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

Zbynek Janoušek¹, Piotr Kaszynski*¹

Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Box 1822 Station B, Nashville, TN 37235, USA

Received 26 April 1999; accepted 7 September 1999

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 SO2. The newly developed homogenous deboronation with SO2 appears to be more efficient than the classical Plešek oxidation especially for highly hyrophilic 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. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Substitued carboranes; 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.

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-C6H5F [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 obtained either from o-carborane 5, or using the recently described reaction of B6H13·L 6 with acetylenes [13,18]. The biphasic Plešek reaction works relatively well for the parent nido-5,6-dicarbadecaborane (3a) but substi-
stitution 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}·L_2 [17,20,21] and a reaction with Me_2S/methanol [22], respectively. 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-decarborane 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 ^11B 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_3Cl precipitates the corresponding ammonium salt 4b-NMe_3, 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 SO₂ as the oxidant, inspired by the observation that SOCl₂ is reduced by polyhedral boron hydrides [26].

The reaction of the free acid 4b-H with SO₂ 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-NBu₄ 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, 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].

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-carbaranes requires higher temperatures. Thus, heating neat alkylocarboranes 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 SO₂, 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-Na₂ upon vacuum distillation at 140°C (Scheme 3). The remaining disodium salt 3c-Na₂ was oxidized with anhydrous CuCl₂ [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
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 those found in the analogous methyl derivatives [27]. As expected, removal of a m 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-
methylammonium salt also affect the resonance of other group adjacent to the cage is shifted downfield by ~1 ppm. Deprotonation of 4b-H and the formation of a tetra-methylammonium salt also affect the resonance of other nuclei and the most significant effect is observed for the cage atoms. The skeletal carbon atoms C-H and C-H nuclei and the most significant effect is observed for the ppm.

The hexyl chain atoms are modestly deshielded in 4b-H and the formation of a tetra- 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 SO₂ produce the nido-carboranes 3 in similar modest yields of

### Table 2

<table>
<thead>
<tr>
<th>Vertex</th>
<th>7-Hexyl-7,8-C₆B₆H₁₂ (4b-H)</th>
<th>7-Hexyl-7,8-C₆B₆H₁₂ NMe₄ (4b-NMe₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>8</td>
<td>−26.76</td>
<td>155</td>
</tr>
<tr>
<td>2</td>
<td>+6.26</td>
<td>162</td>
</tr>
<tr>
<td>3</td>
<td>−14.44</td>
<td>174</td>
</tr>
<tr>
<td>4</td>
<td>+2.53</td>
<td>162</td>
</tr>
<tr>
<td>5</td>
<td>−8.35</td>
<td>153</td>
</tr>
<tr>
<td>6</td>
<td>−6.18</td>
<td>153</td>
</tr>
<tr>
<td>9</td>
<td>−27.84</td>
<td>143</td>
</tr>
<tr>
<td>10</td>
<td>−16.86</td>
<td>147</td>
</tr>
<tr>
<td>11</td>
<td>−27.84</td>
<td>143</td>
</tr>
<tr>
<td>μ-H</td>
<td>−</td>
<td>−</td>
</tr>
</tbody>
</table>

¹ Assignments based on relative intensities and COSY correlation run in benzene-d₆ or in CDCl₃, (in parenthesis).
² Chemical shifts of directly bound hydrogens obtained from ¹H[¹¹B(biselective)] experiments.
³ Skeletal carbon atoms. ¹³C NMR δ 4bH: 68.6 (C²), 87.6 (C³); 4bNMe₄: 49.6 (C⁴), 62.0 (C⁵).
⁴ Signals from the hexyl group: 1.46–1.54 and 1.60–1.68 (m, C-H), 1.18–1.29 (m, C-H), 1.06–1.16 (m, C-H-C-H), 0.95–1.03 (m, C-H), 0.91 (t, J=7.2 Hz, C-H) δ 14.23, 22.91, 29.29, 31.19, 32.13, 32.32, 40.40, (NMe at 55.05).
⁵ Signal from the skeletal C-H unit.

### Table 3

<table>
<thead>
<tr>
<th>Vertex</th>
<th>6-Hexyl-5,6-C₆B₆H₁₁ (3b-I)</th>
<th>5-Hexyl-5,6-C₆B₆H₁₁ (3b-II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>6</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>1</td>
<td>2.02</td>
<td>143</td>
</tr>
<tr>
<td>2</td>
<td>−22.80</td>
<td>177</td>
</tr>
<tr>
<td>3</td>
<td>−3.68</td>
<td>−140</td>
</tr>
<tr>
<td>4</td>
<td>−40.34</td>
<td>150</td>
</tr>
<tr>
<td>7</td>
<td>2.99</td>
<td>144</td>
</tr>
<tr>
<td>8</td>
<td>2.92</td>
<td>143</td>
</tr>
<tr>
<td>10</td>
<td>−5.50</td>
<td>−160</td>
</tr>
<tr>
<td>μ-H</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>μ-H</td>
<td>−</td>
<td>−</td>
</tr>
</tbody>
</table>

¹ Assignments based on relative intensities and COSY correlation run in CD₃CN.
² Chemical shifts of directly bound hydrogens obtained from ¹H[¹¹B(biselective)] experiments.
³ Skeletal carbon atoms.
⁴ Signal from the skeletal CH unit.
⁵ 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% of 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 disproportionation 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 disproportionation 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 $^3$J($^{11}$B–$^1$H) are taken from resolution-enhanced $^{11}$B spectra with digital resolution of $\pm$8 Hz. IR spectra of neat samples were recorded in NaCl using an ATI Mateson g, 60% in mineral oil, twice washed with ether) in ether (5 ml). The mixture was stirred for 1 h at ambient temperature and the yellow supernatant liquid was transferred to a silica gel plug (100 ml) which was stirred overnight with anhydrous CuCl$_2$ (2.0 g) in dry methylene chloride (20 ml). 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 oil was short-path distilled (140°C/10 torr) to give 0.56 g (65% yield) of a colorless oil: $^1$H NMR $\delta$ 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 $\delta$ 14.11, 22.65, 31.53, 31.79, 35.11, 93.6 (br), 125.8 (br); $^{11}$B NMR $\delta$ –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-decarborane (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 $\delta$ –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 oil was short-path distilled (140°C/10 torr) to give 0.56 g (65% yield) of a colorless oil: $^1$H NMR $\delta$ 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 $\delta$ 14.03, 22.52, 31.53, 31.79, 35.11, 93.6 (br), 125.8 (br); $^{11}$B NMR $\delta$ –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$_5$H$_{10}$B$_3$: C, 44.08; H, 10.57. Found: C, 44.93; H, 10.35.

4.3. 1-(4-Bromophenyl)-10-pentyl-1,10-dicarba-closo-decarborane (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-Penty1-1,10-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-bromiodobenzene. The mother liquors were evaporated and the remaining bromiodobenzene 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: 1H 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); 13C 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; 11B NMR δ −12.0 (d, J = 159 Hz); IR (neat) 2956, 2931, 2860, 2599, 1714, 1432, 1307, 1209 cm−1. Anal. Calc. for C13H15B8O2: C, 45.76; H, 6.95.

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

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 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 oily residue was dried under vacuum overnight leaving 4.4 g of colorless viscous oil 1 mixture of FeCl3 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: 1H 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); 13C 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; 11B 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 C13H15B8O2: C, 45.17; H, 6.67. Found: C, 45.76; H, 6.67.

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; 1H NMR δ 0.87 (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); 13C NMR δ 14.02, 22.49, 31.56, 31.71, 35.18, 104.9 (br), 129.9 (br), 171.35; 11B NMR δ −11.5 (d, J = 160 Hz). Anal. Calc. for C13H23B8O2: 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 (FeCl3)

Potassium acetate (47.0 g, 480 mmol) was added to a mixture of FeCl3·6H2O (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 (SO2)

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): 1H NMR δ (300 MHz, CDCl3) 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); 13C NMR δ (CDCl3) 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\(_2\)SO\(_4\) (80 g) and 50% H\(_2\)SO\(_4\) (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-decarbaborane (3b-I)

\(^1^H\) NMR \(\delta\) (C\(_6\)D\(_6\)) 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 \(\delta\) (C\(_6\)D\(_6\)) 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).

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

\(^1^H\) NMR \(\delta\) (C\(_6\)D\(_6\)) 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 \(\delta\) (C\(_6\)D\(_6\)) 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\(_2\)P)\(_2\)PdCl\(_2\) (100 mg), Cul (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 the column the reaction product was collected at 130°C/0.15 torr as a colorless oil: \(^1^H\) NMR (300 MHz) \(\delta\) 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 \(\delta\) 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\(_5\)H\(_{13}\)Br: C, 62.17; H, 6.02. Found: C, 61.94; H, 5.94.

Acknowledgements

This project was supported in part by an NSF CAREER grant (DMR-9703002). One of the authors (Z.J.) was partially supported by the Grant Agency of the Czech Republic (No. 203/97/0060). We are grateful to Dr. James G. Carver of Redstone Arsenal for a generous gift of heptylcarborane and decaborane, Dr. Jiri Fusek of ASCR for providing 2D NMR spectra, and Dr. Jaromil Plešek for helpful discussions.

References
