A RETURN TO THE PLESEK REACTION AND SOME USEFUL VARIATIONS. CARBON-SUBSTITUTED METHYL AND PHENYL DERIVATIVES OF 5,6-DICARBA-*nido*-DECABORANE(12), *nido*-5,6-C₂B₈H₁₂

Bohumil STIBR[a1,b,]*, Josef HOLUB[a2], Tomas JELINEK[a3], Bohumir GRUNER[a4], Jiri FUSEK[a], Zbynek PLZAK[a], Francesc TEIXIDOR[b1,]*, Clara VINAS[b2] and John D. KENNEDY[c]

[a] *Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Rez near Prague, Czech Republic; e-mail: 1 stibr@iic.cas.cz, 2 holub@iic.cas.cz, 3 jelinek@iic.cas.cz, 4 gruner@iic.cas.cz*

[b] *Institute of Material Sciences, Campus de la UAB, 08913 Bellaterra, Spain; e-mail: 1 teixidor@icmab.es, 2 clara@icmab.es*

[c] *School of Chemistry, University of Leeds, Leeds LS2 9JT, England; e-mail: j.kennedy@chemistry.leeds.ac.uk*

We have pleasure in expressing our best wishes to Jaromir Plesek on the occasion of his 70th birthday, and are pleased to dedicate this paper to him in recognition of his outstanding contributions and astute insights into organic and cluster-boron chemistry. There were many chemical tricks the Czech authors had to learn from him.

A modification of the Plesek reaction has been employed to improve the yield in the synthesis of the parent *nido* ten-vertex dicarbaborane 5,6-C₂B₈H₁₂, and to synthesize some of its 5- and 6-substituted derivatives. The method is based on the oxidation of the anions $[7,8-R^1R^2\text{-}nido\text{-}5,6\text{-}C_2B_9H_{10}]^-$ with acidic aqueous of $[Fe(H_2O)_6]Cl_3$ to produce the series of substituted dicarbaboranes $5,6\text{-}R^1R^2\text{-}nido\text{-}5,6\text{-}C_2B_8H_{10}$, where R^1, R^2 = H, H; H, Me; Me, H; Me, Me; H, Ph; Ph, H, and Ph, Ph. The characteristic reaction mode is an oxidative elimination of one boron vertex that is adjacent to the carbon vertex in the open pentagonal face of the starting eleven-vertex *nido* dicarbaborane anion. The products are characterized by mass spectrometry and ¹H and ¹¹B NMR spectroscopy including [¹¹B-¹¹B]-COSY and ¹H-{¹¹B(selective)} measurements that permit complete assignments of all the observed resonances to individual cluster {BH} units.

**Key words:** Carboranes; Ten-vertex dicarbaboranes; 5,6-Dicarba-*nido*-decaboranes.

The most convenient method for the synthesis of the neutral, ten-vertex dicarbaborane *nido*-5,6-C₂B₈H₁₂ was developed by Plesek and Hermanek[1,2] and is based on the elimi-

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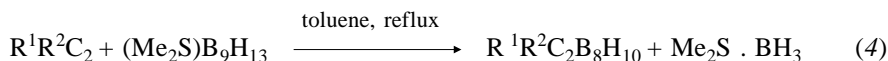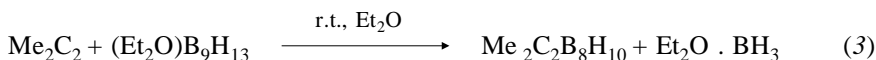* The author to whom correspondence should be addressed.

nation of one boron vertex from the readily available eleven-vertex [*nido*-7,8-$C_2B_9H_{12}$]$^-$ anion[3,4]. This anion can be oxidized by [Fe(H$_2$O)$_6$]Cl$_3$ in acidified aqueous solution to give a 45% yield of *nido*-5,6-$C_2B_8H_{12}$, as in stoichiometric equation (*1*).

$$[C_2B_9H_{12}]^- + Fe^{3+} + 3\ H_2O \longrightarrow C_2B_8H_{12} + B(OH)_3 + Fe^{2+} + 3/2\ H_2 \quad (1)$$
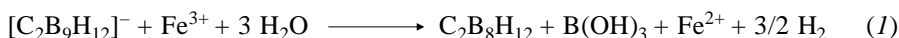
The first report on the synthesis of *nido*-5,6-$C_2B_8H_{12}$ and its 5,6-dimethyl derivative was that by Schaeffer and co-workers[5]. These compounds were isolated from reactions between alkynes and the octaborane *nido*-B_8H_{12} as in Eq. (*2*) (R = H and Me):

$$nido\text{-}B_8H_{12} + R_2C_2 \longrightarrow 5,6\text{-}R_2\text{-}nido\text{-}5,6\text{-}C_2B_8H_{10} + H_2 . \quad (2)$$
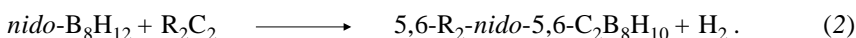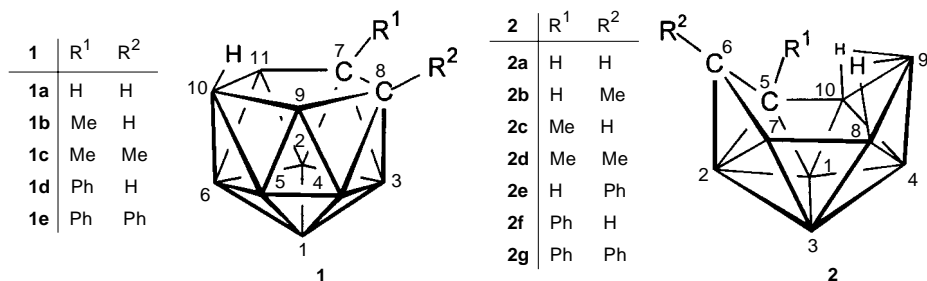
However, this method is rather inconvenient because of the general inaccessibility and instability of the starting borane *nido*-B_8H_{12} (ref.[6]). More conveniently, results from Shore and co-workers[7], and our own recent investigations[8], demonstrate that the reactions between alkynes and the nine-vertex ligand derivatives 4-L-*arachno*-B_9H_{13} (for L = OEt$_2$ (ref.[7]) and SMe$_2$ (ref.[8])) can also be employed usefully for the preparation of *nido*-5,6-$C_2B_8H_{12}$ and its *C*-substituted derivatives (Eqs (*3*) and (*4*)):

$$Me_2C_2 + (Et_2O)B_9H_{13} \xrightarrow{\text{r.t., Et}_2\text{O}} Me_2C_2B_8H_{10} + Et_2O \cdot BH_3 \quad (3)$$

$$R^1R^2C_2 + (Me_2S)B_9H_{13} \xrightarrow{\text{toluene, reflux}} R^1R^2C_2B_8H_{10} + Me_2S \cdot BH_3 \quad (4)$$

(where R^1, R^2 = H, H; Me, Me; Ph, H, and Ph, Ph)[8].

The parent (*i.e.* unsubstituted) ten-vertex dicarbaborane *nido*-5,6-$C_2B_8H_{12}$ has become one of the most essential reagents of dicarbaborane chemistry (see reviews in refs[9–12]). For instance, it has been employed as a starting material for the preparation of several other fundamental dicarbaborane types, such as *closo*-1,2-$C_2B_8H_{10}$, *closo*-1,6-$C_2B_8H_{10}$, *closo*-1,10-$C_2B_8H_{10}$, [*nido*-6,9-$C_2B_8H_{10}$]$^{2-}$, *arachno*-4,6-$C_2B_7H_{13}$ (ref.[13]), *arachno*-6,9-$C_2B_8H_{14}$ (refs[14–16]), [*arachno*-4,5-$C_2B_6H_{11}$]$^-$ (ref.[17]), as well as derivatives of *arachno*-$C_4B_8H_{14}$ (refs[18,19]) and fourteen-vertex methyltricarbaazaboranes[20]. Of recent high interest is that 5,6-$C_2B_8H_{12}$ has become a source of tricarbollides, the first representatives of the eleven-vertex series of tricarbaboranes[21–23].

Here we report an improvement of the Plesek reaction for the synthesis of the parent ten-vertex dicarbaborane 5,6-$C_2B_8H_{12}$, together with an extension of this reaction for the synthesis of mono- and disubstituted derivatives that have one or two methyl or phenyl groups on the cage carbon atoms. Simplified structures and numbering schemes for the compounds discussed in this work are as in the general structures **1** and **2** below; in these schematic structures, the unlettered vertices of individual polyhedra denote cluster BH(*exo*) units.

1	R^1	R^2
1a	H	H
1b	Me	H
1c	Me	Me
1d	Ph	H
1e	Ph	Ph

2	R^1	R^2
2a	H	H
2b	H	Me
2c	Me	H
2d	Me	Me
2e	H	Ph
2f	Ph	H
2g	Ph	Ph

EXPERIMENTAL

General

Aqueous solutions of the K^+ salts of the [7,8-R^1R^2-*nido*-7,8-$C_2B_9H_{10}$]$^-$ anions (where R^1, R^2 = H, H (**1a**) Me, H (**1b**); Me, Me (**1c**); Ph, H (**1d**); and Ph, Ph (**1e**)) were prepared by standard degradation of the corresponding *C*-substituted derivatives of *ortho*-dicarbadodecaborane (*closo*-1,2-$C_2B_{10}H_{12}$)[24] with methanolic KOH (ref.[25]). Hexane and CH_2Cl_2 were dried over CaH_2, and freshly distilled before use. All reactions were carried out under dry nitrogen[26], although some manipulations, such as preparative TLC and column chromatography, were carried out in air. Preparative TLC was carried out using silica gel G with a fluorescent indicator (Aldrich, type UV 254) as the stationary phase on plates of dimensions 200 × 200 × 1 mm, made on glass formers from aqueous slurries followed by drying in air at 80 °C. Column chromatography was performed using silica gel (Silpearl, Kavalier) and the purity of individual chromatographic fractions was checked by analytical TLC on Silufol (Kavalier, silica gel on aluminium foil; detection by UV 254 or iodine vapour, followed by 2% aqueous $AgNO_3$ spray).

Physical Measurements

Low-resolution mass spectra were obtained using a Finnigan MAT MAGNUM ion-trap quadrupole mass spectrometer equipped with a heated inlet option developed by Spectronex AG, Basle, Switzerland (70 keV, EI ionisation). Proton (^1H) and boron (^{11}B) NMR spectroscopies were performed on a variety of instruments, with final data being gathered at *ca* 11.75 T on a Varian Unity-500 instrument. The procedure for [^{11}B-^{11}B]-COSY (refs[27,28]) and ^{1}H-{^{11}B(selective)} (ref.[29]) NMR experiments were essentially as described in other recent papers from our laboratories[30]. NMR chemical shifts δ are given in ppm to high-frequency (low field) of Ξ = 32.083971 MHz (nominally $Et_2O·BF_3$ in $CDCl_3$)

for ^{11}B (quoted ±0.5 ppm) and Ξ = 100 MHz (SiMe$_4$) for ^{1}H (quoted ±0.05 ppm), Ξ being defined as in the literature[31]. Residual solvent ^{1}H resonances were used as internal secondary standards. Coupling constants $^1J(^{11}$B-^{1}H) are taken from resolution-enhanced ^{11}B spectra with digital resolution ±8 Hz and are given in Hz.

HPLC Separations of the Monomethyl Derivatives **2b** and **2c**

Analytical system: Merck–Hitachi, 6200 Intelligent pump, D-6000 Interface, Rheodyne 7125 injection valve with a 20-μl sample loop, L 7450 Diode Array detector with 7000 Manager Software 2.1. Preparative system: Micropump LCP 3001 with preparative option, Rheodyne 7010 injection valve with a 2-ml sample loop, UV-VIS variable wavelength detector LCD 2040 with a preparative cell, TZ 4200 line recorder (ECOM, Prague). Chromatographic conditions: Analytical separation; a CGC column (Tessek Ltd., Prague) 300 × 3 mm packed with Separon SGX (silica, 7 μm), hexane as the mobile phase, flow rate 0.8 ml/min, detection by Diode Array 200–300 nm, sensitivity range 0–2.0 A.U.F.S. Capacity factors (k'), selectivity (α) and resolution values (R_s) for this separation were: k_1' = 0.98 (**2c**), k_2' = 1.05 (**2b**), α = 1.07, R_s = 1.08 (the k' values for biphenyl and terphenyl used as the references under identical chromatographic conditions were 0.81 and 1.16, respectively). Preparative separation; stainless-steel column (250 × 25 mm) packed with Separon SGX (7 μm) (60 000 theoretical plates/m for both isomers), hexane as the mobile phase, flow rate 25 ml/min, detection by UV at 240 nm, sensitivity 3 A.U.F.S.; sample amount 35 mg *per* single injection dissolved in 1 ml of the mobile phase; five successive injections were applied and both isomers were obtained in more than 98% purity (monitoring by analytical HPLC and GC-MS) collecting the eluent from the ascending part of the first peak (**2c**) and the descending part of the second one (**2b**).

Synthesis of *nido*-5,6-C$_2$B$_8$H$_{12}$ (**2a**)

Under intensive stirring and cooling to 0 °C, a 1 mol l^{-1} aqueous solution of K$^+$[7,8-C$_2$B$_9$H$_{12}$]$^-$ (anion **1a**; 20 ml, 20 mmol)[25] was added in several portions into a mixture containing 35 g of [Fe(H$_2$O)$_6$]Cl$_3$, 250 ml of water, 20 ml of concentrated aqueous hydrochloric acid, and 100 ml of hexane. After the initial slightly exothermic reaction had ceased (*ca* 1 h), the mixture was *intensively* stirred for additional 6 h (hydrogen evolution, partial precipitation of yellow materials). The hexane layer was then separated, washed with 100 ml of water, 100 ml of 5% K$_2$CO$_3$, and again with two 50 ml portions of water. The hexane solution thus obtained was dried over MgSO$_4$, filtered, and the filtrate evaporated *in vacuo* at the lowest possible temperature (*ca* 0 °C) to obtain an oily residue which was then quickly dried at ambient temperature or below to obtain **2a** as a crystalline solid. Typically, 1.3–1.4 g (58-62%) of **2a** was isolated as a white crystalline material that should be stored at lower temperatures (below –10 °C) under a dinitrogen atmosphere. The product thus obtained is of sufficient purity for further syntheses. Analytical samples or older batches can be purified by vacuum (oil pump) sublimation at *ca* 50–70 °C (bath) onto a finger cooled below 0 °C. An additional crop of **2a** (300–500 mg) may be obtained if the aqueous layer separated from the original reaction mixture (residual mixture from the first separation of the hexane layer) is covered again with the hexane distillate from the above synthesis (this still contains some **2a** due to its volatility). This mixture is stirred overnight and the hexane layer is then worked up in the same manner as outlined above.

Synthesis of the *C*-Substituted Derivatives 5,6-R^{1}R^2-*nido*-5,6-C$_2$B$_8$H$_{10}$ (R^1, R^2 = H, Me (**2b**); Me, H (**2c**); Me, Me (**2d**); H, Ph (**2e**); Ph, H (**2f**); and Ph, Ph (**2g**))

A similar procedure as in the preceding experiment was applied to 1 mol l^{-1} aqueous solutions of the K$^+$[7,8-R^{1}R^2-*nido*-7,8-C$_2$B$_9$H$_{10}$]$^-$ salts (R^1, R^2 = H, H (**1a**); Me, H (**1b**); Me, Me (**1c**); Ph, H (**1d**);

and Ph, Ph (**1e**)) (5 ml, 5 mmol each). These were added in one portion into a mixture containing 10 g [Fe(H$_2$O)$_6$]Cl$_3$, 50 ml of water, 5 ml of concentrated hydrochloric acid, and 50 ml of hexane. After the initial slightly exothermic reaction had ceased (*ca* 1 h), the mixture was *intensively* stirred for additional 6 h (hydrogen evolution, precipitation of yellow materials). Further work-up as in the preceding experiment gave the title compounds (yields and other characteristics are summarized in Table I) which were characterized by NMR spectroscopy (Table II) and mass spectrometry (Table I). Individual compounds were separated by column or preparative TLC in hexane. The monomethyl derivatives **2b** and **2c** were separated by preparative HPLC as described above, and the monophenyl analogues were separated by repeated preparative TLC in hexane.

RESULTS AND DISCUSSION

The original Plesek synthesis[1,2], consisting of the addition of an acidic solution of [Fe(H$_2$O)$_6$]Cl$_3$ to an aqueous solution of the K$^+$ salt of the [*nido*-7,8-C$_2$B$_9$H$_{12}$]$^-$ anion[25] (**1a**) (see Eq. (*1*)), resulted in the formation of the parent 5,6-C$_2$B$_8$H$_{12}$ dicarbaborane **2a** in 45% yield. Since then, we have repeated the synthesis of **2a** many times and found that the yield can be substantially improved to a standard 58–62% when the reverse addition of reactants is employed. Thus, the reaction is now better carried out by the addition of a 1 mol l^{-1} aqueous solution of the anion **1a** to a dilute, acidic solution of [Fe(H$_2$O)$_6$]Cl$_3$, rather than *vice versa*.

We have now applied a similar procedure (see Eq. (*4*)) to the substituted derivatives of **1a**, using the K$^+$ salts of the [7,8-R^{1}R^2-*nido*-7,8-C$_2$B$_9$H$_{10}$]$^-$ anions (where R^1, R^2 = H, Me (**1b**); Me, Me (**1c**); Ph, H (**1d**); and Ph, Ph (**1e**)) to produce the corresponding series of carbon-substituted derivatives of **2a**, *viz.* the neutral species 5,6-R^{1}R^2-*nido*-5,6-C$_2$B$_8$H$_{10}$ (where R^1, R^2 = H, Me (**2b**); Me, H (**2c**); Me, Me (**2d**); H, Ph (**2e**); Ph, H (**2f**); and Ph, Ph (**2g**)) in yields of 5 to 32% (Table I). Of these, **2b**, **2c** and **2f** are previously

TABLE I
The series of *nido*-5,6-dicarbadecaborane compounds isolated from the modified Plesek synthesis

Compound	Yield, %	R_F, anal. TLC	m/z_{max} (%)	Appearance
5,6-C$_2$B$_8$H$_{12}$ **2a**	58–62	0.42[a]	124	solid
6-Me-5,6-C$_2$B$_8$H$_{11}$ **2b**[b]	27	0.28[c]	138 (10)	liquid
5-Me-5,6-C$_2$B$_8$H$_{11}$ **2c**[b]	9	0.28[c]	138 (4)	liquid
5,6-Me$_2$-5,6-C$_2$B$_8$H$_{10}$ **2d**	32	0.30[c]	152 (15)	liquid
6-Ph-5,6-C$_2$B$_8$H$_{11}$ **2e**[d]	10	0.25[c]	200 (23)	solid
5-Ph-5,6-C$_2$B$_8$H$_{11}$ **2f**[d]	5	0.20[c]	200 (5)	solid
5,6-Ph$_2$-5,6-C$_2$B$_8$H$_{10}$ **2g**	12	0.27[c]	276 (24)	solid

[a] 10% CH$_2$Cl$_2$–hexane. [b] The mixture of **2b** and **2c** was separated by preparative HPLC. [c] Hexane. [d] The mixture of **2e** and **2f** was separated by repeated TLC in hexane.

unreported. As expected, the reaction of Eq. (*4*), when applied to the monosubstituted derivatives of **1** (*i.e.* for $R^2 = H$), leads to a mixture of 5- and 6-substituted derivatives of **2a**. As seen from Table I, the total yields of the derivatives **2** drop progressively with the number of substituents and in the order Me > Ph. Moreover, the yields of individual substituted derivatives are generally lower than those from the recently reported synthesis from $(Me_2S)B_9H_{13}$ (ref.[8]).

$$[R^1R^2C_2B_9H_{10}]^- + Fe^{3+} + 3\ H_2O \longrightarrow R^1R^2C_2B_8H_{10} + B(OH)_3 + Fe^{2+} + 3/2\ H_2 \quad (5)$$

As suggested by Plesek and Hermanek[1,2], the formation of the parent species *nido*-$5,6$-$C_2B_8H_{12}$ (**2a**) is consistent with oxidative elimination of the B(9) boron vertex, which is the one adjacent to the C(7) carbon vertex in the open pentagonal face in structure **I**. This mechanism is also applicable to all the substituted derivatives of **1**. For the monosubstituted derivatives (see Table I and Scheme 1), in which the B(9) and B(11) vertices of the starting eleven-vertex substrates **1b** and **1d** are mutually nonequivalent, the amount of the 6-substituted derivatives **2b** and **2e** in the resulting product mixture is higher than that of the 5-isomers **2c** and **2f** (for R = Me and Ph). This is in agreement with a preferential activation towards elimination of the B(11) atom, *i.e.* the boron site adjacent to the substituted carbon site in structure **1**.
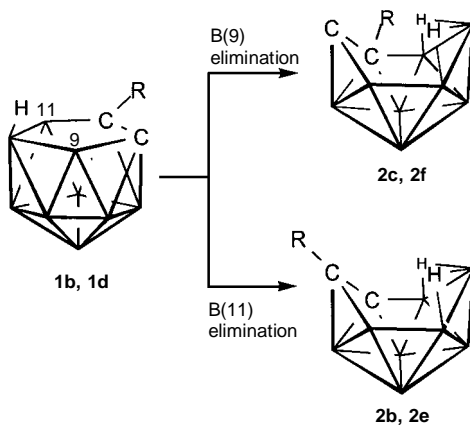
SCHEME 1

The constitution of the substituted derivatives of type **2** was established by NMR spectroscopy. All cluster {BH} and {CH} ^{11}B and ^1H resonances were interrelated by [^{11}B-^{11}B]-COSY (refs[27,28]) and ^1H-{^{11}B(selective)} (ref.[29]) experiments, which permitted complete assignments and thence comparisons with the parent analogue **2a** (ref.[32]). In particular, the results of mass spectrometry (Table I) and the observed NMR data for the previously unreported derivatives of type **2**, specifically **2b**, **2c** and **2f**

(Table II), are in excellent agreement with their formulation as the specified *C*-substituted compounds of the *nido* ten-vertex 5,6-dicarbadecaborane constitution **2**. This general type-**2** constitution was of course previously established unambiguously by single-crystal X-ray crystallography[33] and NMR studies[32]. Intercorrelation of the ^{11}B and ^{1}H chemical shifts for all the *C*-substituted derivatives of **2a** thus far isolated is

TABLE II
NMR data

Compound	Nucleus	δ, ppm (assignment, $^{1}J_{BH}$, Hz)
6-Me-*nido*-5,6-C$_2$B$_8$H$_{11}$ (**2b**)	^{11}B^a	3.5 (B7,~160b^b), 2.25 (B1,8,~165^b), –3.7 (B3,143), –6.3 (B9,161), –9.8 (B10,156^c), –23.0 (B2,177), –41.0 (B4,152)
	^{11}B-^{11}B^d	B7-B8, B7-B3, B7-B2, B1-B3, B1-B10, B1-B10, B1-B2, B1-B4, B8-B3, B8-B4, B3-B2, B3-B4, B9-B10, B9-B4, B10-B4
	^{1}H^e	4.54 (H5), 3.35 (H1), 3.23 (H7), 3.05 (H9), 3.01 (H8), 2.85 (H3), 2.50 (H10), 2.21 (6-Me, 3 H), 1.26 (H2), 0.59 (H4), –2.34 (μH9,10), –2.50 (μH8,9)
5-Me-*nido*-5,6-C$_2$B$_8$H$_{11}$ (**2c**)	^{11}B^d	6.9 (B1,156), 4.5 (B7,149), 1.0 (B8,156), –1.7 (B3,~158^b), –3.0 (B9,~190^b), –6.5 (B10,152^c), –24.9 (B9,177), –39.5 (B4,155)
	^{11}B-^{11}B^c	B1-B3, B1-B10, B1-B2, B1-B4, B7-B8, B7-B3, B7-B2, B8-B3, B8-B9, B8-B4, B3-B2, B3-B4, B9-B10, B9-B4, B10-B4
	^{1}H^e	6.36 (H6), 3.61 (H1), 3.47 (H7), 3.17 (H9), 2.98 (H8), 2.89 (H3), 2.54 (H10), 2.30 (5-Me,3 H), 0.94 (H2), 0.75 (H4), –2.04 (μH9,10), –2.57 (μH8,9)
5-Ph-*nido*-5,6-C$_2$B$_8$H$_{11}$ (**2f**)	^{11}B^a	5.6 (B1,7,~156^b), 3.1 (B8,~150^b), –0.4 (B3,143^b), –1.7 (B9,~180^b), –4.5 (B10,158^b), –23.6 (B2,184), –38.4 (B4,156)
	^{11}B-^{11}B^d	B1,7-B3; B1,7-B4; B8-B3; B8-B4; B3-B2; B9-B4; B10-B4
	^{1}H^e	7.57 (Ph,m,2 H), 3.59 (Ph,m,3 H), 6.74 (H6), 3.93 (H1), 3.59 (H7), 3.24 (H9), 3.13 (H8), 3.06 (H3), 2.79 (H10), 1.19 (H2), 0.87 (H4), –1.72 (μH9,10), –2.30 (μH8,9)

^{a} δ(^{11}B) values in CDCl$_3$ determined from ^{11}B{^{1}H(broadband)} measurements with assignments by [^{11}B-^{11}B]-COSY NMR spectroscopy; all signals are doublets. ^{b} Values uncertain due to peak overlap. ^{c} Additional H splitting. ^{d} Measured under the conditions of {^{1}H(broadband)} decoupling. ^{e} Assignments by ^{1}H-{^{11}B(broadband)} and ^{1}H-{^{11}B(selective)} NMR spectroscopy; all signals are singlets in the ^{1}H-{^{11}B(broadband)} NMR spectrum.

demonstrated graphically in Figs 1 and 2, respectively. The comparison reveals a straightforward similarity for the corresponding resonances to those that are well recognized[32] for the parent compound **2a**. The chemical shift changes observed, of which the most marked are the α and antipodal shifts arising from the Me and Ph substitution[34], are all in agreement with the expected[30] electronic effects of those particular substituents on the designated cage carbon vertices.

In conclusion, therefore, it is now established that *C*-substituted derivatives of **2a** can also be conveniently prepared by the Plesek reaction. In comparison to the recently reported $(Me_2S)B_9H_{13}$ method[8], however, the yields of the substituted derivatives are generally lower. Nevertheless, the Plesek reaction is the only method for the preparation of 5-substituted derivatives of **2a**, which are not available by the $(Me_2S)B_9H_{13}$ method. These mono- and disubstituted derivatives of **2a** have good potential for use as important starting materials for obtaining other substituted compounds in a variety of areas of carborane[9–12,21–23] and heterocarborane[20] chemistry.
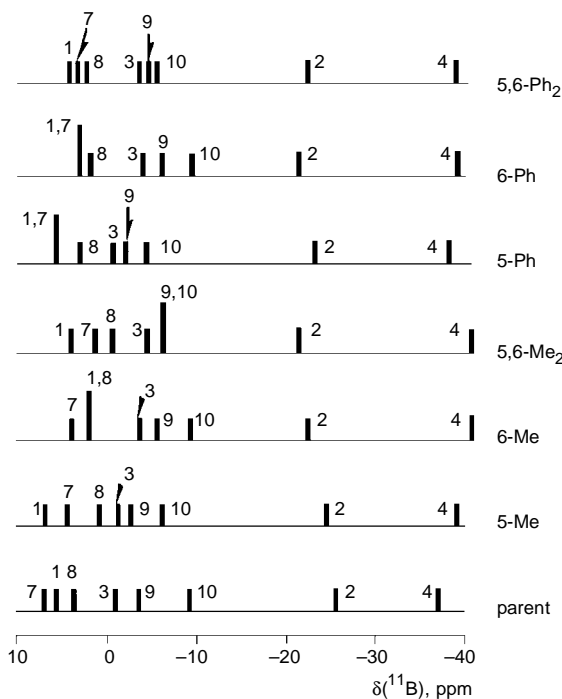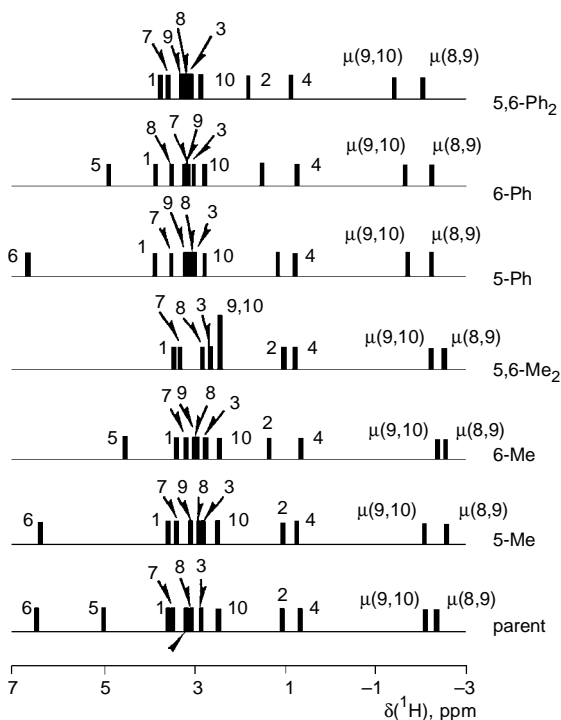

FIG. 1

Stick representation and comparison of the ^{11}B chemical shifts and relative intensities for the unsubstituted 5,6-*nido*-$C_2B_8H_{12}$ (**2a**) (data from ref.[33]) and its 5-Me (**2c**), 6-Me (**2b**), 5,6-Me$_2$ (**2d**) (data from ref.[8]), 5-Ph (**2f**), 6-Ph (**2e**), and 5,6-Ph$_2$ (**2e**) (data from ref.[8]) derivatives

FIG. 2

Stick representation and comparison of the ^{1}H chemical shifts and relative intensities for the unsubstituted 5,6-*nido*-C$_2$B$_8$H$_{12}$ (**2a**) (data from ref.^{33}) and its 5-Me (**2c**), 6-Me (2b), 5,6-Me$_2$ (**2d**) (data from ref.^{8}), 5-Ph (**2f**), 6-Ph (**2e**) (data from ref.^{8}), and 5,6-Ph$_2$ (**2e**) (data from ref.^{8}) derivatives

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