## Synthetic and structural studies on C-ethynyl- and C-bromo-carboranes<sup>†</sup>

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Received 12th December 2005, Accepted 3rd April 2006 First published as an Advance Article on the web 27th April 2006 DOI: 10.1039/b517538k

A high-yield preparation of the C-monoethynyl para-carborane,  $1-Me_3SiC \equiv C-1, 12-C_2B_{10}H_{11}$ , from C-monocopper para-carborane and 1-bromo-2-(trimethylsilyl)ethyne, BrC≡CSiMe<sub>3</sub> is reported. The low-yield preparation of 1,12-(Me<sub>3</sub>SiC $\equiv$ C)<sub>2</sub>-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> from the C,C'-dicopper para-carborane derivative with 1-bromo-2-(trimethylsilyl)ethyne, BrC≡CSiMe<sub>3</sub>, has been re-investigated and other products were identified including the C-monoethynyl-carborane 1-Me<sub>3</sub>SiC=C-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> and two-cage assemblies generated from cage-cage couplings. The contrast in the yields of the monoethynyl and diethynyl products is due to the highly unfavourable coupling process between 1-RC=C-12-Cu- $1,12-C_2B_{10}H_{10}$  and the bromoalkyne. The ethynyl group at the cage carbon C(1) strongly influences the chemical reactivity of the cage carbon at C(12)—the first example of the 'antipodal effect' affecting the syntheses of para-carborane derivatives. New two-step preparations of 1-ethynyl- and 1,12-bis(ethynyl)para-carboranes have been developed using a more readily prepared bromoethyne, 1-bromo-3-methyl-1-butyn-3-ol,  $BrC \equiv CCMe_2OH$ . The molecular structures of the two C-monoethynyl-carboranes,  $1-RC \equiv C-1, 12-C_2B_{10}H_{11}$  (R = H and Me<sub>3</sub>Si), were experimentally determined using gas-phase electron diffraction (GED). For R = H ( $R_G = 0.053$ ) a model with  $C_{SV}$  symmetry refined to give a C=C bond distance of 1.233(5) Å. For R = Me<sub>3</sub>Si ( $R_G = 0.048$ ) a model with  $C_s$  symmetry refined to give a C=C bond distance of 1.227(5) Å. Molecular structures of 1,12-Br<sub>2</sub>-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, 1-HC≡C-12-Br-1,12- $C_2B_{10}H_{10}$  and 1,12-(Me<sub>3</sub>SiC=C)<sub>2</sub>-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> were determined by X-ray crystallography. Substituents at the cage carbon atoms on the  $C_2B_{10}$  cage skeleton in 1-X-12-Y-1,12- $C_2B_{10}H_{10}$  derivatives invariably lengthen the cage C–B bonds. However, the subtle substituent effects on the tropical B–B bond lengths in these compounds are more complex. The molecular structures of the ethynyl-ortho-carborane,  $1-HC \equiv C-1, 2-C_2B_{10}H_{11}$  and the ethene, *trans*-Me<sub>3</sub>SiBrC=CSiMe<sub>3</sub>Br are also reported.

## Introduction

Unlike the more familiar *ortho-* and *meta-*carboranes, the icosahedral  $C_2B_{10}$  cage of *para-*carborane **1** has five-fold symmetry through the axis of the cage carbon atoms (Fig. 1, X, Y = H). The high symmetry of *para-*carborane derivatives, 1-X-12-Y-1,12- $C_2B_{10}H_{10}$ , make them almost ideal for investigating the effects of various substituents on the cage geometry. For example, a *C*-monosubstituted-*para-*carborane 1-X-1,12- $C_2B_{10}H_{11}$  (*i.e.* Y = H in Fig. 1) contains only two distinct boron centres and five unique cage bonds (i, ii, iii, ii2, i2), while a *C*,*C*-disubstituted*para-*carborane (X = Y in Fig. 1) would have only three distinct cage bonds.



**Fig. 1** Cage numbering in 1-X-12-Y-1,12- $C_2B_{10}H_{10}$ . i,  $i_2$  = averaged C–B 'polar-tropical' bond, ii, ii<sub>2</sub> = averaged B–B bond from 'tropical' B–B bonds *e.g.* B2–B3 and iii = averaged 'meridianal' B–B bond *e.g.* B2–B7.

As the cage carbon atoms are easily functionalised,<sup>1,2</sup> there has been much recent attention on the use of this highly symmetrical cage as not only a vehicle to explore cage structures, but also as a linker/building block for the preparation of molecular compounds with liquid crystalline phase behaviour,<sup>3,4</sup> polymers,<sup>5,6</sup> optical materials with large hyperpolarizabilities<sup>7,8</sup> and with the general field of rigid molecular rods.<sup>9-15</sup> The three-dimensional aromaticity associated with these carborane cages has resulted in the robust *para*-carborane bridge  $-CB_{10}H_{10}C$ - also being investigated for its capacity to act as a conduit for electronic effects.<sup>16-22</sup> In

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<sup>†</sup> Electronic supplementary information (ESI) available: Cartesian coordinates of the MP2/6-31G\* optimized geometries of carboranes described in this study. Tables of least-squares correlation matrix ( $\times$  100) for GED structure refinement of **5** and **6** and computed (HF/MP2/B3LYP) geometrical parameters for **6**. Figures for experimental and final weighted difference (experimental–theoretical) molecular scattering intensities for **5** and **6**. See DOI: 10.1039/b517538k

these latter contexts, ethynyl *para*-carboranes have particular appeal, preserving the rigid linear structure and five-fold symmetry associated with the cage, and offering a simple extension to (and mediated through) the tangential C p-orbitals.

The interest in the general area of conjugated materials and molecular species with well-defined linear architectures, and in the development of simple single-source CVD precursors for technologically useful materials, has prompted us to investigate the development of convenient syntheses of C-ethynyl-paracarboranes. Recently we applied our usual carborane coppermediated coupling procedure<sup>19,23</sup> to the reaction of para-carborane 1 with 1-bromo-2-(trimethylsilyl) ethyne 2, from which 1,12bis(trimethylsilylethynyl)-*para*-carborane **3** (X, Y = C $\equiv$ CSiMe<sub>3</sub>) was isolated in low yield; subsequent desilylation of 3 affords the parent species 1,12-bis(ethynyl)-para-carborane  $4(X, Y = C \equiv CH)$ (Scheme 1).<sup>24</sup> A similar low-yielding synthesis of 3 has also been reported by Kaszynski and co-workers.<sup>25</sup> Despite the low yield of these preparative routes, compounds 3 and 4 have been used as precursors to metal complexes (to investigate the potential of the diethynyl cage as a conduit for electronic effects between metal centres)16,20 and incorporated into rigid, rod-like molecular architectures.11,13

Here we report the high yield preparation of monoethynyl *para*carboranes, **5** (X = C $\equiv$ CSiMe<sub>3</sub>, Y = H) and **6** (X = C $\equiv$ CH, Y = H),<sup>26</sup> using procedures similar to the syntheses of **3** and **4** (Scheme 2(a)). The molecular structures of these carboranes have been determined by gas-phase electron diffraction (GED) studies. In seeking to understand the contrasting yields observed in the preparations of the bis(ethynyl) carborane **3** and monoethynyl carborane **6**, we have re-investigated the low yield preparation of **3** shown in Scheme 1. Several carboranyl side-products, including *C*-bromo-*C*-ethynyl-*para*-carboranes and a plethora of products derived from C–C coupling between two carborane cages have been identified. By way of synthetic convenience we have also investigated the use of an alternate, more readily obtained bromo-alkyne, 1-bromo-3-methyl-1-butyn-3-ol 7 (Scheme 2(b)), in place of 1bromo-2-(trimethylsilyl) ethyne **2**. The molecular structures of *C*substituted-*para*-carboranes determined here and elsewhere are discussed in terms of the substituent effects on the structure of the cage framework.

## **Results and discussion**

#### Synthetic aspects

Monoethynyl-*para*-carboranes. The copper-mediated coupling of 1 with one equivalent of 2 proceeded smoothly with 5 being isolated in very good yield (76%) (Scheme 2(a)). Compound 5 was converted to the ethynyl carborane 6 by treatment with KOMe. Attempts to grow suitable crystals of carboranes 5 and 6 at low temperatures for X-ray crystallography were not successful. However, both compounds were sufficiently volatile at ambient temperature for their molecular structures to be determined by gas-phase electron diffraction.

The great attraction of ethyne **2** as a reagent lies in the simple and efficient manner in which the trimethylsilyl protecting group can be removed after the cage C–ethyne C bond forming step. The established, multigram syntheses of **2** involve reaction of bromine with MC=CSiMe<sub>3</sub> (M = MgBr, Li), prepared either by deprotonation of trimethylsilylethyne **8**, or obtained by selective nucleophilic desilylation of bis(trimethylsilyl)ethyne **9** (Scheme 3).<sup>27,28</sup> While both procedures afford **2** in high yield provided that all the starting ethyne was converted into its metal intermediate Me<sub>3</sub>SiC=CM (M = MgBr **10** or Li **11**), careful analysis of the product mixture reveals the formation of tribromoethene **12**, which is a liquid at ambient conditions, by inadvertent bromination of **2**.<sup>29,30</sup> In the





case of preparations involving 9, both 12 and the dibromoethene 13 were obtained, the latter being formed by bromination of  $9.^{31}$ 

Here we also synthesised 2 in good yields by a simpler method using ethyne 8 with butyllithium followed by bromine. An alternative preparation of 2, albeit in low yields, is described here using silver nitrate and *N*-bromosuccinimide on ethyne 8. This mild silver nitrate method was used to convert some terminal alkynes into bromoalkynes in very good yields.<sup>32</sup> The main difficulties in the preparation of 2 are its stability and purification. Attempted purifications of 2 by multigram-scale distillations of product mixtures containing 2 were not successful. Crude 2 was used in the syntheses of 3 and 5.

The difficulties encountered in the purification of **2** together with the significant cost and laborious syntheses of **8** and **9** led us to consider an alternative bromoethyne for use in the preparation of *C*-ethynyl-*para*-carboranes. Multigram quantities of 1-bromo-3-methyl-1-butyn-3-ol, **7**, can be obtained from the readily available ethyne 3-methyl-1-butyn-3-ol, by reaction with an aqueous solution of hypobromite and purified by distillation.<sup>33</sup> We were pleased to discover that the new carborane, 1-(3-hydroxy3-methylbutynyl)-*para*-carborane (14) could be formed in good yield from the copper-mediated coupling of *para*-carborane 1 and 1-bromo-3-methyl-1-butyn-3-ol 7 (Scheme 2(b)). Equally, the high thermal stability of the *para*-carborane cage meant that 1-ethynyl-*para*-carborane (6) could be obtained in good yield following deprotection of carborane 14 upon reaction with NaO<sup>i</sup>Pr in 2-propanol at refluxing temperature.

**Routes to bis(ethynyl)**-*para*-carboranes. Bis(trimethylsilylethynyl)-*para*-carborane **3** was isolated in only low yields (10–15%) from the copper-mediated coupling of *para*-carborane **1** with two equivalents of 1-bromo-2-(trimethylsilyl)ethyne **2** (Scheme 1).<sup>24,25</sup> Schemes 1 and 2(a) differ only in reactant ratios. The monoethynyl*para*-carborane **5**, which could be prepared in high yield from equimolar proportions of reagents (Scheme 2(a)), was also a major product of reactions intended to form the bis(ethynyl) carborane **3**.

The *C*-bromo-*C*-ethynylcarboranes **15** and **16** and bis(carboranes) **17–22** (Fig. 2) were identified as minor products (see Experimental section). Metal–halogen exchange has been



Fig. 2 Minor products identified from the reaction of  $1,12-C_2B_{10}H_{12}$  1 with bromotrimethylsilylethyne 2.

observed with other attempted cage C–C bond formation reactions involving *C*-copper-*para*-carborane with perfluoroheptyl iodide and perfluorohexyl bromide to give *C*-halocarboranes.<sup>34</sup> Compound **20** is related to a structurally characterised derivative featuring heptyne substituents.<sup>4</sup> It is known that the bis(*para*carborane) **17** can be prepared from **1** by sequential reaction with butyllithium and copper(I) chloride.<sup>35</sup> Clearly, this cagecoupling reaction competes with the cross-coupling reaction of the intermediate RC=CCB<sub>10</sub>H<sub>10</sub>CCu with **2** under the reaction conditions described in Scheme 1.

We have also investigated the use of the 1-bromo-3methyl-1-butyn-3-ol 7 as an alternate ethynyl source for the preparation of bis(ethynyl) carborane 4. The carborane 1,12-bis(3-hydroxy-3-methylbutynyl)-*para*-carborane (23) was obtained from *para*-carborane 1 and 7 in a low yield following the usual copper-mediated cross-coupling protocol (Scheme 4). Several side products were also identified, including 1-(3hydroxy-3-methylbutynyl)-*para*-carborane 14 and a significant amount of 2,5-dihydroxy-2,5-dimethyl-3,5-octadiyne 24. The 1,12bis(ethynyl)-*para*-carborane (4) was obtained in good yield from carborane 23 following removal of the protecting group with sodium isopropoxide in refluxing 2-propanol.

The significant yields of the monoethynyl carboranes **5** and **14** (as well as the two-cage products and diynes) in the preparations

of the bis(ethynyl) carboranes **3** and **23** respectively suggest the second coupling reaction rate between  $RC \equiv CCB_{10}H_{10}CCu$  and  $BrC \equiv CR$  is much slower than the first coupling reaction rate between  $HCB_{10}H_{10}CCu$  and  $BrC \equiv CR$ . This contrasts with the moderate-to-high yields of diaryl-*para*-carboranes from *para*-carborane and two equivalents of iodoarenes using our coppermediated coupling methods where the second coupling reaction rate is similar to the first coupling reaction rate.<sup>19</sup> It is assumed here that the ethynyl group  $RC \equiv C$  at cage C(1) deactivates the cage carbon at C(12) significantly enough to prevent coupling with  $BrC \equiv CR$  from taking place to a degree.

We also carried out the copper-mediated coupling reaction between the monoethynyl-*para*-carborane **14** and the bromoalkyne alcohol **7** in the hope that the *C*,*C*'-bis(ethynyl)-*para*-carborane **23** would be formed. Instead we obtained the diyne **26** in good yield (Scheme 5). This result demonstrates facile removal of the acetone protecting group as well as a strong preference for ethyne– ethyne C–C coupling between CuC≡CCB<sub>10</sub>H<sub>10</sub>CH and BrC≡CR over the cage–ethyne C–C coupling between RC≡CCB<sub>10</sub>H<sub>10</sub>CCu and BrC≡CR. We exploited this route to make the symmetrical diyne **27** with *para*-carboranyl moieties at each end using oxygen instead of the bromoalkyne for the ethyne–ethyne C–C coupling step. The diyne **27** can also be considered as a 'building block' for rigid-rod architectures.



In the preparation of the long-known 1-ethynyl-*ortho*-carborane **28** the critical carborane–ethyne C–C bond forming reaction between bromoethyne **2** and a *C*-silyl-*ortho*-carborane was achieved without a copper catalyst (Scheme 6(a)).<sup>36</sup> We repeated the preparation of **3**, but without copper(1) chloride and pyridine. However, instead of the desired trimethylsilylethynyl carboranes **3** and **5** the 1-bromo- and 1,12-dibromo-*para*-carboranes<sup>37</sup> **29** and **30** were obtained in good yield (Scheme 6(b)). *C*-Bromination is favoured over the cage–ethyne coupling process for *para*-carborane in the absence of a copper catalyst here. The molecular structure of the dibromocarborane **30** was determined by X-ray diffraction.

#### Structural aspects

This section describes the molecular structures of the monoethynyl carboranes 5 and 6 determined by GED and the disubstituted carboranes, 3, 4/16 and 30, by X-ray diffraction. The molecular structures of *C*-substituted-*para*-carboranes reported here and elsewhere are examined here for the influence of substituents on the cage geometry. The molecular structure of 1-ethynyl-*ortho*-carborane 28—where the cage carbon atoms are adjacent—is also discussed.

Monosubstituted-para-carboranes. The model used for the GED refinement of 5 was based upon the geometry obtained from the ab initio structure optimizations. The least-squares refinement of the structure resulted in an  $R_{\rm G}$  factor of 0.048 ( $R_{\rm D} = 0.026$ ), with optimized parameters listed in Table 1 and the molecular structure shown in Fig. 3. A summary of final bond distances and amplitudes of vibration is recorded in Table 2. All fifteen geometrical parameters and twenty groups of amplitudes of vibration were refined. Flexible restraints were employed during the refinement using the SARACEN method.<sup>38</sup> Altogether, seven geometric and five amplitude restraints were employed and are listed in Table 3. For a full list of the final bond distances and amplitudes of vibration and a table of the least-squares correlation matrix for the structural refinement see ESI.<sup>†</sup> The success of the final refinement can be assessed on the basis of the molecular scattering curves (see ESI<sup>†</sup>) and radial distribution curve, Fig. 4.

The structure of 5 was refined with a model of  $C_s$  symmetry with local  $C_{sv}$  symmetry for the carborane cage, using fifteen

**Table 1** Geometrical parameters  $(r_{h1})$  for  $5^{a,b}$ 

	Parameter	GED	MP2/6-31G(d)
$p_1$	$rC(1)\cdots C(12)$	3.083(9)	3.076
$p_2$	rC(1)C(13)	1.442(5)	1.437
$p_3$	rC(13)C(14)	1.227(5)	1.234
$p_4$	av[rC(1)B, rC(12)B]	1.718(6)	1.711
$p_5$	av(av rBH, av rCH)	1.145(3)	1.140
$p_6$	dif[rC(1)B, rC(12)B]	0.014(8)	0.016
$p_7$	dif(avrBH, avrCH)	0.113(8)	0.093
$p_8$	av[rC(14)Si(15), rC(16)Si(15)]	1.857(3)	1.864
$p_9$	dif[ <i>r</i> C(16)Si(15), <i>r</i> C(14)Si(15)]	3.5(8)	3.4
$p_{10}$	av[ $\angle$ HC(12)B, $\angle$ C(13)C(1)B]	117.6(2)	117.6
$p_{11}$	av[ $\angle C(1)BH$ , $\angle C(12)BH$ ]	119.0(9)	120.1
$p_{12}$	dif[ $\angle C(12)BH$ , $\angle C(1)BH$ ]	1.3(2)	1.3
$p_{13}$	dif[ $\angle$ HC(1)B, $\angle$ C(13)C(12)B]	1.1(4)	0.7
$p_{14}$	$\angle C(14)Si(15)C(16)$	109.7(4)	108.1
$p_{15}$	∠SiCH	108.6(9)	110.7

<sup>a</sup> Distances in Å, angles in °. <sup>b</sup> See text for parameter definitions.

**Table 2** Bond distances  $(r_a/\text{\AA})$  and amplitudes of vibration  $(u/\text{\AA})$  obtained in the GED refinement of **5** 

Number	Atom pair	<i>r</i> <sub>a</sub>	Amplitude	Restraint
$u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \\ u_7 \\ u_8 \\ u_9 \\ u_{10}$	$\begin{array}{c} C(12)-H(12)\\ B(2)-H(2)\\ C(13)-C(14)\\ C(1)-C(13)\\ B(7)-C(12)\\ C(1)-B(2)\\ B(2)-B(7)\\ B(7)-B(8)\\ B(2)-B(3)\\ C(14)-Si(15) \end{array}$	1.086(4) 1.199(6) 1.226(5) 1.442(5) 1.709(7) 1.719(6) 1.764(8) 1.793(7) 1.793(6) 1.840(5)	0.082(4) 0.090 0.039 0.041(4) 0.082(5) 0.086 0.072 0.072 0.072 0.074(3) 0.054(5)	Tied to $u_1$ Tied to $u_1$ Tied to $u_5$ Tied to $u_9$ Tied to $u_9$
$u_{11}$	Si(15)–C(16)	1.874(5)	0.066(4)	

parameters (Table 4). Parameters  $p_1$ ,  $p_2$  and  $p_3$  correspond to C(cage)–C(cage), C(cage)–C(ethynyl) and C(ethynyl)=C(ethynyl),  $p_4$  defines the average of the bond distance between C(1)–B(2) and C(12)–B(7), while  $p_6$  is the difference between these two distances. The average of C–H and B–H distances is described by parameter  $p_5$ , while  $p_7$  represents the difference between these two bond distances. The average distance between C(14)–Si(15) and Si(15)–C(16/17/18) and the difference are defined by  $p_8$  and  $p_9$  respectively. The average of angles H(12)–C(12)–B and C(13)–C(1)–B



 Table 3
 Flexible restraints used in GED refinement for 5

	Definition	Value/Å or °	Uncertainty/Å or °
$p_6$	dif[ <i>r</i> C(1)B, <i>r</i> C(12)B]	0.016	0.008
$p_7$	dif(avrBH, avrCH)	0.093	0.010
$p_9$	dif[ <i>r</i> C(16)Si(15), <i>r</i> C(14)Si(15)]	0.034	0.010
$p_{11}$	av[ $\angle C(1)BH$ , $\angle C(12)BH$ ]	120.1	1.0
$p_{12}$	dif[ $\angle C(12)BH$ , $\angle C(1)BH$ ]	1.3	0.2
$p_{13}$	dif[ $\angle$ HC(12)B, $\angle$ C(13)C(1)B]	0.7	0.5
$p_{14}$	$\angle C(14)Si(15)C(16)$	108.1	0.5
$u_1$	C(12)–H(12)	0.075	0.005
$u_4$	C(1) - C(13)	0.047	0.005
$u_{10}$	C(14)–Si(15)	0.053	0.005
$u_{17}$	$B(2) \cdots H(2)$	0.127	0.012
$u_{130}$	$B(7) \cdots Si(15)$	0.168	0.030



Fig. 3 Molecular framework showing atom numbering for 5 for the GED refinement.



**Fig. 4** Experimental and difference (experimental-theoretical) radial distribution curves, P(r)/r, for **5**. Before Fourier inversion, the data were multiplied by  $s \times \exp(-0.00002s^2)/(Z_{\rm Si} - f_{\rm Si})(Z_{\rm C} - f_{\rm C})$ .

**Table 4** Geometrical parameters  $(r_{h1})$  for  $6^{a,b}$ 

	Parameter	GED	MP2/6-311G(d)
$p_1$	$rC(1)\cdots C(12)$	3.078(5)	3.079
$p_2$	rC(1)C(13)	1.431(5)	1.438
$p_3$	rC(13)C(14)	1.233(5)	1.220
$p_4$	av[rC(1)B, rC(12)B]	1.716(3)	1.717
$p_5$	av(rBH)	1.184(3)	1.186
$p_6$	dif[rC(1)B, rC(12)B]	0.026(9)	0.015
$p_7$	av(rCH)	1.102(12)	1.076
$p_8$	av $\angle HC(12)B, \angle C(13)C(1)B$	117.2(1)	117.4
$p_9$	$av[\angle C(1)BH, \angle C(12)BH]$	119.3(7)	119.9
$p_{10}$	dif $[\angle C(12)BH, \angle C(1)BH]$	1.3(1)	1.4
$p_{11}$	dif[ $\angle$ HC(12)B, $\angle$ C(13)C(1)B]	1.7(4)	0.6

<sup>*a*</sup> Distances in Å, angles in °. <sup>*b*</sup> See text for parameter definitions.

is described by  $p_{10}$  and their difference is represented by  $p_{13}$ . The angles C(12)–B(7)–H(7) and C(1)–B(2)–H(2) are defined by an average and difference ( $p_{11}$  and  $p_{12}$ ), and  $p_{14}$  represents the angle C(14)–Si(15)–C(16). The methyl group assumes  $C_{3v}$ local symmetry as theoretical methods show no appreciable distortion, and so the angles Si(15)–C–H are represented by a single parameter  $p_{15}$ .

The model used for the GED refinement of **6** was based upon the optimized geometry obtained from the *ab initio* calculations with  $C_{5v}$  symmetry. The least-squares refinement of the structure resulted in an  $R_G$  factor of 0.053 ( $R_D = 0.029$ ), with parameters listed in Table 4 and the structure depicted in Fig. 5. Final bond distances and amplitudes of vibration are summarized in Table 5. All eleven geometrical parameters and eleven groups of amplitudes of vibration were refined. Flexible restraints were employed during the refinement using the SARACEN method. Altogether, six geometric and three amplitudes restraints were employed, as listed in Table 6. For a full list of the final bond distances and amplitudes of vibration and the table containing the least-squares correlation matrix for the structural refinement, see ESI.<sup>†</sup> The success of the final refinement can be assessed on the basis of the molecular scattering curves (see ESI<sup>†</sup>) and radial distribution curve, Fig. 6.



Fig. 5 Molecular framework showing the atom numbering for 6 for the GED refinement.

Eleven geometric parameters were used to describe structure **6** for the refinement procedure, with a model of  $C_{5v}$  symmetry (see ESI†). In analogy to **5** parameters  $p_1, p_2, p_3$  define the distances between the two C(cage) atoms [C(1) ··· C(12)], C(cage)–C(ethynyl) [C(1)–C(13)] and C(13)–C(14), respectively. The average of the bond distances C(1)–B(2) and C(12)–B(11) is defined by parameter

**Table 5** Bond distances  $(r_a/\text{Å})$  and amplitudes of vibration (u/Å) obtained in the GED refinement of **6**. Non-bonded distances are listed in the ESI<sup>†</sup>

Number Atom pair $r_a$ Amplitud	le Restraint
$u_1$ C(14)-H(14) 1.099(12) 0.0726 $u_2$ C(12)-H(12) 1.100(12) 0.075	(fixed) (fixed)
$\begin{array}{cccc} u_3 & C(13)-C(14) & 1.233(5) & 0.037(3) \\ u_4 & C(1)-C(13) & 1.430(5) & 0.040(5) \end{array}$	× ,
$\begin{array}{cccc} u_5 & C(12) - B(7) & 1.704(5) & 0.071 \\ u_6 & B(7) - B(8) & 1.789(6) & 0.070 \end{array}$	Tied to $u_9$ Tied to $u_9$
$\begin{array}{cccc} u_7 & B(2)-C(1) & 1.730(5) & 0.073 \\ u_8 & B(2)-B(3) & 1.798(6) & 0.071 \end{array}$	Tied to $u_9$ Tied to $u_9$
$u_9$ B(2)–B(7) 1.774(4) 0.069(1)	<b>T</b> : 1 /

Table 6 Flexible restraints used in GED refinement for 6

	Definition	Value/Å or $^\circ$	Uncertainty/Å or °
$p_6$	dif[ <i>r</i> C(12)B, <i>r</i> C(1)B]	0.014	0.001
$p_7$	av(rCH)	1.086	0.020
$p_9$	$av[\angle C(1)BH, \angle C(12)BH]$	1.200	0.009
$p_{10}$	dif $[\angle C(1)BH, \angle C(12)BH]$	0.013	0.001
$p_{11}$	dif $\angle$ HC(1)B, $\angle$ C(13)C(1)B]	0.006	0.003
$d_1$	B(2)-B(11)	1.761	0.010
$u_{4}$	C(1) - C(13)	0.046	0.007
$u_{45}$	$C(1) \cdots C(14)$	0.051	0.007
$u_{13}$	$C(1) \cdots C(12)$	0.064	0.009



**Fig. 6** Experimental and difference (experimental–theoretical) radial distribution curves, P(r)/r, for **6**. Before Fourier inversion, the data were multiplied by  $s \times \exp(-0.00002s^2)/(Z_B - f_B)(Z_C - f_C)$ .

 $p_4$  and the difference associated with *these bond lengths* is defined by  $p_6$ . The average hydrogen/boron bond distance between B(2)– H(2) and B(7)–H(7) is described by  $p_5$  while  $p_7$  represents the average hydrogen/carbon bond distance between C(12)–H(12) and C(14)–H(14). Parameter  $p_8$  defines the average angle between H(12)–C(12)–B and C(13)–C(1)–B while the difference between these two angles is represented by  $p_{11}$ . The average of the angles C(1)–B–H and C(12)–B–H is defined by  $p_9$  and the difference between them is  $p_{10}$ .

Disubstituted-para-carboranes. The X-ray structure of the disubstituted carborane 3 has been determined at 100 K. The molecule possesses crystallographic 2/m ( $C_{2h}$ ) symmetry in the space group C2/m. The inversion centre coincides with the centre of the cage, the Si, C(1), C(2), C(3), C(4) and B(2) atoms and their inversion equivalents lie in the mirror plane. The C(1)-C(2)-C(3)-Si fragment is essentially linear. While the present work was in progress, the same structure (studied at 173 K) was reported by Kaszynski and co-workers.25 Apart from a slightly (and spuriously) shorter C≡C bond, 1.193(3) Å at 173 K against 1.204(2) Å at 100 K, and a rotational disorder of one methyl group in each SiMe<sub>3</sub> moiety, the results are identical with ours. High-angle Xray reflections, which are better observed in a low-temperature study, have larger contribution from the core electrons (which do not shift), hence the apparent  $C \equiv C$  bond lengths in the X-ray structures increase with the decrease of temperature.

The difference in the C $\equiv$ C bonds of 1.204(2) Å for the molecular structure of **3** by X-ray diffraction and of 1.227(5) Å for the molecular structure of **5** by GED can be attributed to the fact that the valent electrons of the acetylenic carbon atoms are substantially shifted into the C $\equiv$ C bond area, hence the distance between electron density maxima ('bond distance' as measured

by the X-ray method) is shorter than the (calculated or GED) internuclear distance.

A single crystal grown from an oil consisting of **6** with **4** and **16** present was studied by X-ray diffraction and proved to be a solid solution of **4** and **16** (in a *ca.* 2 : 1 ratio). This solid is isomorphous with pure **4** which crystallises in the similar triclinic lattice with a = 7.287(2), b = 7.579(1), c = 10.953(3) Å, a = 82.73(2),  $\beta = 72.96(2)$ ,  $\gamma = 80.01(2)^{\circ}$  (at 150 K).<sup>24</sup> The latter structure contains two symmetrically non-equivalent molecules, both lying at crystallographic inversion centres. In the mixed crystal both sites are shared by the molecules of **4** and **16**, the latter being disordered between two opposite orientations, related by the inversion centre. The resulting picture is one of the ordered centrosymmetric cage with a superposition of an ethynyl and a bromine substituents (in a 5 : 1 ratio) at positions 1 and 12. The degree of substitution at both molecular sites is equal within experimental error, notwithstanding different packing environments.

The molecule of dibromo-*para*-carborane **30** has crystallographic  $C_i$  symmetry (Fig. 7). Three dibromocarboranes have been structurally characterised previously, 9,10-dibromo-*meta*carborane,<sup>39</sup> 9,12-dibromo-*ortho*-carborane<sup>40</sup> and 1,12-dibromo*ortho*-carborane.<sup>41</sup> The latter molecule is very similar to **30** in shape, but adopts entirely different crystal packing (in chiral space group  $P4_1$ ) due to C–H··· Br hydrogen bonds.<sup>42</sup>



**Fig. 7** X-Ray molecular structure of **30**. C1–Br bond length 1.916(2) Å. Primed atoms are generated by the inversion centre. Thermal ellipsoids are drawn at the 50% probability level.

Discussion of molecular structures of *C*-substituted-*para*carboranes. Tables 7 and 8 list the averaged bond lengths for *para*carborane and its derivatives 1-X-12-Y-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> determined by gas-phase electron and X-ray diffraction respectively. The C<sub>2</sub>B<sub>10</sub> cage geometry in the crystal structure of **4** (X, Y = HC $\equiv$ C) revealed the averaged tropical B–B bond (ii) to be 1.793(3) Å. This is *ca* 0.015 Å longer than the respective bonds (ii, ii<sub>2</sub>) determined for the parent *para*-carborane by X-ray crystallography<sup>43,44</sup> and gas-phase electron diffraction.<sup>45,46</sup> The C–B bond length (i) of 1.726(3) Å in **4** was also longer (*ca*. 0.02 Å) than those measured for the parent *para*-carborane. The molecular structure of **3** (X, Y = Me<sub>3</sub>SiC $\equiv$ C) was also determined here and elsewhere<sup>25</sup> with a similar cage geometry to **4**.

The molecular structure for  $6 (X = HC \equiv C, Y = H)$  determined by GED here gave the expected lengthening of the neighbouring C-B and tropical B-B bonds on ethynyl group substitution at one cage carbon with values of 1.730(5) (i) and 1.799(5) Å (ii) Downloaded by FORDHAM UNIVERSITY on 07 January 2013 Published on 27 April 2006 on http://pubs.rsc.org | doi:10.1039/B517538K

 Table 7
 para-Carborane derivatives 1-X-12-Y-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> studied by GED

$\cup$	Č C/Å	i/Å	ii/Å	iii/Å	$ii_2/$ Å	$i_2/{ m \AA}$	C-X/Å	C≡C/Å	T/K	Ref.
	3.029(5)	1.698(3)	1.784(1)	1.774(4)	1.784(1)	1.698(3)	1.094(8)		343	45
	3.078(5)	1.730(5)	1.799(5)	1.778(4)	1.790(5)	1.704(5)	1.431(5)	1.233(5)	371	This work
	3.083(9)	1.725(6)	1.789(6)	1.765(8)	1.792(7)	1.708(7)	1.442(5)	1.227(5)	418	This work
	3.085(15)	1.706(4)	1.775(3)	1.765(7)	1.775(3)	1.706(4)	1.785(10)		440	47
	~	1.736(11)	1.795(13)	1.760(17)	1.795(13)	1.736(11)	1.553(26)			48
	3.101(25)	1.708(8)	1.777(8)	1.775(11)	1.777(8)	1.708(8)	2.082(14)		503	49
	3.125(9)	1.716(13)	1.777(7)	1.766(20)	1.777(7)	1.716(13)	1.533(19)		343	50

is work 

 Table 8
 X-Ray data for selected para carborane derivatives  $1 - X - 12 - Y - 1, 12 - C_2 B_{10} H_{10}$ . ( $C_2 C_{02} = C_2 SiMe_3 Co_2(dppm)(CO)_4$ )

x	Y	$C \cdots C/ {\rm \AA}$	i/Å	ii/Å	iii/Å	$ii_2/Å$	$i_2/\text{\AA}$	C1-exo/Å	C≡C(N)/Å	T/K	Ref.
C≡N	C≡N	3.056	1.720(2)	1.797(2)	1.758(2)	1.797(2)	1.720(2)	1.455(2)	1.144(2)	173	25
Br	Br	3.064(3)	1.715(3)	1.795(3)	1.767(3)	1.795(3)	1.715(3)	1.916(2)		120	This work
$CO_2H$	$CO_2H$	3.065(2)	1.711(3)	1.784(5)	1.758(3)	1.784(5)	1.711(3)	1.515(1)		293	51
Н	Н	3.071	1.704(3)	1.777(3)	1.765(3)	1.777(3)	1.704(3)			153	44
$C_{r}H_{r}$	Н	3.102	1.719(2)	1.784(2)	1.768(2)	1.782(2)	1.712(2)	1.546(2)		91	8
C≡C(4-py)	C≡C(4-py)	3.103	1.724(2)	1.791(2)	1.764(2)	1.791(2)	1.724(2)	1.447(2)	1.194(2)	150	15
C≡CH	C≡CH	3.104(2)	1.726(3)	1.793(3)	1.761(2)	1.793(3)	1.726(3)	1.451(2)	1.180(3)	150	24
C <sub>6</sub> H₄C≡CPh	Н	3.105(1)	1.725(3)	1.780(3)	1.766(5)	1.782(3)	1.706(3)	1.512	к. 7	123	52
C≡CC <sub>5</sub> H <sub>11</sub>	$CB_{10}H_{10}CC \equiv CC_5H_{11}$	3.116	1.717(2)	1.781(2)	1.759(2)	1.778(2)	1.721(2)	1.451(2)	1.182(2)	173	4
C,Co,	Н	3.119	1.724(3)	1.771(4)	1.765(4)	1.768(7)	1.694(3)	1.510(3)	к. 7	100	22
C≡CSiMe <sub>3</sub>	C≡CSiMe,	3.121	1.726(2)	1.789(2)	1.765(2)	1.789(2)	1.726(2)	1.452(2)	1.193(3)	173	25
C≡CSiMe <sub>3</sub>	C≡CSiMe,	3.122(2)	1.728(2)	1.793(3)	1.769(2)	1.793(3)	1.728(2)	1.453(2)	1.204(2)	120	This work
C <sub>6</sub> H <sub>4</sub> Me	$C_6H_4Me$	3.163	1.727(3)	1.776(3)	1.759(3)	1.776(3)	1.727(3)	1.517(2)		293	53
$C_2Co_2$	$C_2 C_{0_2}$	3.176	1.728(3)	1.776(3)	1.766(3)	1.776(3)	1.728(3)	1.497(2)		100	16

Х	Y	$C \cdots C/ \mathring{A}$	i/Å	ii/Å	iii/Å	ii₂/Å	i <sub>2</sub> /Å	C(1)-exo/Å	C≡C(N)/Å	Point group	Ref.
F	Н	3.040	1.702	1.784	1.761	1.781	1.703	1.363		$C_{5v}$	
Н	Н	3.047	1.703	1.781	1.762	1.781	1.703			$D_{\rm 5d}$	54
Cl	Н	3.054	1.708	1.784	1.761	1.780	1.702	1.751		$C_{5v}$	
C≡N	Н	3.056	1.716	1.790	1.760	1.781	1.703	1.445	1.183	$C_{5v}$	
$CO_2H$	Н	3.057	1.711	1.785	1.761	1.781	1.701	1.512		$C_{s}$	
C≡N	C≡N	3.067	1.716	1.790	1.758	1.790	1.716	1.445	1.183	$D_{\rm 5d}$	47
OH	Н	3.069	1.711	1.778	1.760	1.780	1.702	1.392		$C_{s}$	59
C≡CH	Н	3.073	1.718	1.784	1.761	1.779	1.702	1.439	1.221	$C_{5v}$	
$C \equiv CSiMe_3$	Н	3.076	1.719	1.785	1.761	1.780	1.703	1.437	1.234	$C_{s}$	
Me	Н	3.078	1.711	1.775	1.762	1.779	1.702	1.524		$C_{s}$	
Ph	Н	3.096	1.720	1.776	1.761	1.778	1.701	1.507		$C_{s}$	
$CB_{10}H_{10}CH$	Н	3.096	1.724	1.780	1.760	1.777	1.701	1.533		$C_{s}$	
C≡CH	C≡CH	3.099	1.718	1.784	1.759	1.784	1.718	1.438	1.221	$D_{\rm 5d}$	
$C \equiv CSiMe_3$	C≡CSiMe <sub>3</sub>	3.105	1.719	1.783	1.759	1.783	1.719	1.437	1.235	$C_{\rm s}$	
Ph	Ph	3.142	1.720	1.774	1.761	1.774	1.720	1.506		$C_{\rm s}$	

Table 9MP2/6-31G\* data for selected 1-X-12-Y-1,  $12-C_2B_{10}H_{10}$  carboranes

respectively. The C–B and tropical B–B values of 1.704(5) ( $i_2$ ) and 1.790(5) Å ( $ii_2$ ) observed near the unsubstituted cage carbon are similar to corresponding values in the parent carborane geometry. For the molecular structure of **5** determined by GED, the two C–B bond distances were 1.725(6) (i) and 1.708(7) Å ( $i_2$ ) as expected but the averaged tropical B–B bond lengths of 1.789(6) (ii) and 1.792(7) Å ( $ii_2$ ) were similar. The higher e.s.d.s found in the GED-determined structure of **5** suggest the latter bonds are not precise enough to reveal a difference. The MP2-optimised geometry for **6** shows a difference of 0.016 Å is determined for the two different C–B bond distances (Table 9).

A point worthy of comment here is the variable  $C \equiv C$  bond lengths observed in GED and XRD for the C-ethynyl-carboranes 4 and 6 respectively as well as from 'gas-phase' optimised geometries at different levels of theory. A difference of 0.05 Å found between 4 and 6 is due to the different diffraction methods used. The X-ray diffraction method underestimates the C $\equiv$ C bond length—even at lower temperatures-so this should be taken into account when using the X-ray structure of 4 as a model for longer molecules. The HF/6-31G\*-optimised geometry of 4 has a C=C bond length of 1.185 Å-similar to the X-ray structure—and, again, this is not an appropriate model for longer molecules. The DFT and MP2-optimised geometries with  $C \equiv C$  bond lengths of 1.210<sup>22</sup> and 1.221 Å respectively are in reasonably good agreement with the observed GED value of 1.233(5) Å for 6. Table 9 lists the MP2/6-31G\* data for selected para-carborane derivatives 1-X-12-Y-1,12- $C_2B_{10}H_{10}$ . Moreover, the cage geometries in the DFT and MP2 geometries are in better agreement with the X-ray data for 4 than with the HF geometry.

Unfortunately as shown from the e.s.d.s in Table 7, the majority of reported structures determined by GED for *C*-substituted-*para*carborane derivatives are not sufficiently precise to examine the subtle effects on the cage geometries by substitution at the cage carbon atoms. Nevertheless, the number of accurate molecular structures on *para*-carborane derivatives determined by XRD has grown rapidly in the last five years since the molecular structure of **4** was compared with just three other *para*-carborane derivatives.<sup>24</sup> Relevant XRD data for selected derivatives are given in Table 8.

A previous study<sup>47</sup> on selected *C*-disubstituted-*para*-carboranes at the MP2/6-31G\* level of theory concluded that the  $C \cdots C$  bond distances are related to the induction effect of the substituent. This is supported here by the XRD data in Table 8 and additional MP2/6-31G\* data in Table 9. The substitution effects on the C-B  $(i, i_2)$  and tropical B-B  $(ii, ii_2)$  bonds were not discussed in the reported study on the basis that these changes are insignificantwith ethynyl and aryl groups as substituents we believe that they are significant. The average C–B bond length  $(i, i_2)$  invariably increases on substitution at the cage carbon compared to the parent para-carborane but is longest when the substituent is an ethynyl, C<sub>2</sub>Co<sub>2</sub> cluster or aryl group. The substituent effect on the tropical B-B bonds is interesting. These bonds (ii, ii<sub>2</sub>) lengthen significantly with ethynyl, cyanide and bromo groups as substituents but are unaffected by aryl and C2Co2 cluster groups. It is intriguing that the ethynyl group has the most notable effect on the cage geometry overall and thus mirrors its significant influence on the low-yield syntheses of C, C'-bis(ethynyl)-para-carboranes observed here and elsewhere.24,25

Monoethynyl-ortho-carborane. In 1964, the first C-ethynyl carborane 1-HC=C-1,2-C<sub>2</sub> $B_{10}H_{11}$  28, where the carbons are adjacent in the cage, was reported,55 with its chemistry being explored over the next twenty years.<sup>56</sup> Compound 28 behaves as a typical terminal alkyne, and oxidative coupling affords the carborane terminated diyne. Nickel-catalysed cyclo-trimerisation of 28 affords 1,2,4-tris(1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)C<sub>6</sub>H<sub>3</sub> in good yield.<sup>57</sup> This volatile solid, which polymerises upon UV irradiation, is considered a suitable precursor candidate to boron-carbide (B<sub>4</sub>C) ceramics via MOCVD.<sup>36</sup> The chemistry of 1-ethynyl-para-carborane 6 is expected to be similar to that of its ortho-carborane analogue 28. However the substantially more thermally/chemically stable para-carborane cage with a reduced electron-withdrawing strength relative to the ortho-carborane cage points to some novel chemistry to be discovered with 6. Moreover, the boron-carbide ceramics generated from the volatile ethynyl-para-carboranes would be expected to be more robust than those generated from their orthocarborane analogues.

Monosubstituted *ortho*-carboranes often have rotationally disordered cages in the solid state, with the (unsubstituted) carbon and boron atoms statistically mixed.<sup>42</sup> However, the present Xray diffraction study shows that the molecule of 1-ethynyl-*ortho*carborane **28** (Fig. 8) is ordered in the crystal at 120 K. The C(2) atom was clearly distinguishable from boron atoms both by the electron density peak height and by bond distances. The ordering



Fig. 8 X-Ray molecular structure of 28. The C(1)–C(13) bond length is 1.441(1) Å.

of the  $C_2B_{10}$  cage may be attributed to close intermolecular contacts between positively and negatively charged hydrogen atoms,<sup>42</sup> viz. C(14)-H····H-B(9) (x - 1, y, z - 1) and C(2)-H····H-B(7) (x - 1/2, 1/2 - y, z - 1/2), with *intermuclear* H····H distances of 2.25 and 2.45 Å, respectively (estimated using C/B-H bond lengths from GED). The intra-cage C(1)-C(2) bond is known for its 'elasticity', its length being very sensitive to the nature and even the orientation of the substituents.<sup>58,59</sup> The C(1)-C(2) bond distance of 1.653(1) Å in **28** is some 0.03 Å longer than the C(1)-C(2) bond length determined for the unsubstituted *ortho*carborane.<sup>43,45,60</sup> However, **28** is the first structurally characterised monosubstituted *ortho*-carborane 1-R-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> where the C(1)-C(2) bond is not influenced by the orientation effect of the substituent, as the ethynyl group is cylindrically symmetric.

The triple C(13)=C(14) bond length in **28**, 1.185(2) Å, is consistent with the value of 1.194(2) Å observed in the X-ray structure of the diphenylated derivative, 1-PhC=C-2-Ph-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>.<sup>61</sup> The MP2/6-31G\* optimised geometry of **28** reveals a slightly shorter C(1)–C(2) bond (1.642 Å) and a longer C=C bond (1.221 Å).

#### Spectroscopic aspects

The <sup>11</sup>B NMR peak value for boron atoms B(2)–B(6) on replacing hydrogen at C(1) in para-carborane 1 with a substituent is shifted to high frequency by some 2–3 ppm here and elsewhere.<sup>10</sup> The type of substituent does not influence the value considerably. The longer C-B(2)/(6) bond lengths on substitution of C(1) may well be linked to the high frequency <sup>11</sup>B shift change observed in C-substitutedpara-carboranes compared to para-carborane itself. The C(1) shift value can vary to higher or lower frequency as expected when H is replaced by different substituents. On substitution of H at C(1), the <sup>13</sup>C peak shift for C(12) is changed to low frequency (antipodal effect<sup>62</sup>) in all cases and the shift depends on the type of substituent. We would expect the shift difference for C(1) on substitution at C(1) to be greater than for the antipodal carbon C(12) but the opposite is found for 1-bromo-para-carborane 29. The observed <sup>13</sup>C chemical shifts of 56.5 ppm corresponding to the antipodal C(12) and 58.2 for the substituted C(1) in 29 is unusual when compared with the <sup>13</sup>C shift of 63.5 ppm for para-carborane.

## Conclusions

The low yields of bis(ethynyl)-para-carborane from copper mediated reactions of para-carborane with bromoalkynes, compared to the high yields of monoethynyl-*para*-carborane from similar procedures, are due to the influence of the *C*-ethynyl group on the second cage C–alkyne C coupling process. The readily prepared bromoalkyne 1-bromo-3-methyl-1-butyn-3-ol affords monoethynyl- and bis(ethynyl)-*para*-carborane and is probably the preferred reagent for economy and convenience; however the yield of the disubstituted carborane is low from both bromoalkynes. A convenient high-yield synthesis of bis(ethynyl)-*para*-carborane is therefore still needed to more readily explore and exploit its potential as a precursor to molecular rigid rods or supramolecular assemblies and to metal complexes for investigations into the electronic transmission of the carborane cage.

Gas-phase electron diffraction data for the two *C*-monoethynylpara-carboranes show subtle geometrical effects of the ethynyl group on the highly symmetrical cage geometry and also provide realistic C=C bond lengths, which are underestimated by Xray diffraction data for related ethynyl carboranes, such as the *C*-monoethynyl-*ortho*-carborane determined here and 1,12bis(ethynyl)-*para*-carborane studied elsewhere.<sup>24</sup> The effect of substituents on the *para*-carborane cage geometry is intriguing. Both neighbouring cage C–B bonds and tropical B–B bonds are lengthened significantly by ethynyl groups compared to other substituents.

## Experimental

Reactions were carried out using standard Schlenk techniques under dry high-purity nitrogen. THF and diethyl ether were distilled from potassium and CH<sub>2</sub>Cl<sub>2</sub> from calcium chloride prior to use. Pyridine was distilled after standing over potassium hydroxide for three days. Bromine was dried by shaking with an equal volume of concentrated H<sub>2</sub>SO<sub>4</sub> and then distilled. Trimethylsilylethyne, bis(trimethylsilyl)ethyne and 1-methyl-3butyn-1-ol (Aldrich) were used as supplied. MeLi (1.4 M, diethyl ether), pentane, MeLi-LiBr (1.5 M, diethyl ether), HCl, CdCl<sub>2</sub>, NaCl, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>3</sub>, NaHCO<sub>3</sub> and MgSO<sub>4</sub> (dried in hot oven) were used as supplied. Copper(1) chloride was purified according to a literature procedure.<sup>63</sup>

NMR spectra were measured using Varian Unity-300 (1H, 11B, <sup>13</sup>C), Bruker AM250 (<sup>1</sup>H, <sup>13</sup>C), Bruker Avance 400 (<sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C) and/or Varian Inova 500 (1H, 11B) instruments. All chemical shifts are reported in  $\delta$  (ppm) and coupling constants in Hz. <sup>1</sup>H NMR spectra were referenced to residual protio impurity in the solvent (CDCl<sub>3</sub>, 7.26 ppm). <sup>13</sup>C NMR spectra were referenced to the solvent resonance (CDCl<sub>3</sub>, 77.0 ppm). <sup>11</sup>B NMR spectra were referenced externally to  $Et_2O \cdot BF_3$ ,  $\delta = 0.0$  ppm. Infrared spectra were recorded from KBr discs on Perkin Elmer 1600 series FTIR or Perkin Elmer 1720X FTIR spectrometers. Mass spectra (MS) were recorded on a VG Micromass 7070E instrument under E.I conditions (EI) at 70 eV. Gas chromatography-mass spectra were recorded on a Fisons VG Trio 1000 mass spectrometer coupled directly to a Hewlett Packard 5890 Series II gas chromatograph (Column: HP-1; 25 m; 0.25 mm I.D.; 0.32 µm. 1 m thickness). Values of M show the isotope range  ${}^{10}B_n$  to  ${}^{11}B_n$  including a  ${}^{13}C$ contribution if observed. Elemental carbon and hydrogen analyses were performed using Exeter Analytical CE-440 or Carlo Erba Strumentazione EA Model 1106 instruments.

1-Ethynyl-*ortho*-carborane **28** was prepared by a reported procedure,<sup>55</sup> and confirmed by comparison of spectroscopic data

with that reported elsewhere.<sup>36</sup> Crystals of **28** suitable for Xray diffraction were obtained by slow sublimation at ambient temperature and pressure. 1-Bromo-3-methyl-1-butyn-3-ol **7** was prepared according to a literature procedure.<sup>33</sup> **7**: NMR (CDCl<sub>3</sub>, 298 K),  $\delta$  (<sup>1</sup>H) 3.07 (1H, OH), 1.48 (6H, CH<sub>3</sub>);  $\delta$  (<sup>13</sup>C{<sup>1</sup>H}) 84.5 (*C*=CBr), 66.1 (COH), 42.6 (C=CBr), 31.0 (CH<sub>3</sub>).

# Synthesis of 2-bromotrimethylsilylethyne 2 from trimethylsilylethyne 8 *via* butyllithium

Trimethylsilylethyne 8 (4.9 g, 0.05 mol) was dissolved in  $Et_2O$ (100 ml) under nitrogen. A solution of butyllithium in hexanes (1.6 M, 160 ml, 0.21 mol) was added dropwise at 0 °C and stirred for 20 min before being warmed to r.t. for a further 1 h. The solution was cooled to -78 °C (acetone-dry ice) before bromine (8 g, 0.21 mol) was added dropwise and the mixture stirred for 45 min. The solution was allowed to warm to room temperature giving a light brown transparent solution, which was poured into ice-cold 6 M hydrochloric acid (50 ml). The layers were separated and the dark yellow aqueous phase was extracted with ice-cold pentane (3  $\times$  50 ml). The organic extracts were combined and concentrated using a rotary evaporator. The pale yellow oil (5.6 g) was found to contain 89% of Me<sub>3</sub>SiC=CBr 2(56%)yield), tribromotrimethylsilylethene 12 (5%) and hexanes (6%). The crude compound 2 was stored over molecular sieves under nitrogen in a fridge at 0 °C and used in the syntheses of C-ethynyl carboranes.

**2**<sup>27,64</sup>. Mass (EI) spectrum: typical bromine pattern at m/z161–163 [163,  $M - CH_3$ , 100%], 176–178 [178, M, 2%], C<sub>5</sub>H<sub>9</sub>BrSi requires: M = 177. IR:  $\nu$ (CH) 2960, 2904;  $\nu$ (C $\equiv$ C) 2125; 1251; 867, 844 cm<sup>-1</sup>. NMR (298 K, CDCl<sub>3</sub>)  $\delta$  (<sup>1</sup>H) 0.19 (CH<sub>3</sub>);  $\delta$  (<sup>13</sup>C{<sup>1</sup>H}) 86.9 (BrC $\equiv$ CSi), 61.4 (BrC $\equiv$ CSi), -0.3 (CH<sub>3</sub>).

# Synthesis of 2-bromotrimethylsilylethyne 2 from trimethylsilylethyne 8 *via* Grignard reagent<sup>27</sup>

A solution of BuMgBr was prepared from Mg (4.98 g, 0.2 mol) and bromobutane (28.6 g, 0.2 mol) in diethyl ether (200 ml); little Mg was left after the solution was heated at reflux point for 1 h. Trimethylsilylethyne 8 (20.1 g, 0.2 mol) was added dropwise to the stirred solution, the resulting semi-solid mass was diluted with ether (200 ml) and stirred at room temperature for 18 h by a mechanical stirrer. The solution was cooled to -45 °C (dry ice-acetone bath) and bromine (32.5 g, 0.2 mol) was added dropwise-each drop decolourised as it reached the solution-then warmed slowly to ambient temperature. Water (65 ml) was added slowly and stirred until two phases appeared. The ether layer was separated, washed with water and dried over MgSO<sub>4</sub>. The solvent was removed at 0 °C under vacuum (0.05 mmHg) to afford a light brown residue (36.3 g), which was identified by proton and carbon NMR spectroscopy to be a mixture of 2-bromotrimethylsilylethyne 2 (85%), tribromotrimethylsilylethene 12 (7%) and bromobutane (8%). The crude compound 2 was stored over molecular sieves under nitrogen in a fridge at 0 °C and used in the syntheses of C-ethynyl carboranes.

# Synthesis of 2-bromotrimethylsilylethyne 2 from trimethylsilylethyne 8 *via* silver nitrate

Trimethylsilylethyne **8** (4.9 g, 0.05 mol) was dissolved in acetone (20 ml) under nitrogen and added with silver nitrate (2.83 g, 0.167 mol). The solution containing a suspension of white solid was stirred for 1 hour. A solution of *N*-bromosuccinimide (8.9 g, 0.05 mol) in acetone (100 ml) was added slowly to the stirred solution and the reaction mixture was left to stir for 4 h. Diethyl ether (50 ml) was added to the mixture and the insoluble white solid was filtered off. The filtrate was washed with saturated NaHCO<sub>3</sub> solution (3 × 50 ml) and water (3 × 50 ml), then dried over MgSO<sub>4</sub>. The solution was concentrated using a rotary evaporator to leave an oil (3.5 g) identified as a 3 : 1 mixture of bromotrimethylsilylethyne **2** (*ca.* 29% yield) and ether. The crude compound **2** was stored over molecular sieves under nitrogen in a fridge at 0 °C and used in the syntheses of *C*-ethynyl carboranes.

# Synthesis of 2-bromotrimethylsilylethyne 2 from bis(trimethylsilyl)ethyne 9<sup>28</sup>

Bis(trimethylsilyl)ethyne 9 (34.5 g, 0.2 mol) was dried under vacuum while stirring in a 1 L round bottom flask immersed in an ice bath before THF (110 ml) was added under nitrogen. A solution of methyllithium in diethyl ether (1.5 M, 160 ml, 0.21 mol) at 0 °C was added dropwise, and stirred at 0 °C for 1 h before being warmed to r.t. and stirred for a further 1 h. After this time, examination of an aliquot of the mixture by <sup>13</sup>C NMR confirmed that all the ethyne had converted into the lithium salt, Me<sub>3</sub>SiC=CLi (the <sup>13</sup>C chemical shift assigned to the methyl group of the ethyne is shifted to low frequency by 1.7 ppm on lithiation). The solution was cooled to -70 °C before a solution of bromine (33.6 g, 0.21 mol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) was added dropwise and the mixture stirred for 45 min. The solution was allowed to warm to room temperature giving a light brown transparent solution, which was poured into ice-cold 6 M hydrochloric acid (50 ml). The layers were separated and the dark yellow aqueous phase was extracted with ice-cold pentane (3  $\times$  50 ml). The combined dark orange organic extracts were washed successively with ice-cold 6M HCl  $(3 \times 25 \text{ ml})$ , 20% aqueous CdCl<sub>2</sub> (20 ml), 10% aqueous Na<sub>2</sub>SO<sub>3</sub> (20 ml), saturated NaHCO<sub>3</sub> (20 ml) and saturated NaCl (30 ml), and then dried with MgSO4 for 48 hours. The ether solution was distilled at 0 °C with a Vigreux column under high vacuum (0.01 mmHg). The undistilled residue (23.6 g) was found to contain 93% of Me<sub>3</sub>SiC=CBr 2 (65% yield), tribromotrimethylsilylethene 12 (2%), trans-1,2-dibromo-bis(trimethylsilyl)ethene 13 (2%) and THF (3%). The crude compound 2 was stored over molecular sieves under nitrogen in a fridge at 0 °C and used in the syntheses of C-ethynyl carboranes.

# Formation of tribromotrimethylsilylethene 12 and *trans*-1,2-dibromo-bis(trimethylsilyl)ethene 13 from bis(trimethylsilyl)ethyne 9

Bis(trimethylsilyl)ethyne 9 (23.5 g, 0.14 mol) was dried under vacuum in a 1 L round bottom flask immersed in an ice bath before being dissolved in THF (200 ml), cooled to 0  $^{\circ}$ C and treated dropwise with methyllithium (*ca.* 0.5 M, 115 ml). The

solution was stirred at 0 °C for 30 min and warmed to room temperature and stirred for 30 min to give a colourless solution. A solution of bromine (22.4 g, 0.14 mol) in a mixture of  $CH_2Cl_2$ (20 ml) and pyridine (23 ml) was prepared at -78 °C (acetonedry ice) and warmed to room temperature before being added to the THF solution at -78 °C. The resultant opaque yellow solution was stirred at -78 °C for 30 min and gradually warmed to room temperature to give a cherry red transparent solution and poured into ice-cold 6 M hydrochloric acid (50 ml). The layers were separated and the aqueous phase was extracted with ice-cold pentane (3  $\times$  50 ml). The combined dark brown organic extracts were washed successively with ice-cold 6 M HCl ( $3 \times 25$  ml), 20 ml aqueous solutions of 20% CdCl<sub>2</sub>, saturated NaCl, saturated Na<sub>2</sub>SO<sub>4</sub>, saturated NaHCO<sub>3</sub> and saturated NaCl and then dried with MgSO<sub>4</sub>. The yellow solution was vacuum distilled at 20 °C/0.01 mmHg to remove solvents, then at 50 °C/0.01 mmHg to give 8.0 g (34%) of unreacted bis(trimethylsilyl)ethyne 9 and at 150 °C/0.01 mmHg to give 11.1 g of a 1 : 1 mixture of tribromotrimethylsilylethene 12 (24%) and trans-1,2-dibromobis(trimethylsilyl)ethene65,66 13 (24%). The 1:1 mixture was cooled to 0 °C. After two weeks large crystals of pure 13 were formed and subjected to an X-ray crystallography study which confirmed the trans-conformation of the ethene. The mother liquor was vacuum distilled at 180 °C/0.01 mmHg to give a colourless viscous oil identified as pure tribromotrimethylsilylethene 12.

12. Mass (EI) spectrum: typical bromine pattern at m/z 137– 139, [Me<sub>2</sub>SiBr, 100%], 335–340 [336, M, 19%], C<sub>3</sub>H<sub>9</sub>Br<sub>3</sub>Si requires: M = 337. IR:  $\nu$ (CH) 2956, 2897;  $\nu$ (C=C) 1531; 1251; 891, 846 cm<sup>-1</sup>. NMR (298 K, CDCl<sub>3</sub>)  $\delta$  (<sup>1</sup>H) 0.39 (CH<sub>3</sub>);  $\delta$  (<sup>13</sup>C{<sup>1</sup>H}) 130.7 (BrC=CBr<sub>2</sub>), 94.1 (BrC=CBr<sub>2</sub>), 0.5 (CH<sub>3</sub>).

**13.** Mass (EI) spectrum: m/z 73 [Me<sub>3</sub>Si, 100%], typical bromine pattern 328–332, [330, M, 10%] C<sub>8</sub>H<sub>18</sub>Br<sub>2</sub>Si<sub>2</sub> requires: M = 330. IR: 2971, 2956, 2896; 1251, 1242, 841 cm<sup>-1</sup>. NMR (298 K, CDCl<sub>3</sub>)  $\delta$  (<sup>1</sup>H) 0.37 (CH<sub>3</sub>);  $\delta$  (<sup>13</sup>C{<sup>1</sup>H}) 137.3 (C=C), 0.8 (CH<sub>3</sub>).

#### Preparation of 1-trimethylsilylethynyl-para-carborane (5)

A solution of *para*-carborane (1.44 g, 10 mmol) in monoglyme (45 ml) was treated with BuLi (2.5 M in hexanes, 4.4 ml, 11 mmol). Pyridine (12 ml) and CuCl (1.13 g, 11.3 mmol) were added and the mixture heated at reflux (30 min), then allowed to cool while BrC=CSiMe<sub>3</sub> 2 was introduced (2.0 g, 11.3 mmol) and then returned to reflux overnight. The cooled reaction mixture was diluted with Et<sub>2</sub>O (100 ml). After 4 h, the suspension was filtered and the filtrate washed with dilute HCl (100 ml, 2.5 M), water  $(2 \times 200 \text{ ml})$  and dried over MgSO<sub>4</sub>. The semi-solid obtained after evaporation of the volatiles was dissolved in cyclohexane and passed through a short column packed with chromatographic silica. The cyclohexane was vacuum removed leaving a brown oil. The oil was distilled at 30 °C/0.01 mmHg to give crude paracarborane 1 (0.18 g, 13%), then at 60 °C/0.01 mmHg to give a clear oil (1.82 g, 76% yield) identified as 1-trimethylsilylethynylpara-carborane 5.

5. Mass (EI) spectrum: typical carborane pattern at m/z 221– 228 [225,  $M - CH_3$ , 100%], 238–242, [240, M, 5%] C<sub>7</sub>H<sub>20</sub>B<sub>10</sub>Si requires: M = 240. IR: v(cageCH) 3063(m); v(methylCH) 2960(s), 2899(m); v(BH) 2617(s); v(C $\equiv$ C) 2183(m) cm<sup>-1</sup>. NMR (298 K, CDCl<sub>3</sub>)  $\delta$  (<sup>11</sup>B) -11.5 (5B, d, 168, B2-6), -15.2 (5B, d, 167, B7-11);  $\delta$  (<sup>1</sup>H{<sup>11</sup>B}) 2.61 (1H, C12H), 2.44 (5H, B2-6H), 2.22 (5H, B7-11H), 0.06 (9H, CH<sub>3</sub>);  $\delta$  (<sup>13</sup>C{<sup>1</sup>H}) 100.5 (C-Si), 84.5 (*C*=CSi), 69.6 (cage *CC*=C), 59.9 (cage CH), -0.5 (CH<sub>3</sub>).

#### Preparation of 1-ethynyl-para-carborane (6) from (5)

A sample of Me<sub>3</sub>SiC≡CCB<sub>10</sub>H<sub>10</sub>CH (**5**) (0.5 g, 2 mmol) suspended in 5 ml of methanol was treated with 0.5 ml of methanolic potassium hydroxide solution (0.1 g KOH, 5 g H<sub>2</sub>O, 20 ml methanol). The mixture was stirred at room temperature overnight before being diluted with diethyl ether (40 ml), washed with water (2 × 30 ml) and dried (magnesium sulfate). Evaporation of the ether at room temperature gave an oil which was distilled at 0°/0.05 mmHg with the receiver cooled at -78 °C. A distillate (0.32 g, 91%), consisting of pure 1-ethynyl-*para*-carborane (**6**), was obtained.

6. Mass (EI) spectrum: typical carborane pattern at 158–170, [167, M - H, 100%], [168, M, 95%]  $C_4H_{12}B_{10}$  requires: M =168. IR:  $\nu$ (ethynyl CH) 3305(m); ( $\nu$ (cage CH) 3063(m);  $\nu$ (BH) 2613(vs) cm<sup>-1</sup>. NMR (298 K, CDCl<sub>3</sub>) $\delta$  (<sup>11</sup>B) –11.6 (5B, d, 167, B2-6), -15.1 (5B, d, 167, B7–11);  $\delta$  (<sup>1</sup>H{<sup>11</sup>B}) 2.61 (1H, C12H), 2.41 (5H, B2–6H), 2.16 (5H, B7–11H), 2.05 (1H, C=CH);  $\delta$  (<sup>13</sup>C{<sup>1</sup>H}) 79.6 (C=CH), 67.9 (cage CC=C), 67.7 (C=CH), 60.4 (cage CH).

#### Preparation of 1-(3-hydroxy-3-methylbutynyl)-para-carborane (14)

A stirred solution of *para*-carborane **1** (1.44 g, 10 mmol) in monoglyme (45 ml) was treated with BuLi (2.5 M in hexanes, 4.4 ml, 11 mmol) at ambient temperature. Pyridine (8 ml) and CuCl (1.13 g, 11.3 mmol) were added to the solution and the mixture heated at reflux (30 min) then allowed to cool. A solution of BrC=CCMe<sub>2</sub>OH (7, 2.0 g, 11.3 mmol) in monoglyme (10 ml) was added dropwise to the vigorously stirred solution at 0 °C, and the mixture heated at reflux (30 min). The reaction mixture was cooled, and diluted with Et<sub>2</sub>O (400 ml). The oil obtained after evaporation of the volatiles was passed through a silica column (1 : 1 hexane–dichloromethane) affording *para*-carborane **1** (0.07 g, 5%) and 1-(3-hydroxy-3-methylbutynyl)-*para*-carborane **14** (1.67 g, 74%).

14. Mass (EI) spectrum: typical carborane pattern at m/z 206-214 [211,  $M - CH_3$ , 100%], 221–227, [226, M, 4%] C<sub>7</sub>H<sub>18</sub>B<sub>10</sub>O requires: M = 226. IR:  $\nu$ (OH stretch) 3321(br,s), 3242(br,s);  $\nu$ (cage CH) 3060(w), 3051(m);  $\nu$ (methyl CH) 2983(s), 2932(m);  $\nu$ (BH) 2615(vs);  $\nu$ (C≡C) 2276(vw) cm<sup>-1</sup>. NMR (298 K, CDCl<sub>3</sub>)  $\delta$  (<sup>11</sup>B) –11.6 (5B, d, 168, B2-6), -15.2 (5B, d, 166, B7-11);  $\delta$  (<sup>1</sup>H{<sup>11</sup>B}) 2.63 (1H, C12H), 2.43 (5H, B2-6H), 2.19 (5H, B7–11H), 1.90 (1H, OH), 1.38 (6H, CH<sub>3</sub>);  $\delta$  (<sup>13</sup>C{<sup>11</sup>H}) 83.8 (cage C–C≡C), 78.7 (cage C–C≡C), 69.0 (cage C–C≡C), 64.8 (COH), 59.8 (cage CH), 30.9 (CH<sub>3</sub>). Found, C 37.8, H 8.1; C<sub>7</sub>H<sub>18</sub>B<sub>10</sub>O requires: C 37.2, H 8.0%.

#### Preparation of 1-ethynyl-para-carborane (6) from (14)

A sample of  $HOMe_2CC \equiv CCB_{10}H_{10}CH$  (14) (0.45 g, 2 mmol) suspended in 20 ml of 2-propanol was treated with 0.5 g of sodium metal. The mixture was stirred at room temperature for 2 h, after which time the sodium metal had been consumed and a cloudy solution formed. The reaction mixture was diluted with diethyl ether (40 ml), washed with water (2 × 30 ml), dilute aqueous KOH

solution (2 × 30 ml), water (4 × 30 ml) and dried over magnesium sulfate. Evaporation of the ether at room temperature gave an oil which was distilled at 0 °C/0.05 mmHg with the receiver cooled at -78 °C, to give 1-ethynyl-*para*-carborane (6) (242 mg, 72%).

If a large excess of sodium metal is used in this preparation, ethenyl carboranes are formed in the undistilled material and thus reduce the yield of the ethynylcarborane 7. The mixture of ethenyl carboranes are identified by NMR and GC-MS as 1-(*trans*-HOCMe<sub>2</sub>CH=CH)-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> **31** and 1-(Me<sub>2</sub>C=CHCH<sub>2</sub>)-1,12-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> **32**.

**31.** Mass (EI) spectrum: 43 [MeCO, 100%] typical carborane patterns at 209–215 [213, M – CH<sub>3</sub>, 35%], 225–230 [228, *M*, 1%], C<sub>7</sub>H<sub>20</sub>B<sub>10</sub>O requires: M = 212. NMR (298 K, CDCl<sub>3</sub>) $\delta$  (<sup>11</sup>B) –12.6 (5B, d, B2-6), –15.1 (5B, d, B7-11);  $\delta$  (<sup>1</sup>H) 5.62 (1H, d, 15.2 Hz, Me<sub>2</sub>CCH), 5.43 (1H, d, 15.2 Hz, cage CCH), 2.64 (1H, C12H), 1.20 (6H, Me);  $\delta$  (<sup>13</sup>C{<sup>1</sup>H}) 141.4 (Me<sub>2</sub>CCH), 125.0 (cage CCH), 81.8 (cage CCH), 70.3 (CMe<sub>2</sub>), 58.5 (cage CH), 29.4 (CH<sub>3</sub>).

**32.** Mass (EI) spectrum: 69 [C<sub>3</sub>H<sub>9</sub>, 100%], typical carborane patterns at 176–183 [181, M – C<sub>2</sub>H<sub>7</sub>, 63%], 176–183 [197, M – CH<sub>3</sub>, 55%], 209–214 [212, *M*, 13%] C<sub>7</sub>H<sub>20</sub>B<sub>10</sub> requires: *M* = 212. NMR (298 K, CDCl<sub>3</sub>)  $\delta$  (<sup>11</sup>B) –12.6 (5B, d, B2-6), –15.1 (5B, d, B7-11);  $\delta$  (<sup>1</sup>H) 4.88 (1H, t, 7.6 Hz, CH), 2.61 (1H, C12H), 2.29 (d, 7.6 Hz, 2H, CH<sub>2</sub>) 1.66 (3H, s, *trans*-Me), 1.48 (3H, s, *cis* Me);  $\delta$  (<sup>13</sup>C{<sup>1</sup>H}) 134.5 (*C*Me<sub>2</sub>), 120.2 (CH), 84.7 (cage *C*–CH<sub>2</sub>), 57.9 (cage CH), 36.8 (CH<sub>2</sub>), 25.5 (*trans* Me), 17.6 (*cis* Me).

# Identification of other products (15–22) in the preparation of 1,12-bis(trimethylsilylethynyl)-*para*-carborane (3)<sup>24</sup>

A solution of *para*-carborane **1** (2.88 g, 20 mmol) in monoglyme (80 ml) was treated with BuLi (2.5 M in hexanes, 16.5 ml, 41 mmol). Pyridine (12 ml) and CuCl (4.50 g, 45 mmol) were added and the mixture heated at reflux point (30 min), and allowed to cool before BrC=CSiMe<sub>3</sub> **2** was introduced (7.96 g, 45 mmol) and the mixture heated at reflux for a further 19 h. The cooled reaction mixture was diluted with Et<sub>2</sub>O (400 ml). After 4 h, the suspension was filtered and the filtrate washed with dilute HCl (250 ml, 2.5 M), water (2 × 500 ml) and dried over MgSO<sub>4</sub>. The semi-solid obtained after evaporation of the volatiles was purified by column chromatography on silica. Elution with cyclohexane gave a mixture of 1,12-bis(trimethylsilylethynyl)-*para*-carborane **3** (0.88 g, 13% obtained after trituration of the eluant with ethanol), **5** (19%) and **15** (2%); the latter compounds being obtained by fractional distillation (85 °C/0.05 mmHg) of the ethanol washings.

**15.** Mass (EI) spectrum: typical carborane pattern at 317–321, [319, M, 16%], 300–307 [304, M – Me, 100%] C<sub>7</sub>H<sub>19</sub>B<sub>10</sub>BrSi requires: M = 319.

The distilled fraction of **5** was shown by GC–MS to contain minor impurities of **3** (4%) and **15** (2%). Treatment of the oil containing **5**—with **3** and **15** as minor impurities—with base gave **6** and **4** along with carborane **16**. A single crystal grown from this mixture was studied by X-ray diffraction and proved to be a solid solution of **4** and **16** (in a *ca.* 2 : 1 ratio).

**16.** Mass (EI) spectrum: typical carborane pattern at 242–250, [247, M, 100%] C<sub>4</sub>H<sub>11</sub>B<sub>10</sub>Br requires: M = 247.

Further distillation of the residue at 190  $^{\circ}$ C gave an oil which solidified on cooling. The solid (0.36 g, 5%) was isolated and

characterized as 1,12-bis(trimethylsilylethynyl)-*para*-carborane **3**. Recrystallization of this sample from ethanol gave crystals suitable for X-ray crystallography.

Elution with diethyl ether afforded a fraction (0.6 g) containing the two-cage carborane products **17–21**. The ratio of products was found to be 5:4:3:3 for **18**: **21**: **20**: **17**: **19** by GC-MS. In order of volatility according to GC-MS:

**19.** Mass (EI) spectrum: typical carborane pattern at 296– 314 [309, M - H, 100%]  $C_6H_{22}B_{20}$  requires: M = 310. **17**: Mass (EI) spectrum: typical carborane pattern at 270–289, [285, M -H, 100%],  $C_4H_{22}B_{20}$  requires: M = 286. **21**: Mass (EI) spectrum: typical carborane pattern at 403–410, [406, M - H, 14%], 386–395 [390, M - MeH, 100%]  $C_{11}H_{30}B_{20}Si$  requires: M = 407. **18**: Mass (EI) spectrum: typical carborane pattern at 379–385, [382, M - H, 6%], 363–371 [368, M - MeH, 100%]  $C_9H_{30}B_{20}Si$  requires: M =383. **20**: Mass (EI) spectrum: typical carborane pattern at 475– 482, [479, M, 5%], 459–468 [464, M - Me, 100%]  $C_{11}H_{30}B_{20}Si_2$ requires: M = 479.

Treatment of the reaction mixture with a methanolic solution of NaOMe removed the trimethylsilyl groups, and the resulting mixture of volatile ethynyl carboranes. Analysis of the mixture by GC-MS confirmed the formation of the new compound **22**.

**22.** Mass (EI) spectrum: typical carborane pattern at 403–410, [406, M - H, 14%], 386–395 [390, M - MeH, 100%] C<sub>11</sub>H<sub>30</sub>B<sub>20</sub>Si requires: M = 407.

#### Preparation of 1,12-bis(3-hydroxy-3-methylbutynyl)para-carborane (23)

A solution of para-carborane 1 (2.88 g, 20 mmol) in monoglyme (80 ml) was treated with BuLi (2.5 M in hexanes, 16.5 ml, 41 mmol). Pyridine (12 ml) and CuCl (4.50 g, 45 mmol) were added and the mixture heated at reflux (30 min), allowed to cool and BrC=CCMe<sub>2</sub>OH (7) introduced (7.33 g, 45 mmol) and the reaction mixture heated at reflux for a further 3 h. The cooled reaction mixture was diluted with Et<sub>2</sub>O (400 ml). After 2 h, the suspension was filtered and the filtrate washed with water (4  $\times$ 50 ml) and dried over MgSO<sub>4</sub>. The oil obtained after evaporation of the volatiles was vacuum distilled at 40 °C/0.05 mmHg to give para-carborane (0.21 g, 7%) and then at 70 °C/0.05 mmHg to yield an oil which solidified on cooling. The latter solid was identified by GC-MS and NMR to contain a 1:2 mixture of 1-(3hydroxy-3-methylbutynyl)-para-carborane 14 and 2,5-dihydroxy-2,5-dimethyl-3,5-octadiyne 24. This solid was purified by column chromatography on silica with 1:1 hexane-dichloromethane as eluent yielding carborane 14 (0.95 g, 21% based on carborane used) and diyne 24 (0.73 g, 20% based on ethyne).

**24.** Mass (EI) m/z 166 [M, 1%], 151, [M – CH<sub>3</sub>, 9%], 43 [100]. C<sub>10</sub>H<sub>14</sub>O<sub>2</sub> requires: M = 166. NMR (298 K, CDCl<sub>3</sub>)  $\delta$  (<sup>1</sup>H) 0.06 (CH<sub>3</sub>);  $\delta$  (<sup>1</sup>C{<sup>1</sup>H}) 84.2, 66.5, 65.8, 31.0 (CH<sub>3</sub>).

Sublimation at 180 °C/0.05 mmHg of the residue from the distillation gave a white solid identified as crude 1,12-bis(3-hydroxy-3-methylbutynyl)-*para*-carborane (**23**). This was purified by column chromatography on silica with dichloromethane as eluent to give **23** (0.99 g, 16%).

**23.** Mass (EI) typical carborane pattern at m/z 288–297 [293,  $M - CH_3$ , 100%], 305–310, [308, M, 5%]  $C_{12}H_{24}B_{10}O_2$  requires:

#### Preparation of 1,12-bis(ethynyl)-para-carborane (4) from (23)

A sample of HOMe<sub>2</sub>CC=CCB<sub>10</sub>H<sub>10</sub>CC=CCMe<sub>2</sub>OH (**23**) (0.62 g, 2 mmol) dissolved in 20 ml of 2-propanol was treated with 0.5 g of sodium metal. The mixture was refluxed at room temperature for 2 h, by which time the sodium metal had been consumed. The solution was diluted with diethyl ether (40 ml), washed with dilute aqueous KOH solution (2 × 30 ml), then with water (4 × 30 ml) and dried over magnesium sulfate. Evaporation of the ether at room temperature gave a semi-solid which was sublimed at 20 °C/0.05 mmHg. A sublimate (314 mg, 82%), consisting of pure 1,12-bis(ethynyl)-*para*-carborane (**4**),<sup>24</sup> was obtained.

## Preparation of 1-(5-hydroxy-5-methyl-1,3-hexadiynyl)para-carborane (26)

A stirred solution of ethynylcarborane **14** (1.13 g, 5 mmol) in monoglyme (20 ml) was treated with BuLi (1.6 M in hexanes, 6.5 ml, 11 mmol) at ambient temperature. Pyridine (8 ml) and CuCl (0.63 g, 6.4 mmol) were added to the solution and the mixture heated at reflux for 30 min then allowed to cool. A solution of BrC=CCMe<sub>2</sub>OH (7, 1.0 g, 5.2 mmol) in monoglyme (10 ml) was added dropwise to the vigorously stirred solution at 0 °C, and the mixture heated at reflux for 30 min. The reaction mixture was cooled, and diluted with Et<sub>2</sub>O (400 ml). After filtering off the solids, the oil obtained from the filtrate after evaporation of the volatiles was passed through a silica column (1 : 1 hexane– dichloromethane). The white solid obtained was recrystallised from 2 : 1 hexane–dichloromethane at 0 °C to afford 0.70 g (56%) of 1-(5-hydroxy-5-methyl-1,3-hexadiynyl)-*para*-carborane **26**.

**26.** Mass (EI) spectrum: m/z 43 [MeCO, 100%], typical carborane patterns at m/z 230–237 [235,  $M - CH_3$ , 60%], m/z 246–252, [250, M, 11%] C<sub>9</sub>H<sub>18</sub>B<sub>10</sub>O requires: M = 250. IR: v(OH stretch) 3355(br,s); v(cage CH) 3068(m); v(methyl CH) 2981(s), 2932(m); v(BH) 2617(vs); v(C≡C) 2262(vw) cm<sup>-1</sup>. NMR (298 K, CDCl<sub>3</sub>)  $\delta$  (<sup>11</sup>B) –11.7 (5B, d, 168, B2-6), –15.2 (5B, d, 167, B7-11);  $\delta$  (<sup>14</sup>H<sup>11</sup>B}) 2.66 (1H, C12H), 2.45 (5H, B2-6H), 2.17 (5H, B7–11H), 1.72 (1H, OH), 1.48 (6H, CH<sub>3</sub>);  $\delta$  (<sup>13</sup>C{<sup>1</sup>H}) 84.9 (HOMe<sub>2</sub>C–C≡C), 74.8 (cage C–C≡C), 68.3 (cage C–C≡C), 65.9 (C≡C–C≡C), 65.5 (COH), 63.6 (C≡C–C≡C), 60.6 (cage CH), 30.9 (CH<sub>3</sub>). Found, C 42.0, H 7.4; C<sub>9</sub>H<sub>18</sub>B<sub>10</sub>O requires: C 43.2, H 7.3%.

#### Preparation of 1,4-(1',1"-bis(para-carboranyl))-1,3-butadiyne (27)

A stirred solution of ethynylcarborane **14** (0.55 g, 2.5 mmol) in monoglyme (10 ml) was treated with BuLi (1.6 M in hexanes, 3.25 ml, 5.5 mmol) at ambient temperature. Pyridine (3 ml) and CuCl (0.63 g, 6.4 mmol) were added to the solution and the mixture heated at reflux for 2 h then allowed to cool. Oxygen was bubbled through the vigorously stirred solution at 0 °C for 30 min. The reaction mixture was diluted with Et<sub>2</sub>O (80 ml) and washed with a saturated solution of NaHCO<sub>3</sub> ( $2 \times 30$  ml) and water ( $4 \times 30$  ml). The ether layer was subjected to a rotary evaporator leaving a brown residue which was eluted through a short column of silica using hexanes. The white solid obtained after removal of hexanes was recrystallised from hexane at 0 °C to afford 117 mg (28%) of 1,4-(1',1"-bis(*para*-carboranyl)-1,3-butadiyne **27**.

**27.** Mass (EI) spectrum: typical carborane pattern at m/z 330– 336, [334, M, 100%] C<sub>9</sub>H<sub>18</sub>B<sub>10</sub>O requires: M = 334. IR:  $\nu$ (cage CH) 3058(m);  $\nu$ (BH) 2618(vs);  $\nu$ (C $\equiv$ C) 2266(vw) cm<sup>-1</sup>. NMR (298 K, CDCl<sub>3</sub>)  $\delta$  (<sup>11</sup>B) -11.7 (5B, d, 168, B2-6), -15.1 (5B, d, 167, B7-11);  $\delta$  (<sup>1</sup>H{<sup>11</sup>B}) 2.66 (1H, C12H), 2.42 (5H, B2-6H), 2.20 (5H, B7-11H);  $\delta$  (<sup>13</sup>C{<sup>1</sup>H}) 75.3 (cage C- $C\equiv$ C), 67.7 (cage C- $C\equiv$ C), 63.0 (C $\equiv$ C- $C\equiv$ C), 61.0 (cage CH). Found, C 28.2, H 6.4; C<sub>9</sub>H<sub>18</sub>B<sub>10</sub>O requires: C 28.7, H 6.6%.

# Formation of 1-bromo-*para*-carborane 29 and 1,12-dibromo-*para*-carborane 30

A solution of *para*-carborane **1** (0.72 g, 5 mmol) in diehtyl ether (20 ml) was treated dropwise with BuLi (2.5 M in hexanes, 4.1 ml, 11 mmol). The resulting cloudy solution was heated at reflux (30 min), allowed to cool and BrC=CSiMe<sub>3</sub> (**2**) (2.0 g, 11 mmol) introduced and the reaction mixture returned to reflux for a further 19 h. The solution was diluted with ether (100 ml) and water (50 ml). The ether layer was separated, washed with water and dried over MgSO<sub>4</sub>, and the solvent removed *in vacuo* to give an orange oil. The orange oil was distilled at 40 °C/0.01 mmHg to give unreacted *para*-carborane **1** (0.08 g, 11%) then at 80 °C/0.01 mmHg to give 1-bromo-*para*-carborane **29** (0.28 g, 25%). A further distillate (0.87 g, 57% yield) was obtained at 180 °C/0.01 mmHg and dissolved in chloroform. Slow evaporation of the solvent resulted in large crystals of pure 1,12dibromo-*para*-carborane **30**.

**29.** Mass (EI) typical carborane and bromine pattern at 218– 226,  $C_2H_{11}B_{10}Br$  requires: M = 223. IR:  $\nu$ (CH) 3062;  $\nu$ (BH) 2616 cm<sup>-1</sup>. NMR (298 K, CDCl<sub>3</sub>)  $\delta$  (<sup>11</sup>B) –11.0 (5B, d, 172, B2-6), –14.9 (5B, d, 168, B7-11);  $\delta$  (<sup>1</sup>H{<sup>11</sup>B}) 2.73 (1H, C12H), 2.65 (5H, B2-6H), 2.19 (5H, B7–11H);  $\delta$  (<sup>13</sup>C{<sup>1</sup>H}) 58.2 (CBr), 56.5 (CH).

**30.** Mass (EI) typical carborane and bromine pattern at 297– 306,  $C_2H_{10}B_{10}Br_2$  requires: M = 303. IR:  $\nu(BH)$  2616 cm<sup>-1</sup>. NMR (298 K, CDCl<sub>3</sub>)  $\delta$  (<sup>11</sup>B) -11.0 (d, 174);  $\delta$  (<sup>1</sup>H{<sup>11</sup>B}) 2.65 (BH);  $\delta$ (<sup>13</sup>C{<sup>1</sup>H}) 54.8.

#### Gas-phase electron diffraction

GED data for both substituted *para*-carboranes **5** and **6** were collected at two different camera distances using the Edinburgh apparatus.<sup>67</sup> The data were recorded photographically on Kodak Electron Image films. Three films from each distance were studied for **6** whereas four and three plates at long and short distances, respectively, were used for **5**. The electron-scattering patterns were converted into digital form using an Epson Expression 1600 Pro flatbed scanner with a scanning program as described elsewhere.<sup>68</sup> Electron wavelengths were determined from the scattering pattern of benzene vapour recorded immediately after each carborane run. The weighing points for the off-diagonal weight matrices, correlation parameters, and scale factors for the two camera distances are given in Table 10.

	5		6	
Camera distance/mm	260.92	96.63	261.00	95.26
$T_{\text{sample}}/\text{K}$	400	424	348	365
$T_{\text{nozzle}}/K$	413	426	358	385
$\Delta s/nm^{-1}$	1	2	1	2
$s_{\rm min}/\rm nm^{-1}$	20	80	20	80
$sw_1/nm^{-1}$	40	100	40	100
$sw_2/nm^{-1}$	129	258	131	288
$s_{\rm max}/\rm nm^{-1}$	150	300	152	334
Correlation parameter	0.4968	0.4106	0.4991	0.4759
Scale factor, $k$	0.784(4)	0.828(11)	0.755(4)	0.716(9)
Electron wavelength/pm	6.02	6.02	6.02	6.02

The data reduction and structure analyses were performed using the standard program *ed@ed*,<sup>69</sup> employing the scattering factors of Ross *et al.*<sup>70</sup>

The starting parameters for the  $r_{h1}$  refinement were taken from the theoretical geometry optimised at the MP2(fc)/6-31G\* level for **5** and MP2(fc)/6-311G\* for **6**. For both compounds a theoretical Cartesian force field was obtained with B3LYP/ccpVDZ<sup>71</sup> and converted into a force field described by a set of symmetry coordinates using the program SHRINK.<sup>72</sup> It must be noted that no major differences were seen between the Pople basis set and Dunning's type in the Cartesian force field.

#### Crystallography

Single-crystal X-ray diffraction experiments were carried out on Bruker AXS 3-circle diffractometers with a 1 K CCD or (for **28**) an APEX CCD area detector, using graphite monochromated Mo-K<sub>a</sub> radiation ( $\bar{\lambda} = 0.71073$  Å) from a sealed tube or (for **28**) a 60 W Mo-target microfocus Bede Microsource<sup>®</sup> X-ray generator with glass polycapillary X-ray optics. Reflection intensities of **28**, **30** and **4/16** were corrected for absorption by semi-empirical method based on Laue equivalents, using the SADABS program,<sup>73</sup> and for **13** by numerical integration based on crystal face indexing.

Table 11 Crystal data for 3, 13, 28, 30, and solid solution of 16 in 4

The structures were solved by direct methods (combined with Patterson method for 13 and 4/16) and refined by full-matrix least squares against  $F^2$  of all data, using SHELXTL software package.<sup>74</sup> See Table 11 for crystallographic data.

The molecule of **13** possesses a crystallographic inversion centre at the midpoint of the C=C bond and an approximate 2/m ( $C_{2h}$ ) symmetry. This is the first crystal structure of a symmetrically substituted *trans*-dibromoethene, in which the C=C moiety is not disordered between two mutually perpendicular orientations<sup>75</sup> and thus its geometry can be accurately determined. The alkene C(1) atom is essentially planar, though much distorted from the regular trigonal, coordination.

CCDC reference numbers 292697-292701.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517538k

#### Theoretical methods

All *ab initio* computations were carried out with the Gaussian 98 package.<sup>76</sup> All geometries discussed here were optimised at the HF/6-31G\* level of theory with symmetry constraints. Frequency calculations at HF/6-31G\* levels of theory were carried out and confirmed that the symmetry assumed for all compounds, were local minima. Optimisation of these geometries were then carried out at the MP2/6-31G\* level of theory. Cartesian coordinates of the MP2/6-31G\* optimized geometries in Table 9 are in the ESI.†

Geometry optimizations for compounds **5** and **6** were carried out using  $C_s$  and  $C_{5v}$  symmetry, respectively. Three different methods were used; HF and two methods including electron correlation, B3LYP and MP2. For these methods, basis sets ranging from 6-31G\* to aug-cc-pVDZ were used. Diffuse and polarisation functions were also added to the basis sets. The resultant geometrical parameters are given in ESI.† Frequency calculations at HF/6-31G\*, B3LYP/6-31G\* and B3LYP/ccpVDZ levels of theory allowed the nature of the stationary points to be determined, confirming that the observed  $C_{5v}$  and  $C_s$  structures are true minima on the potential energy surfaces.

	3	13	28	30	4/16
Formula	$C_{12}H_{28}B_{10}Si_2$	$C_8H_{18}Br_2Si_2$	$C_4H_{12}B_{10}$	$C_2H_{10}B_{10}Br_2$	$\frac{2}{3}C_{6}H_{12}B_{10}\cdot\frac{1}{3}C_{4}H_{11}B_{10}Br$
	336.62	330.22	168.24	302.02	210.31
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
a/A	21.734(3)	6.4980(4)	7.0131(4)	7.0941(4)	7.2696(8)
b /Å	7.535(1)	11.101(1)	20.751(1)	7.1764(4)	7.5132(8)
c/Å	6.937(1)	18.698(2)	7.0409(4)	10.851(1)	10.932(1)
a/°	90	90	90	90	83.05(1)
β /°	107.77(1)	90	98.85(1)	104.00(1)	73.66(1)
y/°	90	90	90	90	80.34(1)
$V/Å^3$	1081.8(3)	1348.8(2)	1012.5(1)	536.02(7)	563.1(1)
T/K	100	120	120	120	120
Space group (no.)	C2/m (#12)	<i>Pbca</i> (#61)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	P1 (#2)
Ź	2	4	4	2	2
$\mu/\mathrm{mm}^{-1}$	0.16	6.15	0.05	7.50	1.22
Reflns measured	6764	15332	12934	6070	3946
Reflns unique	1554	1802	3055	1495	1773
$R_{ m int}$	0.031	0.052	0.027	0.024	0.050
$R(F), I > 2\sigma(I)$	0.031	0.020	0.046	0.022	0.071
$wR(F^2)$ , all data	0.083	0.050	0.134	0.055	0.228

The authors wish to thank the EPSRC for financial support. We also thank Dr Sarah Hinchley for scanning the films and for considerable assistance in preparing data for publication and Mr Thomas E. Baines for support in the synthetic work carried out here.

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