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A convenient route to carbon-substituted derivatives of *nido*-5,6-$C_2B_8H_{12}$ [1]

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Abstract

An alternative route to the parent *nido*-5,6-$C_2B_8H_{12}$ dicarbaborane is reported together with a convenient synthesis of its carbon-substituted derivatives. The method is based on reactions between 4-(Me_2S)-*arachno*-B_9H_{13} and alkynes $R^1R^2C_2$ (where R^1R^2 = H,H; Me, Me; Ph,H, and Ph,Ph) in toluene at reflux. The characteristic reaction mode is a dicarbon insertion into the 9-vertex *arachno* cluster to produce a series of the 5,6-R^1R^2-*nido*-5,6-$C_2B_8H_{10}$ species combined with concomitant elimination of one {BH} vertex. The products were characterised by high-field ^1H and ^{11}B NMR spectroscopy and mass spectrometry associated with [^{11}B–^{11}B]-COSY and $^1H\{^{11}B(selective)\}$ measurements that permitted complete assignments of all resonances to individual cluster {BH} units. © 1998 Elsevier Science S.A.

Keywords: Carbon-substituted derivatives; Dicarbaborane; Aqueous solution; Synthesis

1. Introduction

The neutral, 10-vertex *nido* [3] [2–4] dicarbaborane 5,6-$C_2B_8H_{12}$ has become one of the most essential synthons of dicarbaborane chemistry [4] [5,6]. For instance, it has been employed as a starting material for the preparation of other basic dicarbaboranes, 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-$C_2B_7H_{13}$ [7], *arachno*-6,9-$C_2B_8H_{14}$ [8–10], [*arachno*-4,5-$C_2B_6H_{11}$]$^-$ [11], the derivatives of *arachno*-$C_4B_8H_{14}$ [12,13], and 14-vertex methyltricarbaazaboranes [14]. As we have recently reported, 5,6-$C_2B_8H_{12}$ has become a source of tricarbollides, the first representatives of the 11-vertex series of tricarbaboranes [15–17]. The first report on the synthesis of *nido*-5,6-$C_2B_8H_{12}$ and its 5,6-dimethyl derivative is that by Schaeffer's group [18]. These compounds were isolated from reactions between the octaborane *nido*-B_8H_{12} and alkynes as in Eq. (1):

$$nido-B_8H_{12}+R_2C_2 \rightarrow 5,6-R_2-nido-5,6-C_2B_8H_{10}+H_2 \qquad (1)$$

where R = H and Me.

This method is rather inconvenient because of general inaccessibility and instability of the starting B_8H_{12} borane [19]. Plešek and Heřmánek have developed a more convenient method [20,21] starting from the readily available [*nido*-7,8-$C_2B_9H_{12}$] anion [22,23]. This anion can be oxidised by $FeCl_3 \cdot 6\,H_2O$ in an acidified aqueous solution to give a 45% yield of *nido*-5,6-$C_2B_8H_{12}$, as in stoichiometric Eq. (2):

$$[C_2B_9H_{12}]^- + Fe^{+3} + H_3O^+ + 2\,H_2O \rightarrow C_2B_8H_{12} + B(OH)_3 + Fe^{+2} + 2\,H_2 \qquad (2)$$

The disadvantage of this method is that the yields of this reaction decrease significantly when substituted derivatives of the [*nido*-7,8-$C_2B_9H_{12}$]$^-$ anion are employed, which complicates a reasonable synthesis of the

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[1] Dedicated to Professor K. Wade on the occasion of his 65th birthday for his essential contributions to the area of cluster boron chemistry. All cluster chemists know Wade's electron-counting rules and use them for the benefit of chemistry.

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[3] for classification of cluster compounds according to the number of skeletal electrons see, for example, Refs. [1–4].

[4] See, for example, Refs. [5,6].

substituted derivatives of the *nido*-5,6-$C_2B_8H_{12}$ series (B. Štíbr et al., Collect. Czech. Chem. Commun., manuscript in preparation). Preliminary results from our and Shore's groups indicated that also the 9-vertex *arachno* clusters, 4-CB_8H_{14} [24] and $B_9H_{13} \cdot OEt_2$ [25], can be employed as a convenient source for the preparation of the C-substituted derivatives of *nido*-5,6-$C_2B_8H_{12}$. Here we report a convenient synthesis of these derivatives from the stable and readily available ligand-derivative 4-(Me_2S)-*arachno*-B_9H_{13}. Simplified structures and numbering of compounds discussed in this work are in general structures **1**–**3** below, with the vertices of individual polyhedra denoting cluster BH units.

2. Experimental

2.1. General

The Aldrich toluene was dried over Na/benzophenone, hexane and CH_2Cl_2 were dried over CaH_2, and all were freshly distilled before use. Technical acetylene was passed through a −78°C trap and the substituted alkynes (Aldrich) were of reagent grade and used as purchased. All reactions were carried out under dry dinitrogen [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 diiodine vapour, followed by 2% aqueous $AgNO_3$ spray).

2.2. Physical measurements

Low-resolution mass spectra were obtained using a Finnigan Mat Magnum ion trap quadrupole mass spectrometer equipped with a heated inlet option, as developed by Spectronex AG, Basle, Switzerland (70 eV, EI ionisation). Proton (^1H) and boron (^{11}B) NMR spectroscopy was performed at 11.75 T on a Varian X L-500 instrument. The procedure for [^{11}B–^{11}B]-COSY [27,28] and ^1H-{^{11}B(selective)} [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 $\Xi =$ 32.083971 MHz (nominally $F_3B \cdot OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0.5 ppm) and $\Xi = 100$ MHz ($SiMe_4$) for ^1H (quoted ±0.05 ppm), Ξ being defined as in the literature [31]. Residual solvent ^{11}H resonances were used as internal secondary standards. Coupling constants $^1J(^{11}B–^1H)$ are taken from resolution-enhanced ^{11}B spectra with digital resolution 8 Hz and are given in Hz.

2.3. Preparation of 4-(Me_2S)-arachno-B_9H_{13} (**1**)

A modification of the method reported for the Et_2S analogue [32] was employed. A solution of $B_{10}H_{14}$ (1.22 g; 10 mmol) was dissolved in 10 ml of dimethyl sulphide and the solution was left to stand at ambient temperature for 48 h (hydrogen evolution). The excess dimethyl sulphide was then distilled off under vacuum into a −78°C trap (ca. 8 ml recovered). The residual solid was heated with 15 ml of methanol at reflux for 2 h (hydrogen evolution), and the solution obtained was left to crystallise for 12 h. The white crystalline material was isolated by filtration, washed with 20 ml of hexane, and vacuum-dried to give the first crop of **1** (946 mg). To remove possible contaminants, the hexane washings rotaevaporated and subjected to preparative TLC in 50% CH_2Cl_2/hexane (v/v) (column chromatography may be used as well) to collect the main band of R_F 0.5, which was extracted by CH_2Cl_2. Evaporation of the extract gave the second crop (363 mg; total yield 1309 mg, 76%) of **1**, which was identified by NMR spectroscopy.

2.4. Preparation of nido-5,6-$C_2B_8H_{12}$ (**2a**)

Acetylene was bubbled through a solution of compound **1** (861 mg, 5 mmol) in 50 ml of toluene, while the temperature of the reaction mixture was raised to reflux and the bubbling continued intensively for additional 15 min (dihydrogen evolution). The mixture was then cooled to room temperature and the toluene distilled off using a standard rotary evaporator. The residual oily material was dried in vacuo at ambient temperature, and the solid material obtained was sublimed at 50°C (bath) onto a finger cooled to 0°C. The sublimate (the average of 330–368 mg, 53–60%, from several experiments) was then removed and identified as **2a** by NMR spectroscopy.[5]

2.5. Preparation of 5,6-Me_2-nido-5,6-$C_2B_8H_{10}$ (**2b**)

Under cooling to 0°C, to a solution of compound **1** (210 mg, 1.22 mmol) in 20 ml of toluene was added a solution of Me_2C_2 (20 ml of a 0.65 M solution in toluene; 12.9 mmol of Me_2C_2) and the reaction mixture was heated at reflux for 15 min (slow dihydrogen

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[5] A similar BH vertex removal via hydroboration was recently observed in the *nido*-4,5-$C_2B_6H_{10}$ series [33].

evolution). The mixture was then cooled to room temperature and the toluene distilled off as in the preceding experiment. The residual oily material was dried in vacuo at room temperature and the oily material obtained was subjected to preparative TLC using a 10% $CHCl_3$ solution in hexane as the mobile phase. The main band of R_F (prep.) 0.45 was removed by CH_2Cl_2, the extract was evaporated, and the residual liquid dried in vacuo at room temperature. This procedure was followed by distillation into a 0°C trap of the vacuum line to obtain 130 mg (85%) of a liquid compound **2b**. This was identified by NMR spectroscopy (see Table 1) and mass spectrometry [mass calcd. for $^{12}C_4^{11}B_8^1H_{16}$ 152; found 152 (15%)]. For larger-scale preparations, it is convenient to carry out the reaction in benzene, using a sealed ampoule or an autoclave to prevent the volatilisation of the alkyne from the reaction mixture.

*2.6. Preparation of 6-Ph-nido-5,6-$C_2B_8H_{11}$ (**2c**)*

A solution of compound **1** (250 mg, 1.4 mmol) in 20 ml of toluene was heated at reflux with PhC_2H (286 mg, 2.8 mmol) for 15 min (dihydrogen evolution). The orange mixture was then cooled to room temperature and the toluene distilled off. The residual oily material was dried in vacuo at room temperature, and the oily material obtained was subjected to preparative TLC, using hexane as the mobile phase. The main band of R_F (prep.) 0.35 was removed by CH_2Cl_2, the extract was evaporated, and the residual liquid dried in vacuo at room temperature to obtain 144 mg (52%) of compound **2c**, which was identified by NMR spectroscopy (see Table 1) and mass spectrometry [mass calcd. for $^{12}C_8^{11}B_8^1H_{16}$ 200, found 200 (23%)]. Compound **2c** can be isolated as a low-melting solid by careful distillation at ca. 80°C (bath), collecting the distillate on the walls of a sublimation tube at 0°C or in the 0°C trap of a vacuum line.

*2.7. Preparation of 5,6-Ph_2-nido-5,6-$C_2B_8H_{10}$ (**2d**) and 1,2-Ph_2-closo-1,2-$C_2B_8H_8$ (**3a**)*

A solution of compound **1** (250 mg, 1.4 mmol) in 20 ml of toluene was heated at reflux with Ph_2C_2 (498 mg,

Table 1
NMR data

Compound	Nucleus	δ (assignment, $^1J_{BH}$ (Hz))
4-(Me_2S)-*arachno*-B_9H_{13}, **1**	$^{11}B^a$	17.0 (B7, 150), 3.3 (B1, 137), − 17.5 (B5,9, 137), − 22.6 (B6,8,128)^b, −24.8 (B4, 135), −40.4 (B2,3, 146)
	$^{11}B–^{11}B^c$	B7–B6,8; B7–B2,3; B1–B4,5; B1–B4; B1–B2,3; B5,9–B4; B5,9–B2,3; B6,8–B2,3
	$^1H^d$	4.08 (H7), 3.05 (H1), 2.55 (*Me_2*S, 6 H), 1.98 (*exo*-H6,8), 1.83 (H5,9), 0.47 (H2,3), 0.04 (*endo*-H4), −0.01 (*endo* H6,8), −3.52 (μH5,6/μH8,9, 2 H)
5,6-Me_2-*nido*-5,6-$C_2B_8H_{10}$, **2b**	$^{11}B^a$	4.1 (B1, 156), 2.1 (B7, 147), −0.1 (B8, 153), −4.6 (B3, 146), −6.5 (B9,10, ∼156^e), −21.1 (B2, 174), −41.0 (B4, 153)
	$^{11}B–^{11}B^c$	crosspeaks: 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–B4, B10–B4;
	$^1H^d$	3.46 (H1), 3.28 (H7), 3.01(H9 or H10), 2.88 (H8), 2.72 (H3), 2.57 (H10 or H9), 2.15 and 2.13 (5- and 6-Me, 3 · H each), 1.02 (H2), 0.85 (H4), −2.32 (μH9,10), −2.64 (μH8,9)
6-Ph-*nido*-5,6-$C_2B_8H_{11}$ **2c**	$^{11}B^a$	2.8 (B1, 7 ∼ 143^e), 2.0 (B8, 147), −4.0 (B3, 149), −5.6 (B9, 165), −9.8 (B10, 156/28), −21.6 (B2, 181), −39.5 (B4, 152)
	$^{11}B–^{11}B^c$	crosspeaks: B1,7–B8; B1,7–B3; B1,7–B10; B1,7–B2; B1,7–B4; B8–B3; B8–B4; B3–B2; B3–B4; B9–B4, B10–B4;
	$^1H^d$	7.62 (Ph, m, 2 H), 7.43 (Ph, m, 3 H), 4.96 (H5), 3.70 (H1), 3.49 (H8), 3.19(H7), 3.16 (H9), 3.03 (H3), 2.77 (H10), 1.57 (H2), 0.82 (H4), −2.11 (μH9,10), −2.64 (μH8,9)
5,6-Ph_2-*nido*-5,6-$C_2B_8H_{10}$, **2d**	$^{11}B^{a,e}$	4.3 (B1, −^{e}), 3.1 (B7, −^{e}), 2.3 (B8, −^{e}), −3.4 (B3, −^{e}), −4,7 (B^9, −^{e}) −5.3 (B10, −^{e}) −22.6 (B2, 174), −39.2 (B4, 156)
	$^{11}B–^{11}B^c$	crosspeaks: B1–B3; B1–B2; B1–B4; B7–B8^f, B7–B3; B8–B3; B8–B4; B3–B2; B3–B4; B9–B4, B10–B4
	$^1H^d$	7.24-6.76 (5,6-Ph_2, m, 10 H), 3.75 (H1), 3.50 (H7), 3.22 (H8), 3.07 (H3), 3.27 (H9), 2.92 (H10), 1.90 (H2), 0.91 (H4), −1.58 (μH9,10), −2.05 (μH8,9)
1,2-Ph_2-*closo*-1,2-$C_2B_8H_8$, **3a**	$^{11}B^{a,e}$	32.5 (B10, 172), −5.1 (B4, 169), −16.7 (B3,5, 178), −20.6 (B6,9, 166), −23.6 (B7,8, 154)
	$^{11}B–^{11}B^c$	B10–B6,9; B10–B7,8; B4–B3,5; B4–B7,8; B3,5–B6,9; B3,5–B7,8
	$^1H^d$	7.63-6.94 (1,2-Ph_2, m, 10 H), 5.98 (H10), 3.17 (H3,5), 2.78 (H4), 1.51 (H6,9), 1.41 (H7,8)

[a] $\delta(^{11}B)$ values in $CDCl_3$ determined from $^{11}B\{^1H$(broadband)$\}$ measurements with assignments by [$^{11}B–^{11}B$]-COSY NMR spectroscopy.

[b] Broad doublet.

[c] Measured under the conditions of $\{^1H$(broadband)$\}$ decoupling.

[d] Assignments by ^1H-$\{^{11}B$(broadband)$\}$ and ^1H-$\{^{11}B$(selective)$\}$ NMR spectroscopy; unless stated otherwise (m = multiplet), all signals are singlets in the ^1H-$\{^{11}B$(broadband)$\}$ NMR spectrum.

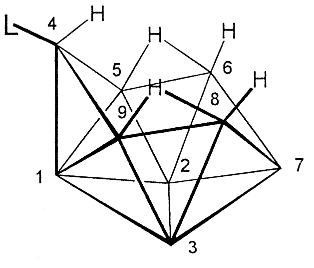
[e] Values uncertain due to peak overlap.

[f] Uncertain crosspeaks due to close proximity of resonances.

2.8 mmol) for 15 min (dihydrogen evolution). The orange mixture was then cooled to room temperature and the toluene distilled off. The residual oily material was dried in vacuo at room temperature and the oily residue obtained was subjected to preparative TLC using hexane as the mobile phase (three subsequent developments on the same TLC plate) to develop two main bands of R_F (prep.) ca. 0.45 and 0.35. These were removed by CH_2Cl_2, the extracts were evaporated, and the residual materials dried in vacuo at room temperature to obtain 131 mg (36%) of the *closo* compound **3a** [mass calcd. for $^{12}\mathrm{C}_{14}{}^{11}\mathrm{B}_{8}{}^{1}\mathrm{H}_{18}$ 274, found 274 (13%)] and 190 mg (52%) of the *nido* species **2d** [mass calcd. for $^{12}\mathrm{C}_{14}{}^{11}\mathrm{B}_{8}{}^{1}\mathrm{H}_{20}$ 276, found 276 (24%)], respectively, from individual bands. Both compounds thus isolated were further identified by NMR spectroscopy (see Table 1). Analytical samples can be purified and isolated as solid materials by careful volatilisation at ca. 80–100°C (bath), collecting the condensate on the walls of a sublimation tube at 0°C.

3. Results and Discussion

Treatment of 4-(Me_2S)-*arachno*-B_9H_{13} (**1**) with approximately a twofold excess of alkynes $R^1R^2C_2$ in toluene (reflux, 15 min) resulted in the formation of a series of the 5,6-R^1R^2-*nido*-5,6-$C_2B_8H_{10}$ species of general structure **2** [where R^1, R^2 = H, H (**2a**); Me, Me (**2b**); Ph, H (**2c**), and Ph, Ph (**2d**)] in yields 53–60, 85, 52, and 52%, respectively. The compounds were isolated by the evaporation of the toluene, followed by preparative TLC separation of the main products in hexane (or its mixtures with CH_2Cl_2 or $CHCl_3$) and further purification by distillation or sublimation. Column chromatography may be employed larger-scale syntheses of individual compounds. As suggested by NMR spectroscopy, the reactions are accompanied, to a variable extent, by the formation of a complex mixture that apparently consists of diverse positional isomers of general formula 7,8-R^1R^2-(Me_2S)-*nido*-7,8-$C_2B_9H_9$ and of the starting compound **1**. This inseparable mixture can be, however, readily removed from compounds of types **2** and **3** by chromatography.



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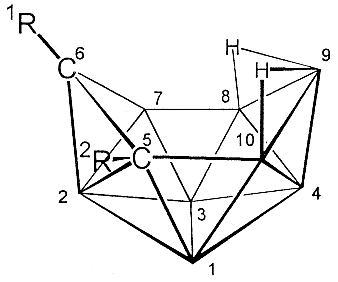
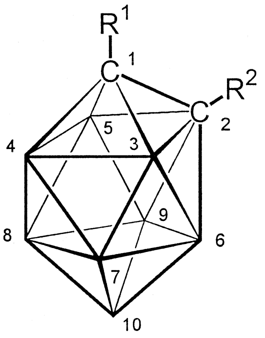


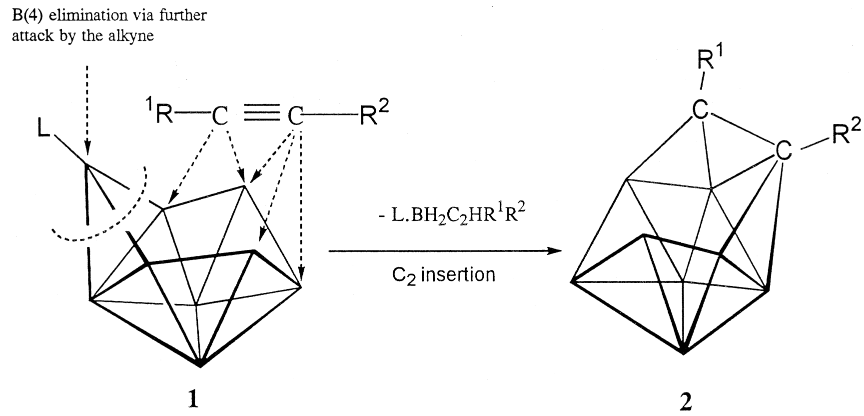
2

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



3

R^1	R^2	
Ph	Ph	**3a**



Scheme 1.

The formation of the *nido* 10-vertex dicarbaboranes of type **2** seems to be in agreement with the stoichiometry as in Eq. (3):

$$2\,R^1R^2C_2 + Me_2S \cdot B_9H_{13} \rightarrow R^1R^2C_2B_8H_{10} + Me_2S \cdot BH_2C_2H\,R^1R^2 \qquad (3)$$

As shown in a simplified Scheme 1 (*exo* and *endo* hydrogens omitted for clarity), the reaction is consistent with the insertion of both alkyne carbons into the 9-vertex *arachno* cage of compound **1**. The reaction proceeds under simultaneous elimination of the B(4) vertex, which may be removed as $Me_2S \cdot BH_2C_2H\,R^1R^2$ by hydroboration at that site [33]. This borane adduct is apparently decomposed by exposure to air during the chromatographical experiment; nevertheless, the fate of the allylborane decomposition products was not followed. It should be noted that the reaction with phenyl acetylene proceeds in a highly regiospecific manner, only with the formation of 6-Ph-*nido*-5,6-$C_2B_8H_{11}$ (**2c**) as a single product of type **2** (without formation of the isomeric 5-Ph-*nido*-5,6-$C_2B_8H_{11}$). This regiospecificity may be consistent with steric requirements of the bulky Ph substituent during the insertion process. In the case of diphenyl acetylene, the reaction is accompanied by the dehydrogenation of **2d** and formation of 1,2-Ph_2-*closo*-1,2-$C_2B_8H_8$ (**3a**), a *closo* counterpart of **2d**; the dehydrogenation being apparently facilitated by electronic effects of the two phenyl rings.

The constitution of the products of types **2** and **3** was established by high-field NMR spectroscopy. All cluster {BH} and {CH} ^{11}B and ^{1}H resonances were interrelated by [^{11}B–^{11}B]-COSY [27,28] and ^{1}H-{^{11}B(selective)} [29] experiments, which permitted complete assignments and comparisons with corresponding parent analogues [20,21,30,34]. The observed NMR data (see Table 1) and the results of mass spectrometry for all compounds of types **2** and **3** are in a good agreement with their formulation as compounds of the 10-vertex *nido* and *closo* constitution, as established before by X-ray crystallography [35], gas-phase electron diffraction [36], and NMR studies [20,21,30,34]. Table 1 summarises more complete NMR data for earlier reported compounds **1** [37] and **2b** [18] together with those obtained for newly prepared compounds **2c**, **2d**, and **3a**. Inspection of this table also reveals a straightforward similarity of the corresponding NMR patterns to those reported for the parent compounds **2a** [20,21,30,34] and *closo*- 1,2-$C_2B_8H_{10}$ [20,21], with changes attributable to the presence of substituents on carbon vertices.

In conclusion, it should noted that the new method for the synthesis of C-substituted compounds of the 10-vertex 5,6-dicarba *nido* constitution presented above represents a notable progress in comparison with other methods so far reported [18,20,21,25] as the yields of individual syntheses exceed in all cases that reported for the parent compound **2a** [20,21]. Another advantage is a simple availability of the borane adduct 4-(Me_2S)-*arachno*-B_9H_{13}. This compound is considerably stable for longer storage and can be prepared directly from the commercially available decaborane. Another positive aspect is the short reaction time of the synthesis (15 min) and facile isolation of the reaction products. The derivatives of **2a** can be used as indispensable starting materials for the development of substitution chemistry in the currently developing areas of dicarbaboranes [5,6], heterocarboranes [14], and tricarbaboranes [15–17].

Acknowledgements

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