

# Monocarborane anion chemistry. An interesting encapsulation of the $\text{Pd}_2\text{I}_2\{\text{P}(\text{C}_6\text{H}_4\text{-4-Me})_3\}_4\}^{2+}$ cation by a pair of $[\text{PhCB}_9\text{H}_4\text{I}(\text{C}_6\text{H}_4\text{Me})_4]^-$ anions

Andreas Franken, Colin A. Kilner, Mark Thornton-Pett and John D. Kennedy

The Department of Chemistry of the University of Leeds, Leeds, UK LS2 9JT.

E-mail: j.kennedy@chemistry.leeds.ac.uk

Received (in Cambridge, UK) 12th June 2002, Accepted 13th July 2002

First published as an Advance Article on the web 16th August 2002

Reaction of the  $[\text{1-Ph-closo-1-CB}_9\text{H}_4\text{-6,7,8,9,10-I}_5]^-$  anion with  $4\text{-MeC}_6\text{H}_4\text{MgBr}$  in the presence of  $[\text{PdCl}_2(\text{PPh}_3)_2]$  gives the  $[\text{Pd}_2\text{I}_2\{\text{P}(\text{C}_6\text{H}_4\text{-4-Me})_3\}_4]^{2+}$  salt of the  $[\text{1-Ph-closo-1-CB}_9\text{H}_4\text{-10-I-6,7,8,9-(C}_6\text{H}_4\text{-4-Me)}_4]^-$  anion, which exhibits an unusual neutral supramolecular assembly in the solid state, in which the dipalladium dication is encapsulated by two four-armed 'tetrapus' anionic units; the anion also has potentialities for four-fold dendrimer construction.

There is increasing contemporary interest in the chemistry of the  $[\text{closo-1-CB}_9\text{H}_{10}]^-$  and  $[\text{closo-1-CB}_{11}\text{H}_{12}]^-$  monocarbaborane anions.<sup>1</sup> Much of this interest involves their substituent chemistry. In this last regard, we have recently reported results<sup>2</sup> on several C-aryl substituted monocarbaboranes derived via the entry reaction of benzaldehyde with *nido*- $\text{B}_{10}\text{H}_{14}$  to give the  $[\text{6-Ph-nido-6-CB}_9\text{H}_{11}]^-$  anion **1**. Upon cluster closure, anion **1** readily yields the  $[\text{1-Ph-closo-1-CB}_9\text{H}_9]^-$  anion **2**,<sup>2a</sup> and here we now report that polyiodination of this last species **2** readily gives the penta-iodinated  $[\text{1-Ph-closo-1-CB}_9\text{H}_4\text{-6,7,8,9,10-I}_5]^-$  anion **3**, which upon arylation with excess  $4\text{-MeC}_6\text{H}_4\text{MgBr}$  in the presence of  $[\text{PdCl}_2(\text{PPh}_3)_2]$  gives the tetra-B-arylated  $[\text{1-Ph-closo-1-CB}_9\text{H}_4\text{-10-I-6,7,8,9-(C}_6\text{H}_4\text{-4-Me)}_4]^-$  anion **4**. Anion **4** exhibits a most interesting encapsulation of the  $[\text{Pd}_2\text{I}_2\{\text{P}(\text{C}_6\text{H}_4\text{-4-Me})_3\}_4]^{2+}$  cation **5** that is also formed in the reaction.

Thus, treatment of the  $[\text{NEt}_4]^+$  salt of the  $[\text{1-Ph-closo-1-CB}_9\text{H}_9]^-$  anion **2** with excess  $\text{ICl}$  in the presence of  $\text{H}_2\text{SO}_4$  gives the  $[\text{1-Ph-closo-1-CB}_9\text{H}_4\text{-6,7,8,9,10-I}_5]^-$  anion **3**, isolatable in ca. 70% yield as its  $[\text{NEt}_4]^+$  salt.<sup>3</sup> Anion **3** then reacts with excess  $[\text{4-Me-C}_6\text{H}_4\text{MgBr}]$  in the presence of an equivalent of the cross-coupling mediator  $[\text{PdCl}_2(\text{PPh}_3)_2]^{1e}$  to form the  $[\text{1-Ph-closo-1-CB}_9\text{H}_4\text{-10-I-6,7,8,9-(C}_6\text{H}_4\text{-4-Me)}_4]^-$  anion **4**, isolatable in ca. 40% yield as the  $[\text{Pd}_2\text{I}_2\{\text{P}(\text{C}_6\text{H}_4\text{-4-Me})_3\}_4]^{2+}$  salt.<sup>4</sup> During the reaction, only four of the five iodo substituents of anion **3** are readily replaced by  $\{\text{C}_6\text{H}_4\text{-4-Me}\}$  moieties. We have been unable to substitute the fifth in experiments so far, even under more forcing conditions. Interesting also is that all the P-phenyl groups on the starting palladium compound are also replaced, as evidenced by the  $[\text{Pd}_2\text{I}_2\{\text{P}(\text{C}_6\text{H}_4\text{-4-Me})_3\}_4]^{2+}$  counter-cation **5**.

The structure of anion **4**, determined by an X-ray diffraction analysis of its salt with the cation **5**,<sup>5</sup> shows that the tetra-arylation has occurred at the four equivalent lower-belt sites distal from the carbon atom, but that the axial iodine substituent antipodal to the carbon site remains (Fig. 1). The prominent four-fold stereochemical protuberance of the four B-aryl substituents is particularly noteworthy, and has implications for dendrimer and coordination-polymer chemistry, for example via methyl group functionalisation. Of more unusual interest is that the anion **4** and the cation **5** seem to exhibit a strong mutual affinity: in our hands so far, we have not been able to separate anion and cation in various attempts using chromatographic and ion-exchange experimentation, although anion and cation are each respectively characterisable individually in the salt by negative and positive ion electrospray mass spectrometry.

The solid-state structure suggests that this mutual affinity arises from a favoured encapsulation of the dication by two of the B-tetra-arylated monoanions to give a stable neutral assembly (Fig. 2). The perspective afforded by the van-der-

Waals-radius representations in Fig. 3 (left) suggests that strong elements of the cohesion arise because the four stereochemically prominent B-aryl arms of the anions interlock intimately into the crevices of the P-aryl groups on the cation, and *vice versa*. The orthogonal view in Fig. 3 (right) shows that the encapsulation by each anion is reminiscent of the way the arms

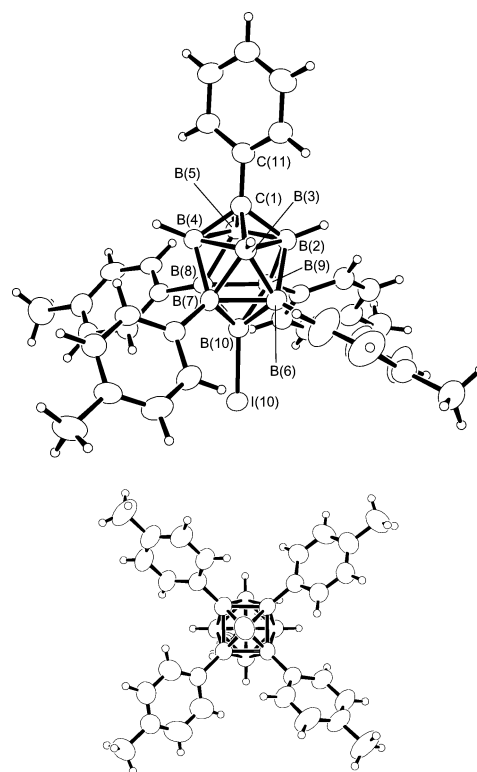


Fig. 1 Two perspectives of the crystallographically determined molecular structure of the  $[\text{1-Ph-closo-1-CB}_9\text{H}_4\text{-10-I-6,7,8,9-(C}_6\text{H}_4\text{-4-Me)}_4]^-$  anion **4**. Selected interatomic distances (Å): C(1)–C(aryl) 1.492(7), B(10)–I 2.179(6), B–C(aryl) 1.583(7)–1.589(7).

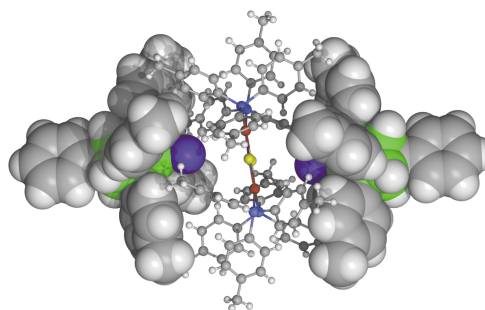
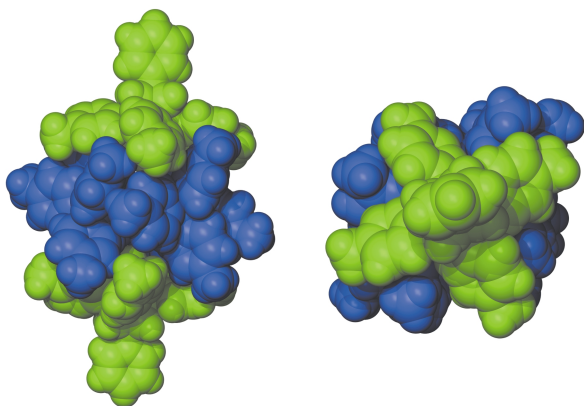


Fig. 2 Representation of the neutral unit within the crystal lattice in which two molecules of monoanion **4** (drawn with van-der-Waals-radius representation) encapsulate one molecule of dication **5** (drawn with ball-and-stick representation). The inherent interionic attraction is augmented by an intimate cation–anion meshing as illustrated in Fig. 3.



**Fig. 3** Two perspectives to illustrate the detail of the interaction of the aryl arms of the monoanions **4** (green) with those of the dication **5** (blue). The left-hand diagram shows how the aryl groups intimately intermesh, and the right-hand diagram shows how an anionic unit enwraps the central cation with its four 'tetrapus' arms.

of a starfish or cephalopod such as an octopus might enwrap its prey. Here however, there are only four arms, so anion **4** would be describable as a 'tetrapus' cation predator.

The phenomenon has clear implications for supramolecular assembly and selective cation sequestration. More generally, this synthesis of this first of a new generation of polyarylated monocarbaborane anions by a simple route in relatively good yield, and in just four steps from the common polyhedral borane starting material  $B_{10}H_{14}$ , significantly augments the range of materials available for 'least-coordinating anion' chemistry. In these contexts, an advantage is that the method is in principle readily adaptable to other cluster substrates and also to other substituents on carbon and boron *via* choice of entry aldehydes<sup>2,6</sup> and choice of Grignard reagent. We therefore currently experiment for cation exchange to examine for encapsulation of other cations, for aryl-group modification for the tailoring and tuning of encapsulation behaviour, and for the extension of the principle to other polyhedral systems. In this last regard, preliminary experiments suggest that the twelve-vertex [1-Ph-closo-CB<sub>10</sub>H<sub>11</sub>]<sup>-</sup> anion can be similarly polyarylated, and that the product exhibits similar cation-sequestration properties; we would hope to be able to report on this more fully in due course.

We thank the UK DTI and the UK EPSRC (grants nos J56929, L49505 and M83360) for support.

## Notes and references

- (a) See, for example, together with references therein: S. H. Strauss, *Chem. Rev.*, 1993, **93**, 927; (b) C. A. Reed, *Acc. Chem. Res.*, 1998, **31**, 133; (c) B. T. King, B. C. Noll and J. Michl, *Collect. Czech. Chem. Commun.*, 1999, **64**, 1001; (d) M. J. Hardie and C. L. Raston, *Chem. Commun.*, 2001, 905; (e) Z. Janoušek, P. Kaszynski and V. G. Young, *Inorg. Chem.*, 1998, **37**, 6361; (f) T. Peymann, C. B. Knobler, S. I. Khan and M. F. Hawthorne, *Angew. Chem., Int. Ed.*, 2001, **40**, 1664; (g) D. Stasko and C. A. Reed, *J. Am. Chem. Soc.*, 2002, **124**, 1148; (h) S. V. Ivanov, J. J. Rockwell, S. M. Miller, O. P. Anderson, K. A. Solntsev and S. H. Strauss, *Inorg. Chem.*, 1996, **35**, 7882; (i) T. Jelínek, J. Plešek, S. Hermánek and B. Štíbr, *Collect. Czech. Chem. Commun.*, 1986, **51**, 819; (j) C.-W. Tsang, Q. Yang, E. T.-P. Sze, T. C. W. Mak, D. T. W. Chan and Z. Xie, *Inorg. Chem.*, 2000, **39**, 3582; (k) B. T. King, B. C. Noll, A. J. McKinley and J. Michl, *J. Am. Chem. Soc.*, 1996, **118**, 10902.
- (a) See, for example, together with references therein: T. Jelínek, C. A. Kilner, M. Thornton-Pett and J. D. Kennedy, *Chem. Commun.*, 2001, 1790; (b) A. Franken, C. A. Kilner, M. Thornton-Pett and J. D. Kennedy, *J. Organomet. Chem.*, 2002, in press, paper no. JOM 11355; (c) A. Franken, C. A. Kilner, M. Thornton-Pett and J. D. Kennedy, *J. Organomet. Chem.*, 2002, in press, paper no. JOM 11359; (d) A. Franken, C. A. Kilner, M. Thornton-Pett and J. D. Kennedy, *Inorg. Chem. Commun.*, 2002, **5**, 581; (e) A. Franken, C. A. Kilner, M. Thornton-Pett and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 2002, 2807.
- Anion **2** ([NET<sub>4</sub>]<sup>+</sup> salt; 0.65 g, 2.0 mmol) was dissolved in CH<sub>3</sub>CN (20 ml), ICl (3.3 g, 20 mmol) was then added, and the mixture stirred for 30 min at room temperature (r.t.). Conc. H<sub>2</sub>SO<sub>4</sub> (1 ml, 18.4 mmol) was added, the mixture stirred for 18 h at r.t., and then cooled to 0 °C. H<sub>2</sub>O (50 ml) and Na<sub>2</sub>SO<sub>3</sub> (2.5 g, 20 mmol) were then added, the CH<sub>3</sub>CN removed *in vacuo*, and the resulting aqueous solution extracted with Et<sub>2</sub>O (3 × 50 ml). Evaporation of the combined ether extracts *in vacuo* gave a colourless oil, which was then dissolved in H<sub>2</sub>O (50 ml); [NET<sub>4</sub>]<sup>+</sup>Cl<sup>-</sup> (0.5 g, 3 mmol) was then added, and the resulting white precipitate filtered off and dried *in vacuo* to yield the colourless [NET<sub>4</sub>]<sup>+</sup> salt of the [1-Ph-closo-1-CB<sub>9</sub>H<sub>4</sub>-6,7,8,9,10-Is]<sup>-</sup> anion **3** (1.38 g, 1.44 mmol, 72%). NMR data [(CD<sub>3</sub>)<sub>2</sub>CO, 294–299 K]: δ(<sup>11</sup>B) for BI(10) +17.5, BH(2,3,4,5) –8.5 [with δ(<sup>1</sup>H) +2.29] and BI(6,7,8,9) –23.5; δ(<sup>13</sup>C)(cluster) +39.6. The Cs<sup>+</sup> salt may be similarly isolated (1.38 g, 1.44 mmol, 72%) by the addition of Cs<sup>+</sup>Cl<sup>-</sup> (0.56 g, 3.3 mmol) to the aqueous solution of the colourless oil.
- Anion **3** (Cs<sup>+</sup> salt; 480 mg, 0.50 mmol) was dissolved in thf (20 ml), 4-Me-C<sub>6</sub>H<sub>4</sub>MgBr (20 ml, 1.0 M solution in thf, 20 mmol) and [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (350 mg, 0.50 mmol) were added, the mixture heated at reflux for 18 h, cooled to 0 °C, and H<sub>2</sub>O (50 ml) added dropwise. Removal of the thf *in vacuo*, extraction with Et<sub>2</sub>O (3 × 50 ml), and evaporation of the ether layers gave an orange residue, of which preparative TLC [silica gel G (Fluka GF254), CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane 70:30], gave one principal component (orange, R<sub>F</sub> 0.46), identified as the [Pd<sub>2</sub>I<sub>2</sub>{P(C<sub>6</sub>H<sub>4</sub>-4-Me)<sub>3</sub>}]<sub>4</sub><sup>2+</sup> salt of anion **4** (39 % from Et<sub>2</sub>O/Me<sub>2</sub>CO); NMR data [(CD<sub>3</sub>)<sub>2</sub>CO, 294–299 K]: δ(<sup>11</sup>B) for BI(10) +16.6, BH(2,3,4,5) –9.1 [with δ(<sup>1</sup>H) +2.53] and B(C<sub>6</sub>H<sub>4</sub>-4-Me)(6,7,8,9) –9.1; δ(<sup>13</sup>C)(cluster) +49.2; δ(<sup>31</sup>P) +30.0. Mass spec. data (electrospray): *m/z* for [Pd<sub>2</sub>I<sub>2</sub>{P(C<sub>6</sub>H<sub>4</sub>-4-Me)<sub>3</sub>}]<sub>4</sub><sup>2+</sup> 841.1 and for anion **4** 682.3 (maximum intensity peak in molecular ion isotopomer envelope).
- Crystallographic data* for the [Pd<sub>2</sub>I<sub>2</sub>{P(C<sub>6</sub>H<sub>4</sub>-4-Me)<sub>3</sub>}]<sub>4</sub><sup>2+</sup> salt of anion **4**; the halogen sites in the cation exhibited some fractional occupancy by Cl/Br instead of I (refined in terms of Cl only): C<sub>77</sub>H<sub>79</sub>B<sub>9</sub>Cl<sub>0.25</sub>I<sub>1.75</sub>Pd: *M* = 1500.97, monoclinic (orange prisms from Et<sub>2</sub>O–Me<sub>2</sub>CO), space group *P*<sub>2</sub><sub>1</sub>/*c*, *a* = 14.23370(10), *b* = 19.1946(2), *c* = 28.6687(3) Å, β = 91.2970(10)°, *U* = 7830.57(13) Å<sup>3</sup>, *D*<sub>c</sub> = 1.273 Mg m<sup>-3</sup>, *Z* = 4, λ(Mo-Kα) = 0.71073 Å, μ = 1.015 mm<sup>-1</sup>, *T* = 150(2) K, *R*<sub>1</sub> = 0.0543 for 11947 reflections with *I* > 2σ(*I*), and *wR*<sub>2</sub> = 0.1578 for all 15331 unique reflections, restraints having been applied so that all the aromatic rings were flat; Methods and programs were standard (Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307; COLLECT, Data Collection Strategy Program, Nonius, 1999). CCDC reference number 184234. See <http://www.rsc.org/suppdata/cc/b2/b205697f/> for crystallographic data in CIF or other electronic format.
- B. Brellocks, in: *Contemporary Boron Chemistry*, ed. M. G. Davidson, A. K. Hughes, T. B. Marder and K. Wade, Royal Society of Chemistry, Cambridge, UK, 2000, p. 212; T. Jelínek, B. Štíbr, J. Holub, M. Bakardjiev, D. Hnyk, D. L. Ormsby, C. A. Kilner, M. Thornton-Pett, H.-J. Schanz, B. Wrackmeyer and J. D. Kennedy, *Chem. Commun.*, 2001, 1756; T. Jelínek, M. Thornton-Pett and J. D. Kennedy, *Collect. Czech. Chem. Commun.*, 2002, **67**, in press, CCCC paper no. 2002/000097.