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Short communication

# Polyhedral monocarbaborane chemistry The C,B-*para*-diphenyl monocarbadodecaborane anion[1] $[1,12\text{-}Ph_2\text{-}closo\text{-}1\text{-}CB_{11}H_{10}]^-$

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**Abstract**

Iodination of $Cs^+[1\text{-}Ph\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$ with $I_2$ in $CH_3COOH$ solution gives $Cs^+[1\text{-}Ph\text{-}closo\text{-}1\text{-}CB_{11}H_{10}\text{-}12\text{-}I]^-$ (78%); reaction of $Cs^+[1\text{-}Ph\text{-}closo\text{-}1\text{-}CB_{11}H_{10}\text{-}12\text{-}I]^-$ with PhMgBr and $[PdCl_2(PPh_3)_2]$ in THF solution thence gives the $[1,12\text{-}Ph_2\text{-}closo\text{-}1\text{-}CB_{11}H_{10}]^-$ anion (49% as its $Cs^+$ salt), characterised by NMR spectroscopy and a single-crystal X-ray diffraction analysis of its $[NEt_4]^+$ salt. 

*Keywords:* Closed monocarbaborane; B-substitution; B-phenylation; C,B-diphenylation; X-ray structures

There is current interest in the *closo*-monocarbaborane anions because their very low basicities permit the examination and exploitation of very acidic systems [1,2]. In this area, the tailoring of the properties of these anions via substituent chemistry attracts attention, and in this context directed arylation has been an important goal [3–5]. Although there are many examples of organyl substitution reactions onto the carbon atom of *closo* monocarbaborane anions and *closo*-dicarbaboranes [6–8], the reported organyl substitution chemistry at the boron atoms of the *closo* monocarbaborane anions is quite sparse. To augment this latter aspect of monocarbaborane chemistry we have started to investigate the B-organylation and B-functionalisation of *closo* twelve-vertex $\{CB_{11}\}$ cluster compounds, and in this context we here report preliminary results on the new C,B-*para*-diphenyl monocarbadodecaborane anion $[1,12\text{-}Ph_2\text{-}closo\text{-}1\text{-}CB_{11}H_{10}]^-$ (species **1**). Concurrently with the preliminary presentation of this work at EUROBORON 2 [3], an alternative synthesis of species **1** was also reported [5]: this alternative synthesis derives from the iodination and subsequent B-phenylation of the parent unsubstituted $[HCB_{11}H_{11}]^-$ anion, followed by a Negishi-type coupling of a second phenyl group at the carbon-vertex.

The preparation described in this present paper has a different approach, and derives from the recently reported C-phenyl *closo* twelve-vertex monocarbadodecaborane anion $[1\text{-}Ph\text{-}closo\text{-}1\text{-}CB_{11}H_{11}]^-$ (species **2**), which we prepare starting with the initial reaction of benzaldehyde with ten-vertex decaborane to give the ten-vertex $[6\text{-}Ph\text{-}nido\text{-}6\text{-}CB_9H_{11}]^-$ anion **3** in 64–94% yield [4]; the reaction of this latter anion **3** with $[BH_3(SMe_2)]$ thence gives the *closo* twelve-vertex species **2** in high yield via the eleven-vertex $[7\text{-}Ph\text{-}nido\text{-}7\text{-}CB_{10}H_{12}]^-$ anionic intermediate [4]. One advantage of this route is that it starts with a pre-phenylated organic precursor, thus avoiding subsequent awkward carbaborane carbon-vertex substitution chemistry. Here, for example, an alternative route to anion **2** uses the unsubstituted $[closo\text{-}1\text{-}CB_{11}H_{12}]^-$ anion **4** as starting material, this anion being prepared via a straightforward, though tedious, multistep synthesis starting from

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[1] Systematic IUPC nomenclature: The 1,12-diphenyl-*closo*-1-carbadodecaborate(1−) anion; characterised crystallographically as its tetraethylammonium salt. This article was freely submitted for publication without royalty. By acceptance of this paper, the publisher and/or recipient acknowledges the right of the authors to retain non-exclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce all or part of the copyrighted paper.

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the commonly used higher borane entry, *nido*-decaborane [9,10]. The C–H bond in the [*closo*-1-$CB_{11}H_{12}$]$^-$ anion **4** is somewhat acidic and can be lithiated with butyllithium [11]; treatment of the lithiated species with iodobenzene in the presence of $ZnCl_2$ and [$PdCl_2(PPh_3)_2$] thence leads to the formation of the [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ anion **2** in a yield of 32% [12].

In terms of B-substitution on the *closo* {$CB_{11}$} cluster, it has been known for some time that the 12-position in the unsubstituted 'parent' [*closo*-1-$CB_{11}H_{12}$]$^-$ anion **4**, i.e. the position antipodal to the carbon atom, is preferentially and readily attacked in electrophilic halogenation, whereas the adjacent 'lower belt' positions 7–11 are somewhat less reactive, with the 'upper belt' positions 2–6 next to the carbon centre being much less reactive [2,13]. Our siting results so far suggest that the C-phenyl substituent in the [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ anion **2** deactivates the boron centres to substitution. For example, although bromination of the unsubstituted anion **4** readily proceeds to the hexabrominated [*closo*-1-$CB_{11}H_6Br_6$]$^-$ anion [13], we have found in preliminary experiments that bromination of the C-phenylated anion **2** beyond the pentabrominated [1-Ph-*closo*-1-$CB_{11}H_6Br_5$]$^-$ anion is not so easily achieved. For the *para*-iodination, however, we find that, under slightly more forcing conditions than those required for the iodination of the [*closo*-1-$CB_{11}H_{12}$]$^-$ anion to give the [*closo*-1-$CB_{11}H_{11}$-12-I]$^-$ anion **5** [13,14], the iodination of species **2** proceeds in $CH_3COOH$ to give [1-Ph-*closo*-1-$CB_{11}H_{10}$-12-I]$^-$ (species **6**) in 78% yield. This new anion **6** has been isolated as its caesium salt.[2] Reaction of this caesium salt in a [$PdCl_2(PPh_3)_2$]-catalysed cross-coupling with the aryl Grignard reagent PhMgBr in THF, in a Kumada-type coupling reaction well known for derivatives of neutral carbaboranes [15–17], thence results in the formation of the C,B-*para*-diphenyl monocarbadodecaborane anion [1,12-$Ph_2$-*closo*-1-$CB_{11}H_{10}$]$^-$ (species **1**), isolated as its $Cs^+$ salt in 49% yield, and characterised by a single-crystal X-ray diffraction analysis of its $[NEt_4]^+$ salt (Fig. 1).[2]

More specifically, elemental $I_2$ (4.0 g, 15.9 mmol) was added to a solution of the $Cs^+$ salt of the [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ anion **2** (1.9 g, 5.4 mmol) in $CH_3COOH$ (40 ml), and the reaction mixture was heated at 100 °C for 18 h. After cooling to room temperature, water (100 ml) and $Na_2[SO_3]$ (1.0 g, 7.9 mmol) were added, and the solution was filtered. $[NEt_4]^+[Cl]^-$ (1.0 g, 6 mmol) was then added to the filtrate and the resulting pale yellow precipitate filtered off and dried in vacuo. Aqueous HCl (10%, 200 ml) and CsCl (2.0 g, 12 mmol) were added to the dried precipitate, the resulting mixture extracted several times with $Et_2O$, and the separated organic layers combined and evaporated in vacuo. The residual oil was dissolved in water (50 ml) and CsCl (2.0 g, 12 mmol) was added. The resulting white precipitate was crystallised from hot water–MeOH (proportions ca. 1:1) to yield the $Cs^+$ salt of the [1-Ph-*closo*-1-$CB_{11}H_{10}$-12-I]$^-$ anion **6** as a white crystalline solid (2.0 g, 4.3 mmol, 78%).[2]

A sample of this $Cs^+$ salt of the [1-Ph-*closo*-1-$CB_{11}H_{10}$-12-I]$^-$ anion **6** (1.43 g, 3.0 mmol) was then dissolved in THF (30 ml) and a solution of PhMgBr in THF (1.0 M, 10 ml), together with [$PdCl_2(PPh_3)_2$] (50 mg, 71 μmol), was added. After heating at reflux for 30 min, the mixture was allowed to cool down to room temperature. An additional aliquot of PhMgBr in THF (1.0 M, 10 ml), together with more [$PdCl_2(PPh_3)_2$] (50

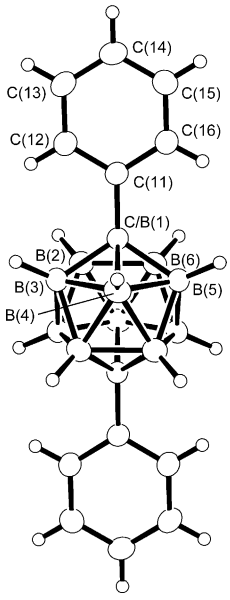


Fig. 1. Drawing of the molecular structure of the [1,12-$Ph_2$-*closo*-1-$CB_{11}H_{10}$]$^-$ anion **1**, as determined crystallographically in its $[NEt_4]^+$ salt. Arising from the extreme geometrical similarities of the C-phenyl and B-phenyl ends of the anion, there is a crystallographic inversion centre at the centre of the twelve-vertex icosahedral cage which mutually disorders the C(1) and B(12) positions so that the two phenylated ends of the ion are crystallographically indistinguishable. For this reason, derived distances are unsuitable for detailed intermolecular comparison with other monocarbaboranes and other arylated borane and heteroborane cluster compounds. Selected derived interatomic distances are C/B(1)–C(11) 1.5525(15) Å with axial–tropical distances from C/B(1) ranging from 1.745(2) to 1.760(2) Å, intratropical distances ranging from 1.774(2) to 1.778(2) Å, and intertropical distances ranging from 1.761(2) to 1.778(2) Å.

[2] Measured NMR data for anions [1,12-$Ph_2$-*closo*-1-$CB_{11}H_{10}$]$^-$ (**1**) and [1-Ph-*closo*-1-$CB_{11}H_{10}$-12-I]$^-$ (**6**), $[NEt_4]^+$ salts in $(CD_3)_2CO$ at 299 K, ordered as assignment $\delta(^{11}B)$/ppm [$\delta(^1H)$/ppm in square brackets]: anion **1**, BPh(12) +1.8, BH(7,8,9,10,11) −12.0 [+1.97], BH(2,3,4,5,6) −13.3 [+1.97]; additionally $\delta(^1H)$(Ph) at +7.59–+6.97 (unresolved multiplets, 10H) and $\delta(^{13}C)$(Ph) at +124.45(1), +126.19(1), +127.2(2), +128.69(2), +128.81(2), +131.95(2), +132.11(1) and +133.12(1) ppm, with $\delta(^{13}C)$(cluster) +70.1 ppm (broad); anion **6**, BH(7,8,9,10,11) −11.2 [+2.18], BH(2,3,4,5,6) −12.9 [+2.11], BI(12) −17.2; additionally $\delta(^1H)$(Ph) at +7.46 to +7.07 (unresolved multiplets, 5H) and $\delta(^{13}C)$(Ph) at +126.60(1), +127.41(2), +128.32(2) and +141.51(1) ppm, with $\delta(^{13}C)$(cluster) +66.1 ppm (broad).

mg, 71 μmol) was added, and the mixture further heated under reflux for 18 h. The solution was then cooled to 0 °C and EtOH (2 ml) and water (50 ml) were added. The THF and EtOH were removed in vacuo, the resulting aqueous solution was acidified with aqueous HCl (5%, 20 ml), CsCl (1.0 g, 6 mmol) was added, and the solution then extracted several times with $Et_2O$. The combined ether extracts were evaporated to dryness to give a brownish yellow oil. This oily residue was dissolved in water (50 ml) and a brownish oily substance was filtered off. CsCl (1.0 g, 6 mmol) was added to the clear filtrate. The resulting white precipitate was filtered off, and crystallised from hot water–MeOH (proportions ca. 1:1) to yield the $Cs^+$ salt of the [1-Ph-12-Ph-*closo*-1-$CB_{11}H_{10}$]$^-$ anion **1** as a white crystalline solid (630 mg, 1.5 mmol, 49%), characterised by NMR spectroscopy.[2] Aqueous HCl (10%, 100 ml) and CsCl (1.0 g, 6 mmol) were added to the dried precipitate, the resulting mixture extracted several times with $Et_2O$, and the separated organic layers combined and evaporated in vacuo. The residual oil was dissolved in water (50 ml) and $[NEt_4]^+[Cl]^-$ (0.50 g, 3.0 mmol) was then added to the filtrate. The resulting colourless precipitate of the $[NEt_4]^+$ salt of the [1-Ph-12-Ph-*closo*-1-$CB_{11}H_{10}$]$^-$ anion **1** was filtered off and dried in vacuo. This $[NEt_4]^+$ salt was dissolved in acetone and layered with diethyl ether which diffused into the acetone solution to give colourless crystals, melting point 157–158 °C, which were suitable for the X-ray diffraction analysis. The $[NEt_4]^+$ salt was also used to characterise the compound by NMR spectroscopy, criteria of purity being clean multinuclear NMR spectra consistent with the all-atom crystallographically determined solid-state structure. The $[N(PPh_3)_2]^+$ salt, prepared similarly from $[N(PPh_3)_2]^+[Cl]^-$, has an interestingly much lower melting point of 69–70 °C, which has auguries for future borane-based ionic liquid chemistry.

The new C-phenylated B-iodinated species **6** and the C,B-diphenylated species **1** have been characterised by $^1H$- and $^{11}B$ NMR spectroscopy, and, in the case of species **1**, by a molecular structure derived from a single-crystal X-ray diffraction analyses of its $[NEt_4]^+$ salt (Fig. 1).[3] In this salt, the target ion **1** was subject to crystallographic disorder, not unexpected in view of the geometric near-symmetry of the anion arising from the extreme similarity of dimension between the 1-phenyl and 12-phenyl molecular extremities. The C-phenyl and B-phenyl ends of the molecules were therefore not distinguished from each other crystallographically, but nevertheless its constitution is clear.

The easy two-step route from decaborane to the C-phenylated [1-Ph-*closo*-1-$CB_{11}H_{11}$]$^-$ anion **2**, and its subsequent conversion to the *para*-C,B-diphenylated [1,12-$Ph_2$-*closo*-1-$CB_{11}H_{10}$]$^-$ anion **1** in a very reasonable preliminary and unoptimised yield, augurs a general ready entry into both homoleptic and mixed C,B-bis(aryl) *closo* {$CB_{11}$} cluster compounds, because both the initial benzaldehyde addition to decaborane, and also the subsequent aryl Grignard addition, will be applicable to a whole spectrum of aromatic residues. Much new aryl-substituted monocarbaborane chemistry should thereby be readily facilitated.

## 1. Supplementary material

Crystallographic data for the $[NEt_4]^+$ salt have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 172018 for anionic compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[3] Crystal data for the $[NEt_4]^+$ salt of anion **1**, $C_{21}H_{40}B_{11}N$: $M = 425.45$, monoclinic (from acetone–diethyl ether 1:5), $0.48 \times 0.42 \times 0.1$ mm, space group $P2_1/c$, $a = 7.5660(2)$, $b = 10.4456(3)$, $c = 16.3637(5)$ Å, $\beta = 98.6260(10)°$, $U = 1278.62(6)$ Å$^3$, $D_{calc} = 1.105$ Mg m$^{-3}$, $Z = 2$, Mo–K$_\alpha$, $\lambda = 0.71073$ Å, $\mu = 0.056$ mm$^{-1}$, $T = 150(2)$ K, $R_1 = 0.0421$ for 2116 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.1143$ for all 2505 unique reflections; CCDC reference number 172018. Methods and programs were standard [18,19].

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