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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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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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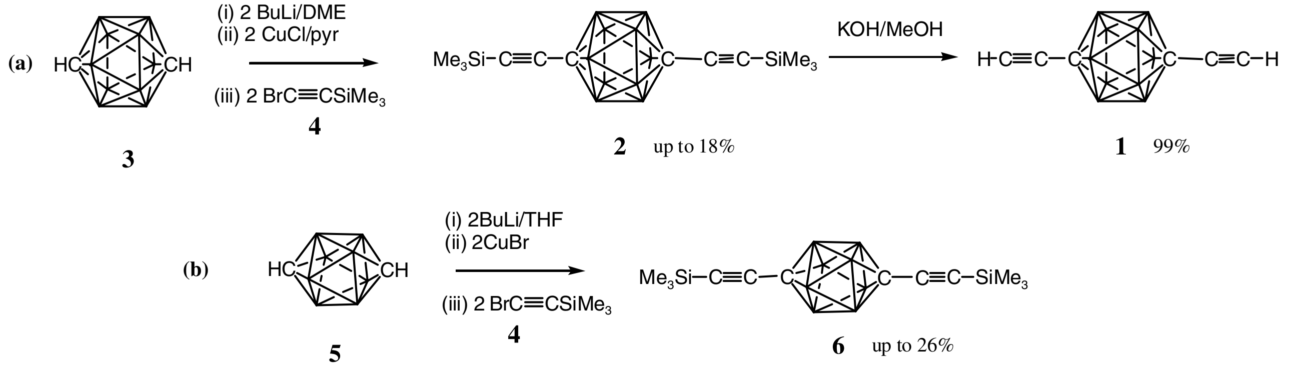
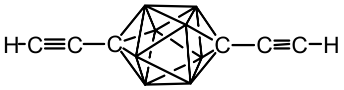


Scheme 1.

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≡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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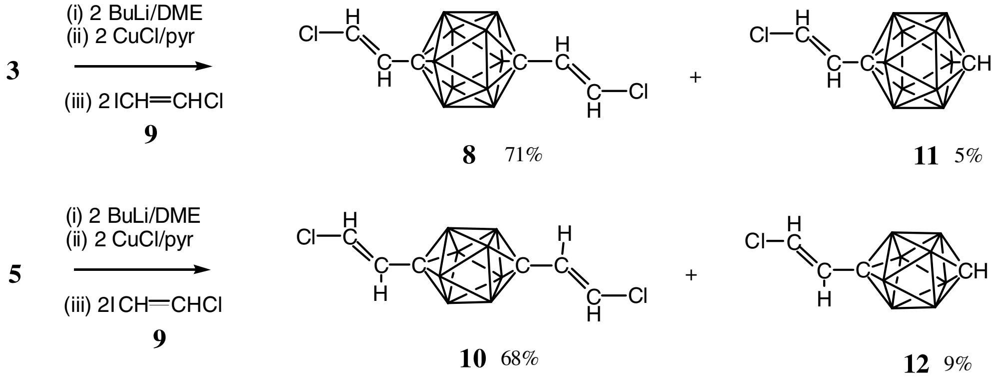
It is apparent that convenient high-yield syntheses of the bis(ethynyl)-*para*-carboranes are needed to more readily explore and exploit the potential of these compounds as precursors to molecular rigid rods/supramolecular assemblies and to metal complexes for investigations of the electronic interactions 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.