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# Carbon Insertion into *arachno*-6,9-$C_2B_8H_{14}$ via Acyl Chlorides. Skeletal Alkylcarbonation (SAC) Reactions: A New Route for Tricarbollides

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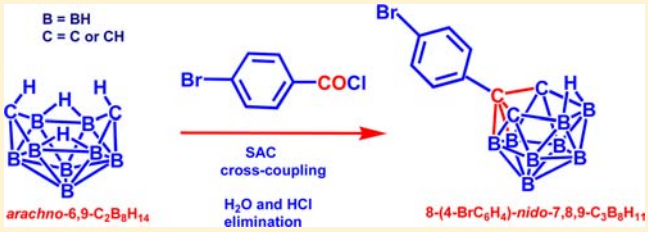
Supporting Information

**ABSTRACT:** Reactions between *arachno*-6,9-$C_2B_8H_{14}$ (**1**) and selected acyl chlorides, RCOCl, in the presence of PS (PS = "proton sponge", 1,8-dimethylamino naphthalene) in $CH_2Cl_2$ for 24 h at reflux, followed by in situ acidification with concentrated $H_2SO_4$ at 0 °C, generate a series of neutral alkyl and aryl tricarbollides 8-R-*nido*-7,8,9-$C_3B_8H_{11}$ (**2**) (where R = $CH_3$, **2a**; $C_2H_5$, **2b**; *n*-$C_4H_9$, **2c**; $C_6H_5$, **2d**; 4-Cl-$C_6H_4$, **2e**; 4-Br-$C_6H_4$, **2f**; 4-I-$C_6H_4$, **2g**; 1-$C_{10}H_7$, **2h**; and 2-$C_{10}H_7$, **2i**). The best yields were achieved for aryl derivatives (80−95%) while the yields of the corresponding alkyl substituted compounds are lower (60−70%). These skeletal alkylcarbonation (SAC) reactions are consistent with an aldol-type condensation between the RCO group and open-face hydrogen atoms on the dicarbaborane **1**, which is associated with the insertion of the carbonyl carbon atom into the structure of *arachno*-6,9-$C_2B_8H_{14}$ (**1**) under elimination of three extra hydrogen atoms as $H_2O$ and HCl. The reactions thus result in an effective R−tricarbaborane cross-coupling. Individual compounds of structure **2** have been purified by chromatography on a silica gel support, using hexane as the mobile phase ($R_F$ = ∼0.3). Deprotonation agents, such as $NEt_3$, NaOH, NaH, etc., convert tricarbaboranes **2** into the corresponding conjugated anions [8-R-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ (**2**$^-$) which were isolated as salts with suitable countercations (for example, $Et_3NH^+$, $Tl^+$, $NEt_4^+$, etc.). The compounds have been characterized by multinuclear ($^{11}B$, $^1H$, and $^{13}C$) NMR spectroscopy, mass spectrometry, and elemental analyses. The structures of anions [8-R-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ (where R = $C_6H_5$, 4-I-$C_6H_4$ and 1-$C_{10}H_7$; **2a**$^-$, **2g**$^-$, and **2h**$^-$) and that of the neutral 8-(1-$C_{10}H_7$)-*nido*-7,8,9-$C_3B_8H_{11}$ (**2h**) have been established by X-ray diffraction analyses.




## INTRODUCTION

Tricarbaboranes are usually prepared by the insertion of one more carbon atom into the structure of dicarbaboranes.[1] L. G. Sneddon's group was the first to develop the concept of so-called skeletal alkylcarbonation (SAC)[2] reactions resulting in the incorporation of the RC unit into the dicarbaborane cage. Excellent examples of such reactions are those between nitriles (RCN) and the [*arachno*-4,6-$C_2B_8H_{12}$]$^-$ anion leading to high-yield formation of the 10-vertex tricarbaboranes [6-R-*nido*-5,6,9-$C_3B_7H_9$]$^-$ (where R = alkyl or aryl) upon elimination of $NH_3$:[3]

$$[arachno\text{-}4,\ 6\text{-}C_2B_7H_{12}]^- + RCN \rightarrow [6\text{-}R\text{-}nido\text{-}5,\ 6,\ 9\text{-}C_3B_7H_9]^- + NH_3 \quad (1)$$

In this case, the three extra hydrogen atoms of the dicarbaborane substrate are capable of interrupting the nitrile RC≡N triple bond.

Another type of SAC reactions occurs in the interaction between the [*arachno*-4,6-$C_2B_7H_{12}$]$^-$ anion and alkynes RC≡CH (where R = polarized group, such as CN, COOMe, and COMe):

$$[arachno\text{-}4,\ 6\text{-}C_2B_7H_{12}]^- + RC_2H \rightarrow [6\text{-}RCH_2\text{-}arachno\text{-}5,\ 6,\ 7\text{-}C_3B_7H_{11}]^- \quad (2)$$

In these reactions, only one of the alkyne carbon atoms has been inserted into the cage to form the 10-vertex tricarbaborane skeleton with three adjacent carbon vertexes.[4]

The best method for the synthesis of 11-vertex tricarbaboranes (tricarbollides) consists of the insertion of the cyanide or isocyanide carbon into the structure of the [*nido*-5,6-$C_2B_8H_{11}$]$^-$ anion:[5]

$$[nido\text{-}5,\ 6\text{-}C_2B_8H_{11}]^- + HCN \rightarrow [7\text{-}(H_2N)\text{-}nido\text{-}7,\ 8,\ 9\text{-}C_3B_8H_{10}]^- \quad (3)$$

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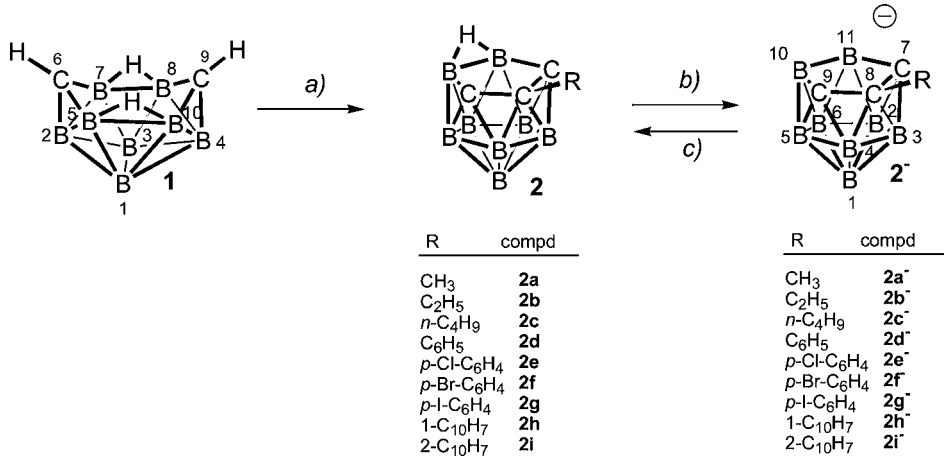
**Scheme 1. Tricarbollide Compounds from the SAC Cross-Coupling via Incorporation of the RC Unit into the Structure of *arachno*-6,9-$C_2B_8H_{14}$ (1) (B = BH, C = CH or C)[a−c]**




| R | compd |
|---|---|
| $CH_3$ | **2a** |
| $C_2H_5$ | **2b** |
| *n*-$C_4H_9$ | **2c** |
| $C_6H_5$ | **2d** |
| *p*-Cl-$C_6H_4$ | **2e** |
| *p*-Br-$C_6H_4$ | **2f** |
| *p*-I-$C_6H_4$ | **2g** |
| 1-$C_{10}H_7$ | **2h** |
| 2-$C_{10}H_7$ | **2i** |

| R | compd |
|---|---|
| $CH_3$ | **2a⁻** |
| $C_2H_5$ | **2b⁻** |
| *n*-$C_4H_9$ | **2c⁻** |
| $C_6H_5$ | **2d⁻** |
| *p*-Cl-$C_6H_4$ | **2e⁻** |
| *p*-Br-$C_6H_4$ | **2f⁻** |
| *p*-I-$C_6H_4$ | **2g⁻** |
| 1-$C_{10}H_7$ | **2h⁻** |
| 2-$C_{10}H_7$ | **2i⁻** |

[a]RCOCl, PS, $CH_2Cl_2$, reflux, 24 h, followed by conc $H_2SO_4$, 0 °C. [b]Deprotonation. [c]Conc $H_2SO_4$, 0 °C.

$$[\textit{nido}\text{-}5,6\text{-}C_2B_8H_{11}]^- + {}^t\text{BuNC} \rightarrow [7\text{-}({}^t\text{BuHN})\text{-}\textit{nido}\text{-}7,8,9\text{-}C_3B_8H_{10}]^- \quad (4)$$

These aminocarbonation processes, in which the amino group has been retained on the cluster carbon, is typical for *nido* clusters.[6] The reason for RNH-retention is that the lone extra hydrogen atom in $[\textit{nido}\text{-}5,6\text{-}C_2B_8H_{11}]^-$ is incapable of interrupting completely the C≡N or N≡C bond in reactions 3 and 4. Further chemical transformations of the amino derivatives generated in turn a long series of tricarbollide compounds, inclusive of the parent *nido* compounds $[7,8,9\text{-}C_3B_8H_{11}]^-$, $7,8,9\text{-}C_3B_8H_{12}$, and $[7,8,10\text{-}C_3B_8H_{11}]^-$ and their derivatives.[5]

The works by Brellochs at al.[7] on degradative insertion of the aldehyde carbon into the structure of the $[6\text{-HO-}\textit{arachno}\text{-}B_{10}H_{13}]^{2-}$ dianion and some metal−carbonyl C-insertion reactions[8] suggested that some specific C═O carbon incorporation procedures might be, in principle, applicable to other cluster systems. This strategy has proved to be justified, and just recently we reported[2] our preliminary results on reactions between acyl chlorides (RCOCl) and the $[\textit{arachno}\text{-}6,9\text{-}C_2B_8H_{13}]^-$ anion in the presence of triethylamine. These so-called skeletal alkylcarbonation (SAC) reactions resulted in a unique incorporation of the CO carbon into the dicarbaborane cage and formation of the symmetrical 8-substituted 7,8,9-tricarbollides. Herein we would like to report full experimental details on the recent "proton-sponge modification" of this novel method which allowed for the synthesis of an extended series of alkyl and aryl derivatives in improved yields.

## RESULTS AND DISCUSSION

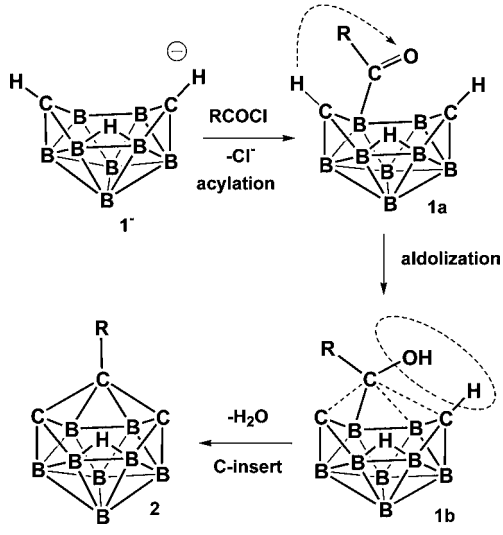
**Syntheses.** Treatment of the *arachno*-6,9-$C_2B_8H_{14}$ (**1**) dicarbaborane[9] with excess acyl chlorides (RCOCl) in the presence of 2 equiv of PS (proton scavenger) in refluxing $CH_2Cl_2$ for 24 h, followed by adding concentrated $H_2SO_4$ at 0 °C (Scheme 1, path a), led to the formation of a series of neutral tricarbollides 8-R-*nido*-7,8,9-$C_3B_8H_{11}$ (**2**). The reaction seems to be of general character, as tested for RCOCl's of varying R substituents (R = *n*-alkyls with 1−5 carbon atoms, aryls $C_6H_5$, 4-X-$C_6H_4$ (X = Cl, Br, and I), and naphthyl isomers 1-$C_{10}H_7$ and 2-$C_{10}H_7$). The yields of compounds **2** were in the ranges 60−70% and 80−95% for alkyls and aryls, respectively, and the reactions appear to be restricted only by the availability of the starting acyl chloride.

The reactions of path a are in accord with a simple stoichiometry of eq 5 comprising the deprotonation of **1** along with the elimination of HCl and $H_2O$:

$$\underset{\mathbf{1}}{\textit{arachno}\text{-}6,9\text{-}C_2B_8H_{14}} + \text{RCOCl} + 2\text{PS} \rightarrow 1\text{PSH}^+[8\text{-R-}\textit{nido}\text{-}7,8,9\text{-}\underset{\mathbf{2}^-}{C_3B_8H_{10}}]^- + \text{PS}\cdot\text{HCl} + H_2O \quad (5)$$

As inferred from Scheme 2, these reactions are consistent with a regiospecific insertion of the 3-electron carbyne RC≡ unit (skeletal alkylcarbonation, SAC) into the *endo*-skeletal area of $\mathbf{1}^-$ identified by B5, C6, C9, and B10 vertexes under extraction of all the three extra hydrogen atoms which are then eliminated as $H_2O$ and HCl. It is also readily seen that the reactions result in an effective cross-coupling between R and

**Scheme 2. Proposed Aldolization Mechanism for the Insertion of the Acyl Chloride RC Unit between the C6 and C9 Positions in $[\textit{arachno}\text{-}6,9\text{-}C_2B_8H_{13}]^-$ ($\mathbf{1}^-$) (B = BH, C = CH or C)**





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the carborane cage of **1** which is then leaving the coupling process enriched in one more carbon vertex.

Although no mechanistic studies have so far been done, it can be reasonably supposed that the reaction starts with acylation of anion $\mathbf{1}^-$ at B5 in the *endo* sphere to form the neutral acyl derivative *endo*-5-(RCO)-*arachno*-6,9-$C_2B_8H_{13}$ (**1a**) (see Scheme 2) which then extracts the *endo* hydrogen atom from the cage C(6)$H_2$ group to form the aldolization product **1b**. Entailing $H_2O$ elimination followed by C-insertion is then leading directly to the formation of the neutral tricarbollide **2**.

All the 8-R-*nido*-7,8,9-$C_3B_8H_{11}$ (**2**) compounds can be deprotonated (Scheme 1, path b) by dissolution in 10% aqueous NaOH, followed by precipitation of the solution with a suitable countercation (for example $Tl^+$, $NEt_4^+$, etc.), to generate very stable anions of general constitution [8-R-*nido*-7,8,9-$C_3B_8H_{10}]^-$ ($\mathbf{2}^-$). However, the most convenient way for ready preparation of these anions is based on treatment of compounds of structure **2** with $NEt_3$ in dichloromethane, which leads to quantitative formation of the corresponding $Et_3NH^+$ salts. These represent a very stable storage form of tricarbollides that can be converted easily into any other salt on dissolution in aqueous NaOH, followed by precipitation with a suitable countercation. $Na^+$ salts can be also generated via reaction of compounds **2** with NaH in $Et_2O$ (for R = aryls) while refluxing THF must be employed for R = alkyls, apparently due to lower acidity of the bridging hydrogen.

**Structural Studies.** The structures of a pair of the anionic [8-(1-$C_{10}H_7$)-*nido*-7,8,9-$C_3B_8H_{10}]^-$ (**2h**$^-$) and the neutral 8-(1-$C_{10}H_7$)-*nido*-7,8,9-$C_3B_8H_{11}$ (**2h**) compounds have already been established unambiguously by X-ray diffraction analyses, as reported in the preliminary communication.[2] The structure of the parent (unsubstituted) anion [*nido*-7,8,9-$C_3B_8H_{11}]^-$ has also been determined just recently by our group.[10] In this work we are adding the structures of the anionic phenyl derivatives $NEt_4^+$[8-$C_6H_5$-*nido*-7,8,9-$C_3B_8H_{10}]^-$ (**2d**$^-$) and $HNEt_3^+$[8-(4-I-$C_6H_4$)-*nido*-7,8,9-$C_3B_8H_{10}]^-$ (**2g**$^-$) shown in Figures 1 and 2, respectively. The data confirm again the overall $C_s$-symmetry and 8-substitution on the central carbon vertex of the pentagonal open face. Comparison of cluster C−C distances

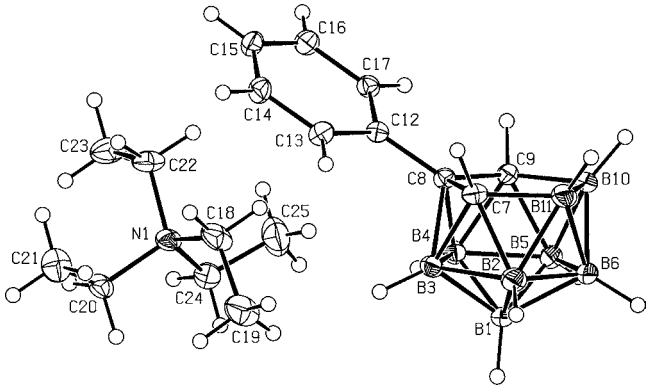


**Figure 1.** ORTEP representation of the molecular structure of $NEt_4^+$[8-($C_6H_5$)-*nido*-7,8,9-$C_3B_8H_{10}]^-$ (**2d**$^-$) anion at 40% probability level. Selected bond lengths (Å) and angles (deg): open face, C7−C8 1.536(3), C7−B11 1.631(4), C8−C9 1.528(3), C9−B10 1.630(4), B10−B11 1.727(5); C8−C7−B11 111.3(2), C7−C8−C9 109.7(2), C8−C9−B10 111.3(2), C7−B11−B10 103.6(2), C9−B10−B11 104.0(2). Interbelt distances: mean C−B, 1.730(4), mean B−B 1.786(4). Lower belt: mean B−B 1.765(4), mean B1−B 1.779(4). The B−H and C−H bond distances and angles fall within usual limits.

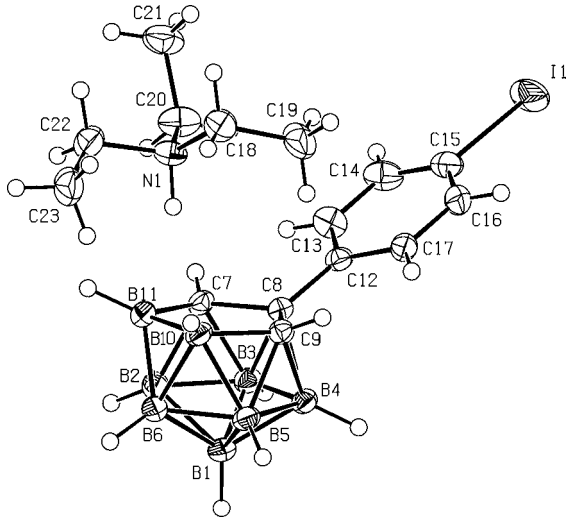


**Figure 2.** ORTEP representation of the molecular structure of $HNEt_3^+$[8-(4−I-$C_6H_4$)-*nido*-7,8,9-$C_3B_8H_{10}]^-$ (**2g**$^-$) anion at 50% probability level. Selected bond lengths (Å) and angles (deg): cg(C1−C2−B3−B4−C5)−N1 3.365(3), I1−C15 2.102(3). Open face: C7−C8 1.529(4), C7−B11 1.621(5), C8−C9 1.519(4), C9−B10 1.624(4), B10−B11 1.724(5); C8−C7−B11 111.6(3), C7−C8−C9 109.6(2), C8−C9−B10 111.2(2), C7−B11−B10 103.3(2), C9−B10−B11 104.0(2). Interbelt distances: mean C−B, 1.733(4), mean B−B 1.789(4). Lower belt: mean B−B 1.766(5), mean B1−B 1.779(5). The B−H and C−H bond distances and angles fall within usual limits.

for anions **2d**$^-$ (mean 1.532 Å) and **2g**$^-$ (mean 1.524 Å) with the equivalent bond vectors in the parent anion (mean 1.515 Å) reveals only a slight lengthening of these distances due to aromatic substitution. The C(7)−C(8)−C(9) angles in anions **2d**$^-$ and **2g**$^-$ (109.7(2)° and 109.6(2)°, respectively) approximate the ideal pentagonal angle, while the corresponding angle in the parent anion is, at 111.00(13)°, slightly larger. Compound **2g**$^-$ crystallizes in the monoclinic space group $P2_1/c$ with four molecules within the unit cell without intermolecular hydrogen bonding. However, the short contact between NH and the upper rim of the carborane core is the reason for forming a layered structure shown in Figure 3.

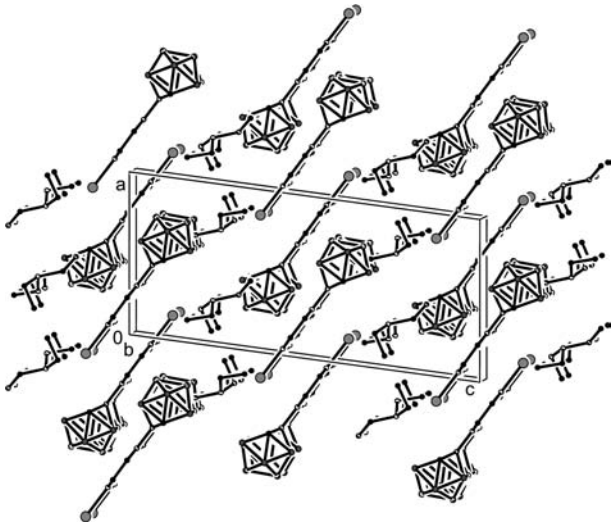


**Figure 3.** Supramolecular architecture of **2g**$^-$, view along the *b* axis.


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**Table 1. NMR Assignments for the Neutral 8-R-*nido*-7,8,9-$C_3B_8H_{11}$ (2) Derivatives**

| | $\delta(^1H)$ and $\delta(^{13}C)^a$ | | | | $\delta(^{11}B)^b$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| R, compd | R signals | CH7,9 | C8 | $\mu$-$H_{10,11}$ | BH2,5 | BH3,4 | BH10,11 | BH6 | BH1 |
| $CH_3$, **2a** | 1.65(3), *22.8* | 2.93 ,*47.0* | –, *75.7* | −2.02 | −0.1, 158, 2.58 | −15.7, 171, 1.90 | −19.8, 147/49, 1.82 | −28.0, 149, 0.78 | −33.5, 150, 1.15 |
| $C_2H_5$, **2b** | 0.98(3), 1.90(2), *30.2, 12.4* | 2.98, *45.2* | –, *81.2* | −2.12 | −0.2, 159, 2.59 | −16.2, 171, 1.83 | −19.9, 144/46, 1.90 | −27.7, 146, 0.91 | −340, 150, 1.25 |
| *n*-$C_4H_9$, **2c** | 1.86(2), 1.43(2), 1.33(2), 0.92(3), *37.2, 36.9, 22.9, 14.2* | 2.72, *44.8* | –, *78.9* | −2.30 | −0.5, 158, 2.71 | −16.8, 169, 1.97 | −20.5, 146/54, 1.94 | −28.2, 147, 0.95 | −34.4, 152, 1.28 |
| $C_6H_5$, **2d** | 7.38(2), 7.34(3), *136.5, 139.0, 129.6(2), 128.2(2)* | 3.29, *47.4* | –, *80.9* | −1.77 | −0.3, 128, 2.67 | −16.4, 171, 2.19 | −19.6, 146/45, 1.96 | −26.6, 147, 0.96 | −33.3, 149, 1.33 |
| 4-$ClC_6H_5$, **2e** | 7.37(4), *135.6, 135.8, 130.1(2), 128.5* | 3.29, *47.5* | –, *79.8* | −1.73 | −0.2, 162, 2.66 | −16.4, 171, 2.14 | −19.4, 150/50, 1.90 | −26.4, 146, 0.97 | −33.3, 149, 1.33 |
| 4-$BrC_6H_5$, **2f** | 7.50(2), 7.31(2), *135.7, 132.5(2), 130.3(2), 123.7* | 3.29, *47.3* | –, *79.9* | −1.75 | −0.3, 162, 2.66 | −16.4, 174, 2.16 | −19.4, 147/46, 1.93 | −26.4, 146, 0.97 | −33.3, 149, 1.33 |
| 4-$IC_6H_5$, **2g** | 7.71(2), 7.17(2), *138.6(2), 136.3, 130.3(2), 95.4* | 3.29, *47.3* | –, *80.0* | −1.74 | −0.3, 162, 2.66 | −16.4, 171, 2.14 | −18.4, 157/46, 1.92 | −26.4, 150, 0.98 | −33.3, 149, 1.33 |
| 1-$C_{10}H_7$, **2h** | 8.01–7.32(7), *130.9–125.4(10)* | 3.28, *49.5* | –, *82.6* | −1.65 | 1.7, 158, 2.88 | −15.2, 171, 2.70 | −19.2, 147/37, 2.08 | −25.9, 147, 1.13 | −33.3, 150, 1.44 |
| 2-$C_{10}H_7$, **2i** | 7.85–7.47, *129.3–125.6(10)* | 3.42, *47.6* | –, *81.1* | −1.66 | −0.2, 162, 2.71 | −16.2, 174, 2.21 | −19.5, 146/46, 2.01 | −26.4, 147, 1.00 | −33.2, 150, 1.37 |

[a]In ppm relative to TMS, $\delta(^{13}C)$ in italics, intensities other than 1 in parentheses, measured in $CD_3CN$. [b]In ppm relative to $BF_3{\cdot}OEt_2$/$^1J$(BH) in Hz/$\delta(^1H)$ for BH cluster units.

**Table 2. NMR Assignments for [8-R-*nido*-7,8,9-$C_3B_8H_{10}$] ($2^-$) Anions ($Et_3NH^+$ Salts)**

| | $\delta(^1H)$ and $\delta(^{13}C)^a$ | | | $\delta(^{11}B)^b$ | | | | |
|---|---|---|---|---|---|---|---|---|
| R, compd | R signals | CH7,9 | C8 | BH6 | BH10,11 | BH2,5 | BH3,4 | BH1 |
| $CH_3$, **2a**$^-$ | 1.28(3), *22.8* | 1.33, *38.5* | –, *46.3* | −18.0, ∼120, 0.81 | −18.0, ∼120, 1.03 | −19.8, ∼170, 1.48 | −19.8, ∼170, 1.12 | −46.3, 137, 0.02 |
| $C_2H_5$, **2b**$^-$ | 1.53(2), 0.87(3), *30.2, 13.0* | 1.37, *36.3* | –, *44.5* | −17.6, ∼120, 0.83 | −17.6, ∼120, 1.34 | −20.3, ∼150, 1.47 | −20.3, ∼150, 1.15 | −46.8, 137, 0.07 |
| *n*-$C_4H_9$, **2c**$^-$ | 1.47(2), 1.35(2), 1.29(2), 0.84(3), *38.0, 31.8, 23.4, 14.1* | 1.33, *37.0* | –, *50.9* | −17.7, ∼130, 0.81 | −17.7, ∼130, 1.03 | −20.1, ∼150, 1.48 | −20.1, ∼150, 1.12 | −46.8, 137, 0.01 |
| $C_6H_5$, **2d**$^-$ | 7.19–7.09(5), *145.2, 128.7(2), 126.5, 126.2(2)* | 1.92, *38.4* | –, *52.9* | −15.8, –, 1.03 | −16.5, ∼140, 1.35 | −19.6, ∼150, 1.73 | −20.6, ∼135, 1.16 | −44.3, 137, 0.27 |
| 4-$ClC_6H_5$, **2e**$^-$ | 7.16(4), *141.1, 131.7, 128.6(2), 127.8(2)* | 1.89, *38.5* | –, *52.2* | −15.8, –, 0.92 | −16.3, ∼140, 1.33 | −19.4, ∼155, 1.69 | −20.6, ∼140, 1.14 | −44.1, 140, 0.29 |
| 4-$BrC_6H_5$, **2f**$^-$ | 7.29(2), 7.10(2), *141.6, 131.6(2), 128.19(2), 119.8* | 1.90, *39.5* | –, *52.2* | −15.5, –, 0.92 | −16.3, ∼140, 1.25 | −19.4, ∼155, 1.65 | −20.6, ∼140, 1.03 | −44.1, 137, 0.29 |
| 4-$IC_6H_5$, **2g**$^-$ | 7.49(2), 6.97(2), *142.3, 137.6(2), 128.3(2), 91.0* | 1.89, *39.4* | –, *54.7* | −15.8, –, 0.92 | −16.3, ∼140, 1.25 | −19.4, ∼155, 1.67 | −20.6, ∼140, 1.05 | −44.1, 141, 0.28 |
| 1-$C_{10}H_7$, **2h**$^-$ | 8.72–7.28(7), *142.6–124.9(10)* | 1.64, *42.9* | –, *54.5* | −16.0, ∼120, 1.07 | −16.0, ∼120, 1.41 | −18.4, 152, 1.35 | −20.1, 168, 2.00 | −45.3, 141, 0.26 |
| 2-$C_{10}H_7$, **2i**$^-$ | 7.75–7.35(7), *139.7–124.0(10)* | 2.10, *38.5* | –, *53.2* | −15.7, –, 1.09 | −16.2, ∼140, 1.32 | −19.4, ∼155, 1.32 | −20.6, ∼140, 1.92 | −44.2, 140, 0.36 |

[a]In ppm relative to TMS, $\delta(^{13}C)$ in italics, intensities other than 1 in parentheses, measured in $CD_3CN$. The $^1H$ resonances due to $Et_3NH^+$ omitted. [b]In ppm relative to $BF_3{\cdot}OEt_2$/$^1J$(BH) in Hz/$\delta(^1H)$ for BH cluster units.

**Table 3. NMR Assignments for Selected [8-R-*nido*-7,8,9-$C_3B_8H_{10}$] ($2^-$) Anions ($Tl^+$ Salts)**

| | $\delta(^1H)$ and $\delta(^{13}C)^a$ | | | $\delta(^{11}B)^b$ | | | | |
|---|---|---|---|---|---|---|---|---|
| R, compd | R signals | CH7,9 | C8 | BH10,11 | BH6 | BH2,5 | BH3,4 | BH1 |
| $C_6H_5$, **2d**$^-$ | 7.30–7.13(5), *140.8, 129.0(2), 127.4, 126.6(2)* | 2.18, *40.0* | –, *56.4* | −9.2, 122, 1.68 | −13.4, 134, 1.35 | −17.2, ∼135, 1.47 | −17.4, ∼150, 1.86 | −40.3, 141, 1.06 |
| 4-$ClC_6H_5$, **2e**$^-$ | 7.26(2), 7.21(2), *140.1, 132.5, 128.7(2), 128.1(2)* | 2.19, *39.8* | –, *54.9* | −10.1, 122, 1.64 | −13.7, 132, 1.31 | −17.8, ∼153, 1.42 | −17.8, ∼153, 1.81 | −40.8, 140, 0.96 |
| 4-$BrC_6H_5$, **2f**$^-$ | 7.34(2), 7.17(2), *140.7, 132.5, 131.7(2), 128.4(2)* | 2.19, *39.4* | –, *54.7* | −10.2, 119, 1.62 | −13.9, 128, 1.29 | −17.8, ∼146, 1.40 | −17.8, ∼146, 1.80 | −40.7, 140, 0.93 |
| 4-$IC_6H_5$, **2g**$^-$ | 7.54(2), 7.06(2), *141.2, 137.8(2), 128.6(2), 91.8* | 2.18, *39.4* | –, *54.7* | −10.0, 119, 1.40 | −13.6, 128, 1.25 | −17.8, ∼150, 1.67 | −17.8, ∼150, 1.05 | −40.7, 141, 0.28 |

[a]In ppm relative to TMS, $\delta(^{13}C)$ in italics, intensities other than 1 in parentheses, measured in $CD_3CN$. [b]In ppm relative to $BF_3{\cdot}OEt_2$/$^1J$(BH) in Hz/$\delta(^1H)$ for BH cluster units.

The 1-naphthyl derivative **2h** has been thus far a single structurally determined[2] tricarbollide of the neutral *nido*-$C_3B_8H_{12}$ series. The main structural difference between this compound and its conjugated base **2h**$^-$ lies in the presence of the $\mu$-$H_{10,11}$ hydrogen bridge,[2] which causes considerable elongation (0.125 Å) of the open face B(10)–B(11) distance.


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**NMR Spectroscopy.** As assessed by multinuclear $^{11}B$, $^{1}H$, and $^{13}C$ NMR spectroscopy (see Tables 1−3), the structures of all the remaining compounds isolated in this study are also in good agreement with 8-substitution by alkyl or aryl substituents. Because of the same $C_s$-symmetry, the NMR characteristics resemble those reported earlier for the parent *nido* tricarbollides $[7,8,9\text{-}C_3B_8H_{11}]^-$ and $7,8,9\text{-}C_3B_8H_{12}$.[5] As shown in Tables 1−3, the $^{11}B$ NMR spectra of compounds of structures **2** and $\mathbf{2}^-$ exhibit striking similarities, indicating that electronic effects exerted by individual alkyl and aryl substituents do not affect chemical shifs at $\beta$- and $\gamma$-boron positions of the cluster too much. The spectra of compounds **2** consist of 2:2:2:1:1 patterns of doublets assigned to boron vertexes B2,5, B3,4, B10,11, B6, and B1 (reading upfield) on the basis of $[^{11}B-^{11}B]$ COSY NMR measurements.[11] Table 2 also demonstrates that anions of constitution $\mathbf{2}^-$ (with countercations other than $Tl^+$) exhibit entirely different 1:2:2:2:1 sets of doublets, the differences being caused by the absence of the open-face bridging $\mu\text{-}H_{10,11}$ hydrogen.[5]

Moreover, as exemplified by the spectra of the phenylated anions $\mathbf{2a}^-$, $\mathbf{2b}^-$, $\mathbf{2c}^-$, and $\mathbf{2d}^-$, those of their $Et_3NH^+$ (Table 2) and $Tl^+$ salts (Table 3) rather differ. The latter salts exhibit a downfield shift (∼5 ppm) of the B10,11 and B1 resonances, which points to (at least partial) coordination of the $Tl^+$ ion to the open pentagonal face in structure $\mathbf{2}^-$. The Tl center would then appear in a position antipodal to the B1 vertex: this type of coordination reminds us of that observed in the structurally similar compound $Tl_2[nido\text{-}C_2B_9H_{11}]$.[12] A similar effect was also observed for $Tl^+$ salts of 7-aminosubstituted derivatives of the $[7,8,9\text{-}C_3B_8H_{11}]^-$anion.[5] As shown in Tables 1−3, apart from the downfield resonances attributed to the exoskeletal 8-R substituent, the $^{1}H$ NMR spectra of compounds **2** and $\mathbf{2}^-$ consist of an intensity 2 singlet attributed to the cage CH7,9 unit; this position is being remarkably shielded (∼1.5 ppm) for anions $\mathbf{2}^-$ when compared to their conjugated acids **2** that exhibit also a typical high-field resonance (approx −2 ppm) due to the $\mu\text{-}H_{10,11}$ bridging hydrogen. Table 3 also shows that conversion into $Tl^+$ salts is associated with a marked downfield shift of the cage CH7,9 signals. Moreover, $^{1}H-\{^{11}B\text{-(selective)}\}$[13] measurements have led to complete assignments of all BH resonances to individual cage positions.

The $^{13}C\{^{1}H\}$ NMR spectra of compounds **2** and $\mathbf{2}^-$ exhibit expectedly two broader ($^{13}C-^{11}B$ coupling) 1:2 singlets attributed to the cage C8 and C7,9 carbon vertexes along with sets of resonances due to aliphatic and aromatic carbon atoms. Within individual series of compounds, all the spectra show striking similarities, similarly as the corresponding $^{11}B$ NMR spectra, as the electronic effects of individual aryl substituents on the $^{13}C$ nuclei do not significantly differ. Deprotonation of compounds **2** results in remarkable shielding of the C8 (∼28 ppm) and C7,9 positions (∼9 ppm), which may be associated with partial localization of the negative charge on the open $C_3B_2$ face. The $^{13}C\{^{1}H\}$ NMR spectra of the corresponding $Tl^+$ salts exhibit a slight deshielding effect in comparison with their $Et_3NH^+$ counterparts. Mass spectra of compounds **2** are entirely in agreement with the calculated $m/z$ values.

## CONCLUSIONS

It has been established undoubtedly that the novel SAC method for carbon insertion appears to be highly effective for the preparation of tricarbollide compounds bearing alkyl and aryl functionalities located symmetrically on the open face of the molecule. The method, based on carbon insertion via acid chlorides, brings new synthetic features into the so far restricted area of 11-vertex tricarbaboranes,[1,5] being extremely flexible and allowing for variations either in molecular shape or substituent design. These synthetic tools may be exploited in cluster engineering and B-cage based biochemistry, for example, by varying substituents on carbon and boron positions in the starting carborane **1** and R in the RCOCl reagent; other tricarbaborane molecular shapes are expected from thermal rearrangement reactions. Metal complexation procedures involving the tricarbollide part of the molecule are expected to provide a series of alkyl and aryl substituted 12-vertex metallatricarbollides[14] that parallel the pioneering work of Sneddon's group in the area of 11- and 10-vertex metallatricarbaborane chemistry.[15] It is also obvious that halophenyl substituted derivatives isolated in this study can be employed as starting components for cross-coupling reactions on the benzene ring.[15g,16] Moreover, experiments involving bifunctional aryl chlorides and development of procedures leading to other substituted derivatives are in progress along with extensive structural investigations. It is also reasonable to expect that the SAC strategy can be applied also to other-than-dicarbaborane cages, which may result in substantial extensions and simplifications in the fields of general carborane and heteroborane chemistry.

## EXPERIMENTAL SECTION

**Materials and Methods.** All reactions were carried out under argon atmosphere, but subsequent operations, such as column LC, were carried out in air. The starting carborane **1** was prepared according to the literature.[9] 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 performed on silica gel (Aldrich, 250−350 mesh), and the purity of individual fractions was checked on Silufol sheets (silica gel on Al foils, detection $I_2$ vapors, followed by $AgNO_3$ spray). Mass spectra were recorded on a Thermo Finnigan LCQ Fleet Ion Trap mass spectrometer. NMR spectroscopy was performed on a Varian Mercury 400 instrument inclusive of standard $[^{11}B-^{11}B]$ COSY[11] (all theoretical cross-peaks were observed) and $^{1}H-\{^{11}B\text{(selective)}\}$[13] NMR experiments leading to complete assignments of all resonances to individual cage BH units. Chemical shifts are given in ppm to high-frequency (low field) of Ξ = 32.083 971 MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for $^{11}B$ (quoted ±0.5 ppm), Ξ = 25.144 MHz for $^{13}C$ (quoted ±0.5 ppm), and Ξ = 100 MHz for $^{1}H$ (quoted ±0.05 ppm), Ξ is defined as in ref 17, and the solvent resonances were used as internal secondary standards.

*Neutral 8-R-7,8,9-$C_3B_8H_{11}$ (2) Compounds (R = $CH_3$, 2a; $C_2H_5$, 2b; n-$C_4H_9$, 2c; $C_6H_5$, 2d; 4-Cl-$C_6H_4$, 2e; 4-Br-$C_6H_4$, 2f; 4-I-$C_6H_4$, 2g; 1-$C_{10}H_7$, 2h; 2-$C_{10}H_7$, 2i).* A solution containing carborane **1** (250 mg, 2 mmol) and PS (900 mg, 4.2 mmol) in dichloromethane (or 1,2-dichloroethane) (30 mL) was cooled to ∼0 °C, and the corresponding RCOCl (∼5 mmol) chloride was then added in small portions under stirring over 0.5 h. The cooling bath was then removed, and the stirring continued for 24 h at reflux temperature. The mixture was then treated with conc $H_2SO_4$ (∼2 mL, dropwise) under intensive cooling and shaking at ∼0 °C. The organic layer was carefully separated from the semiliquid materials sticking on the walls of the reaction flask. The solution thus obtained was then evaporated after adding silica gel (∼5 g). The residual material was mounted onto the top of a column packed with silica gel (∼2.5 cm × 20 cm) which was then eluted with 100% hexane. Combined fractions of $R_F$ (anal.) ∼0.25−0.3 were evaporated to dryness to isolate typically 1.2−1.4 (60−70%) and 1.6−1.9 (80−95%) mmol of the corresponding 8-R-$7,8,9\text{-}C_3B_8H_{11}$ (**2**) derivatives (R = alkyl and aryl, respectively). Akyl derivatives were isolated as liquid or low-melting substances, while aryl compounds were obtained as white crystalline solids that can be crystallized by


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slow evaporation of the hexane solution. For **2a**: liquid; *m*/*z* (max) calcd 148.18, found 148.18; for $C_4H_{14}B_8$ (mw 148.71) calcd 32.30% C, 9.48% H, found 33.10% C, 9.32% H. For **2b**: mp 30−31 °C; *m*/*z* (max) calcd 162.20, found 162.21; for $C_5H_{16}B_8$ (mw 162.74) calcd 36.90% C, 9.91% H, found 36.51% C, 9.61% H. For **2c**: mp 28−29 °C; *m*/*z* (max) calcd 190.23, found 190.24; for $C_7H_{20}B_8$ (mw 190.79) calcd 44.06% C, 10.57% H, found 42.93% C, 10.18% H. For **2d**: mp 82 °C; *m*/*z* (max) calcd 211.19, found 211.20; for $C_9H_{16}B_8$ (mw 210.78) calcd 51.30% C, 7.65% H, found 51.71% C, 7.56% H. For **2e**: mp 84 °C; *m*/*z* (max) calcd 244.16, found 244.17; for $C_9H_{15}B_8Cl$ (mw 245.15) calcd 44.09% C, 6.17% H, found 44.18% C, 6.25% H. For **2f**: mp 85.5 °C; *m*/*z* (max) calcd 289.11, found 289.09; for $C_9H_{15}B_8Br$ (mw 289.60) calcd 37.33% C, 5.22% H, found 38.10% C, 5.34% H. For **2g**: mp 86 °C; *m*/*z* (max) calcd 336.09, found 336.10; for $C_9H_{15}B_8I$ (mw 336.60) calcd 32.11% C, 4.49% H, found 30.91% C, 4.38% H. For **2h**: mp 84 °C; *m*/*z* (max) calcd 260.21, found 260.25; for $C_{13}H_{18}B_8$ (mw 260.77) calcd 59.88% C, 6.96% H, found 60.10% C, 6.82% H. For **2i**: mp 82 °C; *m*/*z* (max) calcd 260.21, found 260.23; for $C_{13}H_{18}B_8$ (mw 260.77) calcd 59.88% C, 6.96% H, found 60.14% C, 6.92% H. For NMR spectra see Table 1.

*[8-R-7,8,9-$C_3B_8H_{10}$]$^-$ ($2^-$) Anions.* For $Et_3NH^+$ salts, details follow. A solution of the corresponding compound **2** (reaction scale 1 mmol) in dichloromethane (15 mL) was treated dropwise with $Et_3N$ (110 mg, 1.1 mmol) under cooling at ∼0 °C. The mixture was then evaporated to dryness at room temperature and the residual white solid dried for 4 h at room temperature to obtain the corresponding $Et_3NH^+$[8-R-7,8,9-$C_3B_8H_{10}$]$^-$ salt as white crystals in quantitative yield. For $Tl^+$ and $Et_4N^+$ salts, details follow. A compound of structure **2** (reaction scale 1 mmol) was dissolved in 0.1 M aq NaOH (20 mL) under shaking, and the solution thus obtained was precipitated by adding 1 M aq $TlNO_3$ or $Et_4NCl$. The white precipitates were isolated by filtration, washed with water (3 × 20 mL), and vacuum-dried to obtain the corresponding salts in practically quantitative yield as white crystalline solids. For metathesis of $Et_3NH^+$ salts, details follow. An arbitrary $Et_3NH^+$ salt of anion $2^-$ (reaction scale 1 mmol) was dissolved in 0.1 M aq NaOH (20 mL) under shaking, and the $Et_3N$ thus evolved was evaporated in vacuo. The residual aqueous solution of the $Na^+$ salt was precipitated as described to obtain the corresponding $Tl^+$ (or $Et_4N^+$) salts that were vacuum-dried. For $\mathbf{2a}^-$ ($Et_3NH^+$ salt): for $C_{10}H_{29}NB_8$ (mw 249.9) calcd 48.06% C, 11.70% H, found 49.10% C, 11.90% H. For $\mathbf{2b}^-$ ($Et_3NH^+$ salt): for $C_{11}H_{31}NB_8$ (mw 263.93) calcd 50.06% C, 11.84% H, found 50.21% C, 11.69% H. For $\mathbf{2c}^-$ ($Et_3NH^+$ salt): for $C_{13}H_{35}NB_8$ (mw 291.98) calcd 53.47% C, 12.08% H, found 52.83% C, 11.84% H. For $\mathbf{2d}^-$ ($Et_3NH^+$ salt): for $C_{15}H_{31}B_8N$ (mw 311.90) calcd 57.76% C, 10.02% H, found 58.10% C, 10.15% H. For $\mathbf{2e}^-$ ($Et_3NH^+$ salt): for $C_{15}H_{30}B_8NCl$ (mw 346.34) calcd 52.02% C, 8.73% H, found 51.83% C, 8.81% H. For $\mathbf{2f}^-$ ($Et_3NH^+$ salt): for $C_{15}H_{30}B_8NBr$ (mw 390.80) calcd 46.10% C, 7.74% H, found 45.53% C, 7.51% H. For $\mathbf{2g}^-$ ($Et_3NH^+$ salt): for $C_{15}H_{30}B_8NI$ (mw 437.80) calcd 41.15% C, 6.91% H, found 40.83% C, 6.68% H. For $\mathbf{2h}^-$ ($Et_3NH^+$ salt): *m*/*z* (max) calcd 260.25, found 260.24; for $C_{19}H_{33}B_8N$ (mw 361.96) calcd 63.05% C, 9.19% H, found 62.80% C, 9.28% H. For $\mathbf{2i}^-$ ($Et_3NH^+$ salt): *m*/*z* (max) calcd 260.25, found 260.25; for $C_{19}H_{33}B_8N$ (mw 361.96) calcd 63.05% C, 9.19% H, found 63.10% C, 9.37% H. For NMR spectra of the $Et_3NH^+$ and selected $Tl^+$ salts see Tables 2 and 3, respectively.

**X-ray Crystallography.** The X-ray data for white crystals of anions $\mathbf{2d}^-$ and $\mathbf{2g}^-$ ($NEt_4^+$ and $HNEt_3^+$ salts) were obtained at 150 K using Oxford Cryostream low-temperature device and a Nonius KappaCCD diffractometer with Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å), a graphite monochromator, and the $\phi$ and $\chi$ scan mode. Data reductions were performed with DENZO-SMN.[18] The absorption was corrected by integration methods.[19] Structures were solved by direct methods (Sir92)[20] and refined by full matrix least-squares based on $F^2$ (SHELXL97).[21] Hydrogen atoms could be mostly localized on a difference Fourier map. However, to ensure uniformity of treatment of crystal structures, they were recalculated into idealized positions (riding model) and assigned temperature factors $U_{iso}(H)$ = $1.2U_{eq}$(pivot atom) or of $1.5U_{eq}$ for the methyl moieties with C−H = 0.96, 0.97, and 0.93 Å for the methyl, methylene, and aromatic hydrogen atoms and 1.1 Å for B−H and C−H bonds in the carborane cage. The hydrogen atom of the N−H group was placed according to the maxima on the Fourier difference map. Crystallographic data for $\mathbf{2d}^-$: $C_{17}H_{35}B_8N$, $M$ = 339.94, monoclinic, $P2_1/c$, $a$ = 9.8570(6) Å, $b$ = 15.3321(9) Å, $c$ = 13.8940(9) Å, $\beta$ = 91.977(5)°, $Z$ = 4, $V$ = 2098.5(2) Å$^3$, $D_c$ = 1.076 g cm$^{-3}$, $\mu$ = 0.055 mm$^{-1}$, $T_{min}/T_{max}$ = 0.988/0.993; $-11 \le h \le 12$, $-18 \le k \le 19$, $-18 \le l \le 17$; 15 241 reflections measured ($\theta_{max}$ = 27.4°), 15 075 independent ($R_{int}$ = 0.0553), 3164 with $I > 2\sigma(I)$, 235 parameters, $S$ = 1.130, R1(obsd data) = 0.0763, wR2(all data) = 0.1664; max, min residual electron density = 0.537, −0.477 e Å$^{-3}$. For $\mathbf{2g}^-$: $C_{15}H_{30}B_8IN$, M = 437.78, monoclinic, $P2_1/c$, $a$ = 9.3060(3) Å, $b$ = 11.1300(8) Å, $c$ = 20.1821(11) Å, $\beta$ = 97.688(4)°, $Z$ = 4, $V$ = 2071.6(2) Å$^3$, $D_c$ = 1.404 g.cm$^{-3}$, $\mu$ = 1.544 mm$^{-1}$, $T_{min}/T_{max}$ = 0.626/0.801; $-12 \le h \le 11$, $-14 \le k \le 14$, $-26 \le l \le 24$; 18 184 reflections measured ($\theta_{max}$ = 27.5°), 18 128 independent ($R_{int}$ = 0.0265), 3892 with $I > 2\sigma(I)$, 242 parameters, $S$ = 1.144, R1(obsd data) = 0.0402, wR2(all data) = 0.0829; max, min residual electron density = 0.894, −0.615 e Å$^{-3}$. Crystallographic data for structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC deposition nos. 898534 and 924312 for $\mathbf{2d}^-$ and $\mathbf{2g}^-$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, U.K. (Fax: +44-1223-336033. E-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk.)

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES


(1) For reviews see: (a) Štíbr, B.; Holub, J.; Teixidor, F. In *Advances in Boron Chemistry*; Siebert, W., Ed.; Royal Society of Chemistry: Cambridge, U.K., 1997; pp 333−340. (b) Štíbr, B. *Proc. Ind. Natl. Sci. Acad.* **2003**, *68A*, 487−497. (c) Grimes, R. N. *Carboranes*, 2nd ed.; Elsevier Science: New York, 2011.

(2) For the term SAC see: Štíbr, B.; Bakardjiev, M.; Holub, J.; Růžička, A.; Padělková, Z.; Olejník, R.; Švec, P. *Chem.—Eur. J.* **2011**, *17*, 13156.

(3) (a) Kang, S. O.; Furst, G. T.; Sneddon, L. G. *Inorg. Chem.* **1989**, *28*, 2339. (b) Ramachandran, B. M.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **2004**, *43*, 3467.

(4) (a) Su, K.; Barnum, B.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1992**, *114*, 2730. (b) Su, K.; Barnum, B.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1993**, *115*, 10004.

(5) (a) Štíbr, B.; Holub, J.; Teixidor, F.; Viñas, C. *Chem. Commun.* **1995**, 795. (b) Štíbr, B.; Holub, J.; Císařová, I.; Teixidor, F.; Viñas, C.; Fusek, J.; Plzák, Z. *Inorg. Chem.* **1996**, *35*, 3635. (c) Holub, J.; Štíbr, B.; Hnyk, D.; Fusek, J.; Císařová, I.; Teixidor, F.; Viñas, C.; Plzák, Z.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1997**, *119*, 7750. (d) Štíbr, B.; Holub, J.; Plešek, J.; Jelínek, T.; Grüner, B.; Teixidor, F.; Viñas, C. *J. Organomet. Chem.* **1999**, *582*, 282. (e) Štíbr, B.; Holub, J.; Císařová, I.; Teixidor, F.; Viñas, C. *Inorg. Chim. Acta* **1996**, *245*, 129. (f) Shedlow, A. M.; Sneddon, L. G. *Collect. Czech. Chem. Commun.* **1999**, *64*, 865.

(6) For other aminocarbonation reactions, see, for example: (a) Hyatt, D. E.; Owen, D. A.; Todd, L. J. *Inorg. Chem.* **1966**, *5*, 1749. (b) Knoth, W. H. *J. Am. Chem. Soc.* **1967**, *89*, 1274. (c) Hyatt, D. E.; Scholer, F. R.; Todd, L. J.; Warner, J. L. *Inorg. Chem.* **1967**, *6*, 2229. (d) Scholer, F. R.; Todd, L. J. *J. Organomet. Chem.* **1968**, *14*, 261. (e) Knoth, W. H. *Inorg. Chem.* **1971**, *10*, 598.

(7) (a) Brellochs, B. In *Contemporary Boron Chemistry*; Davidson, M. G., Hughes, A. K., Wade, K., Eds.; Royal Society of Chemistry: Cambridge, 2000; pp 212−214. (b) Brellochs, B.; Bačkovský, J.; Štíbr, B.; Jelínek, T.; Holub, J.; Bakardjiev, M.; Hnyk, D.; Hofmann, M.; Císařová, I.; Wrackmeyer, B. *Eur. J. Inorg. Chem.* **2004**, 3605. (c) Jelínek, T.; Thornton-Pett, M.; Kennedy, J. D. *Collect. Czech. Chem. Commun.* **2002**, *67*, 1035. (d) Štíbr, B. *Pure Appl. Chem.* **2003**, *75*, 1295 and references therein.

(8) (a) Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Mackinnon, P. I.; Macpherson, I. *J. Chem. Soc., Dalton Trans.* **1987**, 2385. (b) Wegner, P. A.; Guggenberger, L. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1970**, *92*, 3473. (c) Schultz, R. V.; Sato, F.; Todd, L. J. *J. Organomet. Chem.* **1977**, *125*, 115.

(9) (a) Štíbr, B.; Plešek, J.; Heřmánek, S. *Chem. Ind. (London)* **1972**, 649. (b) Štíbr, B.; Plešek, J.; Heřmánek, S. *Collect. Czech. Chem. Commun.* **1974**, *39*, 1805. (c) Štíbr, B.; Janoušek, Z.; Plešek, J.; Jelínek, T.; Heřmánek, S. *Collect. Czech. Chem. Commun.* **1987**, *52*, 103.

(10) Holub, J.; Růžička, A.; Padělková, Z.; Štíbr, B. *J. Organomet. Chem.* **2011**, *696*, 2742.

(11) (a) Kennedy, J . D. In *Multinuclear N. M. R.*; Mason, J., Ed.; Plenum Press, New York, 1987; p 221. (b) Hutton, W. C.; Venable, T. L.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 29. (c) Schraml, J.; Bellama, J. M. *Two-Dimensional NMR Spectroscopy*; Wiley: New York, 1982, and references therein.

(12) Spencer, J. L.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1972**, 1178.

(13) Fontaine, X. L. R.; Kennedy, J. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1573.

(14) See, for example: (a) Štíbr, B.; Holub, J.; Teixidor, F.; Viñas, C. *Collect. Czech. Chem. Commun.* **1995**, *60*, 2023. (b) Holub, J.; Grüner, B.; Císařová, I.; Fusek, J.; Plzák, Z.; Teixidor, F.; Viñas, C.; Štíbr, B. *Inorg. Chem.* **1999**, *38*, 2775. (c) Grüner, B.; Lehtonen, A.; Kivekäs, R.; Sillanpää, R.; Holub, J.; Teixidor, F.; Viñas, C.; Štíbr, B. *Inorg. Chem.* **2000**, *39*, 2577. (d) Perekalin, D. S.; Holub, J.; Golovanov, D. G.; Lyssenko, K. A.; Petrovskii, P. V.; Štíbr, B.; Kudinov, A. R. *Organometallics* **2005**, *24*, 4387. (e) Grüner, B.; Bačkovský, J.; Císařová, I.; Štíbr, B. *J. Organomet. Chem.* **2005**, *690*, 2850. (f) Mutseneck, V.; Perekalin, D. S.; Holub, J.; Lysenko, K. A.; Petrovskii, P. V.; Štíbr, B.; Kudinov, A. R. *Eur. J. Inorg. Chem.* **2006**, 1737. (g) Perekalin, D. S.; Glukhov, I. V.; Štíbr, B.; Kudinov, A. R. *Inorg. Chim. Acta* **2006**, *359*, 3264. (h) Holub, J.; Bakardjiev, M.; Štíbr, B.; Štěpnička, P.; Císařová, I. *Eur. J. Inorg. Chem.* **2010**, 4196. (i) Holub, J.; Štíbr, B.; Štěpnička, P.; Císařová, I. *Dalton Trans.* **2010**, *39*, 2057. (j) Bakardjiev, M.; Štíbr, B.; Holub, J.; Grüner, B.; Padělková, Z.; Růžička, A. *Organometallics* **2013**, *32*, 377.

(15) See, for example: (a) Plumb, C. A.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1992**, *11*, 1665. (b) Plumb, C. A.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1992**, *11*, 1672. (c) Plumb, C. A.; Sneddon, L. G. *Organometallics* **1992**, *11*, 1681. (d) Perez-Gavilan, A.; Carroll, P. J.; Sneddon, L. G. *Collect. Czech. Chem. Commun.* **2010**, *75*, 905. (e) Ramachandran, B. M.; Wang, Y.; Kang, S. O.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **2004**, *23*, 2989. (f) Barnum, B. A.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **1997**, *36*, 1327. (g) Perez-Gavilan, A.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **2012**, *51*, 5903.

(16) For review see, for example: (a) Knappke, C. E. I.; von Wangelin, J. A. *Chem. Soc. Rev.* **2011**, *40*, 4948. (b) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.

(17) Mc Farlane, W. *Proc. R. Soc. London, Ser. A* **1968**, *306*, 175.

(18) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

(19) Coppens, P. In *Crystallographic Computing*; Ahmed, F. R., Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, 1970, p 255.

(20) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(21) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.