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Heterodisubstituted 1,10-dicarba-*closo*-decaboranes from substituted *nido*-carborane precursors

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Abstract

Mono- and heterodisubstituted 1,10-dicarba-*closo*-decaboranes **1** have been prepared from substituted *nido*-carboranes **3** and by carboxylation and arylation of 1-alkyl-*p*-carboranes. Thermal dehydrogenation followed by skeletal rearrangement of **3** furnished **1** in modest yields. Alkyl substituents tolerated the high temperature process whereas the 4-bromophenyl derivative **1d** underwent partial disproportionation. The preparation of the *nido*-carboranes **3** was accomplished in three ways: by acetylene insertion to nonaborane **6**, modified Plešek oxidation of dicarbaundecaborate anions **4** with Fe(III), and a new homogenous oxidation of **4** using gaseous SO_2. The newly developed homogenous deboronation with SO_2 appears to be more efficient than the classical Plešek oxidation especially for highly lypophilic carboranes. The overall yields for the preparation of substituted *p*-carboranes **1** using the three methods from **6** or **4** are about 8% and 14%, respectively.

Keywords: Substitued caboranes; Plešek oxidation; Synthesis

1. Introduction

Differentiation of carbon atoms in *p*-carboranes is an important step in the preparation of compounds for materials applications [1,2]. Recently [3], we developed an efficient route to heterodisubstituted 12-vertex *p*-carboranes *via* silyl derivatives that can, in principle, be extended to 10-vertex *p*-carborane (**1a**). Parent carborane **1a**, however, is a volatile solid whose preparation [4,5] is cumbersome and its heterodisubstituted derivatives might be more conveniently synthesized using appropriately functionalized precursors.

1

a, $R^1=R^2=H$
b, $R^1= n\text{-}C_6H_{13}$, $R^2=H$
c, $R^1= n\text{-}C_5H_{11}$, $R^2=H$
d, $R^1= n\text{-}C_5H_{11}$, $R^2=C_6H_4\text{-}4\text{-}Br$
e, $R^1= n\text{-}C_6H_{13}$, $R^2=COOH$
f, $R^1= n\text{-}C_5H_{11}$, $R^2=COOH$

10-Vertex *p*-carborane is obtained in a similar way to its 12-vertex analog by thermal rearrangement of the corresponding *o*-carborane **2** [6]. The temperatures required for the skeletal rearrangement of the 10-vertex carborane to **1** are in the range of 330–350°C [6], which are lower than the thermal stability limit (~450°C) for 12-vertex alkylcarboranes [7]. Thus the thermal rearrangement of substituted carboranes **2** (Scheme 1) appears to be a viable option for the preparation of 10-vertex *p*-carborane derivatives in contrast to the 12-vertex analogs, which require temperatures above 600°C [8]. In fact, thermal isomerization of C-methyl [6,9], C-phenyl [6] and C-C_6H_4F [10] 10-vertex *closo*-carboranes has been reported to form the 1,10 isomers **1** almost quantitatively at 350°C.

A key intermediate in the preparation of 10-vertex *closo*-carboranes is the *nido*-carborane **3**, which undergoes thermal dehydrogenation to form the *closo* derivative **2** [4,11]. The reaction requires temperatures above 180°C for the parent carborane [4,11] but is much lower for anions [12] and aryl derivatives [13].

The *nido* precursor **3** has been prepared by the carefully controlled Plešek oxidation [11,14] of 11-vertex anion **4** [15–17] obtained either from *o*-carborane **5**, or using the recently described reaction of $B_9H_{13}\cdot L$ (**6**) with acetylenes [13,18]. The biphasic Plešek reaction works relatively well for the parent *nido*-5,6-dicarbadecaborane (**3a**) but substi-

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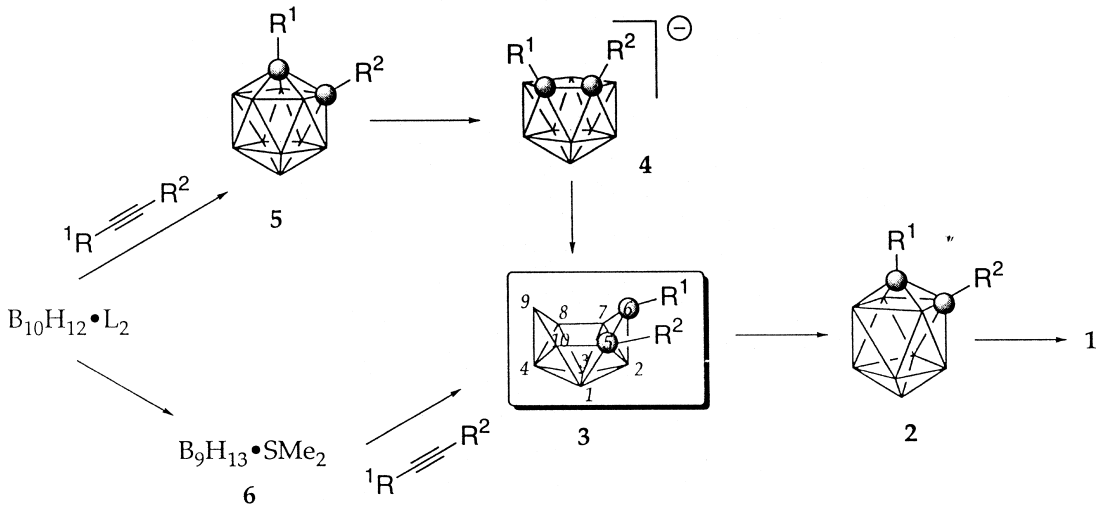


Scheme 1.

tution at the carbon atoms with lipophilic organic groups dramatically diminishes the yields [14]. The nonaborane reaction with two equivalents of acetylene is much less sensitive to the substitution and reported yields of **3** are 50–80% based on **6** [13]. The preparation of C-substituted *nido*-5,6-dicarbadecaboranes by alkyne insertion of octaborane(12) is much less practical due to the limited availability of the borane [19].

Both the carborane **5** and nonaborane **6** are conveniently prepared from decaborane by alkyne insertion to $B_{10}H_{12}\cdot L_2$ [17,20,21] and a reaction with Me_2S/methanol [22], respectively. Alternatively, 1,2-heterodisubstituted *o*-carboranes **5** are easily prepared using 1-(*t*-butyl)dimethylsilyl-*o*-carborane [23,24].

Overall, the preparation of 1,10-dicarba-*closo*-decaborane derivatives **1** relies on the net removal of two boron atoms from and introduction of two carbon atoms to decaborane followed by thermal dehydrogenation/rearrangement. Most of the individual steps in this synthesis have been performed for the parent compounds or their methyl or phenyl derivatives. There has been no attempt, however, to develop a reliable synthetic procedure for preparation of *p*-carboranes **1** disubstituted with aryl and long chain alkyl groups using commercially available precursors.

Here we focus on two aspects of the procedure: (a) preparation of substituted *nido*-carborane **3** using a new homogenous deboronation reaction of the *nido* anion **4** and (b) conversion of **3** to *p*-carborane **1**. We used *n*-hexyl and *n*-pentyl alkyl groups and 4-bromophenyl as a functionalized aryl substituent. Finally, we describe the synthesis of carboxylic acids and the first example of Wade's C-arylation of the monoalkylated *p*-carborane as important intermediates for liquid crystalline materials.

Our synthesis is complemented with 2-D NMR spectroscopy of the products, which allows the complete structural assignment of the ^{11}B NMR signals.

2. Results and discussion

2.1. Synthesis

Treatment of *o*-carborane **5b** with methanolic KOH gave a racemic mixture of the *nido* anion **4b** in analogy to the preparation of the parent anion [15] **4a** and some of its alkylated derivatives [16,17]. Unlike **4a**, the hexyl derivative **4b** is highly lipophilic, and it can be efficiently extracted into hexanes as the corresponding acid **4b-H** upon protonation of its 1 M aqueous solutions. Use of ether, rather than hexanes as solvent, increases the efficiency of extraction of the free acid, which can be easily dissolved in hexanes after removing the ether. The treatment of potassium salt **4b-K** with NMe_4Cl precipitates the corresponding ammonium salt **4b-NMe$_4$**, which is completely soluble in benzene and ether, but only sparingly soluble in hexanes.

2.1.1. nido-5,6-Carboranes

Oxidation of **4b-K** with $FeCl_3$ under Plešek conditions [11,14] was unsuccessful and only traces of the desired *nido* product **3b** were obtained. The relatively low pH of $FeCl_3$ aqueous solutions caused protonation of anion **4b** to **4b-H**, which quickly accumulated in the hexane layer where it was prevented from further contact with the oxidant. Increasing the pH of the solution by the addition of potassium acetate proved helpful. A small increase in the conversion rate was observed when 1 equivalent of AcOK was used, but a 1:3 $FeCl_3$/AcOK ratio turned out to be more practical. No further optimization of the reaction conditions was attempted. The reaction took place over a period of several hours, during which the anion **4b** was slowly extracted to the aqueous phase while the much less acidic product **3b** was accumulated in the hexane layer.

A short path vacuum distillation of the crude product allowed for isolation of **3b** in about 10%–16% yield,

leaving behind a viscous oligomeric material, which was presumably mostly a dimer similar to that reported for oxidation of **3a** under different conditions [25].

In an attempt to improve the yield of the *nido*-carborane **3b**, we turned to homogenous deboronation reactions. In particular, we focused on SO_2 as the oxidant, inspired by the observation that $SOCl_2$ is reduced by polyhedral boron hydrides [26].

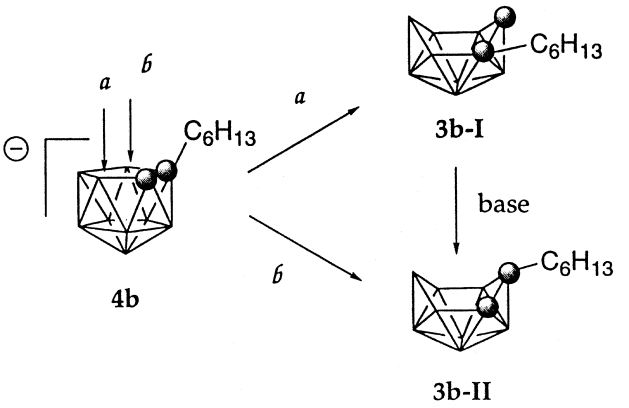
The reaction of the free acid **4b-H** with SO_2 in hexanes proved successful and a 16% yield of the desired *nido* compounds was isolated by distillation. The analogous reaction of the anhydrous salt **4b-NBu$_4$** in benzene did not work and only the unchanged starting material was observed by TLC. This suggests that a proton, or more likely a hydronium ion, is necessary for the reaction to occur. Thus, the stoichiometry of the deboronation reaction can be written as a reduction of S(IV) to elemental sulfur, which is consistent with our observations of formation of a yellow insoluble material.

$$R\text{-}C_2B_9H_{11} - H_3O^+ + SO_2 \rightarrow R\text{-}C_2B_8H_{11} + B(OH)_3 + S_x \quad (1)$$

Unlike the Fe(III) oxidation, the reaction with SO_2 was complicated by the formation of minor quantities of sulfur-containing byproducts according to GCMS. These products were not further characterized and a discussion on their structure and formation will be presented elsewhere. Some of the sulfur-containing species were removed from the reaction mixture by aqueous workup and filtration through a silica gel plug. A short-path vacuum distillation of the resulting crude product typically gave about 15–18% of a mixture of carboranes containing less than 5% of sulfur-containing species, and the yield of the reaction was independent of the **4b-H** drying procedure. A pure mixture of isomeric *nido*-carboranes **3b** can be obtained by chromatographic separation.

In situ generation of SO_2 from aqueous Na_2SO_3 and sulfuric acid in a water/hexane system did not work well and only traces of **3b** were obtained. Other attempts using $SOCl_2$ or SO_2Cl_2 in hexanes or in hexane/water resulted in relatively large amounts of sulfur- and chlorine-containing carboranes as detected by GCMS.

The regiochemistry of the deboronation reactions was rather unexpected. According to a recent literature report, 6-alkyl isomer (**3-II**) was formed in preference to its 5-isomer (**3-I**) in a ratio of about 3:1 under the Fe(III) oxidation conditions [14]. In the present case, however, oxidation of **4b** either with SO_2 or buffered $FeCl_3$ produced the two isomeric products **3b-I** and **3b-II** in almost equal proportions according to the GCMS and NMR analyses. Surprisingly, however, the SO_2 oxidation of a rigorously dried **4b-H** resulted in the preferential formation (~3:1) of the apparently less thermodynamically stable carborane **3b-I**. This is consistent with the removal of the boron vertex from the less hindered position (path a in Scheme 2) in carborane **4**, while the removal of the more hindered boron vertex (path b in Scheme 2) would result in the 6-isomer. Complete isomerization of the 5-isomer **3b-I** to the 6-isomer **3b-II** was observed upon treatment with a base [27].



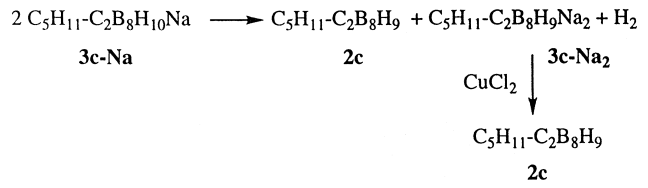
Scheme 2.

Another route to *nido*-carboranes was explored in which carboranes **3c** and **3d** were prepared from nonaborane **6** and appropriate acetylenes in about 50% yields according to the literature method [13]. The isolated carborane **3d** was accompanied by about 30% of the *closo* derivative **2d**.

2.1.2. closo-1,10-Carboranes

The preparation of *p*-carborane **1** from *nido*-carborane **3** was accomplished in two steps: dehydrogenation to the *closo*-carborane **2** and a high temperature skeletal rearrangement. The presence of the aryl substituent in **3d** permits its dehydrogenation at relatively low temperatures and vacuum distillation of the crude reaction mixture at about 200°C afforded the *o*-carborane **2d** in 23% yield based on nonaborane **6**. Similar dehydrogenation of alkyl *nido*-carboranes requires higher temperatures. Thus, heating neat alkylcarboranes **3b** or **3c** at 260°C for 1 h resulted in dehydrogenation to **2b** and **2c**, respectively, and their partial rearrangement to the corresponding *meta* isomers. The resulting *closo*-carboranes were distilled from a polymeric residue to avoid further degradation of the product. The decomposition was particularly pronounced in **3** obtained using SO_2, and is presumably related to the thermal instability of the sulfur-containing species catalyzing product degradation.

To lower the temperature for the formation of **2** and to limit the extent of decomposition of the substrate, the *nido*-carborane **3c** was converted to its sodium salt **3c-Na**, which was disproportionated to form the **2c** and disodium salt **3c-Na$_2$** upon vacuum distillation at 140°C (Scheme 3). The remaining disodium salt **3c-Na$_2$** was oxidized with anhydrous $CuCl_2$ [5] to furnish an additional portion of the *ortho*-carborane **2c**, bringing the total yield to an acceptable level of 23% based on **6**. Thus, the use of the sodium salts increased the yield of the dehydrogenation and also



Scheme 3.

improved the purity of the final carborane **1c** as compared with only the temperature-induced reaction.

The formation of the *para* isomers was accomplished by thermolysis of the distilled alkyl-*closo*-carboranes in a sealed tube at 330°C. The isolated carboranes **1b** and **1c** were sufficiently pure (>97% by NMR and GCMS) for subsequent transformations. Thermolysis of the bromophenyl derivative *closo*-carborane at 300°C resulted in complete rearrangement to the meta isomer with a minimal loss of bromine (~2%). Increasing the temperature to 350°C resulted in complete rearrangement to **1d** and about 10% disproportionation, forming debrominated and dibrominated products according to GCMS.

2.1.3. Functionalization of p-carboranes

Carboxylation of monoalkyl *p*-carboranes **1b** and **1c** according to a general procedure [3,28] has led to the corresponding carboxylic acids **1e** and **1f**, respectively, in about 90% yield (Scheme 4). Wade's arylation [29] of 1-pentyl-*p*-carborane (**1c**) provided an alternative route to the bromophenyl derivative **1d** and represents the first example of such an arylation of a 10-vertex *closo*-carborane. The reaction proceeds in high yield with no byproducts, unlike the synthesis of **1d** from the *nido* precursor **3d**.

2.2. NMR analysis

The structures for the hexyl carboranes have been confirmed by NMR spectroscopy and all ^{11}B and ^{1}H resonances were correlated in ^{11}B–^{11}B COSY [30,31] and ^{1}H{^{11}B(selective)} [32] experiments. ^{11}B chemical shifts observed for hexyl-*o*-carborane **5b** (Table 1) and hexyl-*nido*-carboranes **4b** (Table 2) and **3b** (Table 3) are in agreement with general trends [33] and very similar to those found in the analogous methyl derivatives [27].

Table 1
NMR chemical shifts (δ/ppm) and coupling constants (J/Hz) and their assignments for 1-hexyl-1,2-$C_2B_{10}H_{11}$ carborane **5b**

Vertex[a]	$\delta(^{11}B)$	$^{1}J(^{11}B–^{1}H)$	$\delta(^{1}H)^{b}$
1[c]	–	–	[d]
2[c]	–	–	2.46[e]
3,6	−13.15	152	2.08
4,5	−12.12	142	2.36
7,11	−13.87	161	2.29
8,10	−9.95	150	2.70
12	−6.36	150	2.78
9	−2.95	147	2.90

[a] Assignments based on relative intensities and COSY correlation run in benzene-d_6.

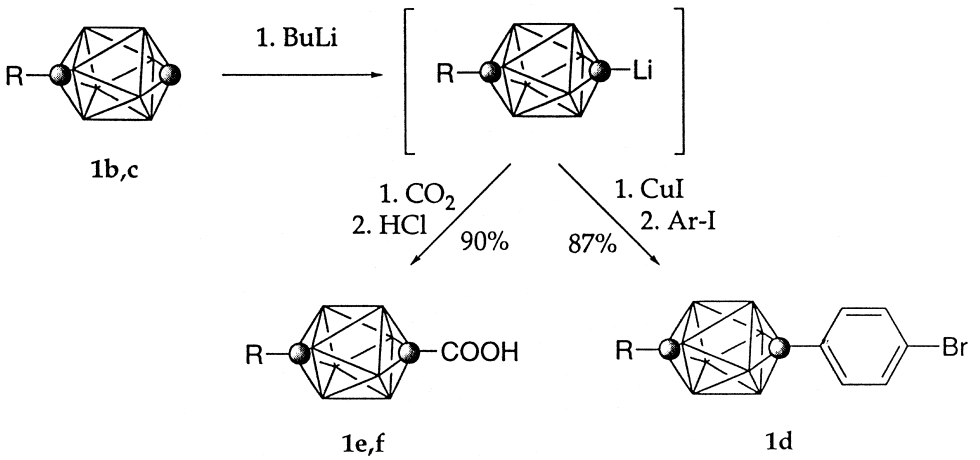
[b] Chemical shifts of directly bound hydrogens obtained from ^{1}H{^{11}B(selective)} experiments.

[c] Skeletal carbon atoms: ^{13}C NMR δ 61.3 (C^2), 75.5 (C^1).

[d] Signals from the hexyl group: 1.55 (t, J=8.6 Hz, C^1H_2), 1.13–1.19 (m, C^2H_2), 0.96–1.03 (m, $C^3H_2C^4H_2$), 0.80–0.84 (m C^5H_2), 0.87 (t, J=7.2 Hz, C^6H_2). ^{13}C NMR δ 14.14 (C^6), 22.75(C^5), 28.67 and 29.16 (C^2C^3), 31.40(C^4), 37.89(C^1); assignments based on a general trend and additivity rules (O.A. Subbotin, T.V. Klimova, V.I. Stanko, Yu.A. Ustynyuk, Russ. J. Gen. Chem. 49 (1979) 363).

[e] Signal from the skeletal C^2H unit.

As expected, removal of a μ proton from the neutral *nido*-carboranes **4b-H** and **3b-II** and the formation of the corresponding anions **4b(−)** and **3b-II(−)** [27] results in a substantial change in the chemical shifts. Deprotonation of **4b-H** results in a 16 ppm shift downfield of the directly affected boron atoms 9 and 11 and an upfield shift by 17 ppm for boron atom 10 (Fig. 1). Boron atoms 2 and 4 antipodal to B9 and B10, respectively, are substantially shifted upfield by 25 ppm whereas B3, antipodal to B10 is unaffected by the deprotonation. Resonances of the re-



Scheme 4.

Table 2
NMR chemical shifts (δ/ppm) and coupling constants (J/Hz) and their assignments for for 7(8)-hexyl-7,8-$C_2B_9H_{12}$ (**4b-H**) 7(8)-hexyl-7,8-$C_2B_9H_{11}$ NMe_4 (**4b-NMe$_4$**)

Vertex[a]	7-Hexyl-7,8-$C_2B_9H_{12}$ (**4b-H**)			7-Hexyl-7,8-$C_2B_9H_{11}$ NMe_4 (**4b-NMe$_4$**)		
	$\delta(^{11}B)$	$^1J(^{11}B-^1H)$	$\delta(^1H)$[b]	$\delta(^{11}B)$	$^1J(^{11}B-^1H)$	$\delta(^1H)$[b]
7[c]	–	–	[d]	–	–	[e]
8[c]	–	–	2.77[f]	–	–	2.39 (1.84)[f]
1	−26.76	155	2.25	−37.64 (−38.57)	137	1.12 (0.42)
2	+ 6.26	162	3.43	−18.36 (−19.42)	125	1.78 (1.13)
3	−14.44	174	1.92	−14.14 (−15.00)	149	2.50 (1.68)
4	+ 2.53	162	3.14	−22.51 (−23.33)	130	1.97 (1.24)
5	− 8.35	153	2.68	−18.36 (−19.42)	125	1.78 (1.13)
6	− 6.18	153	2.77	−18.36 (−18.76)	125	2.20 (1.44)
9	−27.84	143	1.77	−11.65 (−12.67)	134	2.66 (1.94)
10	−16.86	147	2.12	−33.87 (−34.69)	132/60	0.71 (0.00)
11	−27.84	143	1.77	−11.30 (−12.29)	137	2.73 (1.94)
μ-H	–	–	−1.90	–	–	−1.84 (−2.62)

[a] Assignments based on relative intensities and COSY correlation run in benzene-d_6 or in $CDCl_3$ (in parenthesis).
[b] Chemical shifts of directly bound hydrogens obtained from $^1H\{^{11}B(selective)\}$ experiments.
[c] Skeletal carbon atoms: ^{13}C NMR δ **4bH**: 68.6 (C^8), 87.6 (C^7); **4bNMe$_4$**: 49.6 (C^8), 62.0 (C^7).
[d] Signals from the hexyl group: 1.46–1.54 and 1.60–1.68 (m, C^1H_2), 1.18–1.29 (m, C^2H_2), 1.06–1.16 (m, $C^3H_2C^4H_2$), 0.95–1.03 (m, C^5H_2), 0.91 (t, J=7.2 Hz, C^6H_2); ^{13}C NMR δ 14.23, 22.91, 29.29, 31.19, 31.74, 39.17.
[e] Signals from the hexyl group: ^{13}C NMR δ 14.39, 23.09, 30.12, 32.13, 32.32, 40.40, (NMe_4^+ at 55.05).
[f] Signal from the skeletal C^8H unit.

maining boron atoms 1, 5 and 6 are shifted upfield by about 11 ppm.

Deprotonation of **4b-H** and the formation of a tetramethylammonium salt also affect the resonance of other nuclei and the most significant effect is observed for the cage atoms. The skeletal carbon atoms C^7-R and C^8-H are significantly shielded and their resonances are shifted by −26 and −19 ppm, respectively. Similarly, the skeletal C^8-H proton in **4b-NMe$_4$** is more shielded by −0.31 ppm as compared to **4b-H**.

The hexyl chain atoms are modestly deshielded in **4b-NMe$_4$** relative to **4b-H** and the most affected are the proton and carbon atoms of the α-methylene group. The C^1 carbon is shifted downfield by +1.24 ppm. Likewise in ^1H NMR the set of diastereotopic hydrogens of the methylene group adjacent to the cage is shifted downfield by +0.57 ppm.

3. Discussion and conclusions

The two new methods for oxidation of substituted *nido*-dicarbaundecaborates **4** with buffered Fe(III) or with SO_2 produce the *nido*-carboranes **3** in similar modest yields of

Table 3
NMR chemical shifts (δ/ppm) and coupling constants (J/Hz) and their assignments for 6-and 5-Hexyl-5,6-$C_2B_8H_{11}$ carboranes **3b**

Vertex[a]	6-Hexyl-5,6-$C_2B_8H_{11}$ (**3b-I**)			5-Hexyl-5,6-$C_2B_8H_{11}$ (**3b-II**)		
	$\delta(^{11}B)$	$^1J(^{11}B-^1H)$	$\delta(^1H)$[b]	$\delta(^{11}B)$	$^1J(^{11}B-^1H)$	$\delta(^1H)$[b]
5[c]	–	–	4.85[d]	–	–	–
6[c]	–	–	–	–	–	6.60[d]
1	2.02	143	3.27	6.13	156	3.48
2	−22.80	177	1.52	−25.10	174	[e]
3	−3.68	~140	2.73	−2.07	146	2.73
4	−40.34	150	0.50	−38.88	156	0.62
7	2.99	144	3.21	4.30	147	3.39
8	2.02	143	2.84	0.36	~160	2.83
9	−5.50	~160	2.97	−2.07	146	3.08
10	−9.06	156	[e]	−7.02	~160	[e]
μ-H (9,10)	–	–	−2.12	–	–	−1.88
μ-H (8,9)	–	–	−2.52	–	–	−2.39

[a] Assignments based on relative intensities and COSY correlation run in CD_3CN.
[b] Chemical shifts of directly bound hydrogens obtained from $^1H\{^{11}B(selective)\}$ experiments.
[c] Skeletal carbon atoms.
[d] Signal from the skeletal CH unit.
[e] Not identified.

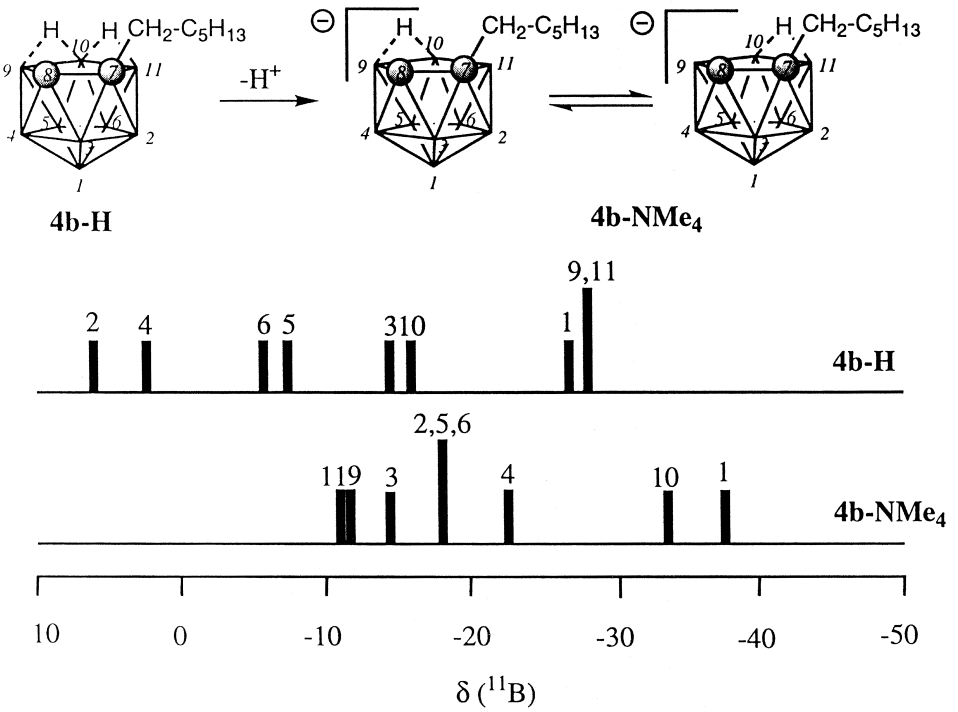


Fig. 1. Stick representation of the ^{11}B NMR chemical shifts for 7(8)-hexyl-7,8-dicarba-*nido*-undecaborane (4b-H) and its tetramethylammonium salt 4b-NMe_4 recorded in benzene-d_6.

about 15% after distillation. The latter deboronation with SO_2 takes place under homogenous conditions which lends itself to extension to highly lipophilic anions **4**. Both methods, however, are less efficient than the synthesis of **3** from nonaborane **6** and acetylenes (>25%).

The conversion of the alkyl *nido*-carboranes **3** to the more chemically stable *closo* compounds is a low yield process during which the reactants and products undergo partial polymerization. The yield of the dehydrogenation and the purity of the final product is improved by using the dispropotionation of the *nido*-carborane sodium salt followed by oxidative cage closure with $CuCl_2$.

The high temperatures required for the skeletal rearrangement of the *closo*-carboranes were tolerated by alkyl groups well but the 4-bromophenyl substituent underwent partial (10%) disproportionation. Filtration of a pentane solution of the *closo*-carboranes **2c** through a short silica gel plug immediately prior to the thermolysis was found to increase the yield.

The overall yields for the preparation of substituted *para*-carboranes are rather low. 1-Hexyl-*p*-carborane **1b** was obtained in about 8% overall yield based on **5b** using either the Fe(III) or the SO_2 methods whereas the pentyl analog **1c** was prepared in 15% overall yield from nonaborane **6**, or 7% yield based on commercial technical grade $B_{10}H_{14}$.

For comparison, the preparation of the parent *p*-carborane (**1a**) from *o*-carborane (**5a**) using the improved Plešek synthesis [14] and the modified anion dispropotionation method can be as high as 45%. Assuming statistical monoalkylation of **1a**, the overall yield for preparation of **1b** or **1c** from either *o*-carborane **5a** or nonaborane **6** should be around 20%. This is higher than the synthesis of the monoalkyl derivatives from substituted precursors. Monoarylation of carboranes [3,29,34] is generally more efficient than monoalkylation and overall yields higher than 20% should be expected for preparation of aryl derivatives of **1a**.

The largest loss of material occurs on the *nido* to *closo* ring closure step and yields higher than 50% have not been observed. This may be due to a reactivity difference between the two isomers 5-alkyl and 6-alkyl-*nido*-carborane. It is possible that one of the isomers is less chemically and thermally stable and/or is less prone to form the *closo* cage and undergoes polymerization whereas the other isomer is largely transformed into the *closo* product. This hypothesis requires further experimental work.

The procedure developed here for preparation of alkyl-*p*-carborane **1** is simple and reliable but the overall yields are lower than those obtained by statistical monoalkylation of the parent *p*-carborane **1a**. Arylation of **1c** to form **1d** is another successful adaptation of reactions typical for 12-vertex *p*-carborane. Alkylation, carboxylation, ethynylation [35], and now arylation constitute a set of key synthetic tools for preparation of liquid crystalline materials [36].

4. Experimental

The ^{1}H, ^{13}C and ^{11}B NMR spectra were obtained in $CDCl_3$ on Bruker instruments operating at 400.1 MHz, 75.5 MHz, and 128.4 MHz, respectively and referenced to the solvent (^{1}H and ^{13}C) or to $B(OMe)_3$ (18.1 ppm) unless specified otherwise. Two dimensional spectra were performed on a Varian XL-500 instrument and coupling constants $^{1}J(^{11}B–^{1}H)$ are taken from resolution-enhanced ^{11}B spectra with digital resolution of ±8 Hz. IR spectra of neat samples were recorded in NaCl using an ATI Mateson instrument. Mass spectrometry was performed using Hewlett–Packard 5890 instrument (GCMS) using a 15 m methylsilicone column. Elemental analysis was provided by Atlantic Microlab, Norcross, Georgia.

*4.1. 1-Hexyl-1,10-dicarba-closo-decaborane (**1b**)*

A crude mixture of *nido* isomers **3b** obtained according to Method A (0.97 g) was heated (Wood's metal bath) in a flask equipped with a Liebig condenser under dry nitrogen atmosphere at 260°C for 1 h. The resulting yellow oil was transferred to a heavy glass tube with aid of a small amount of pentane. The tube was sealed and heated at 330°C for 10 h and the resulting yellow product was short-path distilled (85°C/0.15 torr) to give 0.34 g (35% yield or 8% yield based on **5b**) of a colorless oil: ^{1}H NMR δ 0.93 (t, $J=7.0$ Hz, 3H), 1.25–1.47 (m, 4H), 1.48–1.54 (m, 2H), 1.6 (br d, $J=159$ Hz, 4H), 1.90-1.98 (m, 2H), 2.4 (br d, $J=159$ Hz, 4H), 3.18 (t, $J=8.2$ Hz, 2H), 6.69 (br s, 1H); ^{13}C NMR δ 14.11, 22.65, 29.32, 31.71, 31.85, 35.16, 93.6 (br), 125.8 (br); ^{11}B NMR δ −14.4 (d, $J=165$ Hz, 4B), −12.2 (d, $J=163$ Hz, 4B); IR 3113, 2956, 2930, 2860, 2597, 1465, 1103 cm^{-1}; EIMS, *m*/*e* 205 (M, 1), 166–177 (max at *m*/*e* 175, 27), 153–164 (max at *m*/*e* 161, 86), 71 (66), 57 (40), 43 (100).

Thermolysis of *nido*-carboranes **3b** obtained according to Method B gave 6% of carborane **1b** based on **5b**.

*4.2. 1-Pentyl-1,10-dicarba-closo-decaborane (**1c**)*

A solution of nonaborane **6** (3.45 g, 20 mmol) and 1-heptyne (3.85 g, 40 mmol) in dry toluene (80 ml) was refluxed for 30 min under an atmosphere of dry nitrogen. The solvent was removed under reduced pressure and the yellow oily residue was diluted with hexanes (25 ml) and passed through a silica gel plug (100 ml) which was washed with hexanes (250 ml). The hexane washings were evaporated and the oily residue (3.0 g) was short-path vacuum distilled (155°C/0.5 torr) to give 0.96 g of a colorless oil and 1.48 g of a dark viscous residue. The distilled mixture contained almost equal proportions of the 5-pentyl and 6-pentyl carboranes: GCMS, rt 10.7 and 11.2 min, *m*/*z* 183–194 (max at *m*/*e* 192, 43), 167–180 (max at *m*/*e* 174, 48), 154–163 (max at *m*/*e* 159, 54), 57 (100), 43 (25), 41 (44); ^{11}B NMR δ −40.8, −39.6, −25.6, −23.3, −9.7, −7.5, −6.3, −3.8, −3.1, −2.2, 1.1, 2.2, 3.1, 4.6, 6.4.

The neat distilled *nido* compounds (0.96 g) were heated at 250°C under an atmosphere of dry nitrogen for 1 h and vacuum distilled to give 0.25 g of *closo*-carboranes [(GCMS, rt 9.1 min, *m*/*z* 184–193 (max at *m*/*e* 191, 38), 169–176 (max at *m*/*e* 174, 45), 154–163 (max at *m*/*e* 159, 35), 57 (100), 43 (32), 41 (41)]. Alternatively, a crude mixture of the *nido*-carboranes (2.2 g) was dissolved in dry ether (20 ml) and added to a suspension of NaH (0.50 g, 60% in mineral oil, twice washed with ether) in ether (5 ml). The mixture was stirred for 1 h at ambient temperature and the yellow supernatant liquid was transferred to a dry flask. The remaining excess NaH was washed with ether and the collected ethereal solutions were evaporated to dryness. The resulting viscous oil was short path distilled (155°C/0.5 torr) to yield 0.56 g of a colorless oil and a glassy residue, which was stirred overnight with anhydrous $CuCl_2$ (2.0 g) in dry methylene chloride (20 ml). The resulting dark mixture was passed through a silica gel plug and washed well with hexanes. The filtrate was evaporated and the residue distilled to furnish an additional 0.31 g of a mixture of pentyl-*o*-carboranes **2c**.

The *closo*-carboranes (0.87 g) were dissolved in pentane and passed through a small silica gel plug (a pipette). The resulting colorless solution was evaporated in a heavy wall glass tube which was filled with nitrogen, sealed and heated at 330°C for 12 h. The resulting yellowish product was short-path distilled (140°C/10 torr) to give 0.56 g (65% yield) of a colorless oil: ^{1}H NMR δ 0.93 (t, $J=7.0$ Hz, 3H), 1.25–1.47 (m, 4H), 1.48–1.54 (m, 2H), 1.6 (br d, $J=159$ Hz, 4H), 1.90–1.98 (m, 2H), 2.4 (br d, $J=159$ Hz, 4H), 3.18 (t, $J=8.2$ Hz, 2H), 6.69 (br s, 1H); ^{13}C NMR δ 14.03, 22.52, 31.53, 31.79, 35.11, 93.6 (br), 125.4 (br); ^{11}B NMR δ −14.4 (d, $J=165$ Hz, 4B), −12.2 (d, $J=163$ Hz, 4B); IR (neat) 2958, 2932, 2862, 2594 cm^{-1}; EIMS, *m*/*e* 205 (M, 1), 166–177 (max at *m*/*e* 175, 27), 153–164 (max at *m*/*e* 161, 86), 71 (66), 57 (40), 43 (100). Anal. Calc. for $C_7H_{20}B_8$: C, 44.08; H, 10.57. Found: C, 44.93; H, 10.35.

*4.3. 1-(4-Bromophenyl)-10-pentyl-1,10-dicarba-closo-decaborane (**1d**)*

4.3.1. Method A

A solution of 1-(4-bromophenyl)-1-heptyne (1.56 g, 6.2 mmol) and nonaborane **6** (0.54 g, 3.1 mmol) in dry toluene (30 ml) was refluxed for 30 min. The solvent was evaporated and the viscous residue was treated with hexanes and passed through a SiO_2 plug which was washed with hexanes (100 ml). Evaporation of the hexane eluent left 0.64 g of a yellowish oily mixture of carboranes. The crude mixture (0.64 g) was short-path distilled. The first fraction (0.19 g), collected up to 150°C, was discarded and a second (0.25 g) was collected up to 220°C/0.1 torr. The carboranes were heated at 350°C using

Wood's metal bath under an atmosphere of dry nitrogen for 8 h, cooled down, dissolved in hexanes, and filtered through a silica gel plug. The hexane washings were evaporated and the oily residue was short-path distilled (200°C/0.1 torr) to give 0.21 g of 85% pure product which was purified using chromatography (silica and hexanes).

4.3.2. Method B

1-Pentyl-1,10-dicarba-*closo*-decaborane (**1c**, 0.51 g, 2.7 mmol) was dissolved in dry DME (15 ml) and treated with BuLi (2.3 M, 1.2 ml, 2.8 mmol) at −78°C. The mixture was allowed to reach room temperature, stirred for 20 min, and dry CuI (0.73 g) was added in one portion. The resulting black solution was stirred for 15 min and dry pyridine (1.6 ml) was added, followed by 4-bromo-1-iodobenzene (3.0 g, 10.6 mmol). The resulting mixture was stirred, gently refluxed overnight, cooled, and poured into dilute hydrochloric acid. The product was extracted with hexanes (3×), dried and passed through a silica gel plug. The colorless hexane washings were evaporated. The resulting semicrystalline material (3.6 g) was recrystallized twice from a small amount of pentane yielding starting *p*-bromoiodobenzene. The mother liquors were evaporated and the remaining bromoiodobenzene was sublimed off (125°C/10 torr). The product (0.81 g, 87% yield) was collected at 190°C/0.5 torr as a colorless viscous oil: ^{1}H NMR δ 0.97 (t, J=7.1 Hz, 3H), 1.40–1.57 (m, 4H), 1.91–1.99 (m, 2H), 3.19 (t, J=8.3 Hz, 2H), 7.56 (d, J=8.4 Hz, 2H), 7.65 (d, J=8.4 Hz, 2H); ^{13}C NMR δ 14.03, 22.51, 31.57, 31.77, 34.53, 114.9 (br) 121.4 (br), 122.55, 130.55, 131.43, 137.30; ^{11}B NMR δ −12.0 (d, J=159 Hz); IR (neat) 2956, 2931, 2860, 2593, 1493, 1465, 1069, 1012, 817 cm^{-1}; EIMS, *m*/*e* 340–350 (cluster with max at *m*/*e* 345, 100), 57 (10), 43 (29), 41 (32). Anal. Calc. for $C_{13}H_{15}B_8Br$: C, 45.17; H, 6.71. Found: C, 45.76; H, 6.67.

*4.4. 10-Hexyl-1,10-dicarba-closo-decaborane-1-carboxylic acid (**1e**)*

1-Hexyl-1,10-dicarba-*closo*-decaborane (0.51 g, 2.5 mmol) was dissolved in dry THF (15 ml), treated with BuLi (1.6 1.M, 1.8 ml, 2.9 mmol) at −78°C. The mixture was allowed to reach room temperature and stirred for 20 min and cooled down. Then carbon dioxide generated from dry ice was bubbled through the stirred solution for 1 h. The solvent was removed, the resulting white solid was washed with hexanes, dissolved in water and acidified with conc. HCl. The resulting product was extracted with ether hexane 1:1 mixture (3×10 ml), the organic layer was dried (Na_2SO_4) and the solvent evaporated to yield 0.60 g of crude product. Sublimation (100–110°C/0.15 torr) followed by recrystallization of the product (0.59 g) from pentane (−78°C) gave 0.53 g (86% yield) of white acid **1e**: mp 83–85°C; ^{1}H NMR δ 0.94 (t, J=7.0 Hz, 3H), 1.36–1.44 (m, 4H), 1.50–1.57 (m, 2H), 1.91–1.99 (m, 2H), 3.23 (t, J=8.3 Hz, 2H), 11.7 (br s, 1H); ^{13}C NMR δ 14.09, 22.62, 29.24, 31.65, 31.86, 35.23, 105.1 (br), 130.0 (br), 171.33; ^{11}B NMR δ −11.5 (d, J=159 Hz); IR 3012, 2943, 2924, 2860, 2599, 1714, 1432, 1307, 1209 cm^{-1}. Anal. Calc. for $C_9H_{20}B_8O_2$: C, 43.46; H, 8.91. Found: C, 43.47; H, 8.95.

*4.5. 10-Pentyl-1,10-dicarba-closo-decaborane-1-carboxylic acid (**1f**)*

The acid was obtained according to the procedure described for **1e**: subl. 120°C/0.3 torr; mp 102–103°C; ^{1}H NMR δ 0.97 (t, J=7.0 Hz, 3H), 1.42–1.54 (m, 4H), 1.91–1.99 (m, 2H), 3.22 (t, J=8.3 Hz, 2H), 11.5 (br s, 1H); ^{13}C NMR δ 14.02, 22.49, 31.56, 31.71, 35.18, 104.9 (br), 129.9 (br), 171.35; ^{11}B NMR δ −11.5 (d, J=160 Hz). Anal. Calc. for $C_8H_{20}B_8O_2$: C, 40.94; H, 8.59. Found: C, 41.46; H, 8.70.

*4.6. 5-Hexyl- and 6-Hexyl-5,6-dicarba-nido-decaborane (**3b**)*

4.6.1. Method A ($FeCl_3$)

Potassium acetate (47.0 g, 480 mmol) was added to a mixture of $FeCl_3 \cdot 6H_2O$ (44.0 g, 160 mmol) in water (150 ml) and hexane (100 ml) followed by 1 M solution of **4b-K** (20 ml, 10 mmol), prepared according to a general procedure, added over a period of 30 min. The resulting red reaction mixture was stirred overnight and then refluxed for 4 h, cooled and filtered through Celite. The hexane layer was separated, dried, and solvent removed, leaving 0.50 g of a colorless oil. The aqueous layer was extracted with ether (50 ml). Removal of the ether gave a red oil (4 g) which was extracted with hexanes yielding additional 0.12 g of the crude product. The combined crude products were short-path distilled (125–150°C/0.1 torr) to give 0.40–0.60 g of colorless oil of **3b** (10%–15% yield based on carborane **5b**).

4.6.2. Method B (SO_2)

A 1 M solution of **4b-K** (20 ml, 10 mmol) prepared according to a general procedure [15] was acidified with 10% HCl and the oily product was extracted with ether. The organic layer was dried, solvent evaporated, and the oily residue was dried under vacuum overnight leaving 4.4 g of colorless viscous oil **4b-H** (For more rigorous drying the material was dissolved in hexanes, evaporated, and drying was continued for 12 h at 45°C): ^{1}H NMR δ (300 MHz, C_6D_6) 0.90 (t, J=7.1 Hz, 3H), 0.96–1.04 (m, 2H), 1.06–1.16 (m, 4H), 1.18–1.30 (m, 2H), 1.45–1.55 (m, 1H), 1.58–1.68 (m, 1H), 2.74 (br, 1H); ^{13}C NMR δ (C_6D_6) 14.23, 22.91, 29.29, 31.19, 31.74, 39.17, 68.7 (br), 87.6 (br); EIMS, *m*/*z* 214–219 (max at *m*/*z* 216, 13), 180–188 (max at *m*/*z* 185, 30), 167–175 (max at *m*/*z* 171, 34), 71 (40), 57 (28), 43 (100).

The resulting carborane **4b-H** (4.4 g) was dissolved in hexanes (120 ml) and a slow stream of SO_2, generated from dry Na_2SO_3 (80 g) and 50% H_2SO_4 (80 ml), was passed through the stirred hexane solution over a period of 8 h. The reaction was initially somewhat exothermic, the initial red color changed to yellow, and the mixture become silty. After stirring at rt for the total of 8 h the mixture was filtered through a short silica plug and stirred with water (50 ml) for 2 h. The hexane layer was separated, dried ($MgSO_4$), solvents evaporated, and the residue (0.76 g) vacuum distilled (150°C/0.4 torr) to yield 0.67 g (16% yield based on **5b**) a crude mixture of isomers **3b** contaminated with <5% of sulfur-containing species (GCMS).

*4.7. 5-Hexyl-5,6-dicarba-nido-decaborane (**3b-I**)*

^{1}H NMR δ (C_6D_6) 0.90 (t, J=7.2 Hz, 3H), 1.00–1.35 (m, 8H), 1.9–2.2 (m, 2H), 5.74 (br s, 1H); ^{13}C NMR δ (C_6D_6) 14.23, 22.90, 29.34, 30.66, 31.76, 38.06, 69.2 (br), 139.6 (m); EIMS, rt 11.9 min.: m/e 208–203 (max at 206, 14), 176–168 (max at 173, 17), 162–154 (max at 159, 17), 71 (28), 57 (31), 43 (100).

*4.8. 6-Hexyl-5,6-dicarba-nido-decaborane (**3b-II**)*

^{1}H NMR δ (C_6D_6) 0.87 (t, J=7.2 Hz, 3H), 1.00–1.35 (m, 8H), 1.9–2.2 (m, 2H), 3.86 (br s, 1H); ^{13}C NMR δ (C_6D_6) 14.23, 22.90, 28.70, 29.63, 30.68, 38.45, 91.8 (br), 162 (br m); EIMS, rt 12.5 min.: m/e 208–203 (max at 206, 14), 176–168 (max at 173, 17), 162–154 (max at 159, 17), 71 (28), 57 (31), 43 (100).

4.9. 1-(4-Bromophenyl)-1-heptyne

A mixture of 4-bromo-1-iodobenzene (14.15 g, 50 mmol), 1-heptyne (4.81 g, 50 mmol), $(Ph_3P)_2PdCl_2$ (100 mg), CuI (50 mg) and triethylamine (100 ml) was stirred at rt overnight. The resulting thick suspension of the ammonium salts was decomposed with dilute HCl, and the product was extracted with hexanes. The extracts were dried, filtered through a silica plug and evaporated. The crude product (13.1 g) was short-path distilled. After allowing the traces of bromoiodobenzene to sublime off (120°C/0.5 torr) the main fraction of 11.16 g (89% yield) was collected at 130°C/0.15 torr as a colorless oil: ^{1}H NMR (300 MHz) δ 0.92 (t, J=7.1 Hz, 3H), 1.30–1.47 (m, 4H), 1.55–1.65 (m, 2H), 2.38 (t, J=7.8 Hz, 2H), 7.24 (d, J=8.5 Hz, 2H), 7.41 (d, J=8.5 Hz, 2H); ^{13}C NMR δ 13.98, 19.38, 22.21, 29.31, 31.10, 79.53, 91.78, 121.49, 123.04, 131.37, 133.00; EIMS, m/e 250 and 251 (M, 40), 221 and 223 (38), 195 (73), 142 (100), 129 (72), 128 (55), 116 (94), 115 (55), 114 (51). Anal. Calc. for $C_{13}H_{15}Br$: C, 62.17; H, 6.02. Found: C, 61.94; H, 5.94.

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