

Parent Tricarbollides $[nido-7,8,9-C_3B_8H_{11}]^-$, $nido-7,8,9-C_3B_8H_{12}$, $[nido-7,8,10-C_3B_8H_{11}]^-$, and Their Derivatives

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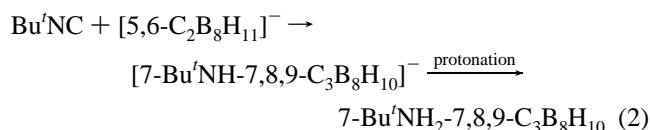
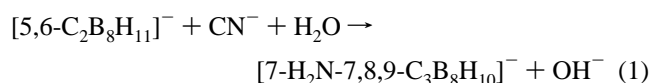
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Abstract: Deamination of 7-(Me₃N)-*nido*-7,8,9-*C*₃*B*₈*H*₁₀ (**1a**) leads either to the parent tricarbollide anion $[nido-7,8,9-C_3B_8H_{11}]^-$ (**2⁻**) or to the neutral tricarbaborane *nido*-7,8,9-*C*₃*B*₈*H*₁₂ (**2a**), together with a small amount of 8-Me-*nido*-7,8,9-*C*₃*B*₈*H*₁₁ (**2b**). Di- and trisubstituted derivatives of **2a**, 7-(Bu^tMeN)-10-Me-*nido*-7,8,9-*C*₃*B*₈*H*₁₀ (**2c**), and 7-(Bu^tMeN)-10,11-Me₂-*nido*-7,8,9-*C*₃*B*₈*H*₉ (**2d**) were obtained as byproducts from the methylation of both 7-(Bu^tNH₂)-*nido*-7,8,9-*C*₃*B*₈*H*₁₀ (**1b**) and 7-(Bu^tMeNH)-*nido*-7,8,9-*C*₃*B*₈*H*₁₀ (**1c**) with MeI in THF under reflux. Heating of **1a** and **2⁻** at 350 °C resulted in the rearrangement of the carbons on the open-face to give high yields of the isomeric tricarbollides 10-(Me₃N)-*nido*-7,8,10-*C*₃*B*₈*H*₁₀ (**3a**) and $[nido-7,8,10-C_3B_8H_{11}]^-$ (**4⁻**), respectively. The structure of **3a** was determined by an X-ray diffraction analysis, and the geometries of the parent compounds **2⁻**, **2a**, and **4⁻** were optimized at the *ab initio* MP2(fc)/6-31G* level. The structures of all compounds also were secured by the excellent agreement between the experimental data and the IGLO/NMR calculations of the ¹¹B chemical shifts for the parent compounds at the DZ//6-31G*, DZ//MP2/6-31G*, and II//MP2/6-31G* levels.

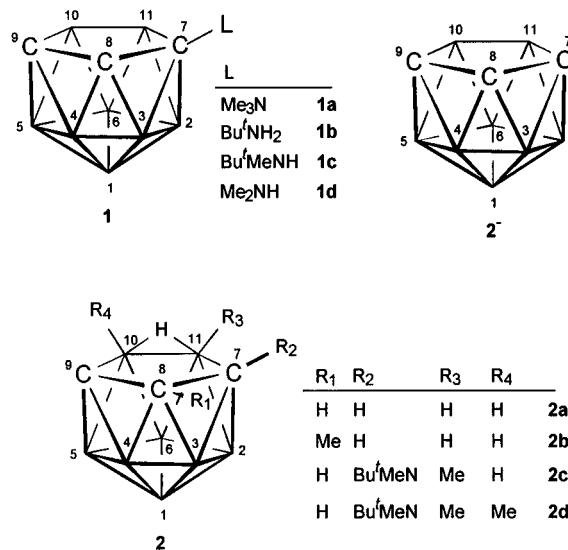
Introduction

We reported recently that reactions of the $[nido-5,6-C_2B_8H_{11}]^-$ anion with either the CN⁻ anion or Bu^tNC result in the formation of moderate to good yields of the zwitterionic adducts with the general formula 7-L-*nido*-7,8,9-*C*₃*B*₈*H*₁₀ (**1**) as exemplified by eqs 1 and 2 for L = NH₂⁻ and Bu^tNH₂.¹ These reactions extended the monocarbon cage-insertion reactions into neutral and anionic dicarbaborane substrates² and generated the first representatives of tricarbollides, the long anticipated compounds of the 11-vertex *nido* series of tricarbaboranes:



In a preliminary communication,^{1a} we reported the synthesis of the parent *nido* tricarbollide anion $[7,8,9-C_3B_8H_{11}]^-$ (**2⁻**) and the neutral species *nido*-7,8,9-*C*₃*B*₈*H*₁₂ (**2a**). Both have three

adjacent cluster carbons in the open pentagonal face of the cage. As predicted by two independent theoretical investigations,³ isomeric tricarbollides with more extended separation of the cage carbons in the open face might arise from the thermal isomerization of such compounds. Indeed, we have now synthesised the first examples of the *parent* and zwitterionic 7,8,10-tricarbaborane systems, via thermal rearrangement of **1a** and **2⁻**.⁴ Sneddon's group also reported preliminary results on the



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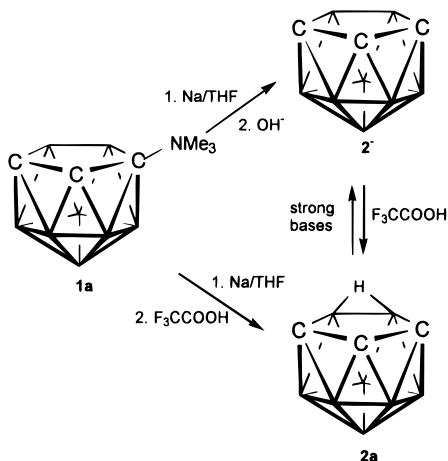
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preparation 7-substituted derivatives of anion **4⁻**, $[7-R-nido-7,8,10-C_3B_8H_{10}]^-$ (where R = Me and PhCH₂) via insertion of

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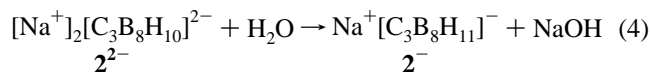
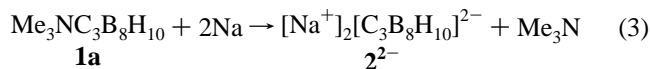
Scheme 1



additional boron vertex into substituted derivatives of the 10-vertex [*nido*-5,6,9- $C_3B_7H_{11}$] $^-$ anion.^{3a} These examples document current interest in the tricarbollide area, particularly from the viewpoint of the synthesis of further types of metallatricarbollide sandwich complexes of the {*closo*- MC_3B_8 } type.⁵ We now report full experimental details of the preparation and some reactions of two isomeric series of *parent* tricarbollide compounds. The experimental results are substantiated by *ab initio* geometry optimizations and IGLO/NMR computations which show excellent agreement between experimental and theoretical ¹¹B NMR chemical shifts for the parent tricarbollides.

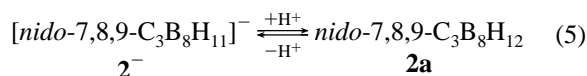
Results and Discussion

Syntheses. Deamination⁶ of the Me_3N derivative **1a** with sodium metal in refluxing THF for 6 h in the presence of naphthalene, followed by careful addition of aqueous CsOH, resulted in the isolation of $Cs^+[nido-7,8,9-C_3B_8H_{11}]^-$, (Cs^+) 2^{2-} (62% isolated yield, also see Scheme 1). Other salts of the parent anion 2^{2-} with stabilizing, bulky counteranions can be isolated in high yields by adding reactants, such as NMe_4Cl , PPh_4Cl , and/or $TiNO_3$ to an alkaline solution of the Cs^+ salt. The parent anion 2^{2-} results from the two-electron deamination reaction (eq 3), followed by hydrolysis of a highly reactive dianionic intermediate [*nido*-7,8,9- $C_3B_8H_{10}$] $^{2-}$ (2^{2-}) (eq 4):



It is reasonable to suppose that the intermediate 2^{2-} contains a free electron pair on one of the cluster carbons.

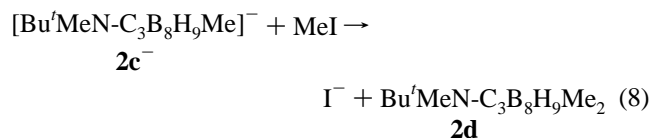
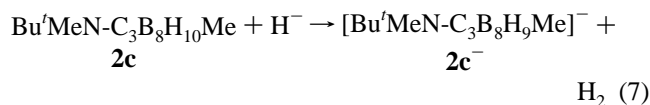
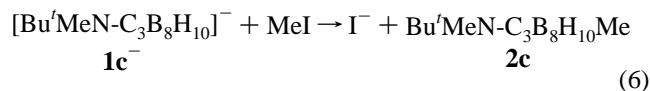
When the deamination reaction (see eq 3) is followed by the acidification with CF_3COOH (see Scheme 1), the main product is the neutral tricarbaborane 7,8,9- $C_3B_8H_{12}$ (**2a**), which is isolated easily by chromatographic separation. We presume that **2a** is formed by diprotonation of the dianion 2^{2-} . As expected, anion 2^{2-} also behaves as a very strong base and can be protonated easily by acids to give a high yield of the neutral tricarbaborane **2a**:



The two adjacent boron atoms in the open pentagonal face of anion 2^{2-} offer a highly favored site for a hydrogen; this facilitates this protonation. An arrangement similar to **2a** is

found in the isostructural [$7,9-C_2B_9H_{12}$] $^-$ anion⁷ (**5⁻**). However, deprotonation to the corresponding dicarbollide dianion [$7,9-C_2B_8H_{12}$] $^{2-}$ only takes place under forcing conditions.⁸ The same applies to **2a**, which can be deprotonated to 2^{2-} only by strong bases, such as H^- , OH^- , and PS (PS = "proton sponge", 1,8-dimethylaminonaphthalene). As a consequence, pure anion 2^{2-} can be isolated conveniently as $[PSH]^+[nido-7,8,9-C_3B_8H_{11}]^-$, (PSH^+) 2^{2-} , by reacting PS with tricarbaborane **2a** in hexane. Under these conditions, the insolubility of the PSH^+ salt shifts the equilibrium (eq 5) quantitatively to the left.

A methyl derivative of **2a**, 8-Me-*nido*-7,8,9- $C_3B_8H_{11}$ (**2b**), was isolated together with 7-(Me_2NH)-*nido*-7,8,9- $C_3B_8H_{10}$ (**1d**)^{1b} as a byproduct from room temperature deamination of **1a** (see eq 3), followed by acidification of the reaction mixture. The formation of **2b** involves an interesting transfer of a methyl group from nitrogen to the C(8) cluster carbon at the β -position. However, the formation of **2b** and **1d** can be suppressed by carrying out the reaction in THF under reflux. Two additional interesting derivatives of **2a** are formed as side products from methylation of the zwitterionic derivatives **1b** and **1c**^{1b} by MeI in the presence of excess NaH in THF under reflux. These derivatives, identified as the neutral compounds 10-Me-7-(Bu^iMeN)-*nido*-7,8,9- $C_3B_8H_{10}$ (**2c**) and 10,11-Me₂-7-(Bu^iMeN)-*nido*-7,8,9- $C_3B_8H_{10}$ (**2d**), were isolated by TLC fractionation in hexane in low yields (5 and 10%, respectively). Although there is no direct evidence for the reaction mechanisms, compounds **2c** and **2d** may be formed by stepwise methylation of **1c**.^{1b} This is deprotonated on the N atom by excess NaH to form the [$7-(Bu^iMeN)$ -*nido*-7,8,9- $C_3B_8H_{10}$] $^-$ anion (**1c⁻**). This anion is methylated at the open-face boron positions B(9) and B(11) for steric reasons rather than on the exoskeletal nitrogen atom:



While the parent compound **2a** is only moderately stable, the amino-substituted derivatives **2c** and **2d** are persistent in air due to the favorable influence of their dialkylamino substituents.

The presence of three adjacent cage CH units in 2^{2-} and in **1a** prompted us to examine their thermal rearrangement reactions. Isomers with separated carbons in the open face of an 11-vertex *nido* cluster are expected to be more stable. The isomerization of the [$7-Ph-7,8-C_2B_9H_{11}$] $^-$ anion to the isomeric

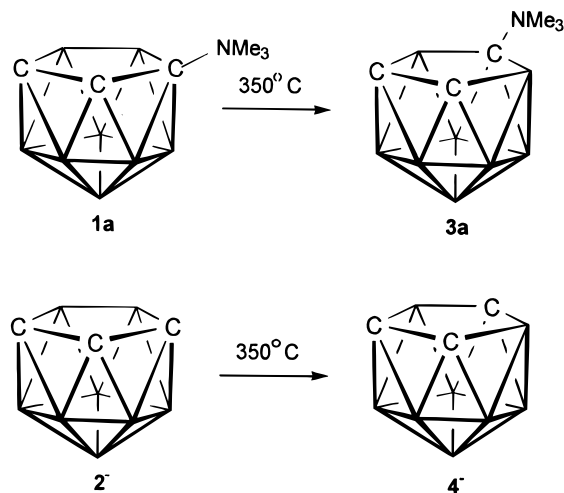
(5) Štíbr, B.; Holub, J.; Teixidor, F.; Viñas, C. *Collect. Czech. Chem. Commun.* **1995**, *60*, 2023–2027.

(6) See, for example: (a) Hyatt, D. E.; Scholer, F. R.; Todd, L. J.; Warner, J. L. *Inorg. Chem.* **1967**, *6*, 2229. (b) Hyatt, D. E.; Owen, D. A.; Todd, L. J. *Inorg. Chem.* **1966**, *5*, 1749. (c) Knoth, W. H.; Little, J. L.; Lawrence, J. F.; Scholer, F. R.; Todd, L. J. *Inorg. Synth.* **1968**, *11*, 33. (d) Plešek, J.; Jelínek, T.; Drdáková, E.; Heřmánková, S.; Štíbr, B. *Collect. Czech. Chem. Commun.* **1984**, *49*, 1559–1562.

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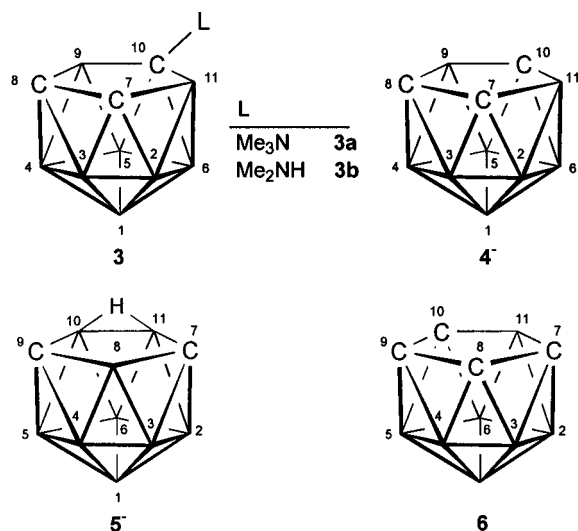
(8) See, for example: Dunks, G. B.; Hawthorne, M. F. In *Boron Hydride Chemistry*; Muettterties, E. L., Ed.; Academic: New York, 1975; Chapter 11, pp 383–430.

Scheme 2



[7-Ph-7,9-C₂B₉H₁₁]⁻ at 300 °C in the 11-vertex *nido* dicarbaborane series affords a good precedent.⁹ In addition, *ab initio* calculations predict that only the 7,8,9 → 7,8,10 isomerization of anion **2⁻** should be highly favored.³ Rousseau et al. also suggested the mechanism including intermediate structures on the rearrangement path.^{3b} We have now realized these theoretical predictions experimentally. Indeed, smooth and high-yield thermal isomerization reactions led to representatives of the isomeric 11-vertex {*nido*-7,8,10-C₃B₈} system.

After heating the zwitterionic compound **1a** (see Scheme 2) in a dry nitrogen atmosphere or, alternatively, in an evacuated sealed tube for 10 min at 350 °C, the isomeric 10-(Me₃N)-*nido*-7,8,10-C₃B₈H₁₀ (**3a**) was isolated in 95% yield. However,



attempted deamination of **3a** by treatment with sodium naphthalide in THF under reflux for 2 h failed. In contrast to the behavior of the isomeric compound **1a**, these experimental conditions resulted in the removal of one methyl from the nitrogen and the formation of 10-(Me₂NH)-*nido*-7,8,10-C₃B₈H₁₀ (**3b**) in 94% yield. Compound **3b** can be reconverted quantitatively to **3a** by treatment with Me₂SO₄ in an alkaline ethanolic solution.

Nevertheless, the Cs⁺ salt of the [*nido*-7,8,10-C₃B₈H₁₁]⁻ anion (**4⁻**) can be prepared in 63% yield by heating the Cs⁺ salt of anion **2⁻** at 350 °C for 30 min (see Scheme 2) and crystallizing the resulting solid from hot water. Treatment of the Cs⁺ salt with 1 equiv of aqueous PPh₄Cl or TiNO₃ led to

essentially quantitative precipitation of the corresponding air-stable PPh₄⁺ and Tl⁺ salts of anion **4⁻**, (PPh₄⁺)**4⁻**, and (Tl⁺)**4⁻**. In contrast to the isomeric anion **2⁻**, anion **4⁻** cannot be converted to the protonated, neutral species by acids as there is no open-face B–H–B bridge possibility. That the neutral tricarbaborane **2a** neither decomposes nor rearranges upon sublimation through a hot tube at 350 °C demonstrates the considerable stability of its B–H–B bridging arrangement.

Structural Studies. The constitution of the zwitterionic compounds of type **1** was established by an X-ray diffraction analysis of the Bu^tMeNH derivative **1c**.^{1b} This confirmed unambiguously the characteristic adjacent disposition of the three cluster carbons (with no extra hydrogen in the open pentagonal face of the molecule), in agreement with the expected 26-electron count for a *nido* skeleton.¹⁰ Unfortunately, neither the Cs⁺ nor Tl⁺ salts of the parent anions **2⁻** and **4⁻** gave crystals suitable for X-ray diffraction analyses; the PPh₄⁺ salts of both anions were extensively disordered as were 7-substituted derivatives of **4⁻**.^{3a} We also were unable to grow suitable crystals of the neutral compounds of type **2**. The calculation of magnetic properties is an increasingly valuable tool to help in determining the structures of boron compounds. The molecular geometries even of relatively large boron clusters can be established by the combined *ab initio*/IGLO¹¹B/NMR method.^{3,12,13} Since ¹¹B chemical shifts are sensitive to small changes in molecular geometry, the reliability of *ab initio* (or experimental) structures can be assessed by comparing the computed with the observed chemical shifts. Structural assignments based on this method have achieved a confidence level that rivals modern X-ray diffraction techniques.¹⁴ As MP2/6-31G* geometries give the best results, this electron-correlated level was employed for the optimization of all the parent tricarbaboranes **2⁻**, **2a**, and **4⁻**. The resulting molecular structures are depicted in Figures 1–3 and intracuster distances shown in Table 1.

The bond distances in **2⁻** (see Table 1) compare excellently to those of the structurally related compound **1c**^{1b} and also are similar to those computed for the isomeric anion **4⁻**. As expected from the generally shorter C–B than B–B distances, the open pentagonal faces in **2⁻** and in **4⁻** are not planar, but

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(13) For electron correlation effects on computed ¹¹B chemical shifts, see: (a) Bühl, M.; Gauss, J.; Hofmann, M.; Schleyer P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 12385. (b) Schleyer P. v. R.; Gauss, J.; Bühl, M.; Greatrex, R.; Fox, M. A. *J. Chem. Soc., Chem. Commun.* **1993**, 1766.

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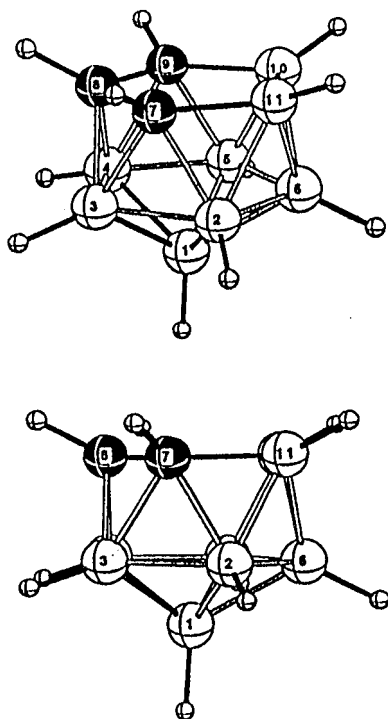


Figure 1. Geometry optimized MP2/6-31G* structure of the [nido-7,8,9-C₃B₈H₁₁]⁻ anion (**2⁻**): (top) perspective and (bottom) side views.

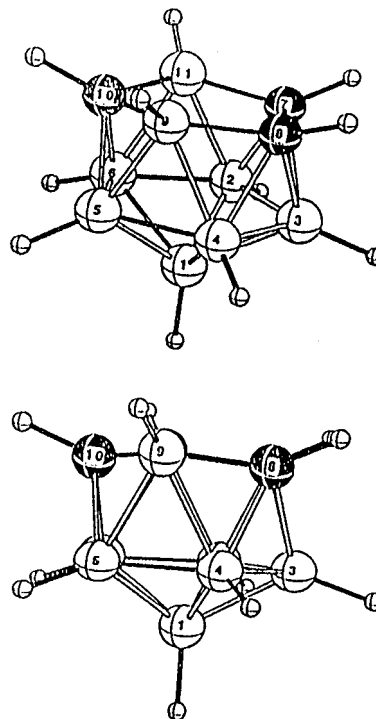


Figure 3. Geometry optimized MP2/6-31G* structure of the [nido-7,8,10-C₃B₈H₁₁]⁻ anion (**4⁻**): (top) perspective and (bottom) side views.

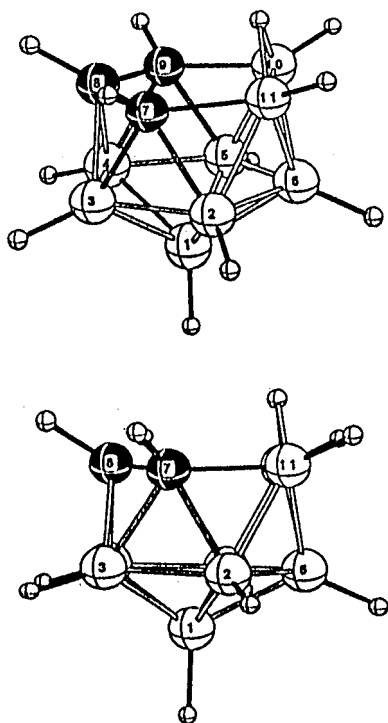


Figure 2. Geometry optimized MP2/6-31G* structure of nido-7,8,9-C₃B₈H₁₂ (**2a**): (top) perspective and (bottom) side views.

are folded into an envelop conformations (see fold angles¹⁵ in Table 1 and side views in Figures 1 and 3). The C(7) and C(9) atoms in **2⁻** are 0.024 Å below the C(8)–B(10)–B(11) plane; the B(9) and B(10) atoms in **4⁻** are situated 0.115 Å above the plane intersecting the three open-face carbons. At MP2/6-31G*, isomer **4⁻** is 18.3 kcal·mol⁻¹ (the corresponding HF values are 21.8, 22.0, and 23.7 kcal·mol⁻¹ for the 6-31G*, II', and DZ basis sets, respectively) more stable than **2⁻** (compare the earlier calculated AM1 and RHF/6-21G* values 10.8 and 32.0 kcal·mol⁻¹, respectively^{3b}). These energy differences may be

Table 1. Salient MP2/6-31G* *ab Initio* Optimized Bond Lengths (Å) and Angles (deg) for the Parent Tricarbollides **2⁻**, **2a**, and **4⁻**

	2⁻	2a	4⁻
distance ^a			
B(1)–B(2)	1.785	1.759	1.773
B(1)–B(3)	1.750	1.775	1.761
B(1)–B(6)	1.811	1.800	1.788
B(2)–B(3)	1.768	1.755	1.768
B(2)–B(6)	1.761	1.778	1.747
B(2)–C(7)	1.717	1.685	1.719
B(2)–B(11)	1.790	1.803	1.800
B(3)–B(4)	1.760	1.767	1.768
B(3)–C(7)	1.734	1.698	1.716
B(3)–C(8) ^b	1.724	1.731	1.716
B(4)–B(9)			1.800
B(5)–B(6) ^c	1.761	1.778	1.783
B(5)–B(9)			1.793
B(5)–C(10)			1.698
B(6)–B(10)	1.790	1.797	
C(7)–C(8)	1.515	1.518	1.545
C(7)–B(11)	1.624	1.656	1.601
B(9)–C(10)			1.624
B(10)–B(11)	1.730	1.828	
mean CH	1.089 ^d	1.086 ^d	1.089
mean B–H	1.197 ^d	1.188 ^d	1.089
B–H (bridge)		1.312	
fold angles ^e			
φ	0.3 ^f		3.6 ^g
θ	2.1 ^h		7.7 ⁱ

^a The number of distances is lower due to the C_s symmetry.

^b Equivalent to B(3)–C(7) for **4⁻**. ^c Equivalent to B(2)–B(6) for **2⁻** and **2a**. ^d Weighted average. ^e Defined with respect to the B(2)–B(3)–B(4)–B(5)–B(6) plane (also see ref 15). ^f For the C(7)–C(8)–C(9) plane. ^g For the C(10), B(9), B(11) plane. ^h For the C(9)–B(10)–B(11)–C(7) plane. ⁱ For the C(7)–C(8)–B(9)–B(11) plane.

compared with the HF/3-21G value of 21.7 kcal·mol⁻¹ calculated for the corresponding methyl derivatives of **2⁻** and **4⁻**.^{3a}

Some bonding details of the neutral compound **2a** differ from its anionic counterpart **2⁻**; C(7) and C(8) in **2a** are 0.073 Å (with respect to the C(8)–B(10)–B(11) plane) closer to the center of the molecule (see side view in Figure 2). The C(7)–C(8)–C(9) angle (116°) deviates most from the ideal 108° value for a regular pentagon. The longer B(10)–B(11) distance (1.828

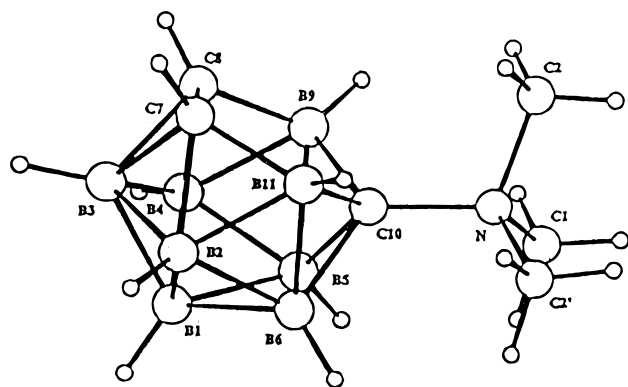


Figure 4. PLUTO representation of the X-ray crystal structure of 10-(Me₃N)-nido-7,8,10-C₃B₈H₁₀ (**3a**).

Table 2. Crystal Data and Structure Refinement for 10-(Me₃N)-nido-7,8,10-C₃B₈H₁₀ (**3a**)

empirical formula	C ₆ H ₁₉ B ₈ N
<i>M</i>	191.78
crystal system	monoclinic
space group	<i>P</i> 2 ₁ / <i>m</i>
<i>a</i> , Å	6.9401(7)
<i>b</i> , Å	10.042(1)
<i>c</i> , Å	8.8174(6)
β , deg	110.614(7)
<i>Z</i>	2
<i>V</i> , Å ³	575.16(9)
μ , mm ⁻¹	0.053
<i>D</i> _{calcd} , mg/m ³	1.107
<i>F</i> (000)	204
θ range, deg	2.47–26.96
scan mode	θ – 2θ
<i>h, k, l</i> collected	<i>h</i> <–8,8>, <i>k</i> <0,12>, <i>l</i> <–11,11>
no. of reflcns measd	2498
no. of unique reflcns	1325 [<i>R</i> _{int}] = 0.093]
no. of params	178
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0478, <i>wR</i> ₂ = 0.1045
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1651, <i>wR</i> ₂ = 0.1450
extinction coeff	0.035(11)
$\Delta\rho$, max., min., e [–] Å ^{–3}	0.181, –0.222

Table 3. Positional Parameters for Non-Hydrogen Atoms in 10-(Me₃N)-nido-7,8,10-C₃B₈H₁₀ (**3a**)

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
B(1)	2236(13)	1492(9)	6569(10)	35(2)
B(2)	–249(14)	1540(10)	6640(12)	31(2)
B(3)	519(7)	2777(8)	5585(5)	39(3)
B(4)	3089(13)	3162(10)	6739(11)	40(2)
B(5)	3889(2)	2155(4)	8441(5)	33(2)
B(6)	1760(10)	1126(6)	8371(7)	29(1)
C(7)	–776(14)	3180(9)	6877(11)	35(2)
C(8)	1109(10)	4051(5)	6938(5)	40(1)
B(9)	2965(11)	3804(6)	8583(7)	37(1)
C(10)	2286(4)	2500	9466(3)	31(1)
B(11)	–134(7)	2290(14)	8488(5)	30(3)
N	3077(4)	2500	11312(3)	35(1)
C(1)	5383(6)	2500	12052(4)	66(1)
C(2)	2324(6)	3706(3)	11921(3)	60(1)

^a Equivalent isotropic displacement parameters Å²·10³ defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

Å) in **2a** reflects the influence of the hydrogen bridge (compare the equivalent separation of 1.95(4) Å found crystallographically for the isostructural anion [nido-7,9-C₂B₉H₁₂][–] (**5[–]**).¹⁶

The structure of the zwitterionic compound **3a** was confirmed by a single-crystal X-ray diffraction study (see Figure 4). The crystal data, selected bond distances, and bond angles are in Tables 2–5. In general, the B–B, C–B, and C–C separations are very similar to those of the parent analog **4[–]**. As expected,

Table 4. Selected Interatomic Distances (Å) for 10-(Me₃N)-nido-7,8,10-C₃B₈H₁₀ (**3a**)

B(1)–B(2)	1.749(11)	B(5)–B(6)	1.786(7)
B(1)–B(3)	1.763(12)	B(5)–B(9)	1.795(8)
B(1)–B(4)	1.767(10)	B(5)–C(10)	1.697(5)
B(1)–B(5)	1.775(9)	B(5)–H(5)	1.06(3)
B(1)–B(6)	1.772(9)	B(6)–C(10)	1.650(6)
B(1)–H(1)	1.09(5)	B(6)–B(11)	1.789(11)
B(2)–B(3)	1.744(13)	B(6)–H(6)	1.05(4)
B(2)–B(6)	1.717(11)	C(7)–C(8)	1.559(7)
B(2)–C(7)	1.715(8)	C(7)–B(11)	1.602(12)
B(2)–B(11)	1.771(11)	C(7)–H(7)	0.99(5)
B(2)–H(2)	1.15(4)	C(8)–B(9)	1.584(8)
B(3)–B(4)	1.757(10)	C(8)–H(8)	0.91(4)
B(3)–C(7)	1.729(9)	B(9)–C(10)	1.673(6)
B(3)–C(8)	1.698(9)	B(9)–H(9)	1.14(4)
B(3)–H(3)	1.08(3)	C(10)–B(11)	1.609(6)
B(4)–B(5)	1.731(9)	C(10)–N	1.524(3)
B(4)–C(8)	1.699(9)	B(11)–H(11)	1.06(3)
B(4)–B(9)	1.779(11)	N–C(1)	1.500(5)
B(4)–H(4)	1.13(5)	N–C(2)	1.491(3)

Table 5. Selected Angles (deg) for 10-(Me₃N)-nido-7,8,10-C₃B₈H₁₀ (**3a**)

B(2)–B(1)–B(3)	59.5(5)	B(9)–B(5)–C(10)	57.2(2)
B(2)–B(1)–B(4)	106.0(7)	B(2)–B(6)–B(1)	60.1(4)
B(3)–B(1)–B(4)	59.7(5)	B(2)–B(6)–B(5)	107.1(5)
B(2)–B(1)–B(6)	58.4(4)	B(2)–B(6)–C(10)	105.1(4)
B(3)–B(1)–B(6)	106.6(5)	B(2)–B(6)–B(11)	60.6(3)
B(4)–B(1)–B(6)	106.5(7)	B(5)–B(6)–B(1)	59.9(3)
B(2)–B(1)–B(5)	106.2(5)	B(5)–B(6)–C(10)	59.0(3)
B(3)–B(1)–B(5)	106.6(5)	B(5)–B(6)–B(11)	103.6(5)
B(4)–B(1)–B(5)	58.5(4)	C(10)–B(6)–B(1)	106.2(4)
B(5)–B(1)–B(6)	60.5(3)	B(11)–B(6)–B(1)	106.8(5)
B(1)–B(2)–B(11)	108.6(6)	B(11)–B(6)–C(10)	55.6(3)
B(3)–B(2)–B(1)	60.6(5)	B(2)–C(7)–B(3)	60.8(6)
B(3)–B(2)–B(11)	105.3(7)	C(8)–C(7)–B(2)	109.3(7)
B(6)–B(2)–B(1)	61.5(4)	C(8)–C(7)–B(3)	61.9(4)
B(6)–B(2)–B(3)	110.0(6)	C(8)–C(7)–B(11)	108.3(7)
B(6)–B(2)–B(11)	61.7(4)	B(11)–C(7)–B(2)	64.4(6)
C(7)–B(2)–B(1)	106.6(7)	B(11)–C(7)–B(3)	114.0(7)
C(7)–B(2)–B(3)	60.0(5)	B(3)–C(8)–B(4)	62.3(4)
C(7)–B(2)–B(6)	105.4(8)	C(7)–C(8)–B(3)	64.0(4)
C(7)–B(2)–B(11)	54.7(6)	C(7)–C(8)–B(4)	113.6(6)
B(1)–B(3)–B(2)	59.8(4)	C(7)–C(8)–B(9)	110.2(5)
B(1)–B(3)–B(4)	60.3(5)	B(9)–C(8)–B(3)	116.2(4)
B(1)–B(3)–C(7)	105.4(5)	B(9)–C(8)–B(4)	65.5(5)
B(4)–B(3)–B(2)	106.7(5)	B(5)–B(9)–B(4)	57.9(4)
B(4)–B(3)–C(7)	103.0(5)	C(8)–B(9)–B(4)	60.4(3)
C(7)–B(3)–B(2)	59.2(4)	C(8)–B(9)–B(5)	106.0(4)
C(8)–B(3)–B(1)	104.6(4)	C(8)–B(9)–C(10)	106.1(4)
C(8)–B(3)–B(2)	101.8(4)	C(10)–B(9)–B(4)	104.7(4)
C(8)–B(3)–B(4)	58.9(4)	C(10)–B(9)–B(5)	58.5(3)
C(8)–B(3)–C(7)	54.1(3)	B(6)–C(10)–B(5)	64.5(3)
B(1)–B(4)–B(3)	60.6(6)	B(9)–C(10)–B(5)	64.4(3)
B(1)–B(4)–B(5)	61.0(4)	B(9)–C(10)–B(6)	115.0(3)
B(3)–B(4)–B(5)	108.9(6)	B(9)–C(10)–B(11)	105.3(5)
C(8)–B(4)–B(1)	104.4(6)	B(11)–C(10)–B(5)	116.3(3)
C(8)–B(4)–B(3)	58.8(4)	B(11)–C(10)–B(6)	66.6(5)
C(8)–B(4)–B(5)	103.9(5)	N–C(10)–B(5)	120.8(2)
C(8)–B(4)–B(9)	54.1(4)	N–C(10)–B(6)	123.2(2)
B(9)–B(4)–B(1)	107.4(7)	N–C(10)–B(9)	116.3(2)
B(9)–B(4)–B(3)	104.0(5)	N–C(10)–B(11)	119.2(3)
B(9)–B(4)–B(5)	61.5(4)	B(6)–B(11)–B(2)	57.7(4)
B(1)–B(5)–C(10)	104.0(4)	C(7)–B(11)–B(2)	60.9(3)
B(4)–B(5)–B(1)	60.5(3)	C(7)–B(11)–B(6)	107.1(4)
B(4)–B(5)–C(10)	105.8(4)	C(7)–B(11)–C(10)	108.3(6)
B(6)–B(5)–B(1)	59.7(3)	C(10)–B(11)–B(2)	104.5(4)
B(6)–B(5)–B(4)	107.4(4)	C(10)–B(11)–B(6)	57.8(3)
B(6)–B(5)–C(10)	56.5(2)	C(1)–N–C(10)	113.1(2)
B(9)–B(5)–B(1)	106.3(4)	C(2)–N–C(1)	107.4(2)
B(9)–B(5)–B(4)	60.6(4)	C(2)–N–C(10)	110.1(2)
B(9)–B(5)–B(6)	103.0(4)		

the open pentagonal face is distorted slightly away from an ideal planar arrangement. In the actual puckered configuration, boron vertices B(9) and B(11) are situated 0.159(11) Å above the C(7)–C(8)–C(10) plane; the dihedral angle between the C(10)–

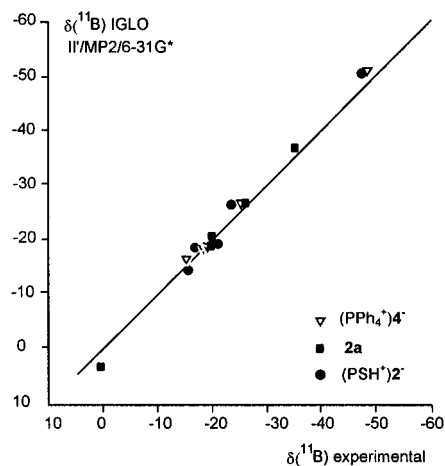


Figure 5. A plot of experimental ^{11}B chemical shifts vs calculated $\text{II}'/\text{MP2}/6\text{-}31\text{G}^*$ IGLO chemical shifts for the parent tricarbollides $[\text{PSH}]^+[\text{nido-}7,8,9\text{-C}_3\text{B}_8\text{H}_{11}]^-$ $[(\text{PSH}^+)2^-]$, *nido-7,8,9-C₃B₈H₁₂* (**2a**), and $[\text{PPh}_4]^+[\text{nido-}7,8,10\text{-C}_3\text{B}_8\text{H}_{11}]^-$ $[(\text{PPh}_4^+)4^-]$.

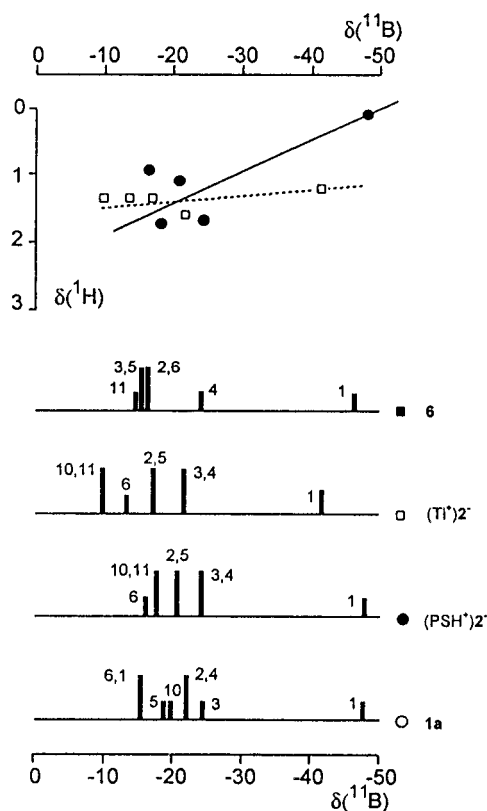


Figure 6. Stick representation and comparison of the ^{11}B chemical shifts and relative intensities for the 11-vertex *nido* compounds 7-(Me₃N)-7,8,9-C₃B₈H₁₀ (**1a**, data from ref 1), $[\text{PSH}]^+[\text{7,8,9-C}_3\text{B}_8\text{H}_{11}]^-$ $[(\text{PSH}^+)2^-]$, $\text{Ti}^+[\text{7,8,9-C}_3\text{B}_8\text{H}_{11}]^-$ $[(\text{Ti}^+)2^-]$, and 7,8,9,10-C₄B₇H₁₁ (**6**) (data from ref 18a) (bottom). The upper diagram is a plot of $\delta(^1\text{H})$ vs $\delta(^{11}\text{B})$ for both salts of anion 2^- .

B(9)–B(11) and the C(7)–C(8)–B(9)–B(11) planes is 12.6(6)°. These two planes have folding angles ($\varphi = 3.6$ and $\theta = 9.1^\circ$), respectively, with respect to the plane of the lower boron pentagon ($\sigma = 0.006$).

NMR Spectroscopy. As is shown in Figure 5, excellent agreement between the computed and observed (see Table 6) ^{11}B chemical shifts for parent molecules 2^- , **2a**, and 4^- was found uniformly; the differences are less than 3.5 ppm at all levels (Table 7). This agreement (along with earlier experience^{12–14,17}) indicates that *ab initio* geometries, particu-

larly those derived at electron correlated level of theory (MP2/6-31G*), afford reasonably good representations of the tricarbollide structures. These computed gas-phase geometries also must approximate those in solution.

In agreement with C_s symmetry, the parent compounds 2^- and 4^- (along with the zwitterionic **3a**) exhibit 1:2:2:2:1 ^{11}B patterns (see Figures 6–8) typified by a cluster of closely spaced resonances of integrated intensity 7 centered around -20 ppm and by the characteristic high-field $^{11}\text{B}(1)$ resonances (-47.5 and -48.5 ppm, respectively). Similar patterns also are found for all isoelectronic compounds of the 11-vertex *nido* series lacking B–H–B bridges on the open face, such as isomeric *nido* tetracarboranes 7,8,9,10-C₄B₇H₁₁ (compound **6** in Figure 6),¹⁸ 2,7,9,10-C₄B₇H₁₁,¹⁸ and 1,7,8,10-C₄B₇H₁₁,^{18,19} along with dicarbaheteroboranes 7,8,10-C₂NB₈H₁₁²⁰ and 7,8,10-C₂SB₈H₁₀.^{21,22} The large shielding of the $^{11}\text{B}(1)$ nucleus is a consequence of high electron density in the open pentagonal face, the area opposite (antipodal)²³ to the B(1)H vertex. Figure 8 shows the excellent correlation of the ^{11}B chemical shifts among all compounds with the 7,8,10-tricarbollide constitution (structures **3** and 4^-) we have isolated so far (compare also the NMR data of the 7-Me and 7-PhCH₂ substituted^{3a} derivatives of 4^-).

Comparison of the shielding properties of the thallium and PSH⁺ salts of 2^- in Figure 6 reveals significant downfield shifts of all resonances of the former salt. This effect is most remarkable for the B(10,11) ($\Delta\delta$ 7.3 ppm) and B(1) ($\Delta\delta$ 5.9 ppm) atoms. Also the $\delta(^{11}\text{B})/\delta(^1\text{H})$ correlation line for the $(\text{Ti}^+)2^-$ compound (dotted line in the upper trace in Figure 5) is much flatter than that for the PSH⁺ salt. These differences reflect the change in electron density (polarization) due to the closer approach of the Ti^+ ion to B(10,11) at the open face of the tricarbollide anion as shown by a preliminary *ab initio* computation (compare thallium derivatives of the isoelectronic $[\text{7,8-C}_2\text{B}_9\text{H}_{11}]^{2-}$ dicarbollide dianion²⁴). On the other hand, the ^{11}B and ^1H chemical shifts for the thallium salt of the isomer 4^- do not differ too much from those for the PPh_4^+ salt (see Table 6 and upper part of Figure 8), which may be due to the more central cation location in agreement with an ionic formulation $\text{Ti}^+[\text{7,8,10-C}_3\text{B}_8\text{H}_{11}]^-$, $(\text{Ti}^+)4^-$.

Due to the presence of a B–H–B bridge^{22,23} on the open pentagonal face in **2a**, there are pronounced differences both in the order and the position of individual boron resonances in comparison to 2^- (see Figure 7). Protonation of the open face of 2^- results in a marked deshielding of the corresponding $^{11}\text{B}(1)$ nucleus in **2a** (-35.2 ppm; compare -36.6 ppm for the isostructural thiaanalogue $[\text{nido-}7\text{-SB}_{10}\text{H}_{11}]^-$).²² Figure 7 also reveals straightforward NMR and structural relationships between **2a** and its anionic dicarbon analog 5^- which has the same type of open-face hydrogen bridge.⁷ Figure 7 shows the similarities among all neutral tricarbollide compounds of general constitution **2** thus far isolated. The asymmetric derivatives **2c** and **2d** exhibit eight different boron resonances including signals

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Table 6. NMR Data

compound	nucleus	δ (assignment, J_{BH} (Hz))
$\text{Cs}^+[\text{nido-7,8,9-C}_3\text{B}_8\text{H}_{11}]^-, (\text{Cs})^+2^-$	$^{11}\text{B}^a$	-15.5 (B6, $\sim 156^b$), -16.5 (B10,11, $\sim 125^b$), -20.5 (B2,5, 143), -23.5 (B3,4, 158), -47.3 (B1, 134)
	$^{11}\text{B}-^{11}\text{B}^c$	cross-peaks: B6-B10,11; B6-B2,5; B6-B1; B2,5-B3,4; B2,5-B1; B3,4-B1
	$^1\text{H}^d$	2.09 (H8), 1.48 (H7,9), 1.47 (H3,4), 1.13 (H10,11), 1.08 (H2,5), 0.96 (H6), 0.05 (H1)
$[\text{PSH}]^+[\text{nido-7,8,9-C}_3\text{B}_8\text{H}_{11}]^-, [\text{PSH}]^+2^-$	$^{11}\text{B}^a$	-15.5 (B6, ~ 135), -16.6 (B10,11, ~ 125), -20.6 (B2,5, 144), -23.6 (B3,4, 153), -47.5 (B1, 143)
	$^{11}\text{B}-^{11}\text{B}^c$	cross-peaks: B6-B10,11; ^c B6-B2,5; B6-B1; B2,5-B3,4; B2,5-B1; B3,4-B1
	$^1\text{H}^d$	7.39 (PSH ⁺ , 4 H), 6.39 (PSH ⁺ , 2 H), 2.79 (PSH ⁺ , 12 H) ~ 2.15 (H8), 1.50 (H7,9), 1.55 (H10,11), 1.47 (H3,4), 1.09 (H2,5), 0.97 (H6), 0.05 (H1)
$\text{TI}^+[\text{nido-7,8,9-C}_3\text{B}_8\text{H}_{11}], (\text{TI})^+2^-$	$^{11}\text{B}^a$	-9.3 (B10,11, 122), -12.6 (B6, 137), -16.7 (B2,5, 153), -21.7 (B3,4, 161), -41.6 (B1, 141)
	$^{11}\text{B}-^{11}\text{B}^c$	cross-peaks: B10,11-B6; B10,11-B2,5; B6-B2,5; B6-B1; B2,5-B3,4; B2,5-B1; B3,4-B1
	$^1\text{H}^d$	2.66 (H8), 1.76 (H8), 1.65 (H3,4), 1.43 (H10,11), 1.39 (H6), 1.39 (H2,5), 1.24 (H1)
<i>nido-7,8,9-C</i> ₃ <i>B</i> ₈ <i>H</i> ₁₂ , 2a	$^{11}\text{B}^a$	0.45 (B2,5, 158), -19.0 (B3,4, ~ 170), -20.0 (d, B10,11, $\sim 125/39^f$), -25.9 (d, B6, 146), -35.2 (d, B1, 152)
	$^{11}\text{B}-^{11}\text{B}^c$	cross-peaks: B2,5-B3,4; B2,5-B10,11; B2,5-B6; B3,4-B1; B10,11-B6; B6-B1
	$^1\text{H}^d$	3.76 (H8), 3.08 (H7,9), 2.65 (H2,5), 1.85 (H3,4), 1.84 (H10,11), 1.15 (H1), 0.91 (H6), -2.19 ($\mu\text{H10,11}$)
8-Me- <i>nido-7,8,9-C</i> ₃ <i>B</i> ₈ <i>H</i> ₁₁ , 2b	$^{11}\text{B}^a$	0.2 (B2,5, 160), -15.8 (B3,4, 172), -19.9 (B10,11, 140/36 ^f), -28.2 (B6, 147), -33.6 (B1, 150)
	$^{11}\text{B}-^{11}\text{B}^c$	cross-peaks: B2,5-B3,4; B2,5-B10,11; B2,5-B6; B3,4-B1; B10,11-B6; B6-B1
	$^1\text{H}^d$	2.95 (H7,9), 2.61 (H2,5), 1.84 (H10,11), 1.68 (Me, 3 H), ~ 1.70 (H3,4), ^b 1.15 (H1), 0.79 (H6), -2.00 ($\mu\text{H10,11}$)
10-Me-7-(Bu ^{<i>u</i>} MeN)- <i>nido-7,8,9-C</i> ₃ <i>B</i> ₈ <i>H</i> ₁₀ , 2c	$^{11}\text{B}^{a,g}$	-0.7 (B2, 158), -3.0 (B5, 160), -9.5 (B10), -18.7 (B3, 170), -19.3 (B4, 172), -20.2 (d, B11), -24.2 (B6, 153), -35.2 (B1, 155)
	$^{11}\text{B}-^{11}\text{B}^c$	cross-peaks: B2-B11; B2-B6; B2-B1; B5-B6; B5-B1; B10-B6; B3-B1; B3-B4; ^c B4-B1; B11-B6
	$^1\text{H}^d$	3.97 (H8), 3.11 (H2), 2.60 (H9), 2.38 (Bu ^{<i>u</i>} MeN, 3 H), 2.50 (H5), 2.04 (H4), 1.99 (H3), 1.69 (H11), 1.24 (Bu ^{<i>u</i>} MeN, 9 H), 1.10 (H1), 0.32 (Me10, 3 H), -2.13 ($\mu\text{H10,11}$)
10,11-Me ₂ -7-(Bu ^{<i>u</i>} MeN)- <i>nido-7,8,9-C</i> ₃ <i>B</i> ₈ <i>H</i> ₉ , 2d	$^{11}\text{B}^{a,g}$	-0.5 (B2, 155), -5.8 (B5, 156), -10.5 (s, B11), -11.5 (s, B10), -22.1 (B3, 172), -23.3 (B4, 173), -24.7 (B6, 146), -36.9 (B1, 150)
	$^{11}\text{B}-^{11}\text{B}^c$	cross-peaks: B2-B11; B2-B3; B2-B6; B2-B1; B5-B10; B5-B4; B5-B6; B5-B1; B11-B6; B10-B6; B3-B1; B4-B1
	$^1\text{H}^d$	3.92 (H8), 2.81 (H2), 2.49 (H9), 2.49 (Bu ^{<i>u</i>} MeN, 3 H), 2.38 (H5), 1.82 (H4), 1.78 (H3), 1.25 (Bu ^{<i>u</i>} MeN, 9 H), 1.03 (H1), 0.31 (Me11, 3 H), 0.26 (Me10, 3 H), -2.01 ($\mu\text{H10,11}$)
10-(Me ₃ N)- <i>nido-7,8,10-C</i> ₃ <i>B</i> ₈ <i>H</i> ₁₀ , 3a	$^1\text{H}-^1\text{H}^h$	selected cross-peaks: H8-H9; H9-Me10; H9-H5; H2-Me11
	$^{11}\text{B}^{a,g}$	-16.1 (B5,6, 147), -17.3 (B3, 157), -20.8 (B9,11, 135), -25.6 (B2,4, 152), -49.0 (B1, 144)
	$^{11}\text{B}-^{11}\text{B}^c$	cross-peaks: B5,6-B9,11; B5,6-B2,4; B5,6-B1; B3-B2,4; B3-B1; B9,11-B2,4; B9,11-B2,4; B2,4-B1
10-(Me ₂ NH)- <i>nido-7,8,10-C</i> ₃ <i>B</i> ₈ <i>H</i> ₁₀ , 3b	$^{11}\text{B}^a$	-16.4 (B5,6, 153), -17.7 (B3, ~ 150), -20.2 (B9,11, 136), -26.1 (B2,4, 149), -49.0 (B1, 143)
	$^{11}\text{B}-^{11}\text{B}^c$	cross-peaks: B5,6-B9,11; B5,6-B2,4; B5,6-B1; B3-B2,4; B3-B1; B9,11-B2,4; B2,4-B1
	$^1\text{H}^d$	6.92 (s, br, Me ₂ NH), 2.81 (t, Me ₂ NH, 6 H, $J \sim 15$ Hz), 1.81 (H3), 1.78 (H9,11), 1.70 (H5,6), 1.50 (H7,8), 1.06 (H2,4), -0.01 (H1)
$\text{Cs}^+[\text{nido-7,8,10-C}_3\text{B}_8\text{H}_{11}]^-, (\text{Cs})^+4^-$	$^{11}\text{B}^a$	-15.5 (B3, 158), -17.8 (B5,6, $\sim 145^b$), -18.0 (B9,11, 132), -25.3 (B2,4, 147), -48.1 (B1, 140)
	$^{11}\text{B}-^{11}\text{B}^c$	cross-peaks: B3-B2,4; B3-B1; B5,6-B9,11; ^c B5,6-B2,4; B5,6-B1; B9,11-B2,4; B2,4-B1
	$^1\text{H}^d$	1.77 (H3), 1.51 (H9,11), 1.22 (H5,6), 1.22 (H7,8), 0.97 (H2,4), 0.56 (H10), -0.10 (H1)
$\text{PPh}_4^+[\text{nido-7,8,10-C}_3\text{B}_8\text{H}_{11}]^-, (\text{PPh}_4)^+4^-$	$^{11}\text{B}^a$	-15.6 (B3, 156), -18.0 (B9,11, $\sim 130^b$), -18.3 (B5,6, $\sim 140^b$), -25.4 (B2,4, 143), -48.5 (B1, 140)
	$^{11}\text{B}-^{11}\text{B}^c$	cross-peaks: B3-B2,4; B3-B1; B9,11-B2,4; B9,11-B5,6; ^c B5,6-B2,4; B5,6-B1; B2,4-B1
	$^1\text{H}^d$	1.76 (H3), 1.50 (H9,11), 1.22 (H5,6), 1.17 (H7,8), 0.96 (H2,4), 0.52 (H10), -0.14 (H1)
$\text{TI}^+[\text{nido-7,8,10-C}_3\text{B}_8\text{H}_{11}], (\text{TI})^+4^-$	$^{11}\text{B}^a$	-15.3 (B3, - ^b), -16.0 (B9,11, $\sim 120^b$), -20.1 (B5,6, 143), -23.3 (B2,4, 159), -46.9 (B1, 140)
	$^{11}\text{B}-^{11}\text{B}^c$	cross-peaks: B3-B1; B9,11-B5,6; B5,6-B2,4; B5,6-B1; B2,4-B1
	$^1\text{H}^d$	1.47 (H2,4), 1.27 (H7,8), 1.15 (H9,11), 1.11 (H5,6), 0.99 (H3), 0.60 (H10), 0.15 (H1)

^a $\delta(^{11}\text{B})$ values (in CD₃CN and for compounds of type **2** in CDCl₃) determined from $^{11}\text{B}\{^1\text{H}(\text{broadband})\}$ measurements with assignments by [$^{11}\text{B}-^{11}\text{B}$]-COSY NMR spectroscopy. ^b Values uncertain due to peak overlap. ^c Measured under the conditions of $\{^1\text{H}(\text{broadband})\}$ decoupling. ^d Assignments by $^1\text{H}-\{^{11}\text{B}(\text{broadband})\}$ and $^1\text{H}-\{^{11}\text{B}(\text{selective})\}$ NMR spectroscopy; unless stated otherwise, all signals are singlets in the $^1\text{H}-\{^{11}\text{B}(\text{broadband})\}$ NMR spectrum. ^e Uncertain cross-peaks due to close proximity of resonances. ^f Secondary μH splitting. ^g J_{BH} coupling constants determined by [$^1\text{H}-^{11}\text{B}$] correlation spectroscopy. ^h Measured under the conditions of $\{^{11}\text{B}(\text{broadband})\}$ decoupling.

shifted (ca. 10–11 ppm) downfield due to 10-Me and 10,11-Me₂ substitution. The spectrum of the C_s symmetry 8-Me derivative **2b** is similar to that of **2a**, with downfield shifts attributable to the presence of the substituent.

Plots at the top of Figures 6–8 show the approximately linear correlations between the proton and ^{11}B shifts for the cluster BH vertices despite the presence of three CH units in the open face of the tricarbollide cages discussed above. Also the ^1H resonances for the CH(cage) protons (see Table 6) also are

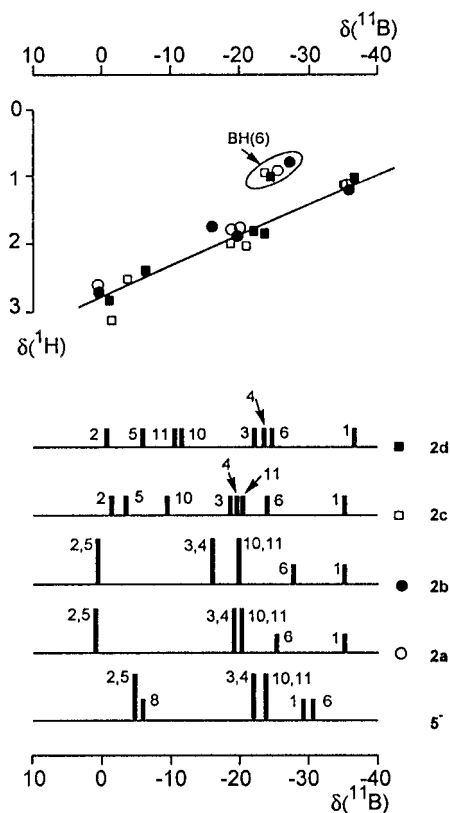
within the usual range for the 11-vertex *nido* carborane series.^{7,18,19}

Conclusion

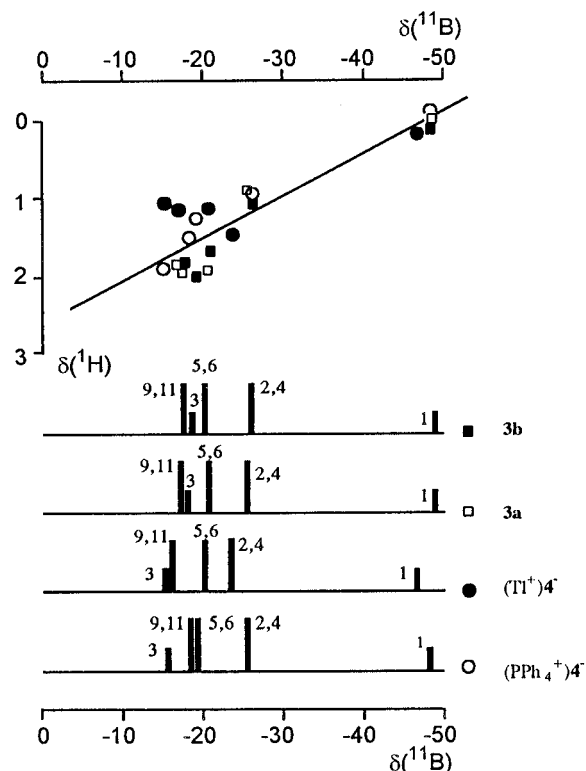
The reactions reported above lead to three new *parent* tricarbaboranes **2**⁻, **2a**, and **4**⁻. Unsubstituted tricarbaboranes so far reported include the “bare-carbon” *closo*-C₃B₅H₇²⁵ as well as *nido*-2,3,4-C₃B₃H₇²⁶ and *hypho*-C₃B₄H₁₂.²⁷ However, “*closo*-C₃B₅H₇” and “*hypho*-C₃B₄H₁₂” were found recently to be *closo*-

Table 7. Calculated IGLO ^{11}B NMR Shifts^a for the Parent Tricarbollides 2^- , 2a , and 4^-

level of theory//geometry	assignments for 2^-				
	B(1)	B(2,5)	B(3,4)	B(6)	B(10,11)
DZ//6-31G*	-50.5	-19.5	-26.9	-14.8	-18.9
DZ//MP2/6-31G*	-50.5	-22.2	-26.2	-14.0	-20.1
II'/MP2/6-31G*	-51.0	-20.4	-24.2	-12.9	-19.0
experiment	-47.5	-20.6	-23.6	-15.5	-16.6
level of theory//geometry	assignments for 2a				
	B(1)	B(2,5)	B(3,4)	B(6)	B(10,11)
DZ//6-31G*	-36.7	3.4	-20.7	-26.4	-21.4
DZ//MP2/6-31G*	-36.8	2.2	-21.4	-28.1	-22.9
II'/MP2/6-31G*	-36.5	3.7	-19.1	-26.7	-20.8
experiment	-35.2	0.5	-19.0	-25.9	-20.0
level of theory//geometry	assignments for 4^-				
	B(1)	B(2,4)	B(3)	B(5,6)	B(9,11)
DZ//6-31G*	-50.8	-28.1	-16.6	-18.4	-17.9
DZ//MP2/6-31G*	-50.6	-28.2	-16.8	-19.7	-19.0
II'/MP2/6-31G*	-51.2	-26.4	-14.0	-17.2	-18.5
experiment	-48.5	-25.4	-15.6	-18.3	-18.0

^a In ppm relative to $\text{BF}_3 \cdot \text{OEt}_2$.**Figure 7.** Stick representation and comparison of the ^{11}B chemical shifts and relative intensities for $\text{Cs}^+[\text{nido-7,9-C}_2\text{B}_9\text{H}_{12}]^-$ (5^-) (data from ref 7) and the neutral tricarbollides 7,8,9- $\text{C}_3\text{B}_8\text{H}_{12}$ (2a), 8-Me-7,8,9- $\text{C}_3\text{B}_8\text{H}_{12}$ (2b), 10-Me-7-(Bu^{Me}N)-*nido*-7,8,9- $\text{C}_3\text{B}_8\text{H}_{10}$ (2c), and 10,11-Me₂-7-(Bu^{Me}N)-*nido*-7,8,9- $\text{C}_3\text{B}_8\text{H}_{10}$ (2d) (bottom). The upper diagram is a plot of $\delta(^1\text{H})$ vs $\delta(^{11}\text{B})$ for all compounds of structure 2 .

2,3- $\text{C}_2\text{B}_5\text{H}_7$ ²⁸ and 1-Me-*arachno*-2,5- $\mu\text{-CH}_2$ -1- CB_4H_7 ,²⁹ respectively, and also the synthesis and identity of *nido*-2,3,4- $\text{C}_3\text{B}_7\text{H}_7$ were reinvestigated.³⁰ Moreover, these long-anticipated parent 11-vertex *nido* parent species 2^- , 2a , and 4^- facilitate the

(25) Thompson, M. L.; Grimes, R. N. *J. Am. Chem. Soc.* **1971**, *93*, 6677–6679.(26) (a) Bramlett, C. L.; Grimes, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 4269–4270. (b) Grimes, R. N.; Bramlett, C. L. *J. Am. Chem. Soc.* **1967**, *89*, 2557–2560. (c) Franz, D. A.; Grimes, R. N. *J. Am. Chem. Soc.* **1971**, *93*, 387–394.**Figure 8.** Stick representation and comparison of the ^{11}B chemical shifts and relative intensities for the isomeric 11-vertex *nido* compounds $[\text{PPh}_4]^+[\text{7,8,10-C}_3\text{B}_8\text{H}_{11}]^-$ $[\text{PPh}_4^+]4^-$, $\text{TI}^+[\text{7,8,10-C}_3\text{B}_8\text{H}_{11}]^-$ $[(\text{TI}^+)4^-]$, 10-(Me₃N)-7,8,10- $\text{C}_3\text{B}_8\text{H}_{10}$ (3a), and 10-(Me₂NH)-7,8,10- $\text{C}_3\text{B}_8\text{H}_{10}$ (3b) (bottom). The upper diagram is a plot of $\delta(^1\text{H})$ vs $\delta(^{11}\text{B})$ for all these compounds.

expansion of tricarbollide^{1,4} chemistry and its extension to metallatricarbollide⁵ and metallatricarbaborane³¹ areas which are scarcely represented. We also are investigating boron-elimination and expansion reactions leading to new types of nonmetallic tricarbaborane species. The recent synthesis of the first unsubstituted 10-vertex tricarbaborane *arachno*-5,6,9- $\text{C}_3\text{B}_7\text{H}_{13}$ ⁴ via boron elimination from anion 4^- is an example of such reactions in the tricarbollide series.

Experimental Section

General Procedures. All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver,³² although some operations, such as preparative TLC and column chromatography, were carried out in air. The starting tricarbaboranes 1a-c were prepared as reported previously^{1b} and sublimed before use. The metallic Na was purchased from Aldrich and used as received. The Aldrich tetrahydrofuran (THF) was dried over Na/benzophenone, hexane and CH_2Cl_2 were dried over CaH_2 and freshly distilled before use. Other chemicals were reagent or analytical grade

(27) Greatrex, R.; Greenwood, N. N.; Kirk, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1510–1511.(28) Fox, M. A.; Greatrex, R. *J. Chem. Soc., Dalton Trans.* **1994**, 3197.(29) Fox, M. A.; Greatrex, R.; Hofman, M.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *33*, 2298–2300.(30) Fox, M. A.; Greatrex, R.; Nikrahi, A. *J. Chem. Soc., Chem. Commun.* **1996**, 175–176.(31) (a) Howard, J. W.; Grimes, R. N. *J. Am. Chem. Soc.* **1969**, *91*, 6499–6500. (b) Howard, J. W.; Grimes, R. N. *Inorg. Chem.* **1972**, *11*, 263–267. (c) Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 943–958. (d) Siebert, W. *Pure Appl. Chem.* **1987**, *59*, 947–954. (e) Siebert, W. *Pure Appl. Chem.* **1988**, *60*, 1345–1348. (f) Attwood, A. T.; Fonda, K. K.; Grimes, R. N.; Brodt, G.; Hu, D.; Zenneck, U.; Siebert, W. *Organometallics*, **1989**, *8*, 1300–1303. (g) Brodt, G.; Kuhlman, T.; Siebert, W. *Chem. Ber.* **1989**, *122*, 829–831. (h) Plumb, C. A.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1992**, *11*, 1665–1671. (i) Plumb, C. A.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1992**, *11*, 1672–1680. (j) Plumb, C. A.; Sneddon, L. G. *Organometallics* **1992**, *11*, 1681–1685. (k) Barnum, B. A.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **1997**, *36*, 1327–1337.

and were used as purchased. Preparative TLC was carried out using silica gel (Aldrich, type 254 nm) as the stationary phase on plates of dimensions 200 × 200 × 1 mm, made on glass formers from aqueous slurries followed by drying in air at 80 °C. The purity of individual chromatographic fractions was checked by analytical TLC on Silufol (Kavalier, silica gel on aluminum foil; detection by diiodine vapor, followed by 2% aqueous AgNO₃ spray). Melting points were measured in sealed capillaries under nitrogen and are uncorrected. 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). Proton (¹H) and boron (¹¹B) NMR spectroscopy was performed at 7.05 and 11.75 Tesla on Bruker ARX 300 and Varian XL-500 instruments, respectively. The [¹¹B-¹¹B]-COSY and ¹H-¹¹B-(selective)} NMR experiments were essentially as described in other related papers from our laboratories.³³ Chemical shifts are given in ppm to high-frequency (low field) of $\Xi = 32.083\,971$ MHz (nominally F₃B·OEt₂ in CDCl₃) for ¹¹B (quoted ± 0.5 ppm) and $\Xi = 100$ MHz (SiMe₄) for ¹H (quoted ± 0.05 ppm), Ξ being defined as in ref 34. Solvent resonances were used as internal secondary standards. Coupling constants ¹J(¹¹B-¹H) are taken from resolution-enhanced ¹¹B spectra with digital resolution ± 8 Hz and are given in Hz; in some cases these were determined from [¹H-¹¹B]-correlation spectra³⁵ with enhanced resolution of ca. ± 1 Hz. IR spectra were obtained on a EU 9512 Pye-Unicam Fourier transform spectrometer. Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic.

Salts of the [nido-7,8,9-C₃B₈H₁₁]⁻ Anion (2⁻). (a) Cs⁺ salt from **1a**: In a typical experiment, a solution of 192 mg (1 mmol) of **1a** in 20 mL of THF was treated with ca. 100 mg (2.17 mmol) of finely cut sodium metal and 100 mg (0.78 mmol) of naphthalene under heating at reflux for 6 h. The colored mixture was then treated (dropwise) with aqueous 1 M solution of CsOH (5 mL) under stirring and cooling to 0 °C. The THF was evaporated, and the white precipitate dissolved under heating in a minimum amount of water and filtered. The filtrate was left to crystallize to give typically 165 mg (62%) of the Cs⁺ salt. For 2⁻ (Cs⁺ salt): IR (KBr) 3428 (m), 2596 (s), 2576 (s), 2520 (s), 2476 (s), 1632 (w), 1610 (w), 1452 (w), 1100 (w), 1060 (w), 1032 (m), 986 (w), 958 (m), 894 (w), 870 (m) cm⁻¹. Anal. Calcd: C, 13.51; H, 4.16. Found: C, 13.40; H, 4.09. (b) Cs⁺ salt from **2a**: A solution of 135 mg (1 mmol) of **2a** in 20 mL of THF was treated with aqueous 1 M solution of CsOH (5 mL) under stirring at room temperature for 6 h. The THF was evaporated, and the white precipitate dissolved under heating in a minimum amount of water and filtered. The filtrate was left to crystallize to give typically 256 mg (0.96 mmol, 96%) of the Cs⁺ salt of 2⁻. The Cs⁺ salt can be converted in essentially quantitative yields to NMe₄⁺, PPh₄⁺, and Tl⁺ salts by heating a concentrated aqueous solution with NMe₄Cl, PPh₄Cl, and TlNO₃ for 30 min, followed by cooling to ambient temperature, filtration, and drying in vacuo at 50 °C for 6 h. For Tl⁺[nido-7,8,9-C₃B₈H₁₁]: IR (KBr) 3548 (sh), 3420 (m), 2576 (s), 2508 (s), 2492 (s), 2456 (s), 1616 (w), 1094 (w), 1052 (w), 1024 (m), 978 (m), 946 (w), 892 (w), 866 (m), 810 (w), 742 (w) cm⁻¹. Anal. Calcd: 10.62; H, 3.27. Found: C, 10.11; H, 3.05. (c) PSH⁺ salt from **2a**: A solution of 67.3 mg (0.5 mmol) of **2a** in 10 mL of hexane was treated with a solution of 107 mg (0.5 mmol) of PS in 10 mL of hexane, and the mixture was left to stand for 6 h. The white precipitate was isolated by filtration and vacuum dried at ambient temperature to give 165 mg (95%) of the PSH⁺ salt of 2⁻, which was identified by NMR spectroscopy.

nido-7,8,9-C₃B₈H₁₂ (2a), 8-Me-nido-7,8,9-C₃B₈H₁₁ (2b), and 7-(Me₂NH)-nido-7,8,9-C₃B₈H₁₀ (1d). In a typical experiment, a solution of 192 mg (1 mmol) of **1a** in 20 mL of THF was treated with ca. 100 mg (2.17 mmol) of finely cut sodium metal and 100 mg (0.78 mmol) of naphthalene for 12 h at room temperature to develop a green-brown coloration of the mixture. The mixture was filtered using a Schlenk apparatus, and the filtrate treated with ca. 0.5 mL F₃CCOOH under

cooling at 0 °C. The THF was evaporated, the residue dissolved in a minimum amount of CH₂Cl₂ and subjected to preparative TLC in hexane to develop three major bands of *R_f* (prep.) 0.45, 0.30, and 0–0.05. The compound isolated by extraction with CH₂Cl₂ and evaporation from the second band, identified as pure **2a** via analytical TLC in hexane (*R_f* 0.20), was sublimed in vacuo at 50–70 °C/bath to give the first crop of **2a** (39 mg, 29%). Repeated TLC of the first band in hexane and a more detailed separation of pure fractions (checked by analytical TLC), followed by sublimation (50–70 °C/bath) of the solid materials obtained by the evaporation of the CH₂Cl₂ extracts led to the isolation of pure compounds **2a** (26 mg, 16%, total yield 65 mg, 0.45 mmol, 45%) and **2b** (13 mg, 9%) as white crystalline solids, moderately stable in air, but reasonably stable under inert atmosphere. The compound mixture isolated from the third band by extraction with acetone was repurified by preparative TLC in 10% MeCN/CH₂Cl₂ to isolate the main band of *R_f* (prep.) 0.48 by extraction with acetone, evaporation, and vacuum sublimation of the residue at 50–70 °C/bath to give 15.5 mg (9%) of **1d**, which was isolated as a white, air-stable solid. For **2a**: mp 185 °C, *R_f* (anal.) (hexane) 0.15, IR (KBr) 3068 (w), 2920 (w), 2576 (s), 2356 (sh), 2328 (sh), 1290 (w), 1254 (w), 1162 (w), 1164 (w), 1060 (sh), 1046 (m), 1018 (sh), 1004 (sh), 966 (w), 926 (w), 916 (w), 884 (m), 856 (w), 800 (sh), 792 (w), 750 (sh), 7236 (w), 652 (w), 634 (w), 578 (sh), 552 (w), 510 cm⁻¹ (w). Anal. Calcd: C, 26.75; H, 8.98. Found: C, 27.05; H, 8.75. Mass calcd for ¹²C₃¹¹B₈¹H₁₂ 136, found 136 (25%), 133 (100%). For **2b**: mp 100 °C, *R_f* (anal.) (hexane) 0.20. Anal. Calcd: C, 32.30; H, 10.17. Found: C, 33.41; H, 10.31. Mass calcd for ¹²C₄¹¹B₈¹H₁₄ 150, found 150 (2%), 146 (100%). For **1d**: mp 213 °C, *R_f* (anal.) (20% MeCN/CH₂Cl₂) 0.22, IR (KBr) 3084 (vs), 3028 (s), 2788 (m), 2708 (w), 2588 (sh), 2548 (vs), 2512 (vs), 2476 (vs), 1462 (s), 1448 (s), 1430 (s), 1396 (m), 1360 (m), 1290 (w), 1226 (w), 1188 (w), 1156 (w), 1124 (w), 1074 (sh), 1050 (m), 1000 (vs), 962 (m), 916 (m), 856 (m), 824 (w), 782 (w), 694 (w), 666 (w), 606 cm⁻¹ (w). Mass calcd for ¹²C₅¹¹B₈¹⁴N¹H₁₇ 179, found 179 (30%), 161 (100%). When the same experiment was carried out under heating at reflux for 12 h, the only reasonably isolable preparative TLC fraction was that of *R_f* (prep.) 0.30 from which 84 mg (0.62 mmol, 62%) of **2a** was isolated as described above.

10-Me-7-(Bu¹Me₂N)-nido-7,8,9-C₃B₈H₁₀ (2c) and 10,11-Me₂-7-(Bu¹Me₂N)-nido-7,8,9-C₃B₈H₉ (2d). (a) From **1b**: To a suspension of 180 mg (7.5 mmol) of NaH (obtained from 60% mineral oil suspension by washing with hexane) in 20 mL of glyme was added a solution of **1b** (600 mg, 2.91 mmol) in 20 mL of glyme (hydrogen evolution) together with 2.13 g (15 mmol) of MeI. The mixture was heated at reflux for 3 h, and the glyme was then removed by evaporation. Under cooling to 0 °C, the residue was treated with 50 mL of CH₂Cl₂, 50 mL of water (dropwise), and then with 2 mL of concentrated HCl. The bottom layer was separated, dried with MgSO₄, and evaporated. The oily residue was dissolved in a minimum amount of MeCN and separated by preparative TLC in 5% MeCN/CH₂Cl₂ to isolate three major bands of *R_f* (prep.) 0.82 (fraction A), 0.54 (fraction B), and 0.31 (fraction C). The fractions B and C were purified by repeated preparative TLC to give 152 mg (0.69 mmol, 24%) of **1c** and 208 mg (1.1 mmol, 37%) of **1a**, respectively (see ref 1b). A compound mixture from fraction A was separated by preparative TLC in 20% CH₂Cl₂/hexane to isolate two major bands of *R_f* (prep.) 0.55 (fraction D) and 0.24 (fraction E) on extraction with CH₂Cl₂. Evaporation of the fraction E to dryness and vacuum distillation of the residual liquid at ca. 100 °C (bath) onto a cold finger (ca. 0 °C) gave 28 mg (0.12 mmol, 4%) of **2c** as white, air-stable crystals. For **2c**: mp 41 °C, *R_f* (anal.) (hexane) 0.05, IR (KBr) 3084 (w), 2964 (s), 2908 (sh), 2816 (sh), 2588 (vs), 1462 (m), 1388 (m), 1360 (m), 1314 (m), 1286 (m), 1262 (w), 1230 (m), 1212 (m), 1184 (w), 1162 (m), 1106 (w), 1088 (sh), 1054 (m), 1014 (m), 990 (m), 966 (m), 926 (w), 834 (w), 736 cm⁻¹ (w). Anal. Calcd: C, 46.04; H, 10.73. Found: C, 45.28; H, 10.82. Mass calcd for ¹²C₉¹¹B₈¹⁴N¹H₂₅ 235, found 235 (8%), 233 (90%). Fraction D (identified by ¹¹B NMR as a mixture of substituted derivatives of **2a**) was evaporated to dryness, dissolved in 5 mL of glyme, and heated at reflux for 3 h upon addition of 24 mg (1 mmol) of NaH and 50 mg (0.35 mmol) of MeI. The volatile materials were evaporated, and, under cooling to 0 °C, the residue was treated with 10 mL of CH₂Cl₂, 10 mL of water (dropwise), and then with 1 mL of concentrated HCl. The bottom layer was separated, dried with MgSO₄, and evaporated. The oily residue was dissolved in a minimum amount

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of CH_2Cl_2 and separated by preparative TLC in hexane to isolate the major band of R_f (prep.) 0.45, from which 60 mg (0.24 mmol, 8%) of **2d** was isolated by evaporation and vacuum distillation similarly as compound **2c** to obtain white, air-stable crystals. For **2d**: mp 68 °C, R_f (anal.) (hexane) 0.15, IR (KBr) 2981 (s), 2910 (s), 2875 (sh), 2833 (m), 2629 (vs), 2601 (vs), 2580 (vs), 2538 (vs), 1469 (s), 1398 (s), 1363 (s), 1321 (vs), 1307 (s), 1244 (m), 1173 (m), 1117(m), 1061 (m), 1019 (s), 991 (sh), 963 (m), 857 (w), 815 (m), 759 (m), 723 (m), 674 (m), 597 (w), 576 (m), 548 cm^{-1} (m). Anal. Calcd: C, 48.28; H, 10.94. Found: C, 47.16; H, 11.22. Mass calcd for $^{12}\text{C}_{10}^{11}\text{B}_8^{14}\text{N}^1\text{H}_{27}$ 249, found 249 (4%), 247 (48%). (b) From **1c**: The reaction of **1c** (642 mg, 2.91 mmol) in 20 mL of glyme with 2.13 g (15 mmol) of MeI, performed exactly under the same conditions as part (a) resulted in the recovery of 95 mg (0.43 mmol, 15%) of **1c** and the isolation of 202 mg (1.07 mmol, 36%) of **1a**, 35 mg (0.15 mmol, 5%) of **2c**, and 83 mg (0.33 mmol, 11%) of **2d**.

10-(Me₃N)-nido-7,8,10-C₃B₈H₁₀ (3a). Compound **1a** (192 mg, 1 mmol) was heated in a sealed glass ampoule at 350 °C for 20 min. After being cooled to ambient temperature, the contents were removed by CH_2Cl_2 , and the product was purified by preparative TLC in 10% hexane/ CH_2Cl_2 to isolate the only fraction of R_f (prep.) 0.50 by extraction with CH_2Cl_2 . The extracts were evaporated, and the crystalline residue was washed with 5 mL of hexane and vacuum dried to give 186 mg (97%) of **3a**. The analytical product can be obtained by sublimation at 150–200 °C. For **3a**: mp 290 °C, R_f (anal.) (CH_2Cl_2) 0.73, IR (KBr) 3100 (w), 3051 (w), 3028 (m), 2959 (w), 2573 (s), 2552 (s), 2545 (s), 2523 (s), 2453 (s), 1983 (s), 1462 (s), 1441 (sh), 1406 (s), 1096 (m), 1005 (m), 948 (s), 906 (s), 878 (w), 822 (w), 808 (w), 759 (w), 745 (w), 534 cm^{-1} (m). Anal. Calcd: C, 37.57; H, 9.98. Found: C, 37.71; H, 10.15. Mass calcd for $^{12}\text{C}_6^{11}\text{B}_8^{14}\text{N}^1\text{H}_{19}$ 193, found 193 (40%), 192 (100%).

10-(Me₂NH)-nido-7,8,10-C₃B₈H₁₀ (3b). In a typical experiment, a solution of 192 mg (1 mmol) of **3a** in 20 mL of THF was treated with ca. 100 mg (2.17 mmol) of finely cut sodium metal and 100 mg (0.78 mmol) of naphthalene under heating at reflux for 2 h. The colored mixture was then treated (dropwise) with 20 mL of water and ca. 1 mL of F_3CCOOH while cooling to 0 °C. The THF was evaporated, and the residual mixture extracted with three 20 mL portions of CH_2Cl_2 . The combined organic layers were reduced in volume and subjected to column chromatography or preparative TLC using CH_2Cl_2 to isolate the main fraction of R_f 0.10. This was isolated by evaporation and recrystallization of the solid residue from concentrated CH_2Cl_2 solution that was overlaid by a 2-fold amount of hexane to give 161 mg (94%) of **3b**. For **3b**: mp 158 °C, R_f (anal., CH_2Cl_2) 0.10, IR (KBr): 3444 (w, br), 3160 (s), 3028 (w), 2724 (w), 2540 (s), 2492 (sh), 1466 (s), 1430 (s), 1402 (m), 1382 (s), 1368 (s), 1258 (w), 1202 (m), 1156 (w), 1096 (m), 1052 (w), 1008 (s), 986 (m), 962 (s), 948 (s), 906 (m), 866 (m), 846 (m), 800 (m), 740 (m) 680 (w), 656 (w), 532 (m), 316 cm^{-1} (m). Anal. Calcd: C, 34.97; H, 9.97. Found: C, 35.10; H, 9.82. Mass calcd for $^{12}\text{C}_5^{11}\text{B}_8^{14}\text{N}^1\text{H}_{17}$ 179, found 179 (40%), 178 (100%).

Salts of the [nido-7,8,10-C₃B₈H₁₀]⁻ Anion (4⁻). Compound 2⁻ (Cs⁺ salt) (267 mg, 1 mmol) was heated under nitrogen at 350 °C for 20 min. After being cooled to ambient temperature, the contents were recrystallized from a minimum amount of water. The white crystalline material separated after cooling at 0 °C was isolated by filtration and dried in vacuo at 50 °C for 6 h to give 168 mg (63%) of the Cs⁺ salt of 4⁻. For 4⁻ (Cs⁺ salt): R_f (anal.; 33% MeCN in CHCl_3) 0.22. Anal. Calcd: C, 13.51; H, 4.16. Found: C, 13.20; H, 4.02. Alternatively, a hot solution of the Cs⁺ salt was precipitated by equivalent amounts of PPh_4Cl or TiNO_3 to isolate 308 mg (65%) and 227 mg (67%) of the PPh_4^+ and Ti^+ salts, respectively. For 4⁻ (PPh_4^+ salt): R_f (anal.; 33% MeCN in CHCl_3) 0.75; IR (KBr): 3416 (w, br), 3232 (sh), 3076 (w), 3056 (w), 3028 (w), 2512 (s), 1582 (w), 1480 (m), 1434 (s), 1388 (sh), 1336 (w), 1314 (w), 1180 (w), 1162 (w), 1106 (s), 1028 (w), 994 (m), 954 (w), 934 (w), 912 (w), 754 (w), 722 (m), 686 (s), 518 cm^{-1} (s). For 4⁻ (Ti^+ salt): R_f (anal.; 33% MeCN in CHCl_3) 0.16.

Single-Crystal Diffraction Analysis of 3a. The white single crystals of **3a** were grown by slow evaporation of a saturated Me_2CO solution at room temperature. A crystal of dimensions 0.3 × 0.2 × 0.2 mm was measured on a CAD4-MACHII-PC four-circle diffractometer using $\text{Mo K}\alpha$ X-radiation ($\lambda = 0.71069 \text{ \AA}$) at 293(2) K. A brief summary of crystal data and data collection parameters are given in Table 2. Three standard reflections monitored every 1 h showed 2% intensity variation

during the measurement. The data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods using SHELXS86³⁶ and was refined by full-matrix least squares using SHELXL93.³⁷ The function minimized was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/[\sigma(F_o^2) + (0.0704P)^2]$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms were located on a Fourier difference map and refined isotropically. The molecule is located on a mirror plane in the $P2_1/m$ space group; the atoms N, C(1), and C(10) are placed in special positions 2e, and each remaining atom occupies two positions with occupation factor 0.5.

Computational Methods. Geometries were fully optimized in C_s symmetry using standard *ab initio* methods³⁸ beginning at the SCF level with the 3-21G and 6-31G* basis sets. The 6-31G* frequency calculations confirmed the structures to be minima. The final optimization employed second-order Møller–Plesset (MP2) perturbation theory in the frozen-core (fc) approximation (denoted as MP2/6-31G*; with fc omitted for simplicity). All calculations were carried out on a Cray YMP-8 computer using the Gaussian 94 program.³⁹ Chemical shieldings were computed with the IGLO (individual gauge for localized orbitals) program¹¹ using Huzinaga basis sets:⁴⁰ first DZ, i.e., (7s3p) contracted to [4111, 21] for B, C and (3s) contracted to [21] for H, and second II', i.e., (9s5p1d) contracted to [51111, 2111, 1] for B, C and (3s) contracted to [21] for H. The calculated relative chemical shieldings are presented in Table 7 below. DZ results were obtained with an IGLO lobe version whereas for II' calculations the direct IGLO program (DIGLO)^{11d} was used.

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Supporting Information Available: Listings of MP2/6-31G* calculated coordinates for 2⁻, 2a, and 4⁻ (1 page). Tables of crystal data and structure refinement, atomic coordinates for non-hydrogen atoms, bond lengths and bond angles, calculated hydrogen positional parameters and isotropic displacement (16 pages) for **3a**. See any masthead page for ordering and Internet access instructions.

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