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# Unusual Closure of the Ten-Vertex Nido Cage via Alkylation: Regiospecific Synthesis of 3-Alkyl Derivatives of *closo*-1,2-$C_2B_8H_{10}$

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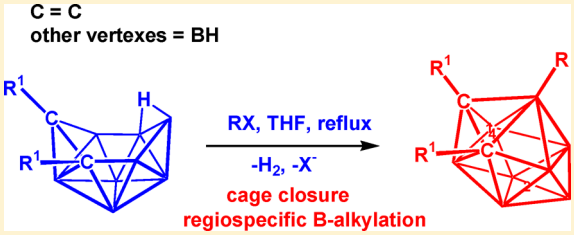
Supporting Information

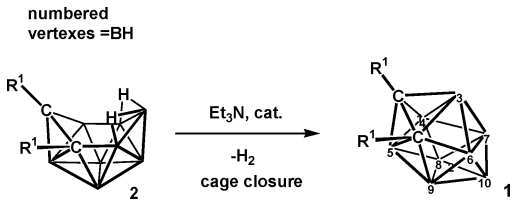
**ABSTRACT:** Alkylation of the [*nido*-5,6-$R^1_2C_2B_8H_9$]$^-$ anions (where $R^1$ = H and Me) with alkyl halides (RX, where R = primary and secondary alkyls) in boiling tetrahydrofuran (THF) proceeds via unusual $H_2$ elimination, followed by cage closure to give a series of the neutral *closo*-1,2-$R^1_2C_2B_8H_7$-3-R derivatives in ∼70−80% yields. In contrast, treatment of the unsubstituted [*nido*-5,6-$C_2B_8H_{11}$]$^-$ anion with *tert*-butyl bromide (*t*-BuBr) led to the formation of the parent *closo*-1,2-$C_2B_8H_{10}$ in >85% yield. The constitution of all compounds isolated has been confirmed unambiguously by multinuclear ($^{11}$B, $^1$H, and $^{13}$C) nuclear magnetic resonance measurements and α-shift correlation assessments.




## INTRODUCTION

The dicarbaborane *closo*-1,2-$C_2B_8H_{10}$ and its C-substituted derivatives (general structure **1**) were isolated as side products from alkyne insertion into *nido*-$B_8H_{12}$[1] and 4-L-*arachno*-$B_9H_{13}$,[2,3] or from the oxidation of the [*nido*-$C_2B_9H_{12}$]$^-$ anion.[4,5] Apart from other chemistry of *nido*-5,6-$R_2C_2B_8H_{10}$ carboranes (**2**) (where $R^1$ = H or alkyl) of type **2**,[6−13] we have just recently reported that they undergo a high-yield dehydrogenation in refluxing acetonitrile in the presence of a catalytic amount of triethylamine to afford closo derivatives **1** (see Scheme 1).[14] This reaction is supposed to proceed via

**Scheme 1. Closure of the 10-Vertex Nido Dicarbaborane Cage (2) via $Et_3N$-Promoted Catalytic Dehydrogenation**




triethylammonium salts which in turn undergo dehydrogenation under skeletal closure:

$$[nido\text{-}5,6\text{-}R_2C_2B_8H_9]^-HNEt_3^+ \rightarrow closo\text{-}1,2\text{-}R_2C_2B_8H_8 + Et_3N + H_2 \quad (1)$$

Despite numerous reports[15−19] on the synthesis, reactions and structure of the *closo*-1,2-$R_2C_2B_8H_8$ dicarbaboranes, 10-vertex analogs of the popular *o*-carborane, only the methylation at the C-vertexes via standard LiBu/MeI method[17] and electrophilic halogenation at B9 and B10 sites[18] have been published; no other reports on reactions leading to direct substitution of the carborane cage in compounds **1** have so far been available.

In this article we wish to report on an important route to boron substituted derivatives of **1** bearing alkyl substituents on the B3 vertex which is connected to both cluster-carbon vertexes. The main feature of this synthesis consists in an unusual dehydroalkylation of the [*nido*-5,6-$R^1_2C_2B_8H_9$]$^-$ (**2**$^-$) anions leading regioselectively to a series of asymmetrically substituted *closo*-1,2-$R^1_2C_2B_8H_7$-3-R derivatives.

## RESULTS AND DISCUSSION

**Syntheses.** In view of the fact that that the alkylation of the [*nido*-$B_{10}H_{13}$]$^-$ anion takes place mostly at the apex B6 site,[20−22] it was reasoable to examine the comparable B-alkylation of the isoelectronic [*nido*-5,6-$R^1_2C_2B_8H_9$]$^-$ anions (**2**$^-$). As illustrated in Scheme 2, reactions between the **2a**$^-$ anion[12] ($Na^+$ salt, generated in situ by treatment of the neutral *nido*-5,6-$C_2B_8H_{12}$ (**2a**) carborane with excess NaH) and selected alkyl halides (RX) (where RX = MeI, EtBr, *n*-PrBr, *i*-PrBr, *n*-BuBr, and $PhCH_2Br$) in boiling thetrahydrofuran (THF) result in the isolation of a series of B-substituted *closo*-1,2-$C_2B_8H_9$-3-R (**4a−4f**) derivatives (see eq 2 and Scheme 2).

$$[nido\text{-}5,6\text{-}C_2B_8H_{11}]^- (\mathbf{2a}^-) + RX \rightarrow closo\text{-}1,2\text{-}C_2B_8H_9\text{-}3\text{-}R\ (\mathbf{4a−4f}) + H_2 + X^- \quad (2)$$

Interestingly, the reaction with allyl bromide resulted in clean formation of the *n*-Pr derivative **4c**, obviously due to internal hydrogenation of the double bond:

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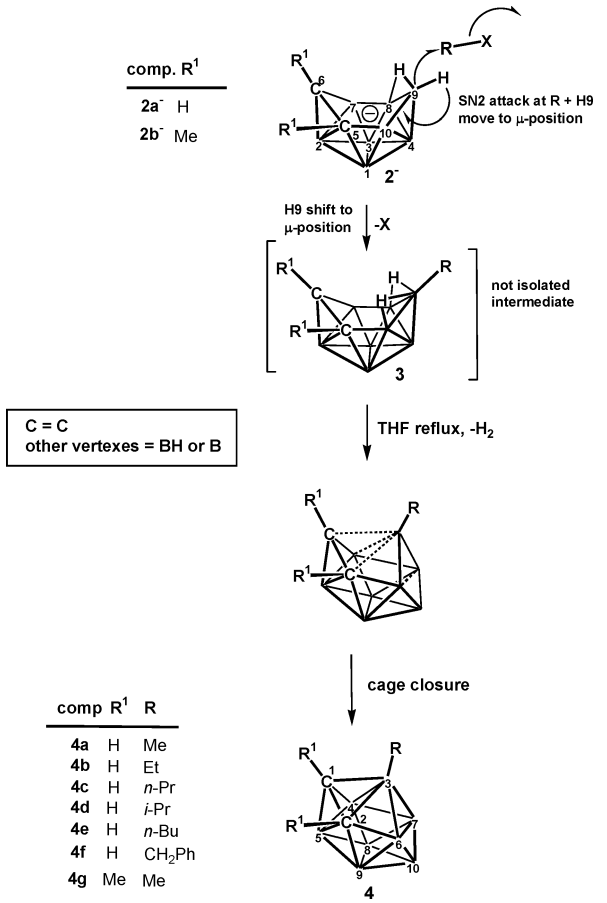
**Scheme 2. Proposed Mechanisms and Stereochemistry of the Formation of the 1,2-$R^1_2$-*closo*-1,2-$C_2B_8H_7$-3-R (4) Derivatives**




$$[nido\text{-}5,6\text{-}C_2B_8H_{11}]^- + C_3H_5Br \rightarrow closo\text{-}1,2\text{-}C_2B_8H_9\text{-}3\text{-}n\text{-}C_3H_7\ (\mathbf{4c}) + Br^- \quad (3)$$

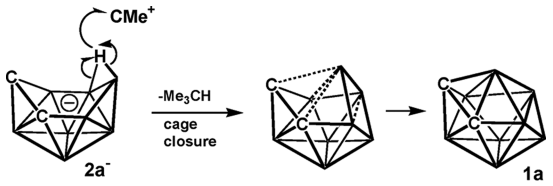
The main reaction mode (2), dehydroalkylation, (see also Scheme 2) is predominant and fast (yields 70−80%) when R = primary alkyls. The reaction with *i*-PrBr was much more sluggish and had to be carried out at a higher temperature (~100 °C) in a Pyrex tube, being at the same time accompanied by hardly separable rearrangement coproducts. In all cases, the resulting compounds of structure **4** can be purified by LC chromatography on a silica gel support. The compounds are usually isolated as liquid or semiliquid substances unsuitable for X-ray diffraction analysis. A similar reaction of the carbon disubstituted [5,6-$Me_2$-*nido*-5,6-$C_2B_8H_{10}]^-$ (**2b**$^-$) anion with MeI in refluxing THF gave the trimethylated species *closo*-1,2- $Me_2C_2B_8H_7$-3-Me (**4g**) (yield ~80%) as the main product.

Although no mechanistic studies have been done, the formation of compounds **4** might be consistent with a SN2-type attack by the electronegative B9-vertex in anion **2**$^-$ (see also Figure S2) at the substituted RX carbon atom, followed by $X^-$ and $H_2$ elimination upon H9-move to the bridging site and skeletal closure, as shown in Scheme 2. The apex-substituted intermediate **3** has not been isolated even at room temperature, because of its fast dehydrogenation to **4**.

It should also be noted that the main reaction mode (2) is sometimes (especially for R = Me, Et, and $CH_2Ph$) accompanied by side (~5%) formation of the unsubstituted *closo*-1,2-$C_2B_8H_{10}$ (**1a**) via RH elimination (see eq 4); fortunately, **1a** can be separated from the main product **4** by LC chromatography. Consistent with the reaction mode (4) is, however, the high-yield (>85%) formation of the parent carborane **1a** on treatment of the **2a**$^-$ anion with *t*-BuBr in refluxing THF (see Scheme 3). The reaction may proceed via SN1 mechanism with the $Me_3C^+$ carbocation acting as $H^-$ acceptor:

$$[nido\text{-}5,6\text{-}C_2B_8H_{11}]^- + RX \rightarrow closo\text{-}1,2\text{-}C_2B_8H_{10}\ (\mathbf{1a}) + RH + X^- \quad (4)$$

**Scheme 3. Possible SN1 Mode in Oxidative Extrusion of the $H^-$ Anion from the Cage of 2a$^-$ by the Action of the $Me_3C^+$ Carbocation under $Me_3CH$ Elimination**




Reaction 4 seems to be associated with $H^-$ extraction from **2a**$^-$ by the $R^+$ carbocation, followed by cage closure (Scheme 3).

**NMR Spectra.** All the NMR spectra ($^{11}B$, $^1H$, and $^{13}C$) of the 3-alkyl derivatives of general structure **4** are graphically illustrated in Figures 1 and S1 along with complete assignments. As an example of NMR measurements, see those of the *n*-Pr derivative in Figures 2 and 3 (for a broader selection of other NMR spectra, see the SI, Figures S3−S21). The $^{11}B$ NMR spectra of the asymmetrical 3-R-substituted closo derivatives **4** display one B(3)-singlet and seven doublets assigned by [$^{11}B-^{11}B$]-COSY NMR measurements[23] to boron vertexes B10, B4, and B5 and to the less resolved B7, 8, and B6/9 signals (reading upfield); the spectra excellently correlate with that of the parent **1a**.[14] Moreover, $^1H$-{$^{11}B$(selective)}[24] measurements led to complete assignments of BH resonances to individual cage positions, at least in the well resolved area. Though individual 3-alkyl substituents do not differ too much in their shielding properties at the substituted ($\alpha$) site, there is a trend for $\alpha$-shielding decreasing in the order Me > $PhCH_2$ > Et > *n*-Pr > *i*-Pr > *n*-Bu (see the $\alpha$-shift correlation (ASC) diagram[25] of Figure 4). The diagram is in agreement with a straightforward linear correlation between $\alpha$-shifts (*x*-axis) and substituent chemical shift (SCS) values in unsubstituted cage positions (*y*-axis; individual correlation lines are indexed as *g*/assignment[25]). An important ASC feature is that the linearity applies to all nuclei involved in the skeletal bonding, i.e., $^{11}B$, $^1H$, and $^{13}C$.[25] This ASC analysis also suggests that $\beta$-positions are, along with the $\gamma$-*trans* B5 vertex, the most sensitive sites to $\alpha$-shift changes at position B3 with sensitivities decreasing in the order: C1 > C2 ≫ B4.

Apart from resonances derived from the R-substituent, the $^1H$ and $^{13}C$ NMR spectra (see framed text in Figure S1) exhibit two distinct CH or CMe singlet resonances. The spectra, however, do not show broad variations due to rather similar structures. Of diagnostic value are certainly the broad $^{13}C$ signals due to B(3)-C substitution in the high-field area as a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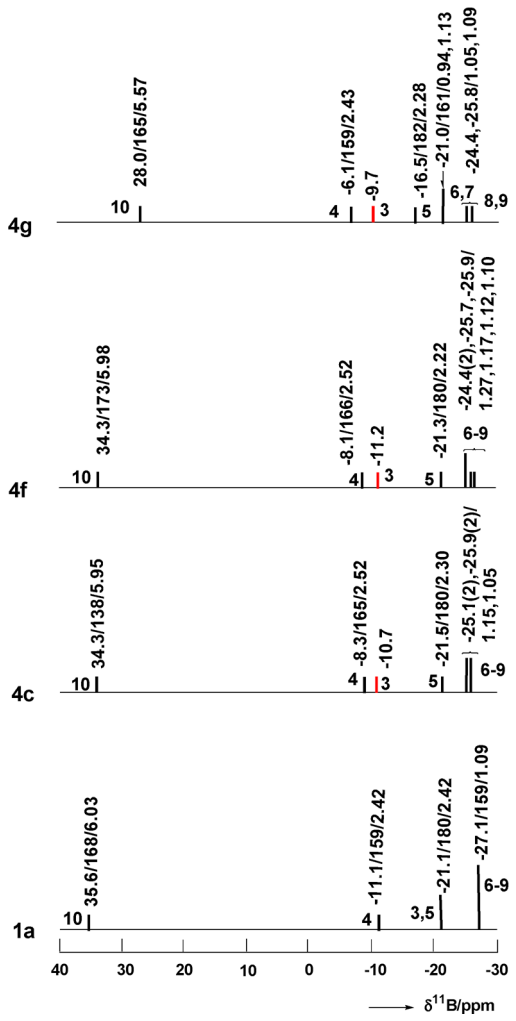


**Figure 1.** Stick diagrams comparing the 128.3 or 190.2 MHz $^{11}$B NMR chemical shifts in $CDCl_3$ and relative intensities for the parent **1a** derivative with those for the 3-alkylated derivatives **4** exemplified by **4c**, **4f**, and **4g**. The data are ordered as $\delta(^{11}B)/^{1}J_{BH}/\delta(^{1}H)_{BH}$, singlets in red. For NMR data of all derivatives, see the Supporting Information, Figure S1).

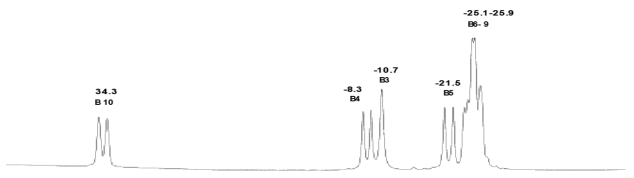


**Figure 2.** $^{11}$B NMR spectrum (128.3 MHz, $CDCl_3$) of *closo*-1,2-$C_2B_8H_9$-3-Pr (**4c**).

consequence of the $^{1}J(^{13}C-^{11}B)$ coupling (see Figure S6, for example).

## CONCLUSIONS

While the long-known alkylation of the $[nido\text{-}B_{10}H_{13}]^-$ anion takes place mostly at the apex B6 site,[20−23] a comparable B-alkylation of the isoelectronic $[nido\text{-}5,6\text{-}R^1{}_2C_2B_8H_9]^-$ anions ($\mathbf{2}^-$) with primary alkyl halides proceeds most likely at the equivalent apex B9-position, too. However, the anticipated 9-R substituted *nido* intermediates **3** tend to spontaneously loose dihydrogen, affording regioselectively 3-alkyl substituted *closo*-1,2-dicarbadecaboranes **4** (for structural work in the area of

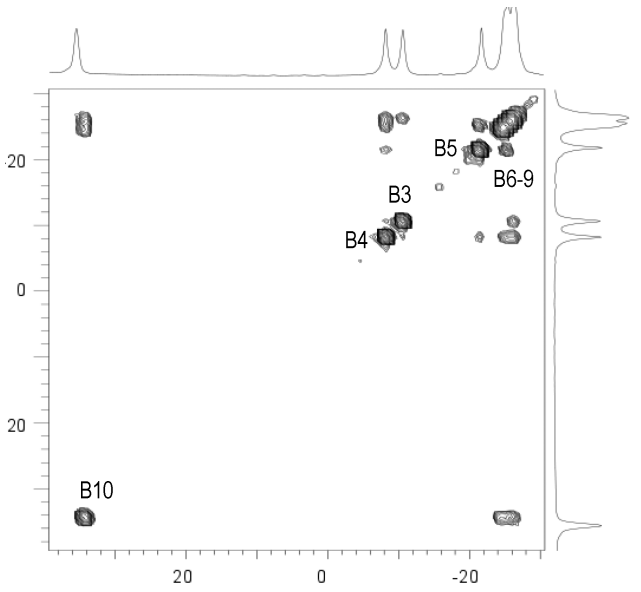


**Figure 3.** $^{11}$B−$^{11}$B COSY NMR spectrum (128.3 MHz, $CDCl_3$) of *closo*-1,2-$C_2B_8H_9$-3-Pr (**4c**).

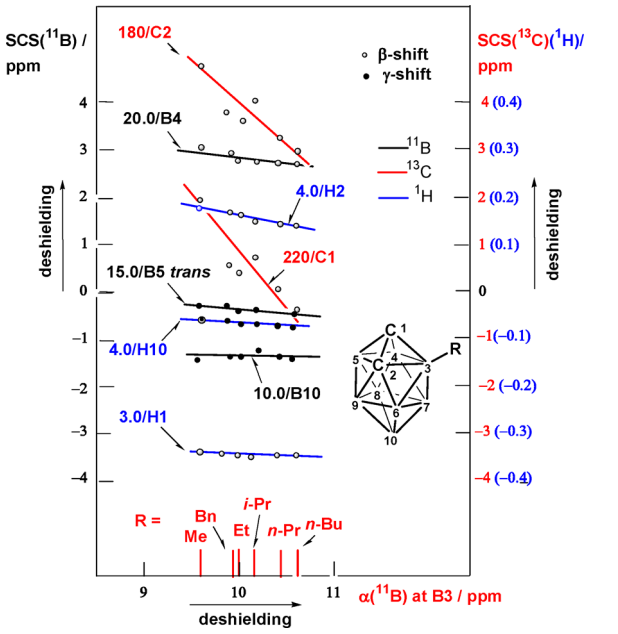


**Figure 4.** ASC diagram for selected cage positions in **4** as a plot of SCS ($^{11}$B) (black), ($^{13}$C) (red), and ($^{1}$H) (blue) for unsubstituted cluster positions vs $\alpha(^{11}B)_{exp}$-shifts.

type-**1** carboranes, see refs 14 and 18), even under relatively mild conditions employed in this work (refluxing THF). In contrast, a similar reaction of the parent $\mathbf{2a}^-$ anion with *t*-BuBr represents an alternative access to the unsubstituted *closo*-1,2-$C_2B_8H_{10}$ dicarbaborane **1a**. It is also evident that compounds of structure **4** can be used as "boron labels" for various syntheses in the dicarbaborane or metalladicarbaborane area and as starting materials for various substitution reactions, either on the cage-carbon or boron vertexes. All these aspects may perhaps help renew interest in this less explored area of carborane chemistry.



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## EXPERIMENTAL SECTION

All the syntheses have been performed in an inert atmosphere, but subsequent operations, such as column LC, were carried out in air. Dichloromethane and hexane were dried over $CaH_2$ and freshly distilled before use; THF was distilled from sodium diketyl. Other chemicals were of reagent or analytical grade and were used as purchased. Column chromatography was performed on a silica gel support (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 in the $ESI^-$ mode and NMR spectroscopy was performed at 400 and 600 Mz (for $^1H$). Standard [$^{11}B-^{11}B$]-COSY[23] (and $^1H$-{$^{11}B$(selective)}[24] NMR experiments led to complete assignments of all resonances to individual cage BH units, at least in the well resolved area. Chemical shifts are given in parts per million (ppm) and referenced to $F_3B{\cdot}OEt_2$ (for $^{11}B$, quoted ±0.5 ppm) and TMS (for $^1H$ and $^{13}C$, quoted ±0.05 and 0.5 ppm, respectively) and the solvent resonances were used as internal secondary standards. The starting carboranes of structure **2** have been prepared according to methods previously reported.[3,4,8]

***closo*-1,2-$R^1_2C_2B_8H_7$-3-R (4) Carboranes (Where $R^1$, R = H, Me 4a; H, Et 4b; H, *n*-Pr 4c; H, *i*-Pr 4d; H, *n*-Bu 4e; H, $PhCH_2$ 4f; Me, Me 4g).** A solution of the corresponding *nido*-5,6-$R^1_2C_2B_8H_{10}$ (**2**) carborane (where $R^1$ = H **2a** and Me **2b**; reaction scale 1−2 mmol) in THF (10 mL) was treated with about a 2-fold excess of sodium hydride under stirring at room temperature. After the hydrogen evolution had ceased, the supernatant NaH was removed by filtration or centrifugation. The clear yellowish solution of the corresponding $\mathbf{2}^-$ salt was treated with methyl iodide or with the corresponding alkyl bromide (1−2 mL) and the mixture was heated at reflux for ∼6 h. The mixture was filtered after cooling down to ambient temperature, treated with silica gel (∼5 g) under cooling to 0 °C and the volatiles were then distilled off on a rotary evaporator. The residual material was mounted onto the top of a column packed with silica gel (∼2.5 × 20 cm) which was then eluted with 10% $CH_2Cl_2$ in hexane to collect a combined main fraction of $R_F$ (anal, benzene) ∼ 0.4, which was then evaporated and subjected to sublimation at 100−120 °C (bath) onto a 0 °C glass finger. The compounds of structure **4** thus isolated in 70−80% yields are colorless or off-white semisolids, whose identity was checked by NMR. For **4a**: *m*/*z* (max) calcd 135.17, found 135.16; for $C_3H_{12}B_8$ (mw 134.62) calcd 26.77% C, 8.99% H, found 26.64% C, 8.51% H. For **4b**: *m*/*z* (max) calcd 149.19 found 149.20; for $C_4H_{14}B_8$ (mw 148.64) calcd 32.32% C, 9.49% H, found 32.10% C, 9.31% H. For **4c**: *m*/*z* (max) calcd 163.20, found 163.25; for $C_5H_{16}B_8$ (mw 162.67) calcd 36.92% C, 9.91% H, found 36.84% C, 9.80% H. For **4d**: *m*/*z* (max) calcd 163.20 found 163.35; for $C_5H_{16}B_8$ (mw 162.67) calcd 36.92% C, 9.91% H, found 36.53% C, 9.78% H. For **4e**: *m*/*z* (max) calcd 177.22 found 177.28; for $C_6H_{18}B_8$ (mw 176.70) calcd 40.78% C, 10.27% H, found 40.71% C, 10.10% H. For **4f**: *m*/*z* (max) calcd 211.20 found 211.25; for $C_9H_{16}B_8$ (mw 210.71) calcd 51.30% C, 7.65% H, found 51.17% C, 7.39. For **4g**: *m*/*z* (max) calcd 163.20 found 163.24; for $C_5H_{16}B_8$ (mw 162.67) calcd 36.92% C, 9.91% H, found 36.14% C, 9.70% H. For NMR spectra, see Figure S1.

***closo*-1,2-$C_2B_8H_{10}$ (1a).** A solution of the *nido*-5,6-$C_2B_8H_{12}$ (**2a**) carborane (123 mg, 1 mmol) in THF (10 mL) was treated with a 2-fold excess of sodium hydride (50 mg) under stirring at room temperature. After the hydrogen evolution had ceased, the supernatant NaH was removed by vacuum filtration. The clear yellowish filtrate containing the $\mathbf{2a}^-$ salt was treated with *t*-BuBr (2 mL), and the mixture was heated at reflux for ∼6 h. The mixture was evaporated on a rotary evaporator and the residue subjected to vacuum sublimation (bath temperature ∼90 °C) onto a glass finger cooled to ∼−15 °C to isolate 106 mg (86%) of **1a** which was identified by $^{11}B$ NMR (see Figure 1).

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b02783.

Stick diagrams involving all NMR data and a selection of authentic NMR spectra of compounds of type **4** (PDF)

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### Notes

The authors declare no competing financial interest.

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