.68 (d,  $J = 9.0$  Hz, 1H,  $\text{C}_6\text{H}_4(\text{CH}_2)_2$ ), 3.60 (s, 24H,  $\text{C}_{12}\text{H}_{24}\text{O}_6$ ), 3.24 (d,  $J = 15.0$  Hz, 1H,  $\text{C}_6\text{H}_4(\text{CH}_2)_2$ ), 2.95 (d,  $J = 15.0$  Hz, 1H,  $\text{C}_6\text{H}_4(\text{CH}_2)_2$ ), 1.70 (s, 1H,  $\mu\text{-H}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  138.62, 127.02, 125.55 ( $\text{C}_6\text{H}_4(\text{CH}_2)_2$ ), 48.66, 39.16 ( $\text{C}_6\text{H}_4(\text{CH}_2)_2$ ), 70.09 ( $\text{C}_{12}\text{H}_{24}\text{O}_6$ ), the cage carbon atoms were not observed;  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$   $-8.78$  (1B),  $-13.06$  (4B),  $-22.39$  (3B),  $-37.01$  (1B),  $-39.73$  (1B); IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{BH}}$  2525 (vs), 2460 (s), 2379 (m). Anal. Calc. for  $\text{C}_{22}\text{H}_{43}\text{B}_{10}\text{K}_6\text{O}_6$ : C, 47.97; H, 7.87. Found: C, 47.82; H, 8.05%.

‡ **Crystal data** for **1**:  $\text{C}_{60}\text{H}_{114}\text{B}_{20}\text{K}_4\text{N}_2\text{O}_{18}$ ,  $M = 1524.13$ , triclinic, space group  $P\bar{1}$ ,  $a = 11.645(1)$ ,  $b = 12.209(1)$ ,  $c = 16.194(1)$  Å,  $\alpha = 97.77(1)$ ,  $\beta = 103.46(1)$ ,  $\gamma = 104.23(1)^\circ$ ,  $V = 2124.7(2)$  Å $^3$ ,  $D_c = 1.191$  g  $\text{cm}^{-3}$ ,  $Z = 1$ ,  $2\theta_{\text{max}} = 50^\circ$ ,  $\mu(\text{Mo-K}\alpha) = 0.269$  mm $^{-1}$ , 11 476 reflections used, 7439 unique,  $R_1 = 0.060$  ( $I > 2.0\sigma(I)$ ),  $wR_2 = 0.158$  on  $F^2$ .

For **2**:  $\text{C}_{22}\text{H}_{43}\text{B}_{10}\text{K}_6\text{O}_6$ ,  $M = 550.76$ , monoclinic, space group  $P2_1/n$ ,  $a = 8.953(1)$ ,  $b = 18.667(2)$ ,  $c = 18.642(2)$  Å,  $\beta = 101.12(1)^\circ$ ,  $V = 3056.9(6)$  Å $^3$ ,  $D_c = 1.197$  g  $\text{cm}^{-3}$ ,  $Z = 4$ ,  $2\theta_{\text{max}} = 50^\circ$ ,  $\mu(\text{Mo-K}\alpha) = 0.208$  mm $^{-1}$ , 14 719 reflections used, 4787 unique,  $R_1 = 0.063$  ( $I > 2.0\sigma(I)$ ),  $wR_2 = 0.171$  on  $F^2$ .

Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo-K $\alpha$  radiation. An empirical absorption correction was applied using the SADABS program.<sup>7</sup> All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on  $F^2$  using the SHELXTL program package.<sup>8</sup> CCDC reference numbers 160868 and 160869. See <http://www.rsc.org/suppdata/cc/b1/b102131c/> for crystallographic data in CIF or other electronic format.

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