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Journal of Organometallic Chemistry 691 (2006) 3889–3894

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Improved syntheses of bis(ethynyl)-*para*-carboranes, 1,12-$(RC{\equiv}C)_2$-1,12-$C_2B_{10}H_{10}$ and 1,10-$(RC{\equiv}C)_2$-1,10-$C_2B_8H_8$ (R = H or Me_3Si)

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Received 3 May 2006; accepted 19 May 2006
Available online 6 June 2006

Abstract

Copper-mediated cross-coupling reactions of the 12-vertex and 10-vertex *para* carboranes, 1,12-$C_2B_{10}H_{12}$ and 1,10-$C_2B_8H_{10}$, with *trans*-1-iodo-2-chloroethene gave the bis(*trans*-2-chloroethenyl) carboranes, 1,12-$(ClCH{=}CH)_2$-1,12-$C_2B_{10}H_{10}$ and 1,10-$(ClCH{=}CH)_2$-1,10-$C_2B_8H_8$, respectively, in good yield. The molecular structures of both compounds were determined by X-ray crystallography, verifying the *trans* disposition of the chloride and carboranyl substituents across the double bonds. These vinyl carboranes can be converted to bis(ethynyl) carboranes, 1,12-$(RC{\equiv}C)_2$-1,12-$C_2B_{10}H_{10}$ and 1,10-$(RC{\equiv}C)_2$-1,10-$C_2B_8H_8$ (R = H or Me_3Si), easily, and in high yields. These findings provide the most convenient routes to bis(ethynyl) carboranes from the commercially available carboranes, 1,12-$C_2B_{10}H_{12}$ and 1,10-$C_2B_8H_{10}$ reported to date.

Keywords: Carborane; Carbaborane; Alkyne; Alkene; Cross-coupling

1. Introduction

Since the beginning of this century, there has been substantial interest in the 12-vertex bis(ethynyl)-*para*-carborane, 1,12-$(HC{\equiv}C)_2$-1,12-$C_2B_{10}H_{10}$ (**1**), (Scheme 1) and its trimethylsilyl analogue, 1,12-$(Me_3SiC{\equiv}C)_2$-1,12-$C_2B_{10}H_{10}$ (**2**). These compounds have found use as precursors to molecular rigid rods, and by extension as components in supramolecular assemblies with defined and persistent shape. In addition to the structural properties offered by these rod-like building blocks, which offer approximately cylindrical symmetry along the long molecular axis, the "three dimensional" aromaticity offered by the cage [1], and the analogy with 1,4-diethynyl benzene, 1,4-$(HC{\equiv}C)_2C_6H_4$, has prompted consideration of diethynylcarboranes as conduits for electronic effects [2–4].

The reaction of the 12-vertex *para*-carborane (**3**) with 1-bromo-2-(trimethylsilyl)ethyne (**4**) using our usual copper-mediated cross-coupling procedure [5] gave 1,12-bis(trimethylsilylethynyl)-*para*-carborane (**2**) in low yields; subsequent desilylation of **2** affords the parent species 1,12-bis(ethynyl)-*para*-carborane (**1**) (Scheme 1(a)) [6,7]. A low-yielding synthesis of **2** has been reported by Kaszynski *et al.* [8] while we have also used 1-bromo-3-methyl-1-butyn-3-ol instead of **4** in a two-step synthesis of **1** in low yields [7]. Herzog *et al.* reported multi-step syntheses of **1** and **2** from **3** in overall yields of 64% [9]. These yields are considerably improved with respect to the simple two-step syntheses from **1** and, whilst elegant, the complete synthetic procedure is somewhat tedious.

In 2000, Kaszynski and co-workers reported that the reaction of the 10-vertex *para*-carborane, 1,10-$C_2B_8H_{10}$ (**5**), with ethyne **4** using a copper-mediated coupling procedure gave 1,10-bis(trimethylsilylethynyl)-*para*-carborane (**6**) in low yields [10] (Scheme 1(b)). It was suggested that the degree of electronic communication of the apical substituents with the 10-vertex carborane cage may be comparable to that in benzene analogues and greater than that found in the 12-vertex cage. However, the expense of the 10-vertex precursor and the low yield of **6** have so far

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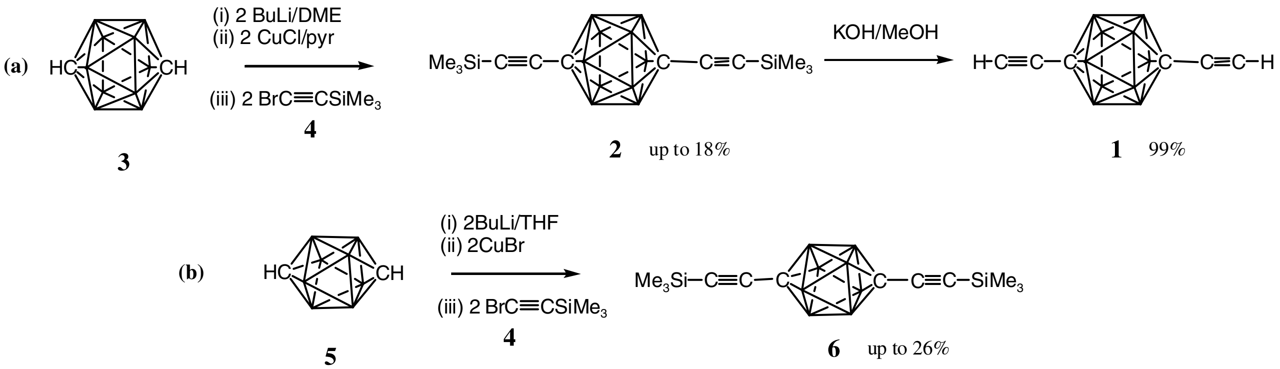
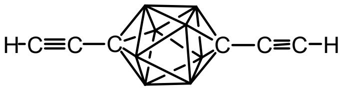
doi:10.1016/j.jorganchem.2006.05.044



Scheme 1.

precluded the widespread use of **6** as a precursor of compounds to explore this point. It is noteworthy that not even the 10-vertex analogue of **1**, 1,10-$(HC{\equiv}C)_2$-1,10-$C_2B_8H_8$ (**7**), was known prior to the present study, although calculations of this species have been reported at the HF/6-31G* level of theory [8,9].



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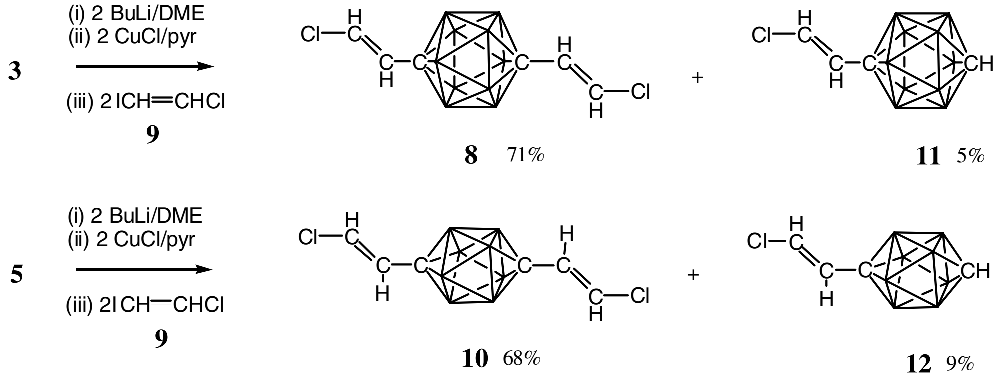
It is apparent that convenient high-yield syntheses of the bis(ethynyl)-*para*-carboranes are needed to more readily explore and exploit the potential of these compounds as precursors to molecular rigid rods/supramolecular assemblies and to metal complexes for investigations of the electronic interactions through the carborane cage. Here we report the syntheses of the desired bis(ethynyl)-*para*-carboranes, **1**, **2**, **6** and **7**, in good yields by two-step syntheses from their parent carboranes **3** and **5**.

2. Results and discussion

The bis(*trans*-2-chloroethenyl) carboranes, 1,12-$(ClCH{=}CH)_2$-1,12-$C_2B_{10}H_{10}$ (**8**), and 1,10-$(ClCH{=}CH)_2$-1,10-$C_2B_8H_8$ (**10**) are readily obtained directly from the appropriate parent carboranes **3** and **5** and *trans*-1-iodo-2-chloroethene (**9**) via a copper mediated coupling procedure. Similar reaction conditions have been previously employed for the coupling of haloaryls with *C*-copper carborane derivatives (Scheme 2) [5], and a related coupling protocol has been reported for the synthesis of 1,7-(*trans*-$ClCH{=}CH)_2$-1,7-$C_2B_{10}H_{10}$ from *meta*-carborane, 1,7-$C_2B_{10}H_{12}$ [11]. Compound **8** (together with the *cis* isomer) has been prepared on a previous occasion in three steps from **3** [9].

The divinyl carboranes **8** and **10** are easily converted into diethynyl carboranes **1** and **7**, respectively, by treatment with methyllithium, and subsequent work-up. The protected acetylenes **2** and **6** were likewise obtained from sequential reaction of **8** and **10** with methyllithium and chlorotrimethylsilane. The overall yields of **1**, **2**, **6** and **7** from *para*-carboranes **3** and **5** are 69%, 67%, 63% and 48%, respectively, which are superior to reported yields of up to 26% from previous single/two-step syntheses [6–8,10]. The convenience of a two-step route is also an obvious advantage in effort and cost over the more elaborate multi-step syntheses, which afford the ethynyl carboranes in comparable yield to those described here [9].

Molecular structures were determined for both bis(ethenyl)-*para*-carboranes, **8** and **10**, by X-ray crystallographic studies (Figs. 1 and 2). The ethenyl groups are found in the



Scheme 2.

expected *trans*-conformations with C═C bond lengths of 1.311(2) and 1.287(3) Å for **8** and **10**, respectively. As previously noted for other pairs of 10- and 12-vertex cage derivatives [8–10,12], the single bond C1–C2 between the ethene and cage is longer in the 12-vertex **8** than in the 10-vertex **10** with values of 1.495(2) and 1.479(3) Å for **8** and **10**, respectively.

The influence of the substituents on the cage geometry of 1,12-disubstituted-*para*-carboranes has been discussed in detail elsewhere [7]. The effect on the cage framework by the ethenyl groups in **8** is somewhat comparable to the effects by aryl and ethynyl groups. While there are many structurally characterised 1,12-disubstituted-*para*-carboranes, only three 1,10-disubstituted-*para*-carboranes, 1,10-X_2-1,10-$C_2B_8H_8$, have been characterised by X-ray crystallography [3,10]. The cage geometries in these compounds are summarised in Table 1 along with **10** and MP2-optimised [13] geometries of **5** and **7**. The ethenyl groups in **10** have a similar effect on the C_2B_8 cage geometry compared to the ethynyl groups in **6** and **7**.

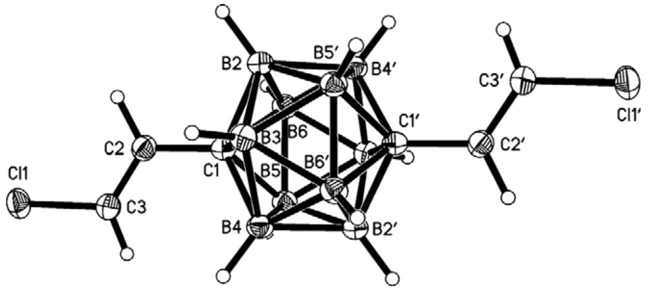


Fig. 1. Molecular structure of 1,12-(ClCH═CH)$_2$-1,12-$C_2B_{10}H_{10}$ (**8**). Thermal ellipsoids are at 50% probability level. Primed atoms are generated by the inversion centre. Selected bond lengths (Å) and angles (°); C3–Cl1 1.7366(12), C–B(av) 1.723(2), B–B (belt, av) 1.784(2), B–B (interbelt, av) 1.764(2), C1…C1′ 3.126, C1–C2–C3 123.9(1), C2–C3–Cl1 122.3(1).

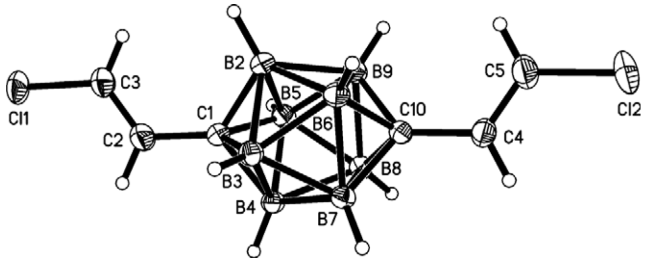


Fig. 2. Molecular structure of 1,10-(ClCH═CH)$_2$-1,10-$C_2B_8H_8$ (**10**). Selected bond lengths (Å) and angles (°); C3–Cl1 1.731(2), C5–Cl2 1.737(2), C1–C2–C3 124.7(2), C10–C4–C5 124.0(2), C2–C3–Cl1 124.0(2), C4–C5–Cl2 123.5(2).

3. Conclusions

The bis(ethynyl)-*para*-carboranes were formed in good yields (48–69%) from 12- and 10-vertex *para*-carboranes in two synthetic steps. These results represent a significant improvement in the syntheses of bis(ethynyl)-*para*-carboranes compared to previous work. The 10-vertex cage compound, 1,10-(HC≡C)$_2$-1,10-$C_2B_8H_8$, is reported here for the first time. It is hoped that these findings will stimulate further research on these bis(ethynyl)carboranes, especially the 10-vertex analogues, as precursors to molecular rigid rods or supramolecular assemblies and to metal complexes for investigations into the transmission of electronic effects through the carborane cage.

4. Experimental

Reactions were carried out using standard Schlenk techniques under dry high-purity nitrogen. Pyridine was distilled after standing over potassium hydroxide for three days. Copper(I) chloride was purified according to the literature procedure [14]. Acetylene from a cylinder was purified by passing through a trap kept at −78 °C, water, H_2SO_4 and KOH pellets. Iodine monochloride was purified by distillation at atmospheric pressure. The *para*-carboranes, 1,12-$C_2B_{10}H_{12}$ and 1,10-$C_2B_8H_{10}$, were purchased from KatChem (Prague, Czech Republic). The dihalovinyl reagent, *trans*-1-chloro-2-iodoethene, ClCH═CHI, was prepared according to the literature procedure [15].

NMR spectra were measured using Varian Unity-300 (^{1}H, ^{11}B, ^{13}C), Bruker AM250 (^{1}H, ^{13}C), Bruker Avance 400 (^{1}H, ^{11}B, ^{13}C) and/or Varian Inova 500 (^{1}H, ^{11}B) instruments. All chemical shifts are reported in δ (ppm) and coupling constants in Hz. ^{1}H NMR spectra were referenced to residual protio impurity in the solvent ($CDCl_3$, 7.26 ppm). ^{13}C NMR spectra were referenced to the solvent resonance ($CDCl_3$, 77.0 ppm). ^{11}B NMR spectra were referenced externally to $Et_2O \cdot BF_3$, $\delta = 0.0$ ppm. Infrared spectra were recorded from KBr discs (unless otherwise stated) on Perkin–Elmer 1600 series FT-IR or

Table 1

Comparison of bond distances (Å) in the cage geometries of 1,10-X_2-1,10-$C_2B_8H_8$ derivatives determined by X-ray crystallography and by optimisations at the MP2/6-31G* level of theory

X	C(1)…C(10)	C–B	B2–B3 (belt)	B2–B6 (interbelt)	References
C≡N	3.341	1.612(2)	1.869(2)	1.805(2)	[10]
H **5**	*3.356*	*1.599*	*1.843*	*1.806*	This work
HC≡C **7**	*3.383*	*1.611*	*1.848*	*1.801*	This work
Me_3SiC≡C **6**	3.386	1.614(2)	1.855(3)	1.809(3)	[10]
CH═CHCl **10**	3.387	1.609(3)	1.847(3)	1.808(3)	This work
Cp(CO)$_2$Fe	3.476	1.609(5)	1.800(6)	1.799(6)	[3]

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. film 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.

4.1. Preparation of 1,12-bis(trans-2-chloroethenyl)-para-carborane (8)

A solution of *para*-carborane **3** (0.72 g, 5 mmol) in monoglyme (20 ml) was treated with BuLi (1.6 M in hexanes, 6.4 ml, 10.2 mmol) which resulted in a cloudy solution. Pyridine (3 ml) and CuCl (1.06 g, 10.7 mmol) were added and the black mixture was heated at reflux (20 min). The dark reaction solution was cooled to 0 °C, and ClCH=CHI (**9**) (2.2 g, 11.7 mmol) was introduced dropwise, and the mixture returned to reflux for 3 h. After this time, the reaction mixture was cooled, and diluted with Et_2O (100 ml). After 4 h, the suspension was filtered and the filtrate washed with dilute HCl (50 ml, 2.5 M), water (2 × 100 ml) and dried over $MgSO_4$. The semi-solid obtained after evaporation of the volatiles was dissolved in hexanes and passed through a short column packed with chromatographic silica. The organic solvent was removed in vacuo leaving a light brown semi-solid. The solid was sublimed at 30 °C/0.01 mmHg to give pure 1-(*trans*-2-chloroethenyl)-*para*-carborane (**11**) (51 mg, 5%), then at 180 °C/0.01 mmHg to give a white solid (0.94 g, 71% yield) identified [9] as 1,12-bis(*trans*-2-chloroethenyl)-*para*-carborane (**8**). Crystals of **8** suitable for X-ray crystallography were grown from slow evaporation of dichloromethane.

1-(*trans*-2-Chloroethenyl)-*para*-carborane (**11**): mass (EI) spectrum: typical carborane pattern at *m*/*z* 195–208 [203, $M-1$, 100%], $C_4H_{13}B_{10}Cl$ requires: $M = 204$. IR: ν(vinyl CH) 3081(w); ν(cage CH) 3062(w); ν(BH) 2612(s); ν(C=C) 1622(m) cm^{-1}. NMR (298 K, $CDCl_3$) δ (^{11}B) −12.6 (d, 164, B2-6), −14.9 (d, 164, B7-11); δ ($^1H\{^{11}B\}$) 6.03 (1H, d, 13.6, CHCl), 5.65 (1H, d, 13.6, CH), 2.68 (1H, C12H), 2.30 (5H, B2-6H), 2.22 (5H, B7-11H); δ ($^{13}C\{^1H\}$) 130.9 (CHCl), 123.1 (*C*=CHCl), 80.0 (cage *C*C=C), 59.4 (cage CH). $C_4H_{13}B_{10}Cl$ requires: C, 23.5; H, 6.4. Found: C, 23.2; H, 6.3%.

1,12-bis(*trans*-2-Chloroethenyl)-*para*-carborane (**8**): mass (EI) spectrum: typical carborane pattern at *m*/*z* 258–270 [264, *M*, 100%], $C_6H_{14}B_{10}Cl_2$ requires: $M = 264$. IR: ν(vinyl CH) 3081(m); ν(BH) 2609(s); ν(C=C) 1628(m) cm^{-1}. NMR (298 K, $CDCl_3$) δ (^{11}B) −12.7 (d, 166); δ ($^1H\{^{11}B\}$) 6.03 (2H, d, 13.6, CHCl), 5.65 (2H, d, 13.6, CH), 2.33 (10H, BH); δ ($^{13}C\{^1H\}$) 130.0 (CHCl), 123.3 (*C*=CHCl), 76.1 (cage C). $C_4H_{14}B_{10}Cl_2$ requires: C, 27.2; H, 5.3. Found: C, 26.9; H, 5.3%.

4.2. Preparation of 1,10-bis(trans-2-chloroethenyl)-1,10-dicarbadecaborane (10)

In a manner entirely analogous to that described above, a solution of 1,10-dicarbadecaborane (**5**) (0.60 g, 5 mmol) in monoglyme (20 ml) was treated with BuLi (1.6 M in hexanes, 6.4 ml, 10.2 mmol) which resulted in a cloudy solution. Pyridine (3 ml) and CuCl (1.06 g, 10.7 mmol) were added and the black mixture was heated at reflux (20 min). The solution was cooled to 0 °C and treated with ClCH=CHI **9** (2.2 g, 11.7 mmol) dropwise, and then returned to reflux for 3 h. After this time the reaction mixture was cooled and diluted with Et_2O (100 ml). After 4 h, the suspension was filtered and dried over $MgSO_4$. The semi-solid obtained after evaporation of the volatiles was dissolved in hexanes and passed through a short column packed with chromatographic silica. The organic solvent was removed in vacuo leaving a light brown coloured oil. The oil was distilled at 30 °C/0.01 mmHg to give an oil consisting of pure 1-(*trans*-2-chloroethenyl)-1,10-dicarbadecaborane (**12**) (81 mg, 9%), then at 180 °C/0.01 mmHg to give a viscous oil which crystallised on standing to give a white solid (0.82 g, 68% yield) identified as 1,10-bis(*trans*-2-chloroethenyl)-1,10-dicarbadecaborane (**10**). The crystals of **10** obtained were suitable for X-ray crystallography.

1-(*trans*-2-Chloroethenyl)-1,10-dicarbadecaborane (**12**): mass (EI) spectrum: typical carborane pattern at *m*/*z* 173–184 [180, M−1, 100%], $C_4H_{11}B_8Cl$ requires: $M = 181$. IR(neat): ν(cageCH) 3112(w); ν(vinylCH) 3073(w); ν(BH) 2597(s); ν(C=C) 1617(m) cm^{-1}. NMR (298 K, $CDCl_3$) δ (^{11}B) −10.6 (4B, d, 164, B2-5), −13.1 (4B, d, 167, B6-9); δ ($^1H\{^{11}B\}$) 7.24 (1H, d, 13.6, CH), 6.89 (1H, C10H), 6.84 (1H, d, 13.6, CHCl), 2.16 (4H, B2-5H), 2.06 (4H, B6-9H); δ ($^{13}C\{^1H\}$) 130.3 (CHCl), 123.5 (*C*=CHCl), 117.4 (cage *C*C=C), 97.5 (cage CH). $C_4H_{11}B_8Cl$ requires: C, 26.5; H, 6.1. Found: C, 25.9; H, 5.9%.

1,10-bis(*trans*-2-Chloroethenyl)-1,10-dicarbadecaborane (**10**): mass (EI) spectrum: typical carborane pattern at *m*/*z* 234–246 [241, M, 100%], $C_6H_{12}B_8Cl_2$ requires: $M = 241$. IR: ν(vinyl CH) 3073(m); ν(BH) 2599(s); ν(C=C) 1615(m) cm^{-1}. NMR (298 K, $CDCl_3$) δ (^{11}B) −11.0 (d, 167); δ ($^1H\{^{11}B\}$) 7.21 (1H, d, 13.2, CH), 6.83 (1H, d, 13.2, CHCl), 2.20 (8H, BH); δ ($^{13}C\{^1H\}$) 129.8 (CHCl), 123.8 (*C*=CHCl), 113.5 (cage C). $C_4H_{12}B_8Cl_2$ requires: C, 29.8; H, 5.0. Found: C, 29.3; H, 4.9%.

4.3. Preparation of 1,12-bis(trimethylsilylethynyl)-para-carborane (2)

A stirred solution of **8** (200 mg, 0.76 mmol) in THF (10 ml) was treated dropwise with methyllithium (2.0 ml, 1.6 M in ether, 3.2 mmol) at 0 °C. After 30 min stirring at ambient temperature, chlorotrimethylsilane (1 g, 9 mmol) was added dropwise at 0 °C. After 1 h at ambient temperature, the solvents were removed in vacuo. The residue was dissolved in hexanes and passed through a short column of chromatographic silica. The organic solvent was removed in vacuo leaving a yellow solid. The solid was sublimed at 180 °C/0.01 mmHg to give a white solid (243 mg, 95% yield) identified [6] as 1,12-bis(trimethylsilylethynyl)-*para*-carborane (**2**).

4.4. Preparation of 1,10-bis(trimethylsilylethynyl)-1,10-dicarbadecaborane (6)

A stirred solution of **10** (200 mg, 0.83 mmol) in 10 ml of THF was treated dropwise with methyllithium (3.2 ml, 1.6 M in ether, 5.1 mmol) at 0 °C. After 2 h stirring at ambient temperature, chlorotrimethylsilane (1 g, 9 mmol) was added dropwise at 0 °C resulting in a cloudy solution. After 1 h at ambient temperature, the solvents were removed in vacuo. The residue was dissolved in hexanes and passed through a short column of chromatographic silica. The organic solvent was removed in vacuo leaving a yellow solid. The solid was sublimed at 180 °C/0.01 mmHg to give a white solid (242 mg, 93% yield) identified [10] as 1,10-bis(trimethylsilylethynyl)-1,10-dicarbadecaborane (**6**).

1,10-Bis(trimethylsilylethynyl)-1,10-dicarbadecaborane (**6**): mass (EI) spectrum: typical carborane pattern at m/z 295–301 [298, M−CH_3, 100%], 310–315, [313, M, 6%] $C_{12}H_{26}B_8Si_2$ requires: $M = 313$. IR: ν(methylCH) 2959(s), 2930(m), 2904(w); ν(BH) 2619(s); ν($C{\equiv}C$) 2181(m) cm^{-1}. NMR (298 K, $CDCl_3$) δ (^{11}B) −10.0 (d, 175); δ ($^1H\{^{11}B\}$) 2.30 (8H, BH), 0.29 (18H, CH_3); δ ($^{13}C\{^1H\}$) 101.1 (C–Si), 100.7 (cage $\mathit{C}C{\equiv}C$), 90.9 ($\mathit{C}{\equiv}CSi$), −0.3 (CH_3).

4.5. Preparation of 1,12-bis(ethynyl)-para-carborane (1)

A stirred solution of **8** (200 mg, 0.76 mmol) in 10 ml of THF was treated dropwise with methyllithium (2.0 ml, 1.6 M in ether, 3.2 mmol) at 0 °C. After 30 min stirring at ambient temperature, the solvents were removed in vacuo. The residue was dissolved in hexanes and passed through a short column packed with chromatographic silica. The organic solvent was removed in vacuo leaving an off-white solid. The solid was sublimed at 50 °C/0.01 mmHg to give a white solid (142 mg, 97% yield) identified [6] as 1,12-bis(ethynyl)-*para*-carborane (**1**).

4.6. Preparation of 1,10-bis(ethynyl)-1,10-dicarbadecaborane (7)

A stirred solution of **10** (170 mg, 0.7 mmol) in THF (10 ml) was treated dropwise with methyllithium (2.0 ml, 1.6 M in ether, 3.2 mmol) at 0 °C. After 30 min stirring at ambient temperature, the solvents were carefully removed in vacuo using a rotary evaporator. The residue was dissolved in hexanes and passed through a short column packed with chromatographic silica. The organic solvent was carefully (to avoid loss of the volatile product) removed in vacuo leaving an off-white solid. The solid was sublimed at 20 °C/0.01 mmHg using a dry ice cooled finger to give a white crystalline solid (84 mg, 71% yield) identified as 1,10-bis(ethynyl)-1,10-dicarbadecaborane (**7**).

Table 2
Crystal data for **8** and **10**

Compound	**8**	**10**
Formula	$C_6H_{14}B_{10}Cl_2$	$C_6H_{12}B_8Cl_2$
M (g/mol)	265.17	241.54
Crystal system	Triclinic	Orthorhombic
a (Å)	7.1733(3)	13.380(2)
b (Å)	7.2766(3)	9.2945(14)
c (Å)	7.3405(3)	20.077(3)
α (°)	91.555(2)	90
β (°)	91.039(2)	90
γ (°)	119.321(2)	90
V (Å^3)	333.73(2)	2496.7(6)
T (K)	120(2)	120(2)
Space group	$P\bar{1}$	$Pbca$
Z	1	8
μ (mm^{-1})	0.449	0.476
Reflections measured	5195	16627
Reflections unique [R_{int}]	2290 [0.0339]	3087 [0.0446]
Goodness-of-fit (on F^2)	1.039	1.071
$R(F)$, $I > 2\sigma(I)$	0.0347	0.0499
$wR(F^2)$, all data	0.0915	0.1200

1,10-Bis(ethynyl)-1,10-dicarbadecaborane (**7**): mass (EI) spectrum: typical carborane pattern at m/z 165–173, [169, M, 100%] $C_6H_{10}B_8$ requires: $M = 169$. IR: ν(ethynyl C–H) 3312(w), 3292(s); ν(BH) 2614(s) cm^{-1}. NMR (298 K, $CDCl_3$) δ (^{11}B) −9.8 (d, 170); δ ($^1H\{^{11}B\}$) 2.88 (2H, CH), 2.35 (8H, BH); δ ($^{13}C\{^1H\}$) 99.8 (cage $\mathit{C}C{\equiv}C$), 79.9 ($\mathit{C}{\equiv}CH$), 73.7 ($C{\equiv}\mathit{C}H$). $C_6H_{10}B_8$ requires: C, 42.7; H, 6.0. Found: C, 41.9; H, 6.0%.

4.7. Crystallographic section

Diffraction data were collected on Bruker three-circle diffractometers with SMART 6 K (for **8**), APEX (for **10**) CCD area detectors, using graphite-monochromated sealed-tub Mo Kα radiation. The data collection was carried out at 120 K using cryostream (Oxford cryosystem) open flow N_2 cryostats. Reflection intensities were integrated using the SAINT V6.45 program [16]. The crystal structures were solved using direct-methods and refined by full matrix least-squares against F^2 of all data using SHELXTL software [17]. All non-hydrogen atoms where refined in anisotropic approximation. Hydrogen atoms were either located by a difference map (for all hydrogen atoms in **8** and boron-coupled hydrogen atoms in **10**) or placed in calculated positions (for all carbon-coupled hydrogen atoms in **10**) and refined isotropically using a riding model. Crystal data and experimental details are listed in Table 2. CCDC 605996 and 605997 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank the EPSRC and ONE NorthEast for generous financial support of this work. We also thank Dr. Dmitry S. Yufit for assistance with crystallographic data.

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