Unusual interaction of alkynes with nine-vertex *arachno*-monocarbaboranes 4-CB_8H_{14} and [4-CB_8H_{13}]$^-$

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Alkynes $R^1R^2C_2$ react with the neutral monocarbaborane *arachno*-4-CB_8H_{14} (**1**) at elevated temperatures (115–120 °C) under the formation of the derivatives of the ten-vertex dicarbaborane *nido*-5,6-$C_2B_8H_{12}$ (**2**) of general formula 9-Me-5,6-R^1,R^2-*nido*-5,6-$C_2B_8H_9$ (where R^1,R^2 = H,H **2a**; Me,Me **2b**; Et,Et **2c**, H,Ph **2d**, and Ph,Ph **2e**) in moderate yields (26–52%). Side reaction with PhC_2H also yields 1-Ph-6-Me-*closo*-1,2-$C_2B_8H_8$ (**3d**). In contrast, the reaction between [*arachno*-4-CB_8H_{13}]$^-$ anion (**1**$^-$) and PhC_2H produces a mixture of the *closo* anions [1-CB_7H_8]$^-$ (**4**$^-$) and [1-CB_6H_7]$^-$ (**5**$^-$) (yields 32 and 24%, respectively). Individual compounds were isolated and purified by liquid chromatography and characterized by NMR spectroscopy (^{11}B, ^{1}H and ^{13}C) combined with two-dimensional [^{11}B–^{11}B]–COSY and ^{1}H–{^{11}B(selective)}NMR techniques.

Introduction

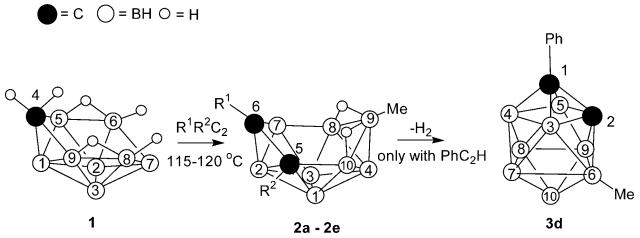
The nine-vertex monocarbaborane *arachno*-4-CB_8H_{14} (**1**), was prepared for the first time in 1976 *via* oxidative degradation of the [*nido*-6-CB_9H_{12}]$^-$ anion.[1] Improved synthesis is based on the reaction between [*nido*-7,9-$C_2B_{10}H_{13}$]$^-$ and Me_2S in the presence of concentrated hydrochloric acid.[2] The most convenient route to carborane **1** is, however, the acidic oxidation of the [*arachno*-6-CB_9H_{14}]$^-$ anion.[3,4] Kennedy *et al.* reported the preparation of the C-phenyl derivative, 4-Ph-4-CB_8H_{13}.[5] Deprotonation of **1**[1,6] leads to anions [*arachno*-4-CB_8H_{13}]$^-$ (**1**$^-$) and [*arachno*-4-CB_8H_{12}]$^{2-}$, and treatment with Et_3N generates the [*closo*-1-CB_7H_8]$^-$ anion.[4] Dehydrogenation of **1** at elevated temperatures produces a useful carborane *nido*-1-CB_8H_{12},[1] which was employed for the synthesis of the *closo* anions [1-CB_8H_9]$^-$ and [2-CB_6H_7]$^-$.[3,7] In this work we would like to extend the non-metallic chemistry of **1** and **1**$^-$ by reactions with selected alkynes that, instead of expected formation of tricarbaboranes, lead to derivatives of the ten-vertex dicarbaborane *nido*-5,6-$C_2B_8H_{12}$[8] and to removal of boron vertices, respectively.

Results and discussion

Syntheses

Treatment of the neutral monocarbaborane *arachno*-4-CB_8H_{14} (**1**) with alkynes $R^1R^2C_2$ at elevated temperatures (115–120 °C) did not yield the expected eleven-vertex tricarbaboranes $C_3B_8H_{12}$[9] but the main reaction mode was the formation of the ten-vertex dicarbaboranes 9-Me-5,6-R^1,R^2-*nido*-5,6-$C_2B_8H_9$ (where R^1,R^2 = H,H **2a**; Me,Me **2b**; Et,Et **2c**, H,Ph **2d**, and Ph,Ph **2e**) in moderate yields (26–52%, see Scheme 1). The process is thus consistent with the stoichiometry as in eqn (1):

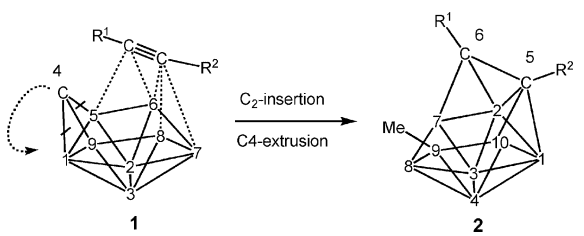
$$R^1R^2C_2 + 4\text{-}CB_8H_{14} \rightarrow 9\text{-}CH_3\text{-}5,6\text{-}R^1,R^2\text{-}5,6\text{-}C_2B_8H_9 + H_2 \quad (1)$$



Scheme 1 Formation of the 9-Me-5,6-R^1,R^2-*nido*-5,6-$C_2B_8H_9$ derivatives and 1-Ph-6-Me-*closo*-1,2-$C_2B_8H_8$ (**3d**) from 4-CB_8H_{14} (**1**) *via* alkyne insertion and dehydrogenation.

The reactions are carried out in refluxing toluene or by heating in hexane at 120 °C using a stainless steel vessel and the products were isolated by liquid chromatography in hexane.

Although no detailed mechanistic studies have been done, the reactions are in agreement with the dicarbon insertion pathway shown in Scheme 2 (extra hydrogen atoms omitted for clarity). According to this scheme, both alkyne carbons are inserted into the area identified by B-vertices 5,6,7, and 8 in the cage of **1**, while the C4 vertex is expelled into the exoskeletal site, forming thus a Me substituent at position B9 (numbering as in **1**). This process is evidently associated with interruption of the original C4–B1 and C4–B5 connectivities. One of the alkyne carbons (at R^1) becomes three-coordinate (C6 in compound **2** formed) and that at R^2 forms the tetra-coordinate C5 vertex in **2**. It should be noted that a similar removal of the cluster carbon atom, called de-insertion, was observed recently in the [*nido*-$C_2B_{10}H_{13}$]$^-$ → [*closo*-CB_9H_{10}]$^-$



Scheme 2 Proposed mechanism of the alkyne insertion.

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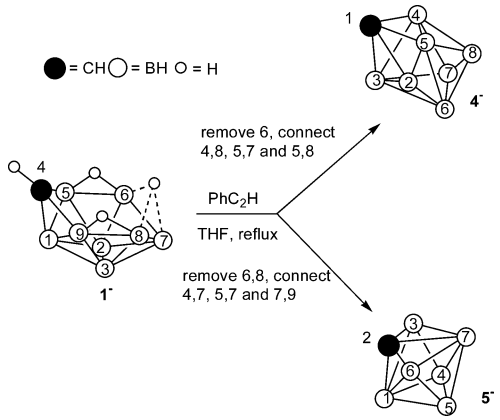
conversion.[10a] The reaction with PhC_2H is highly regiospecific, giving only 5-Ph-9-Me-*nido*-5,6-$C_2B_8H_{10}$ (**2d**). It should also be noted that, in this case, the formation of **2d** is accompanied by its dehydrogenation to 1-Ph-6-Me-*closo*-1,2-$C_2B_8H_8$ (**3d**). Partial dehydrogenation of **2e** to 1,2-Ph_2-6-Me-*closo*-1,2-$C_2B_8H_7$ (**3e**) at the reaction temperature was also observed in the reaction with Ph_2C_2, but the product could not be isolated in pure state from the mixture of other trace components.

Also the reaction between [*arachno*-4-CB_8H_{13}]$^-$ anion (**1**$^-$) and PhC_2H in THF at reflux did not produce tricarbaboranes. Instead of these, a mixture of the *closo* anions [1-CB_7H_8]$^-$ (**4**$^-$) and [1-CB_6H_7]$^-$ (**5**$^-$) (yields 32 and 24%, respectively) was isolated. Both anions were separated as their PPh_4^+ salts by liquid chromatography in CH_2Cl_2 and identified by NMR spectroscopy as reported earlier.[4,7] It seems highly probable that the reaction is based on removal of one (B6) or two (B6,8) boron vertices *via* hydroboration, followed by closure of the rest of the cage (see Scheme 3 and eqn (2) and (3)):

$$[4\text{-}CB_8H_{13}]^- + PhC_2H \rightarrow [1\text{-}CB_7H_8]^- + PhCH{=}CH{-}BH_2 + H_2 \quad (2)$$

$$[4\text{-}CB_8H_{13}]^- + 2\,PhC_2H \rightarrow [1\text{-}CB_6H_7]^- + 2\,PhCH{=}CH{-}BH_2 \quad (3)$$



Scheme 3 Formation of anions [1-CB_7H_8]$^-$ (**4**$^-$) and [1-CB_6H_7]$^-$ (**5**$^-$) from [4-CB_8H_{13}]$^-$ (**1**$^-$).

NMR spectroscopy

Graphical intercomparison of the ^{11}B NMR shifts (see Fig. 1) shows that the positions of the B9 singlet and the B4 doublet are remarkably affected by combined antipodal (A) and γ effects from the organic substituents on the C6 and C5 vertices. Most remarkably affected by the vicinal (β) C-substitution are the B2-shifts, followed by vicinal B7, B10, and B1 shifts. The ^{11}B NMR spectrum of the *closo* compound **3d** exhibits seven different doublet resonances and one B6 singlet due to Me-substitution. The four high-field doublets assigned to B5,6,7 and 9 coincidentally overlap.

Graphical interrelations of the ^{13}C NMR properties (see Fig. 2) of derivatives of type **2** shows that, besides signals attributed to the organic C-substituents, the spectra consist of downfield resonances of the cage C6 atoms (range 158–128 ppm), intermediate-field C5-resonances (range 89–65 ppm), and little varying high-field resonances of the exoskeletal 9-Me group (range −1.4 to −3.5 ppm). It is readily seen that the organic C-substituents exert

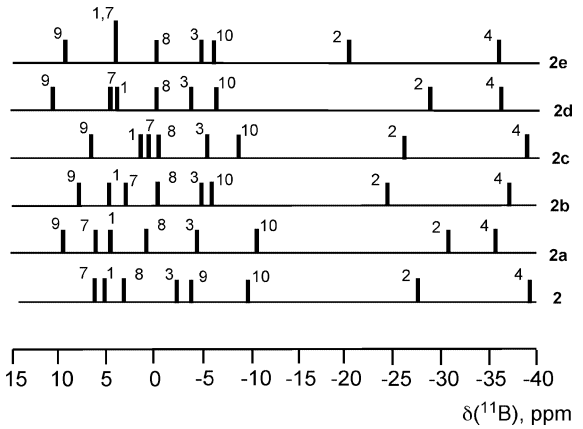


Fig. 1 Stick representation of the ^{11}B NMR spectra of compounds **2a–2e**.

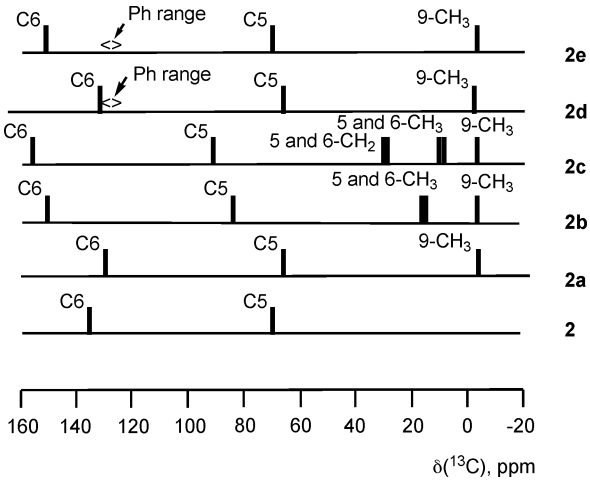


Fig. 2 Stick representation of the ^{13}C NMR spectra of compounds **2a–2e**.

remarkable combined α + β effects at the substituted carbon sites with shieldings decreasing in the order H > Ph > Me > Et. The ^{13}C NMR spectrum of the *closo* compound **3d** exhibits two distinct C1 and C2 resonances (62.4 and 54.9 ppm) along with typical 1-Ph (range 133.5–128.8 ppm) and 6-Me (30.5 ppm) resonances of these exosleletal substituents.

The ^{1}H NMR spectrum of compound **2a** exhibits two typical low-field singlet resonances of the cage CH6 and CH5 units, while that of **2d** shows only one CH6 singlet due to 5-Ph substitution. The spectra of all compounds of type **2** show a typical resonance of intensity **3** due to the 9-Me subsitution (range 0.62–0.78 ppm) along with two different, broad high-field resonances of the μ-9,10 (range −1.03 to −1.90) and μ-8,9 (range −1.61 to −2.22) hydrogen bridges. Beside these resonances, the ^{1}H–{^{11}B} NMR spectra reveal seven singlet signals due to unsubstituted BH units. The ^{1}H NMR spectrum of the *closo* compound **3d** exhibits one distinct H2 resonance (3.19 ppm) along with typical 1-Ph (7.83 and 7.57 ppm) and 6-Me (0.24 ppm) resonances due to the exoskeletal substituent.

Experimental

General

All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver,[10b] although some operations, such as column LC, were carried out in air. The starting carborane **1** was prepared according to the literature.[4] Fluka dichloromethane and hexane were dried over CaH_2 and freshly distilled before use. Other chemicals were of reagent or analytical grade and were used as purchased. Column chromatography was carried out using silica gel (Aldrich, 130–270 mesh) as the stationary phase. The purity of individual chromatographic fractions was checked by analytical TLC on Silufol (silica gel on aluminium foil; detection by I_2 vapour, followed by 2% aqueous $AgNO_3$ spray). 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, Basel, Switzerland (70 eV, EI ionisation). ^1H and ^{11}B, NMR spectroscopy was performed at 9.4 T on a Varian Mercury 400 instrument. The [^{11}B–^{11}B]–COSY[11] and ^1H–{^{11}B(selective)}[12] NMR experiments were made essentially as described earlier.[13] Chemical shifts are given in ppm to high-frequency (low field) of $\Xi = 32.083971$ MHz (nominally $F_3B.OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0.5 ppm), $\Xi = 25.144$ MHz ($SiMe_4$) for ^{13}C (quoted ±0.5 ppm), and $\Xi = 100$ MHz ($SiMe_4$) for ^1H (quoted ±0.05 ppm), Ξ being defined as in as in ref. 14. Solvent resonances were used as internal secondary standards. NMR data for all compounds isolated are listed in Table 1.

Synthesis of 9-CH_3-5,6-R^1,R^2-*nido*-5,6-$C_2B_8H_9$ (2) compounds (where R^1,R^2 = H,H 2a; Me,Me 2b; Et,Et 2c, H,Ph 2d, and Ph,Ph 2e)

A solution of alkynes $R^1R^2C_2$ (6 mmol, excess) and compound **1** (225 mg, 2 mmol) in hexane (20 ml) was heated in a 100 ml-stainless steel vessel at 120 °C for 2 h. In the case of acetylene the reaction was carried out by bubbling through the solution of **1** in toluene (20 ml) for 2 h at reflux. After cooling to room temperature, the solvents were evaporated and the desired compounds of type **2** were isolated by liquid chromatography on silica gel, using hexane as a mobile phase. Yields, R_f values, and other properties of compounds **2** isolated in this manner are in Table 2.

Alternative synthesis of *closo* anions [1-CB_7H_8]$^-$ (4^-) and [2-CB_6H_7]$^-$ (5^-)

A solution of compound **1** (171 mg, 1.52 mmol) in THF (30 ml) was treated with NaH (100 mg, 4.16 mmol) under stirring for *ca.* 2 h until the hydrogen evolution ceased. The mixture was filtered and the filtrate treated with phenylacetylene (932 mg, 9.12 mmol) and then heated at reflux for 120 h. After cooling

Table 1 NMR data

Compound	Nucleus	Chemical. shifts
5,6-$C_2B_8H_{12}$ (**2**)	$^{13}C\{^1H\}^a$	137.5 (q, J_{CB} = 55 Hz, C6), 69.5 (s, C5)
9-Me-5,6-$C_2B_8H_{11}$ (**2a**)	$^{11}B^{a,b}$	9.6 (s, –, B9), 6.5 (d, 149, B7), 4.5 (d, 159, B1), 1.1 (d, 155, B8), −4.6 (d, 144, B3), −11.4 (d, 152/43, B10), −31.0 (d, 177, B2), −36.4 (d, 152, B4), all [^{11}B–^{11}B]–COSY cross-peaks observed
	$^1H\{^{11}B\}^{a,c}$	6.37 (s, H6), 4.91 (s, H5), 3.50 (s, 2H,H1,7), 2.96 (s, H8), 2.87 (s, H3), 2.48 (s, H10), 0.91 (s, H4), 0.86 (s, H2), 0.67 (s, 3H,9-Me), −1.69 (s, μ-H9,10), −1.99 (s, μ-H8,9)
	$^{13}C\{^1H\}^{a,c}$	128.5 (br. s, C6), 64.7 (s, C5), −3.5 (s, 9-Me)
5,6-Me_2-9-Me-5,6-$C_2B_8H_9$ (**2b**)	$^{11}B^{a,b}$	7.5 (s, –, B9), 4.4 (d, *ca.* 160, B1), 3.2 (d, *ca.* 150, B7), −0.9 (d, 150, B8), −5.0 (d, *ca.* 150, B3), −6.6 (d, *ca.* 160/37, B10), −24.0 (d, 174, B2), −37.4 (d, 149, B4), all [^{11}B–^{11}B]-COSY cross-peaks observed
	$^1H\{^{11}B\}^{a,c}$	3.39 (s, H1), 3.23 (s, H7), 2.71 (s, H8), 2.63 (s, H3), 2.42 (s, H10), 2.15, 2.08 (s, 3H, 5- and 6-Me), 0.80 (s, H2), 0.70 (s, H4), 0.62 (s, 3H, 9-Me), −1.78 (s, μH8,9), −2.21 (s, μH9,10)
	$^{13}C\{^1H\}^a$	152.0 (br. s, C6), 84.0 (s, C5), 23.0, 21.7 (5- and 6-Me) −2.5 (s, 9-Me)
5,6-Et_2-9-Me-5,6-$C_2B_8H_9$ (**2c**)	$^{11}B^{a,b}$	6.6 (s, –, B9), 2.2 (d, 144, B1), 1.3 (d, 131, B7), −1.2 (d, 149, B8), −6.0 (d, 144, B3), −8.5 (d, 149/27, B10), −26.6(d, 177, B2), −38.6 (d, 150, B4), all [^{11}B–^{11}B]-COSY cross-peaks observed
	$^1H\{^{11}B\}^{a,c}$	3.36 (s, H1), 3.26 (s, H7), 2.76 (s, H8), 2.62 (s, H3), 2.57 (s, H10), 2.50, 2.38 (s, 2H, 5- and 6-Et), 1.20, 1.13 (s, 3H, 5- and 6-Et), 0.81 (s, H2), 0.70 (s, H4), 0.62 (s, 3H, 9-Me), −1.90 (s, μ-H9,10), −2.22 (s, μ-H8,9)
	$^{13}C\{^1H\}^a$	158.0 (br. s, C6), 89.3 (s, C5), 28.5, 28.2 (5- and 6-Et), 14.2, 13.9 (5- and 6-Et) −2.1 (s, 9-Me)
5-Ph-9-Me-5,6-$C_2B_8H_{10}$ (**2d**)	$^{11}B^{a,b}$	10.7 (s, –, B9), 4.6 (d, *ca.* 150, B7), 3,7 (d, *ca.* 150, B1), −0.3 (d, 146, B8), −3.2 (d, 147, B3), −6.8 (d, 155, B10), −28.3 (d, 177, B2), −36.8 (d, 153, B4), all [^{11}B–^{11}B]–COSY cross-peaks observed
	$^1H\{^{11}B\}^{a,c}$	7.60–7.39 (m, 5H, Ph), 6.66 (s, H6), 3.90 (s, H1), 3.59 (s, H7), 2.99 (s, 2H, H3,8), 2.67 (s, H10), 1.03 (s, 2H, H2,4), 0.71 (s, 3H, 9-Me), −1.16 (s, μ-H9,10), −1.82 (s, μ-H8,9)
	$^{13}C\{^1H\}^a$	133.6 (br. s, C6), 132.0 – 127 (m, 6C, Ph), 92.7 (s, C5), −1.8 (s, 9-Me)
1-Ph-6-Me-5,6-$C_2B_8H_{10}$ (**3d**)	$^{11}B^{a,b}$	32.0 (d, 168, B10), −7.3 (d, 144, B4), −9.3 (s, –, B6), −17.3 (d, 177, B3), −24.7 (d, 4B, 177, B5,7 and 6,9), all [^{11}B–^{11}B]–COSY cross-peaks observed except for B6–B10
	$^1H\{^{11}B\}^{a,c}$	7.83 (s, 3H, Ph), 7.57 (s, 2H, Ph), 5.92 (s, H10), 3.19 (s, H2), 2.87 (s, H4), 2.51 (s, H3), 1.26, 1.21, 1.16 (s, 2H, 1H, 1H, H5,6,7, 9), 0.24 (s, 3H, 6-Me)
	$^{13}C\{^1H\}^a$	133.5–128.8 (m, 5-Ph), 62.4 (s, C1), 54.9 (s, C2), 30.5 (s, 6-Me)
5,6-Ph_2-9-Me-5,6-$C_2B_8H_9$ (**2e**)	$^{11}B^{a,b}$	8.6 (s, –, B9), 3.6 (d, 2B, *ca.* 150, B1,7), 0.2 (d, 133, B8), −5.0 (d, 153, B3), −6.6 (d, *ca.* 155, B10), −20.3 (d, 177, B2), −36.6 (d, 152, B4), all [^{11}B–^{11}B]–COSY cross-peaks observed
	$^1H\{^{11}B\}^{a,c}$	7.58–6.82 (m, 10H, Ph), 3.71 (s, H1), 3.50 (s, H7), 2.81 (s, H10), 1.72 (s, H2), 1.04 (s, H4), 0.78 (s, 3H, 9-Me), −1.03 (s, μ-H9,10), −1.61 (s, μ-H8,9)
	$^{13}C\{^1H\}^a$	153.7 (br. s, C6), 139.6–126.9 (m, 12C, Ph), 91.6 (s, C5), −1.4 (s, 9-Me)

[a] In $CDCl_3$. [b] $\delta(^{11}B)$ (multiplicity, $^1J_{BH}$ in Hz, assignment). [c] $\delta(^1H$ and $^{13}C)$ (multiplicity, assignment).

Table 2 Characteristics of products of reactions between alkynes $R^1R^2C_2$ and *arachno*-4-CB_8H_{14} (**1**) at 115–120 °C

Alkyne	Product(s)	Yield (%)	R_f[a]	mp/°C	*m/z* (found)[b]	Calcd[c]	Found[c]
C_2H_2	**2a**	26	0.25	*ca.* −10	138(50), 137(100)	26.37, 10.33	25.92, 10.15
Me_2C_2	**2b**	29	0.26	*ca.* −20	166(50), 165(100)	36.47, 11.02	36.20, 10.95
Et_2C_2	**2c**	37	0.40	32	194(55), 193(100)	43.62, 11.51	43.33, 11.24
PhC_2H	**2e**	32	0.45	74	214(55), 213(100)	50.82, 8.53	50.71, 8.41
	3d	14	0.61	78	212(55), 211(100)	50.94, 7.60	51.01, 7.42
Ph_2C_2	**2e**	52	0.16	82	290(60), 289(100)	62.38, 7.68	61.94, 7.41

[a] In hexane. [b] Ordered as *m/z* values corresponding to M^+ (%), most intensive *m/z* (%). [c] Ordered as %C, %H.

to ambient temperature, the volatiles were evaporated using a rotary evaporator and the remaining materials were digested with a mixture of water (30 ml) and dichloromethane (30 ml) under stirring. The aqueous layer was separated, treated with a solution of PPh_4Cl (570 mg, 1.52 mmol) in water (30 ml) and the resulting white precipitate was isolated by filtration and dried *in vacuo*. The mixture of the PPh_4^+ salts of anions $\mathbf{4}^-$ and $\mathbf{5}^-$ thus obtained was separated on a silica gel column using dichloromethane as a mobile phase. Fractions of R_f 0.12 and 0.05 were collected and compounds obtained by evaporation were identified by NMR spectroscopy as $PPh_4^+[2\text{-}CB_6H_7]^-$ ($\mathbf{5}^-$) (154 mg, 24%) and $PPh_4^+[1\text{-}CB_7H_8]^-$ ($\mathbf{4}^-$) (212 mg, 32%), respectively, as reported earlier.[4,7]

Conclusions

We have shown that the insertion of alkynes $R^1R^2C_2$ to the nine-vertex monocarbaborane *arachno*-4-CB_8H_{14} (**1**) at elevated temperatures results in the formation of the ten-vertex dicarbaboranes 9-Me-5,6-R^1,R^2-*nido*-5,6-$C_2B_8H_9$, the typical feature being the extrusion of the cage CH_2 vertex in **1** into the exoskeletal position. In this respect this reaction reminds us of the reaction between $R^1R^2C_2$ and 4-(Me_2S)–B_9H_{13}, also generating C-substituted 5,6-R^1,R^2-*nido*-5,6-$C_2B_8H_{10}$ derivatives under complete elimination of one boron vertex from the nine-vertex *arachno* core.[15] It was also demonstrated that the reaction between [*arachno*-4-$CB_8H_{13}]^-$ anion ($\mathbf{1}^-$) and PhC_2H proceeds in an entirely different manner, producing a mixture of the *closo* anions $[1\text{-}CB_7H_8]^-$ ($\mathbf{4}^-$) and $[1\text{-}CB_6H_7]^-$ ($\mathbf{5}^-$) under elimination of one or two boron vertices. This reaction represents an improved access to the seven-vertex anion $\mathbf{5}^-$ that has so far been hardly available.[7] In general, we hope that the substituted derivatives of **2** reported in this paper can be used as source compounds for various mechanistic studies and the preparation of C- and B-substituted compounds in the area of dicarbaborane and tricarbaborane chemistry. Relevant studies in these areas of cluster-boron chemistry are in progress.

Acknowledgements

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