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Monocarbaborane anion chemistry. The substantiation of the C-arylated $[PhCB_6H_6]^-$ seven-vertex *closo* cluster anion by single-crystal synchrotron X-ray diffraction analysis

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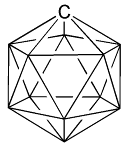
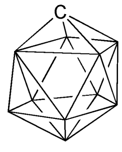
Single-crystal synchrotron X-ray diffraction analysis of the $[NEt_4]^+$ salt of the [2-Ph-*closo*-2-$CB_6H_6]^-$ anion, obtained from [4-Ph-*arachno*-4-CB_8H_{13}] and NEt_3 in refluxing toluene, substantiates the anion as the first structurally characterised seven-vertex monocarbaborane.

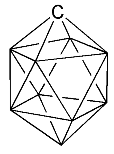
The general chemistry of the monocarbaboranes, compared to boranes on one hand and dicarbaboranes on the other, is sparsely investigated.[1] One reason for this has been an absence of convenient synthetic protocols. The Brellochs Reaction[2] of aldehydes with $B_{10}H_{14}$ in alkaline solution now gives ready access to ten-vertex $\{CB_9\}$ residues, which, *via* cluster-Aufbau and cluster-dismantling reactions, can then effect entries also into eight-vertex $\{CB_7\}$, nine-vertex $\{CB_8\}$, eleven-vertex $\{CB_{10}\}$ and twelve-vertex $\{CB_{11}\}$ systems.[2–6] For example, using the benzaldehyde entry into the $\{PhCB_9\}$ system as a model, we have recently reported the complete series of *closo* C-phenylated monocarbaborane anions [1-Ph-*closo*-1-$CB_{11}H_{11}]^-$ **1**, [2-Ph-*closo*-2-$CB_{10}H_{10}]^-$ **2**, [1-Ph-*closo*-1-$CB_9H_9]^-$ **3a**, [2-Ph-*closo*-2-$CB_9H_9]^-$ **3b**, [4-Ph-*closo*-4-$CB_8H_8]^-$ **4** and [1-Ph-*closo*-1-$CB_7H_7]^-$ **5** (schematic cluster structures **I**, **II**, **IIIA**, **IIIB**, **IV** and **V** respectively).[4–6] In the consideration of this sequence, it may be noted that C-arylation of monocarbaborane anions has hitherto often been recognised as a difficult target.[7]



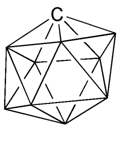
I



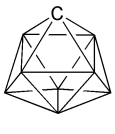
II



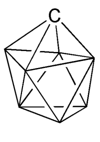
IIIA



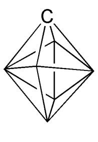
IIIB



IV



V



VI

The next member in this descending sequence is the seven-vertex [2-Ph-*closo*-2-$CB_6H_6]^-$ anion **6** (schematic cluster structure **VI**). Descriptions of $\{CB_6\}$ cluster species are essentially unknown,[1] but anion **6** has very recently been tentatively identified by NMR spectroscopy in a product mixture from which the eight-vertex [1-Ph-*closo*-1-$CB_7H_7]^-$ anion **5** was obtained as the major product.[5] We can now support this NMR identification by DFT B3LYP/6-31G* geometry optimizations of the molecular structure (Fig. 1, right), and thence by a confirmatory prediction using DFT-GIAO//B3LYP/6-31G* calculations of the boron nuclear shieldings that reasonably match the observed ^{11}B NMR chemical shifts.‡ The unsubstituted analogue $[HCB_6H_6]^-$ has similarly been identifiable very recently in a $[HCB_7H_7]^-$ product mixture.[8] More definitively, however, we now report the unequivocal structural substantiation of the C-phenylated species **6** by single-crystal synchrotron X-ray diffraction work. As far as we are aware this is the first clear structural substantiation in this hitherto elusive $\{CB_6\}$ monocarbaborane cluster system.

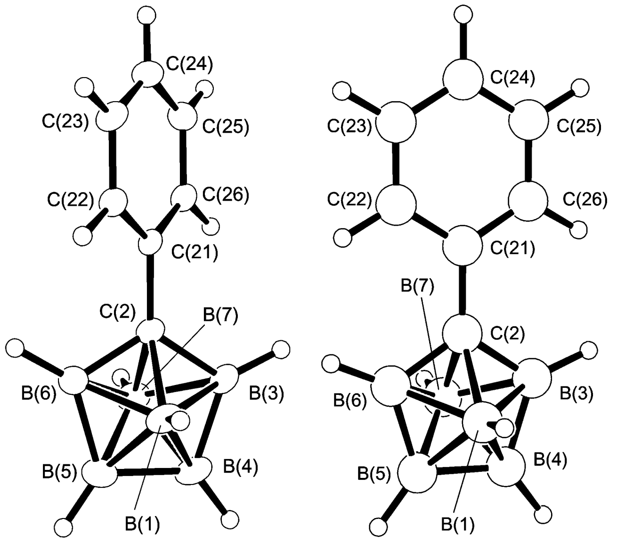


Fig. 1 Crystallographically determined (left) and DFT B3LYP/6-31G* geometry-optimized (right) molecular structures of the [2-Ph-*closo*-2-$CB_6H_6]^-$ seven-vertex cluster anion **6**. Selected dimensions in Å are as follows: from the crystallographic determination: C(2)–C(21) 1.492(2), C(2)–B(1) 1.744(2), C(2)–B(3) 1.559(2), C(2)–B(6) 1.555(2), C(2)–B(7) 1.736(2) and interboron distances 1.645(3) to 1.825(3); for the calculated structure: C(2)–C(21) 1.518, C(2)–B(1) 1.753, C(2)–B(3) 1.538, C(2)–B(6) 1.538, and C(2)–B(7) 1.753 and interboron distances 1.611 to 1.798.

Thus, a solution of [4-Ph-*arachno*-4-CB_8H_{13}] (compound **7**, 0.5 g, 2.7 mmol)[5] and NEt_3 (5 ml) in toluene (15 ml) was heated at reflux for 18 hours under dinitrogen, cooled to room temperature, and the volatile organic solvents removed *in vacuo*. In air, the residue was dissolved in 5% aqueous HCl (50 ml), filtered, and $[NEt_4]^+Cl^-$ (0.5 g, 3.0 mmol) in water (30 ml) added. The resulting white precipitate was filtered off and dried *in vacuo*, and shown by NMR spectroscopy to be a mixture of the $[NEt_4]^+$ salts of the [1-Ph-*closo*-1-$CB_7H_7]^-$ anion **5** and the new [2-Ph-*closo*-2-$CB_6H_6]^-$ anion **6** (combined amount 0.37 g,

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ca. 2.2 mmol, *ca.* 82%) in a ratio of **5** : **6** of 60 : 40, corresponding to unseparated yields of *ca.* 50 and 30% respectively. The extreme similarities of the solubility and chromatographic properties of salts of **5** and **6** have so far precluded a clean bulk separation in our hands. However, crystallisation from a concentrated solution in $(CH_3)_2CO$ that was overlayered with a *ca.* five-fold excess of Et_2O gave a mixture of crystals of the $[NEt_4]^+$ salts of both **5** and **6**. Manual separation of individual crystals, followed by unit-cell measurements on each using conventional sealed-tube X-radiation, distinguished the salt of **6** (orthorhombic, $a = 14.438(3)$, $b = 15.762(3)$ and $c = 16.877(4)$ Å at 150 K) from that previously established[5] for the salt of **5** (monoclinic, $a = 9.5758(2)$, $b = 16.5323(4)$, $c = 12.2821(3)$ Å and $\beta = 98.0110(10)°$ at 150 K). Crystals of the air-stable $[NEt_4]^+$ salt of the anion **6** thus isolated were very small, and required the use of synchrotron X-radiation (wiggler-generated from 2 GeV electrons at 150–250 mA, station 9.8, CCLRC, Daresbury, UK)[9] for sufficient diffraction intensity for molecular structure determination. The analysis of the diffraction data gave a clean result, with no disorder apparent.

The solid-state structure of anion **6** thus determined (Fig. 1, left)§ clearly mimics the pseudo-gas-phase structure arising from DFT calculations (Fig. 1, right). The only notable difference is in the rotamer angle about the C(cluster)–C(phenyl) bond-axis, but this difference is not significant, as energy barriers to phenyl-group/cluster-group contrarotation will be small[10] and easily overcome by crystal-packing forces. The seven-vertex cluster architecture is that of a pentagonal bipyramidal closed deltahedron, in accord with the Williams–Wade paradigm.[11] The all-boron analogue $[closo\text{-}B_7H_7]^{2-}$ was recognised some time ago,[12] but has not been structurally characterised, although the perbrominated $[closo\text{-}B_7Br_7]^{2-}$ species has,[13] and seven-vertex closed dicarbaboranes are well-established.[1] In anion **6** the carbon atom takes one of the positions of lower cluster-connectivity four, rather than one of higher cluster-connectivity five, also in accord with long-recognised general behavioural patterns.[11,14] The identification and substantiation of this new, stable, fundamental monocarbaborane type augurs well for the continued development of monocarbaborane chemistry, for example in an extension of the 'least-coordinating anion' chemistry[15] of the cluster species of *closo* $\{CB_n\}$ character for the study of and application of very acidic systems. We currently plan experimentation to attempt to increase the proportion of anion **6** in the product mixture at the expense of **5**, and also to attempt to find conditions for efficient bulk separation and purification.

Acknowledgements

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Notes and references

‡ Measured NMR data for the $[2\text{-Ph-}closo\text{-}2\text{-}CB_6H_6]^-$ anion **6**, $[NEt_4]^+$ salt in $(CD_3)_2CO$ at 294–299 K, ordered as assignment $\delta(^{11}B)$/ppm [$\delta(^1H)$/ppm], are as follows: BH(3,6) +6.4 [+4.11], BH(4,5) +0.5 [+3.55], BH(1,7) −19.5 [−0.16]; additionally $\delta(^1H)$(Ph) *ca.* +7.39 to +7.03 (5H, compact overlapping multiplet), and $\delta(^1H)$(Et) at +3.47 (8H, quartet), +1.39 (12H, triplet), also $\delta(^{13}C)$(Ph) +143.02 (1C), +127.66 (2C), +127.16 (2C) and +124.25 (1C), with $\delta(^{13}C)$(cluster) +85.8 and $\delta(^{13}C)$(Et) +7.07 and +52.47 ppm. Calculated $\delta(^{11}B)$ values by DFT-GIAO//B3LYP/6-31G* are as follows:[16] B(3,6) +2.8, B(4,5) −2.1 and B(1,7) −19.7 ppm.

§ Crystal data for the $[NEt_4]^+$ salt of the $[2\text{-Ph-}closo\text{-}2\text{-}CB_6H_6]^-$ anion **6**: $C_{15}H_{31}B_6N$: $M = 290.27$, orthorhombic, colourless rod, 300 × 30 × 30 µm, from $(CH_3)_2CO–Et_2O$, space group *Pbca*, $a = 14.438(3)$, $b = 15.762(3)$, $c = 16.877(4)$ Å, $U = 3840.6(14)$ Å^3, $D_{calc} = 1.004$ Mg m^{-3}, $Z = 8$, $\lambda = 0.6883$ Å, $\mu = 0.052$ mm^{-1}, $T = 150(2)$ K, $R_1 = 0.0701$ for 3385 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.1792$ for all 4073 unique reflections. CCDC reference number 186128; methods and programs were standard.[17] See http://www.rsc.org/suppdata/dt/b2/b205016c/ for crystallographic data in CIF or other electronic format. Crystal data for the $[NEt_4]^+$ salt of the $[1\text{-Ph-}closo\text{-}1\text{-}CB_7H_7]^-$ anion **5** were previously deposited; CCDC reference number 172016.

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