Metal-Promoted Cage Rearrangements in the Tricarbollide Series: Conversion of Ligand Derivatives 7-L-*nido*-7,8,9-$C_3B_8H_{10}$ (L = H_3N, *t*BuH_2N, Me_2HN) into Neutral 8-R-*nido*-7,8,9-$C_3B_8H_{11}$ (R = H_2N, *t*BuHN, Me_2N) Compounds

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Keywords: Boranes / Carboranes / NMR spectroscopy / Rearrangement / N ligands

Deprotonation of the eleven-vertex tricarbaborane zwitterions 7-L-*nido*-7,8,9-$C_3B_8H_{10}$ [**1**: L = H_3N (**1a**), *t*BuH_2N (**1b**), Me_2HN (**1c**)], followed by reactions with metal reagents [FeI_2, $NiCl_2$, and $Ni(C_5H_5)_2$] at higher temperatures and in situ acidification, led to the 7 → 8 rearrangement of the *N*-substituted cage carbon atom to yield a series of 8-amino-substituted derivatives of *nido*-7,8,9-$C_3B_8H_{12}$. These were characterized as 8-R-*nido*-7,8,9-$C_3B_8H_{11}$ [**2**: R = H_2N (**2a**), *t*BuHN (**2b**), Me_2N (**2c**)]. A possible rearrangement mechanism for their formation has been proposed. Deprotonation of compound **2a** with proton sponge [PS = 1,8-bis(dimethylaminonaphthalene)] generated the [8-*t*BuHN-*nido*-7,8,9-$C_3B_8H_{10}]^-$ (**2b**$^-$) anion, which can be reprotonated to give the original compound **2b** and not the tautomeric zwitterion 8-*t*BuH_2N-*nido*-7,8,9-$C_3B_8H_{10}$ (**3b**). All compounds were characterized by high-field (^{11}B and ^1H) NMR and IR spectroscopy, and mass spectrometry. The molecular structures of the neutral carbaborane **2b** and its salt PSH$^+$**2b**$^-$were determined by single-crystal X-ray diffraction analyses.

Introduction

Over the last decade, there has been a growing interest in the chemistry of ten- and eleven-vertex tricarbaboranes.[1−6] The first representatives of the eleven-vertex family (tricarbollides), ligand derivatives 7-L-*nido*-7,8,9-$C_3B_8H_{10}$ (L = amines)[2,6] and the parent tricarbollides *nido*-7,8,9-$C_3B_8H_{12}$ and [*nido*-7,8,9-$C_3B_8H_{11}]^-$, were discovered in 1995.[3,6] An extension of this chemistry has led to the isolation of the isomeric [*nido*-7,8,10-$C_3B_8H_{10}]^-$ anion,[3] its 7-substituted (alkyl and aryl)[4a] and amine-ligand derivatives,[2,4b,4c,6] and finally to the synthesis of isomeric 7-R-*nido*-2,7,10-$C_3B_8H_{11}$ (R = alkyl and aryl)[5] compounds. Later efforts in this area were directed to the exploration of metal complexation properties since $[C_3B_8H_{11}]^-$-type anions can be regarded as cyclopentadienide analogues.[6−12] This research led, in turn, to the isolation of a whole series of metallatricarbollides in which the tricarbaborane core acts as an η^5-coordinating ligand.[6−12] We report herein that, with certain metal reagents, the expected complexation reaction of the [7-R-7,8,9-$C_3B_8H_{10}]^-$ anions (R = H_2N, *t*BuHN, and Me_2N) fails, leading instead to an unexpected 7 → 8 migration of the R−C(cage) carbon atom with the formation of new 8-R-*nido*-7,8,9-$C_3B_8H_{11}$ compounds in moderate to good yields. These are 8-amino-substituted derivatives of *nido*-7,8,9-$C_3B_8H_{12}$ [2,3] and are tautomeric with regards to the nonexistent zwitterions of the 8-L-*nido*-7,8,9-$C_3B_8H_{10}$ compounds. The numbering system for the eleven-vertex compounds used in this work can be seen in Schemes 1 and 2, and in Figures 1−3. The unmarked vertices in Schemes 1 and 2 denote cage BH units.

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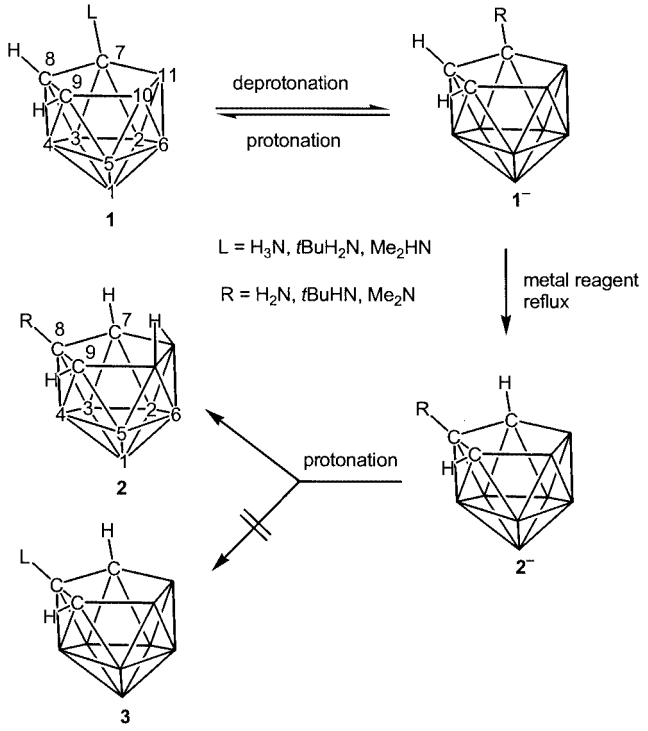
Results and Discussion

Syntheses

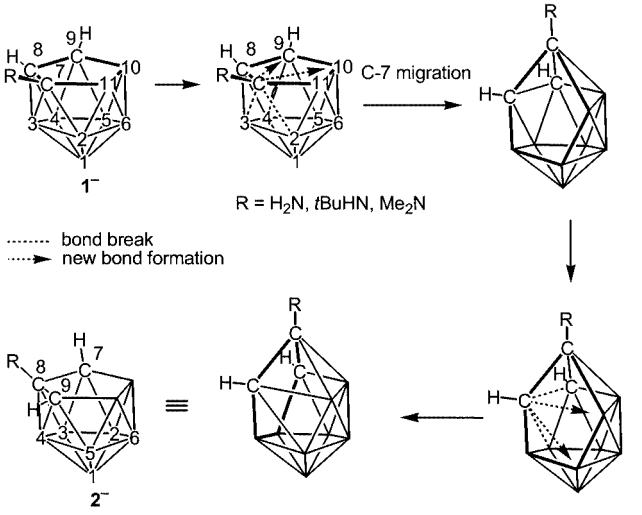
As shown in Scheme 1, selected zwitterionic compounds of the type 7-L-*nido*-7,8,9-$C_3B_8H_{10}$ [**1**: L = H_3N (**1a**), *t*BuH_2N (**1b**), Me_2HN (**1c**)] were deprotonated in situ at the exoskeletal N site by gentle heating with sodium hydride in DME (1,2-dimethoxyethane) or diethylene glycol dimethyl ether (diglyme) (see Table 1) to give the anions [7-R-*nido*-7,8,9-$C_3B_8H_{10}]^-$ [**1**$^-$: R = H_2N (**1a**$^-$), *t*BuHN (**1b**$^-$), Me_2N (**1c**$^-$)]. These were treated with selected metal reagents [FeI_2, $NiCl_2$, $NiCp_2$ (Cp = $C_5H_5^-$)] at elevated temperatures (95−140 °C, see Table 1) to give the isomeric anions [8-R-*nido*-7,8,9-$C_3B_8H_{10}]^-$ [**2**$^-$: R = H_2N (**2a**$^-$), *t*BuHN (**2b**$^-$), Me_2N (**2c**$^-$)]. Final acidification of the reaction mixture gave a series of neutral compounds of general formulation 8-R-*nido*-7,8,9-$C_3B_8H_{11}$ [**2**: R = H_2N (**2a**), *t*BuHN (**2b**), Me_2N (**2c**)]. As seen from Scheme 1, the net result of

these reactions is, instead of the expected metal complexation, an unusual migration of the amine functionality into the adjacent C-8 position. When compared to structures **1**, compounds **2** thus formed, have lost their original zwitterionic character, being transformed into the tautomeric 8-amino-substituted derivatives of the neutral tricarbaborane *nido*-7,8,9-$C_3B_8H_{12}$.[3] It should be noted that the reactions do not proceed without deprotonation of compounds **1** preceding the reaction with individual metal reagents. The role of the metal reagents is quite obscure, as no sign of complex formation is observed during the reactions, nevertheless, the reactions do not proceed in the absence of the metal reagent. Moreover, the reactions never come to completion (see Table 1) and the starting compounds can easily be recovered by chromatography.



Scheme 1

Although there is no direct evidence on the reaction mechanisms, the formation of anions of type $\mathbf{2}^-$ from anions of type $\mathbf{1}^-$ is consistent with a simple C-7 vertex-swing mechanism outlined in Scheme 2. The mechanism is similar to that proposed recently by Sneddon et al.[5] and involves the formation of two new bonds together with a cleavage of two original bonds around the C-7 vertex. The new system, thus formed, has one of the skeletal carbon atoms in an unfavorable high-connectivity position and is therefore rearranged in a similar manner to the isomeric anions $\mathbf{2}^-$.



Scheme 2

An interesting aspect is the final protonation of the $\mathbf{2}^-$ anions as there are two ways in which the proton can be added (see Scheme 1). In contrast to the anions $\mathbf{1}^-$, the protonation of $\mathbf{2}^-$does not occur on the exoskeletal nitrogen atom with the anticipated formation of the 8-L-*nido*-7,8,9-$C_3B_8H_{10}$ zwitterions (compounds of type **3**), but exclusively on the open-face B-10−B-11 edge to give the tautomeric 8-R-*nido*-7,8,9-$C_3B_8H_{11}$ (**2**) compounds, 8-substituted derivatives of the parent tricarbollide 7,8,9-$C_3B_8H_{12}$ (**4**).[3]

As demonstrated by a separate experiment, the deprotonation of compound **2b** with PS (see also Scheme 1) proceeds by abstraction of the μ_{10-11} bridging proton with the formation of anion $\mathbf{2b}^-$, which by reprotonation returns to the original compound **2b**, and not the zwitterionic compound **3b**.

Structural Studies

The structures of the neutral compound **2b** and the corresponding salt $PSH^+\mathbf{2b}^-$ were determined by single-crystal

Table 1. Conditions for the formation of 8-amino-substituted derivatives of type **2**

Starting compound	Metal reagent	Conditions	Product	Yield (%)
1a	FeI_2	DME, reflux, 2 h	**2a**	43 (50)[a]
1b	FeI_2	diglyme, 120 °C, 16 h	**2b**	48 (67)[a]
1b	$NiCl_2$	DME, reflux, 16 h	**2b**	51 (64)[a]
1b	$NiCl_2$	diglyme, 140 °C, 16 h	**2b**	60
1b	$NiCp_2$	diglyme, 140 °C, 24 h	**2b**	30
1c	$NiCl_2$	DME, reflux, 42 h	**2c**	18 (66)[a]

[a] Yields based on recovered starting compounds **1** in parentheses.

X-ray diffraction analyses (see Figures 1−3). The molecular structure of the latter salt shows that the arrangement of the substituent at the C8 site and the whole cage remain unaltered by deprotonation. Both structures confirm the adjacent position of all three of the cage carbon atoms in the *nido* cage and the substitution on the central C8 atom. Two symmetrically independent molecules in the unit cell of **2b** differ only slightly in the orientation of the *t*Bu moiety. Selected interatomic distances and angles for both species (see Table 2) show all expected features, with the shortest distances between carbon atoms. The longest interboron distances are those between the open-face B10−B11 vertices. This distance is even more elongated by the presence of the hydrogen bond in **2b** [1.841(3) Å] in comparison with the corresponding separation in PSH^+**2b**$^-$ [1.727(2) Å]. The latter distance is similar to that found for B10−B11 in the zwitterionic compound 7-*t*BuHMeN-7,8,9-$C_3B_8H_{10}$ [1.725(3) Å].[2b]

The structures of all remaining amino derivatives **2a** and **2c** were proposed from the structurally determined com-

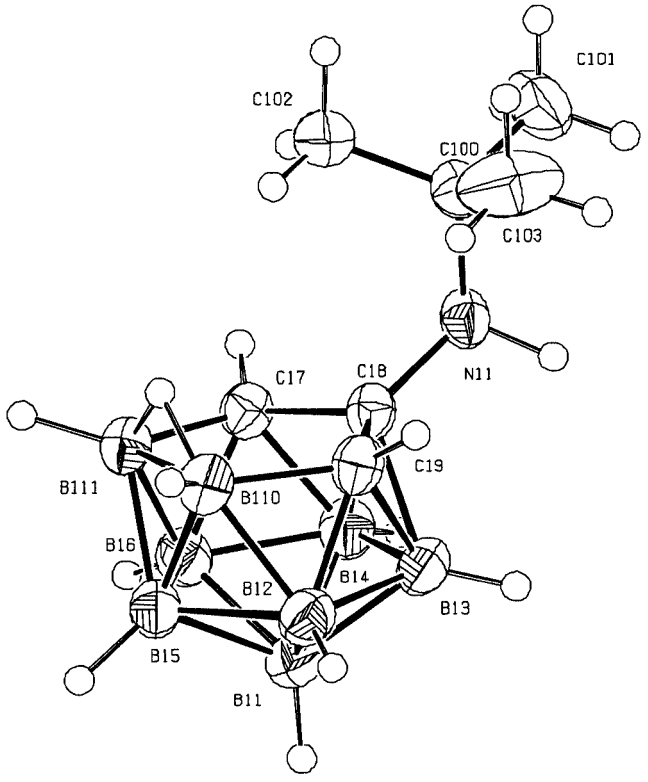


Figure 1. Perspective view of the first molecule of **2b** with atom-numbering scheme (PLATON, displacement ellipsoids at the 50% probability level)

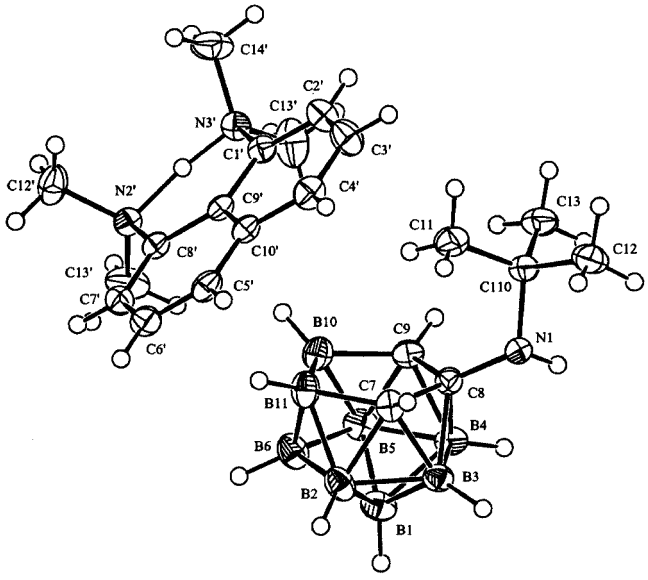


Figure 3. View of the first molecule of PSH^+**2b**$^-$ with atom-numbering scheme (PLATON, displacement ellipsoids at the 50% probability level)

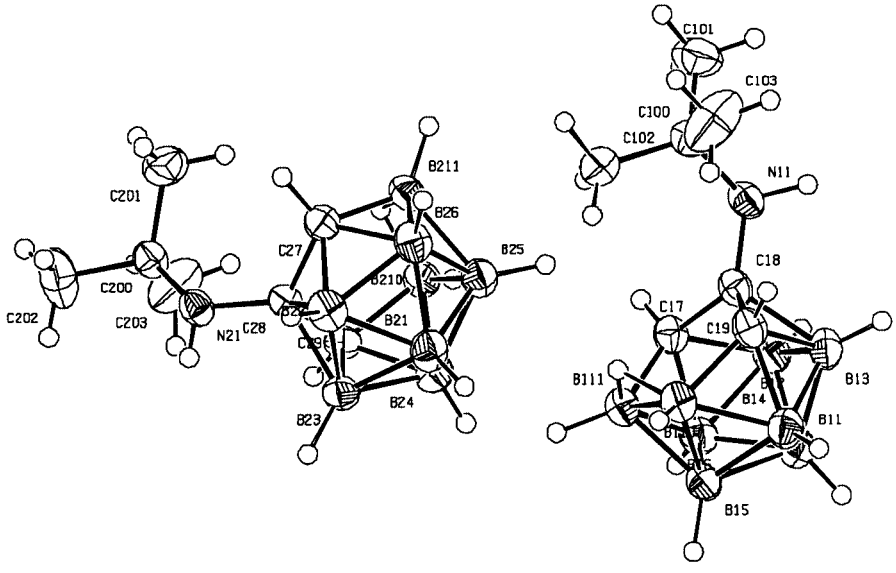


Figure 2. ORTEP representation of two symmetrically independent molecules differing slightly in the orientation of the *t*Bu group present in the unit cell of **2b**

Table 2. Selected interatomic distances [Å] and angles [°] for **2b** and PSH^+**2b**$^-$

Compound	**2b**, molecule 1 * = 1	**2b**, molecule 2 * = 2	PSH^+**2b**$^-$ * = blank
C(*7)−C(*8)	1.529(3)	1.527(3)	1.5283(15)
C(*7)−B(*11)	1.654(3)	1.652(3)	1.6223(18)
C(*8)−N(*1)	1.427(3)	1.419(3)	1.4351(15)
C(*8)−C(*9)	1.536(3)	1.530(3)	1.5359(16)
C(*9)−B(*10)	1.653(3)	1.640(3)	1.6199(19)
B(*10)−B(*11)	1.840(3)	1.841(3)	1.727(2)
N(*1)−C(*10)	1.481(3)	1.506(2)	1.4896(15)
C(*8)−C(*7)−B(*11)	109.92(16)	109.39(16)	111.74(10)
C(*7)−C(*8)−C(*9)	113.86(16)	114.27(16)	109.04(9)
C(*8)−C(*9)−B(*10)	109.86(17)	109.72(16)	111.59(10)
C(*9)−B(*10)−B(*11)	102.69(17)	102.85(16)	103.75(10)
B(*10)−B(*11)−C(*7)	102.78(16)	102.66(16)	103.66(6)
N(*1)−C(*8)−C(*7)	118.32(18)	117.82(17)	117.89(9)
N(*1)−C(*8)−C(*9)	121.20(17)	121.35(17)	124.62(10)
C(*8)−N(*1)−C(*10)	120.70(16)	119.70(15)	119.05(9)
B(*10)−H(*01)	1.28(2)	1.28(2)	
B(*11)−H(*01)	1.16(2)	1.27(2)	

pound **2b**, on the basis of close similarities in their NMR spectroscopic shielding behavior. The comparison revealed (see Figure 4) straightforward similarities between corresponding ^{11}B and ^{1}H resonances for all amino derivatives of **2**. The observed NMR spectroscopic data for this class of compounds (see Exp. Sect.), together with the results of mass spectrometry, are in excellent agreement with their formal descriptions as 8-amino-substituted derivatives of the previously reported parent tricarbaborane **4**.[3] All the cluster ^{11}B and ^{1}H resonances were interrelated by [^{11}B-^{11}B]-COSY[13] and/or ^{1}H{^{11}B(selective)}[14] experiments, which permitted complete assignments and thence comparisons with the known, but isomeric, 7-*t*BuMeN-10-Me-7,8,9-$C_3B_8H_{10}$ and 7-*t*BuMeN-10,11-Me_2-7,8,9-$C_3B_8H_9$ amine derivatives.[2b]

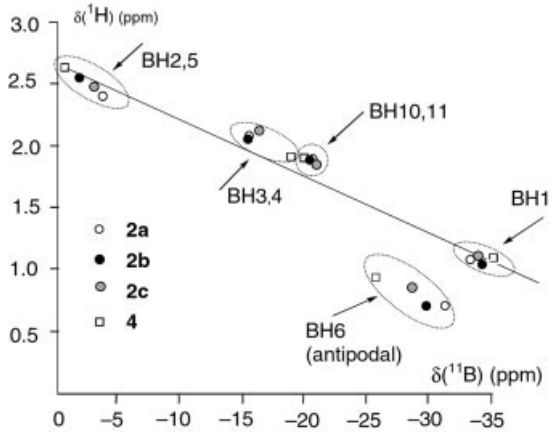


Figure 4. Graphical correlation between the ^{1}H and ^{11}B NMR chemical shifts for compounds **2a**, **2b**, and **2c**, and for the parent tricarbaborane **4**

As shown in Figure 4, the most significant feature of the compounds **2** is the 2:2:2:1:1 patterns of the ^{11}B resonances. These are very similar to those of the parent compound **4**, which is of the same C_s symmetry,[3] the most remarkable feature being the upfield shift of resonances assigned to the antipodal B-6 vertex. A similar effect was also observed in the spectrum of 8-Me-7,8,9-$C_3B_8H_{11}$,[3] the only 8-substituted derivative of **4** isolated so far. The ^{11}B NMR spectrum of PSH^+**2b**$^-$, showing (2+2+1):2:1 patterns of doublets (incidental overlap), is consistent with the same C_s symmetry. As expected, most of the peaks are markedly shifted upfield in comparison with adequate resonances observed for **2b** due to the absence of hydrogen bonding. This correlates closely with the observed bridge effect found in the ^{11}B NMR spectra for the couple of unsubstituted compounds **4** and [7,8,9-$C_3B_8H_{11}$]$^-$ (**4**$^-$).[3] Moreover, ^{1}H NMR spectra of compounds **2a**−**2c** clearly reveal, besides the 7,9-H resonance of intensity 2, a broad high-field singlet due to the presence of the μ_{10-11} bridging proton. As demonstrated graphically in Figure 4, there is an approximately linear correlation between the ^{11}B and ^{1}H chemical shifts for all derivatives of **2**, with the exception of data points for the antipodal B-6-H positions.

Mass spectrometric results along with similar chromatographic and solubility properties are all consistent with the proposed structures of the neutral derivatives of type **2**. Across the series, enhanced solubility in less polar solvents and higher R_f values were observed for **2** in comparison with the corresponding characteristics of the starting zwitterions of structure **1**.

Conclusions

It was shown that the zwitterionic tricarbollides **1** undergo an unusual metal-promoted cage rearrangement upon deprotonation and reaction with some metal reagents to generate isomeric compounds of type **2**. The net result of the rearrangement is a shift of the amine functionality to the adjacent position without changing the configuration of the cage carbon atoms. In contrast to the starting zwitterionic compounds of **1**, the rearranged compounds adopt the tautomeric neutral configuration of **2** and *not* the zwitterionic structure of **3** (see Scheme 1). The relation between structures **2** and **3** falls into the category of H-tautomerism as the two forms differ only in the positioning of the extra hydrogen atom. In structure **2** this hydrogen atom resides in the bridging open-face position, while in the zwitterionic structure **3** it would reside on the exoskeletal nitrogen atom. This interesting aspect of tautomerism in the eleven-vertex tricarbaborane series was encountered for the first time in the 7-substituted series of compounds of the general form 7-*t*BuMeN-10,11-R^1R^2-7,8,9-$C_3B_8H_9$ (R^1, R^2 = H or Me). For R^1 = R^2 = H these compounds exist exclusively in the zwitterionic form 7-*t*BuMeHN-7,8,9-$C_3B_8H_{10}$ (**1d** for L = *t*BuMeHN), while the formally *B*-mono- and *B*,*B*-dimethylated derivatives of **1d**, exist only in the neutral tautomeric forms 7-*t*BuMeN-10-Me-7,8,9-$C_3B_8H_{10}$ and 7-*t*BuMeN-10,11-Me_2-7,8,9-$C_3B_8H_9$.[2b] It seems highly probable that both the electron density on the nitrogen center and the type of substitution of the tricarbaborane core play decisive

roles in determining the preferences for individual tautomeric forms. It is also highly probable that compounds of the general structure **2**, isolated in this work, act as intermediates in the metal complexation reactions of anions of type $\mathbf{1}^-$.[6−12] We are currently studying the aspects of tautomerism and associated rearrangements of tricarbaborane cages occurring during the metal complexation process in more detail. Studies on further interesting rearrangement reactions of compounds of the type **2** and $\mathbf{2}^-$, at high temperatures, are also in progress.

Experimental Section

General Procedures: All reactions were carried out with the use of standard vacuum or inert gas techniques as described by Shriver,[15] although some operations, such as preparative LC, were carried out in air. The starting compounds **1** were prepared according to the literature.[2] The Aldrich DME and diglyme were dried with sodium metal and freshly distilled from sodium diphenylketyl or NaH. Hexane and benzene were dried with CaH_2, CH_2Cl_2 and P_2O_5 and then freshly distilled prior to use. Other chemicals were reagent grade and used as purchased. Preparative liquid chromatography was carried out using Aldrich silica gel (60−230 mesh) as the stationary phase under nitrogen. Analytical TLC on Macherey−Nagel plates with a UV indicator (silica gel on aluminium foil; detection by UV at 254 nm followed by 2% aqueous $AgNO_3$ spray) was used to check the purity of individual chromatographic fractions. Melting points were measured in sealed capillaries and are uncorrected. Elemental analyses were performed in the IIC analytical laboratories using standard procedures. 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 ionization). Proton (^{1}H) and boron (^{11}B) NMR spectroscopy was performed at 11.75 Tesla with a Varian UNITY-500 instrument. The [^{11}B-^{11}B]-COSY[13] and ^{1}H{^{11}B(selective)}[14] NMR experiments were essentially as described in other related papers from our laboratories.[16] Chemical shifts are given in ppm to high-frequency (low field) of Ξ = 32.083971 MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for ^{11}B (quoted ± 0.5 ppm) and Ξ = 100 MHz ($SiMe_4$) for ^{1}H (quoted ± 0.05 ppm), Ξ being defined as in ref.[17] Residual solvent ^{1}H resonances were used as internal secondary standards. Coupling constants $^1J_{BH}$ are taken from resolution-enhanced ^{11}B NMR spectra with a digital resolution of ± 8 Hz and are given in Hz.

General Conditions for the Synthesis of the 8-R-*nido*-7,8,9-$C_3B_8H_{11}$ Derivatives 2 [R = H_2N (2a), *t*BuHN (2b), Me_2N (2c)]: A slurry of the starting compound **1** (reaction scale 1.5 mmol), NaH (3.15 mmol) and solvent (DME or diglyme, 20 mL) was stirred at room temperature for 1 h and then heated at 90 °C (bath) for an additional hour whilst stirring. Excess metal reagent (see Table 1) (reaction scale 4.5 mmol) was then added and the mixture was stirred under the conditions given in Table 1. The solvent was rotaevaporated and the residue treated with a mixture of Et_2O (20 mL) and water (20 mL), and the aqueous layer was acidified with dilute hydrochloric acid to pH = 3.0 under cooling. The organic layer was then separated and the aqueous phase extracted with additional portions of Et_2O (2 × 20 mL). The combined ethereal extracts were concentrated and the residue treated with CH_2Cl_2 (15 mL) and silica gel (10 g). The solvent was evaporated, the solids were placed on top of a silica gel column (25 × 2 cm) and eluted with a CH_2Cl_2/pentane (1:1, v/v) mixture. The purity of individual fractions was checked by analytical TLC (for R_F values see Table 1). Essentially pure compounds of type **2** were obtained by concentration of the corresponding chromatographic fractions and the products were repurified by crystallization from hexane. Compound **2b** was purified by vacuum sublimation at 120 °C. Subsequent elution with CH_2Cl_2 or its mixtures with CH_3CN (up to 1:1 composition) recovered, in most cases, the starting compounds of type **1**. Reaction conditions for individual derivatives and yields are summarized in Table 1.

2a: R_f (CH_2Cl_2) = 0.40; m.p. 132 °C. ^{11}B NMR ($CDCl_3$): δ = −4.1 (d, $^1J_{B\text{-}H}$ = 159 Hz, 2 B, B-2,5), −15.5 (d, $^1J_{B\text{-}H}$ =171 Hz, 2 B, B-3,4), −20.4 (d, $^1J_{B\text{-}H}$ = 183 Hz, 2 B, B-10,11), −31.4 (d, $^1J_{B\text{-}H}$ = 153 Hz, 1 B, B-6), −32.8 (d, $^1J_{B\text{-}H}$ = 150 Hz, 1 B, B-1) ppm, all theoretical [^{11}B-^{11}B]-COSY cross-peaks observed. ^{1}H{^{11}B} NMR ($CDCl_3$): δ = 2.93 (s, 2 H, 7,9-H), 2.39 (s, 2 H, 2,5-H), 2.16 (br. s, 2 H, NH_2), 2.05 (s, 2 H, 3,4-H), 1.86 (s, 2 H, 10,11-H), 1.18 (s, 1 H, 1-H), 0.62 (s, 1 H, 6-H), −1.92 (s, 1 H, 10,11-μ-H). MS (70 eV, EI): *m*/*z* (%) = 151 (16) $[M]^+$, 150 (100) $[M - H]^+$. $C_3H_{13}B_8N$ (149.6): calcd. B 57.80; found 57.54.

2b: R_f (CH_2Cl_2) = 0.62; m.p. 95 °C. ^{11}B NMR ($CDCl_3$): δ = −1.5 (d, $^1J_{B\text{-}H}$= 162 Hz, 2 B, B-2,5), −15.4 (d, $^1J_{B\text{-}H}$ = 171 Hz, 2 B, B-3,4), −19.9 (d, $^1J_{B\text{-}H}$ = 192 Hz, 2 B, B-10,11), −29.9 (d, $^1J_{B\text{-}H}$ = 147 Hz, 1 B, B-6), −32.6 (d, $^1J_{B\text{-}H}$ = 150 Hz, 1 B, B-1).) ppm, all theoretical [^{11}B-^{11}B]-COSY cross-peaks observed. ^{1}H{^{11}B } NMR ($CDCl_3$): δ = 3.28 (s, 2 H, 7,9-H), 2.66 (s, 2 H, 2,5-H), 2.56 (br. s, 1 H, NH), 2.04 (s, 2 H, 3,4-H), 1.94 (s, 2 H, 10,11-H], 1.19 (s, 9 H, *t*Bu), 1.08 (s, 1 H, 1-H), 0.71 (s, 1 H, 6-H), −2.34 (s, 1 H, 10,11-μ-H) ppm. IR (KBr): $\tilde{\nu}$ = 2579 (B−H) cm^{-1}. MS (70 eV, EI): *m*/*z* = 207 (15) $[M]^+$, 206 (100) $[M - H]^+$. $C_7H_{21}B_8N$ (205.7): calcd. B 42.04, found 41.92.

2c: R_f (CH_2Cl_2) = 0.50; m.p. 75 °C. ^{11}B NMR (CD_3CN): δ = −3.76 (d, $^1J_{B\text{-}H}$ = 158 Hz, 2 B, B-2,5), −16.4 (d, $^1J_{B\text{-}H}$ = 168 Hz, 2 B, B-3,4), −20.6 (d, $^1J_{B\text{-}H}$ = 195 Hz, 2 B, B-10,11), −30.6 (d, $^1J_{B\text{-}H}$ = 140 Hz, 1 B, B-6), −33.6 (d, $^1J_{B\text{-}H}$ = 153 Hz, 1 B, B-1) ppm, all theoretical [^{11}B-^{11}B]-COSY cross-peaks observed. ^{1}H{^{11}B} NMR (CD_3CN): δ = 3.00 (s, 2 H, 7,9-H), 2.43 (s, 2 H, 2,5-H), 2.36 (s, 2 H, 3,4-H), 2.16 (m, 6 H, Me), 1.98 (s, 2 H, 10,11-H), 1.02 (s, 1 H, 1-H), 0.72 (s, 1 H, 6-H), −1.98 (s, 1 H, 10,11-μ-H) ppm. IR (KBr): $\tilde{\nu}$ = 2556 (B−H) cm^{-1}. MS (70 eV, EI): *m*/*z* = 179 (18) $[M]^+$, 178 (100) $[M - H]^+$. $C_5H_{17}B_8N$ (177.7): calcd. B 48.67; found 48.34.

PSH^+[8-*t*BuHN-7,8,9-$C_3B_8H_{10}$]$^-$ (PSH^+2b$^-$): A solution of PS (107 mg, 0.5 mmol) in hexane (15 mL) was added dropwise to a stirred solution of **2b** (100 mg, 0.48 mmol) in hexane (15 mL) over a period of 10 min. The mixture was stirred for an additional 30 min and a white, voluminous precipitate formed. The precipitate was isolated by filtration, washed with hexane (3 × 5 mL) and vacuum-dried to yield 188 mg (92%) of $PSH^+\mathbf{2b}^-$, which was identified by NMR spectroscopy. **PSH^+2b$^-$:** ^{11}B NMR (CD_3CN): δ = −18.5 (d, $^1J_{B\text{-}H}$ = 170 Hz, 2 B, B-10,11), −19.7 (d, $^1J_{B\text{-}H}$ =158 Hz, 5 B, B-2,3,4,5,6), −47.7 (d, $^1J_{B\text{-}H}$ = 139 Hz, 1 B, B-1) ppm, all theoretical [^{11}B-^{11}B]-COSY cross-peaks observed. ^{1}H{^{11}B } NMR (CD_3CN): δ = 18.81 (s, 1 H, PSH^+), 7.35−9.96 (m, 6 H, PS-aromatic), 3.21 (br. s, 6 H, PS-Me), 2.66 21 (br. s, 6 H, PS-Me), 2.17 (s, 2 H, 7,9-H), 1.30, 1.53, 1.80 (s, 1 H, 2 H, 2 H, 2,3,4,5,6-H), 1.13 (s, 9 H, *t*Bu), 0.97 (s, 2 H, 10,11-μ-H), 0.17 (s, 1 H, 1-H) ppm.

Protonation of PSH^+[8-*t*BuHN-7,8,9-$C_3B_8H_{10}$]$^-$ (PSH^+2b$^-$): A solution of $PSH^+\mathbf{2b}^-$ (126 mg, 0.3 mmol) in CH_2Cl_2 (20 mL) was treated with several drops of concentrated H_2SO_4 whilst stirring for 1 h and cooling to 0 °C. The organic layer was then separated and

Table 3. Crystal data and structure refinement for **2b** and $PSH^+\mathbf{2b}^-$

	2b	$PSH^+\mathbf{2b}^-$
Empirical formula	$C_7H_{21}B_8N_1$	$C_7H_{20}B_8N_1\cdot C_{14}H_{19}N_2$
Formula mass	205.75	420.03
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	13.9799(4)	13.8910(2)
b [Å]	13.4980(5)	10.1050(2)
c [Å]	13.9760(5)	18.1420(3)
β [°]	100.258(2)	101.127(1)
Z	8	4
V [Å^3]	2595.13(15)	2498.70(7)
μ [mm^{-1}]	0.051	0.060
$D_{calcd.}$ [Mg/m^3]	1.053	1.117
Wavelength [Å]	0.71073	0.71073
F(000)	880	904
θ range [°]	1.51−26	1−27.5
Scan mode	and ω	and ω
h, k, l collected	$-16 \le h \le 17$, $-15 \le k \le 16$, $-16 \le l \le 17$	$-18 \le h \le 18$, $-13 \le k \le 13$, $-23 \le l \le 23$
No. of reflections measured	16548	46448
No. of unique reflections	5209 (R_{int} = 0.048)	5713 (R_{int} = 0.035)
No. of parameters	386	344
GOF[a] all data	1.043	1.065
Final R[a] indices [$I > 2\sigma(I)$]	$R1$ = 0.052, $wR2$ = 0.122	$R1$ = 0.044, $wR2$ = 0.112
R[a] indices (all data)	$R1$ = 0.073, $wR2$ = 0.135	$R1$ = 0.063, $wR2$ = 0.122
w_1/w_2	0.087/0.1561	0.0605/0.4392
Δρ(max./min.) [e Å^{-3}]	0.244/−0.197	0.191/0.180

[a] Definitions: $R(F) = \Sigma||F_o| - ||F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_o^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; GOF $= \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{reflns} - N_{params})\}^{1/2}$; weighting scheme $w = [\sigma^2(F_o^2) + (w_1P) + w_2P]^{-1}$; $P = [\max.(F_o^2,0) + 2F_c^2]/3$.

the solvents were evaporated to give 59 mg (96%) of **2b**, which was identified by NMR spectroscopy by comparison with the characteristics of an authentic sample.

X-ray Crystallography: The crystal of **2b** was obtained by slow vacuum sublimation of the tricarbaborane at 120 °C and that of the $PSH^+\mathbf{2b}^-$ salt by slow concentration of the $CHCl_3$ solution in a glass tube. The colorless crystals of **2b** and $PSH^+\mathbf{2b}^-$ of dimensions 0.4 × 0.3 × 0.17 and 0.3 × 0.27 × 0.22 mm, respectively, were mounted on glass fibers with epoxy cement and measured with a four-circle diffractometer Nonius Kappa CCD equipped with a CCD area detector at 150(2) K with Mo-K_α radiation. The crystallographic details for both compounds are summarized in Table 3. The structures were solved by the direct method (SIR97)[18] and that of $PSH^+\mathbf{2b}^-$ was refined by a full-matrix least-squares procedure based on F^2 (SHELXL-97).[19] However, the crystal of **2b** underwent pseudomerohedral twinning, as discovered during the structure solution. The phase problem was therefore solved using the $P2_1$ space group and the model was later transformed into the $P2_1/c$ space group. The symmetry of the diffraction pattern is consistent with the orthorhombic space group $C222_1$ as the result of twinning due the matrix:

h' 0 0 1 h
k' 0 1 0 k
l' 1 0 0 l

The data were corrected accordingly during the refinement by a full-matrix least-squares procedure based on F^2 (SHELXL-97),[19] which yielded a ratio of twin parts 0.472/0.528. The absorption was neglected. All hydrogen atoms, except for those of the methyl groups, were localized on a difference Fourier map and refined isotropically. For $PSH^+\mathbf{2b}^-$, hydrogen positions of the methyl groups and those of the PSH^+ CH moieties were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or $1.5\ U_{eq}$ for the methyl moiety, others were localized on a difference Fourier map and refined isotropically. The final difference maps for both compounds had no peaks of chemical significance. Scattering factors were those implemented in the SHELX programs. CCDC-184057 and -190913 contain the supplementary crystallographic data for compounds **2b** and $PSH^+\mathbf{2b}^-$, respectively. These can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors gratefully acknowledge Drs. J. Fusek, Z. Plzák, and E. Večerníková from the Institute of Inorganic Chemistry, ASCR for providing NMR, mass, and IR spectra. The work was supported by the Ministry of Education of the Czech Republic (project no. LN 00A028) and Grant Agency of the Czech Republic (grant nos. 203/00/1042 and 203/99/M037, the latter is appreciated for the purchase of the Kappa CCD equipment).

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Received October 10, 2002
[I02558]