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The Derivatives of the 7,8,9- Series of Tricarbollides. Preparation and Structural Characterization of the 11-Vertex Tricarbaboranes 7-L-*nido*-7,8,9-$C_3B_8H_{10}$ (L = Amines)

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Reactions leading to the first representatives of the tricarbollide series are reported. These are based on monocarbon insertion into the neutral *nido*-5,6-$C_2B_8H_{12}$ (**1**) and its anion [*nido*-5,6-$C_2B_8H_{11}$]$^-$ (**2**), using the CN^- anion and Bu^tNC as monocarbon insertion agents, to give the ligand derivatives of the 11-vertex *nido* family of general formula 7-L-*nido*-7,8,9-$C_3B_8H_{10}$ (**3**), where L = H_2N^- (**3a**) or Bu^tNH_2 (**3b**) as a result of *endo* attack by the C-atom of the carbon-insertion reagent in the open hexagonal face of the dicarbaborane substrate. The second product from the CN^- reaction is the [9-CN-*arachno*-5,6-$C_2B_8H_{12}$]$^-$ anion (**4**) arising from an *exo* attack by the N-atom at the B(9) vertex of **2**. Methylation of **3a** and **3b** leads to the isolation of N-methyl derivatives of type **3**, where L = Me_3N (**3c**) and Bu^t(Me)NH (**3d**). Compounds of the general structure **3**, namely **3c**, are essential starting materials for the parent tricarbollide chemistry. Single-crystal X-ray diffraction analysis of **3d**·Me_2CO shows a regular 11-vertex *nido* constitution with a slightly perturbed pentagonal open face with three adjacent {CH} vertices. Crystal data for **3d**·Me_2CO: $C_{11}H_{29}B_8NO$, $M = 277.83$, $a = 13.8400(10)$ Å, $b = 10.6400(10)$ Å, $c = 16.439(2)$ Å, $\alpha = 90°$, $\beta = 134.725(8)°$, $\gamma = 90°$, $Z = 4$, $V = 1719.9(3)$ Å^3, $\mu = 0.058$ mm^{-1}, $D_{\text{calcd}} = 1.073$ Mg/m^3, $R_1 = 0.0472$, w$R_2 = 0.1247$.

Introduction

In this paper we report an extension of the monocarbon cage-insertion reactions based on reactions between polyhedral boron substrates and either the CN^- anion[1] or isonitriles.[2] Both of these monocarbon insertion processes may be reasonably supposed to proceed in an endo-substitution manner[3] via ligand-substituted derivatives *endo*-L·(B-substrate) (where L = CN^- or RNC) that undergo ligand−carbon cluster insertion under specific reaction conditions to form amine adducts of general formula RNH_2·(CB-substrate). This process is associated with the hydrogenation of the N≡C triple bond by the extra hydrogens of the boron substrate under simultaneous carbon insertion into the cluster area that generates exopolyhedral amine functionality on the inserted cluster carbon, as exemplified by reactions in eqs 1 and 2:[1,3]

$$[B_{10}H_{13}]^- + CN^- \xrightarrow{H_2O} [\textit{endo}\text{-6-NC-}\textit{arachno}\text{-}B_{10}H_{13}]^{2-} \xrightarrow{\text{acidification}} 7\text{-}H_3N\text{-}\textit{nido}\text{-7-}CB_{10}H_{12} + 7\text{-}H_3N\text{-}\textit{nido}\text{-7-}CB_9H_{11} \tag{1}$$

$$SB_9H_{11} + Bu^tNC \xrightarrow{\text{THF, RT}} \textit{exo}\text{-9-}(Bu^tNC)\text{-}\textit{arachno}\text{-6-}SB_9H_{11} + \textit{endo}\text{-9-}(Bu^tNC)\text{-}\textit{arachno}\text{-6-}SB_9H_{11} \xrightarrow{\text{10 min, RT}} 7\text{-}(Bu^tNH_2)\text{-}\textit{nido}\text{-7,8-}CSB_9H_9 \tag{2}$$

Sneddon's group has recently extended the monocarbon insertion concept using MeCN[4] and polarized alkynes, RC_2H (where R = CN, COOMe, or COMe),[5] as monocarbon insertion reagents in reactions with anionic polyhedral boron substrates of enhanced polarization of positive and negative charges in the open, reactive face of the molecule. This polarization was shown to strongly facilitate the C-insertion by adding the oppositely polarized ends of the triple bonded organic reagent to those of the polyhedral anionic reactant, analogous to the case of the formation of cyclic organic compounds via reactions of polarized alkynes with organic nucleophiles.[6] A typical example of this structurally tailored "anionic" synthetic strategy is exemplified by the high-yield reaction in eq 3, resulting in the incorporation of the acetonitrile {MeC} moiety into the cage of the [*arachno*-4,6-$C_2B_7H_{12}$]$^-$ anion accompanied by complete reduction of the C≡N bond by the extra hydrogens of the dicarbaborane:

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$$[\mathit{arachno}\text{-}4,6\text{-}C_2B_7H_{12}]^- + MeCN \xrightarrow{\text{reflux}} 6\text{-Me-}\mathit{nido}5,6,9\text{-}C_3B_7H_{10} + NH_3 \quad (3)$$

This "nitrile" synthetic approach, however, leads inevitably to C-substituted tricarbaboranes, and therefore it seemed viable to examine a combination of the classical cyanide and isonitrile monocarbon insertion methods[1,2] with the newly developed "anionic" strategy.[4,5] As we have reported in two preliminary communications, this merger of the two methods, the reactions between anion **2** and CN^- or Bu^tNC, resulted in the formation of the tricarbollides of the {7,8,9-C_3B_8} tricarbaborane class[7] which readily undergo straightforward thermal isomerization to {7,8,10-C_3B_8} species.[8] Both of these tricarbaborane types are, together with the recently reported substituted compounds [7-R-7,8,10-$C_3B_8H_{10}$]$^-$ (R = Me and PhCH2),[9] the first examples of the long anticipated 11-vertex *nido* family of tricarbaboranes. Here we wish to report full details of the synthesis of the basic starting materials of the 7,8,9-tricarbollide chemistry, ligand derivatives 7-L-7,8,9-$C_3B_8H_{10}$, along with some extension of this chemistry. The numbering system for the 10-vertex *nido* and *arachno* and the 11-vertex *nido* cages used in this paper are in structures **1** and **3**.

Experimental Section

All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver,[10] although some operations, such as preparative TLC chromatography, were carried out in air.

Materials. The starting *nido*-5,6-$C_2B_8H_{12}$ dicarbaborane was prepared as reported previously[11] and sublimed before use. Bu^tNC, MeCN, NaCN, and NaH (60% suspension in mineral oil, washed by hexane under nitrogen and then vacuum dried) were purchased from Aldrich and used as received. The Aldrich 1,2-dimethoxyethane (glyme) and tetrahydrofuran (THF) were dried over Na/benzophenone, hexane and CH_2Cl_2 were dried over CaH_2, and all were freshly distilled before use. Preparative TLC was carried out using silica gel (Aldrich, type UV 254) 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. Column chromatography was performed using silica gel Silpearl (Kavalier), and the purity of individual chromatographic fractions was checked by analytical TLC on Silufol (Kavalier, silica gel on aluminum foil; detection by UV 254 or diiodine vapor, followed by 2% aqueous $AgNO_3$ spray).

Physical Measurements. 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, Basle, Switzerland (70 eV, EI ionization). Proton (^1H) and boron (^{11}B) NMR spectroscopy was performed at 7.05 and 11.75 T on Bruker AM 300 and Varian XL-500 instruments, respectively. The [$^{11}B-^{11}B$]-COSY and $^1H\{^{11}B(\text{selective})\}$ NMR experiments were essentially as described in other recent papers from our laboratories.[12] Chemical shifts are given in ppm to high frequency (low field) of $\Xi = 32.083971$ MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0.5 ppm) and $\Xi = 100$ MHz ($SiMe_4$) for ^1H (quoted ± 0.05 ppm), Ξ being defined as in ref 13. Solvent resonances were used as internal secondary standards. Coupling constants $^1J(^{11}B-^1H)$ are taken from resolution-enhanced ^{11}B spectra with digital resolution ±8 Hz and are given in hertz; in some cases these were determined from [$^1H-^{11}B$]-correlation spectra[14] with enhanced resolution of *ca.* ±1 Hz. Infrared 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 Czech Academy of Sciences.

[7-H_2N-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ (3a) and [9-CN-*arachno*-5,6-$C_2B_8H_{12}$]$^-$ (4) (NMe_4^+ and PPh_4^+ Salts). To a solution of 1.24 g (10 mmol) of *nido*-5,6-$C_2B_8H_{12}$ (**1**) in 20 mL of hexane was added a solution of 2.0 g (40 mmol) of NaCN, and the mixture was stirred at room temperature for 24 h. The aqueous layer was separated, acidified with 15 mL of dilute HCl (1:2, v/v, dropwise, gas and HCN evolution!) and precipitated with NMe_4Cl (2.20 g, 20 mmol). The white precipitate was isolated by filtration, washed with water and diethyl ether, and vacuum dried to give 670 mg (2.96 mmol, 30%) of the NMe_4^+ salt of **3a**. For **3a** (PPh_4^+ salt, isolated from the NMe_4^+ salt by reprecipitation with 1 equiv of aqueous PPh_4Cl): IR (KBr) 3408 (br), 3216 (br), 3056 (m), 2948 (br), 2512 (m), 1610 (br), 1480 (m), 1434 (s), 1388 (m), 1336 (m), 1314 (m), 1106 (s), 994 (m), 722 (s), 686 (s), 518 (s) cm^{-1}. Anal. (NMe_4^+ salt) Calcd: C, 38.57; H, 10.69; N, 12.47. Found: C, 37.41; H, 10.38; N, 12.20. The PPh_4^+ salts of anions **3a** and **4** can be obtained alternatively by precipitation of the aqueous layer with a concentrated aqueous solution of PPh_4Cl (3.74 g, 10 mmol) and separation of a mixture of the dry PPh_4^+ salts thus obtained by column chromatography on silica gel, using a mixture of CH_2Cl_2 and MeCN (9:1, v/v). Isolation of fractions of R_f (anal., MeCN/$CHCl_3$ 1:2, v/v) 0.25 and 0.55 by evaporation and recrystallization from CH_2Cl_2−hexane (1:1) gave PPh_4^+ salts of anions **3a** and **4** in yields of 31% and 45%, respectively. For **4** (PPh_4^+ salt): Anal. Calcd: C, 66.47; H, 6.57. Found: C, 64.91 ; H, 6.45.

7-(Bu^tNH_2)-*nido*-7,8,9-$C_3B_8H_{10}$ (3b). (a) From 2: In a typical experiment, to a suspension of NaH (192 mg, 8 mmol) in 20 mL of glyme was added dropwise a solution of 492 mg (4 mmol) of *nido*-5,6-$C_2B_8H_{12}$ (**1**) under stirring at room temperature for 1 h to generate anion **2**. This was followed by the addition of Bu^tNC (592 mg, 8 mmol), and stirring was continued for 2−4 days at ambient temperature. The glyme was then evaporated and the oily residue digested with CH_2Cl_2 and water (30 mL each), followed by acidification with concentrated HCl (pH *ca.* 4). The CH_2Cl_2 layer was separated, dried with $MgSO_4$, evaporated to dryness, dissolved in a minimum amount of MeCN, and subjected to preparative TLC, using a mixture of hexane and CH_2Cl_2 (3:2, v/v) as the mobile phase. The main strong band of R_f (prep.) *ca.* 0.13 was isolated by extraction with acetone, evaporation, and drying in vacuo for 2 h to give 370 mg (53%) of **3b** (in many experiments with variable amounts of reactants the yields varied in the range 45−60%). An analytical sample can be obtained by vaccum distillation/sublimation at 150−200 °C/bath as a white, air-stable, crystalline material. For **3b**: mp 145 °C, R_f (anal.) (CH_2Cl_2) 0.20, IR (KBr) 3213 (m), 3128 (m), 3079 (m), 2981 (w), 2938 (w), 2601 (sh), 2573 (sh), 2559 (sh), 2509 (s), 2446 (s), 2404 (sh), 1567 (s), 1476 (m), 1384 (s), 1370 (sh), 1181 (s), 1012 (s), 956 (m) cm^{-1}. Anal. Calcd: C, 40.67; H, 10.24. Found: C, 39.85; H, 10.42. Mass calcd for $^{12}C_7{}^{11}B_8{}^{14}N^1H_{21}$ 207, found 207 (4%), 190 (100%). (b) From **1**: A solution of 492 mg (4 mmol) of dicarbaborane **1** in 30 mL of benzene was treated with Bu^tNC (592 mg, 8 mmol) while being stirred at room temperature for 4 days. The mixture was then evaporated and the oily pale yelow residue subjected to preparative TLC as in the preceeding experiment to isolate the main band of R_f (prep.) 0.13 from which 105 mg (15%) of 3a was isolated by evaporation and vacuum sublimation at 150−200 °C (bath).

7-(Me_3N)-*nido*-7,8,9-$C_3B_8H_{10}$ (3c). (a) From **1**: A solution of **1** (4.11 g, 33.1 mmol) in 50 mL of hexane was stirred with a solution of NaCN (6.83 g, 139 mmol) in 100 mL of water for 12 h at ambient temperature. The hexane layer was then separated and the remaining aqueous solution treated with solid NaOH (5 g, 125 mmol) and 20 mL

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of dimethyl sulfate (dropwise) while being stirred at room temperature for 1 h. The resulting white precipitate was isolated by filtration, washed with water and diethyl ether, and vacuum-dried to obtain 1.73 g (9.31 mmol, 28.1%) of **3c**. An analytical sample can be obtained by crystallization form a concentrated CH_2Cl_2 solution that was overlaid by a 2-fold amount of hexane or, alternatively, by vacuum sublimation at 150−200 °C (bath) as white air-stable crystals. Addition of 2.20 g (20 mmol) of NMe_4Cl to the aqueous filtrate resulted in the precipitation of 3.54 g (15.9 mmol, 48%) of the NMe_4^+ salt of anion **4**, which was filtered and vacuum dried. For **3c**: mp 290 °C, R_f (anal.) (MeCN−CH_2Cl_2 1:5, v/v) 0.30, IR (KBr) 3100 (w), 3030 (w), 2959 (w), 2934 (m), 2854 (w), 2559 (vs), 2509 (vs), 2362 (w), 1483 (s), 1462 (s), 1413 (m), 1040 (m), 1005 (s), 949 (s), 906 (w), 808 (w) cm^{-1}. Anal. Calcd: C, 31.31; H, 9.98. Found: C, 30.79; H, 10.58. Mass calcd. for $^{12}C_5{}^{11}B_8{}^{14}N^1H_{19}$ 193, found 193 (15%), 192 (100%). For **4**: R_f (anal.) (MeCN−$CHCl_3$ 1:2, v/v) 0.17, IR (KBr) 3380 (sh), 3252 (m), 3020 (w), 2972 (w), 2560 (m), 2520 (m), 2420 (m), 2264 (w), 2144 (m), 1632 (w), 1484 (m), 1414 (m), 1382 (m), 1308 (m), 1194 (w), 1148 (w), 1078 (w), 1032 (sh), 1014 (m), 972 (m), 948 (m), 916 (m), 772 (m), 722 (sh), 708 (m), 638 (w), 538 (w), 472 (w) cm^{-1}. (b) From **3b**: To a suspension of 180 mg (7.5 mmol) of NaH in 20 mL of glyme was added a solution of **3b** (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. After cooling to 0 °C, the residue was treated with 50 mL of CH_2Cl_2, with 50 mL of water (dropwise), and then with 2 mL of concentrated HCl. The bottom layer was separated, dried with $MgSO_4$, and evaporated. The oily residue was dissolved in a minimum amount of MeCN and separated by preparative TLC in 5% MeCN−CH_2Cl_2 to isolate two major bands of R_f (prep.) 0.54 and 0.31. Both fractions were purified by repeated preparative TLC to give 152 mg (0.69 mmol, 24%) of **3d** and 208 mg (1.1 mmol, 37%) of **3c**, respectively, upon workup as described above.

7-[Bu^t(Me)NH]-*nido*-7,8,9-$C_3B_8H_{10}$ (3d). (a) From **2**: In a typical experiment, to a suspension of NaH (192 mg, 8 mmol) in 20 mL of glyme was added dropwise a solution of 492 mg (4 mmol) of *nido*-5,6-$C_2B_8H_{12}$ (**1**) under stirring at room temperature for 1 h to generate anion **2**. This was followed by the addition of Bu^{t}NC (592 mg, 8 mmol), continued stirring for 48 h at ambient temperature, and dropwise addition of 631 mg (5 mmol) of Me_2SO_4 after cooling to 0 °C. The stiring was then continued for an additional 1 h, and the volatile materials were removed by rotary evaporation. The residual viscous oily residue was treated subsequently with 50 mL of CH_2Cl_2, 20 mL MeCN, and 2 mL of 25% aqueous NH_3. The bottom organic layer was separated, dried with $MgSO_4$, filtered, and subjected to multiple preparative TLC treatments using 5% MeCN−CH_2Cl_2 as the liquid phase. The main band of R_f (prep.) 0.53 was extracted with acetone and evaporated to dryness, and the residual solid was vacuum-dried to obtain 415 mg (1.88 mmol, 47%, with the yields from many experiments varying in the range 45−63%) of white air-stable crystals of **3d**. An analytical sample can be obtained by vacuum sublimation at 150−200 °C. For **3d**: mp 200 °C, R_f (anal.) (5% MeCN−CH_2Cl_2) 0.40, IR (KBr) 3093 (vs), 3051 (m), 2995 (m), 2805 (w), 2734 (w), 2566 (vs), 2523 (s), 2453 (s), 2369 (sh), 1476 (s), 1455 (s), 1399 (s), 1377 (vs), 1181 (s, br), 1117 (m), 1005 (s), 998 (sh), 970 (m), 752 (m) cm^{-1}. Anal. Calcd: C, 43.71; H, 10.55. Found: C, 43.12; H, 10.23. Mass calcd. for $^{12}C_8{}^{11}B_8{}^{14}N^1H_{23}$ 221, found 221 (4%), 163 (100%). (b) From **3b**: while being stirred and cooled at 0 °C, 400 mg (3.15 mmol) of Me_2SO_4 was added dropwise to a solution containing 280 mg (1.06 mmol) of **3b** and 88 mg (2.2 mmol) of NaOH in 30 mL of ethanol. The mixture was then left stirring for 2 h and the ethanol evaporated after the addition of 30 mL of water. The white precipitate thus formed was filtered with suction, washed with 30 mL of water and 10 mL of Et_2O, and vacuum-dried to obtain 224 mg (1.02 mmol, 96%) of **3d**, which was identified by IR and NMR spectroscopy. The acetone solvate **3d**·Me_2CO was obtained as described below.

Single-Crystal Diffraction Analysis of 3d. The white single crystals of **3d**·Me_2CO were grown by slow evaporation of a saturated Me_2CO solution at room temperature. A crystal of dimensions 0.7 × 0.6 × 0.35 mm^3 was placed inside a capillary tube which was then sealed with glue. The crystallographic measurement was carried out at 293(2) K on a CAD4-MACHII-PC diffractometer using Mo Kα X-radiation (λ = 71.069 pm). A brief summary of crystal data and data collection parameters is given in Table 1.

Table 1. Crystal Data and Structure Refinement for 7-[Bu^t(Me)NH]-*nido*-7,8,9-$C_3B_8H_{10}$·Me_2CO (**3d**)

empirical formula	$C_{11}H_{29}B_8NO$
M	277.83
crystal system	monoclinic
space group	$P21/c$
a, Å	13.8400(10)
b, Å	10.6400(10)
c, Å	16.439(2)
α, deg	90
β, deg	134.725(8)
γ, deg	90
Z	4
V, Å3	1719.9(3)
μ, mm^{-1}	0.058
D_{calcd}, Mg/m^3	1.073
F(000)	600
radiation, λ, Å	0.71069
θ range, deg	2.07−24.95
scan mode	$\omega-2\theta$
h, k, l collected	$h \langle -16,11\rangle$, $k \langle 0,12\rangle$, $l \langle 0,19\rangle$
no. of reflections measured	3127
no. of unique reflections	3015 [$R_{(int)} = 0.0292$]
no. of parameters	282
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0472$, $wR_2 = 0.1247$
R indices (all data)	$R_1 = 0.0747$, $wR_2 = 0.1419$
$\Delta\rho$, max, min, e·Å^{-3}	0.233, −0.246

Three standard reflections monitored every 1 h showed a 30% intensity decrease during the measurement. The data were corrected appropriately, and corrections were applied for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods using SHELXS86[15] and was refined by full-matrix least squares using SHELXL93.[16] The function minimized was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma(F_o^2) + (0.0821P)^2]$ and $P = (F_o^2 + 2\,F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the acetone methyl groups were placed in theoretical positions, and the cluster hydrogen atoms were located on a Fourier difference map and freely refined with individual isotropic thermal parameters.

Results

Syntheses. We realized in retrospect that we had isolated the first compound of the tricarbollide series, the [7-H_2N-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ anion (**3a**), many years ago from the reaction between the dicarbaborane *nido*-5,6-$C_2B_8H_{12}$ (**1**) and NaCN but did not unambiguously recognize its tricarbaborane constitution from sheer NMR results. We had been unable to grow a suitable crystal for an X-ray diffraction analysis and had no comparable NMR data at hand. The reaction is carried out by stirring a hexane solution of **1** with aqueous NaCN at room temperature to obtain a mixture of anions **3a** and [9-CN-*arachno*-5,6-$C_2B_8H_{12}$]$^-$ (**4**) as in eqs 4 and 5 in typical yields ranging from 30% to 48%, respectively:

$$[nido\text{-}C_2B_8H_{11}]^- + CN^- + H_2O \rightarrow [nido\text{-}H_2N\text{-}C_3B_8H_{10}]^- + OH^- \quad (4)$$

$$nido\text{-}C_2B_8H_{12} + CN^- \rightarrow [arachno\text{-}CN\text{-}C_2B_8H_{12}]^- \quad (5)$$

The mixture of the sodium salts of anions **3a** and **4**, contained in the aqueous phase, can be processed in different ways. Acidification with dilute hydrochloric acid destroys anion **4** and addition of NMe_4Cl then precipitates only the tricarbaborane anion **3a**. Alternatively, both anions **3a** and **4** can be copre-

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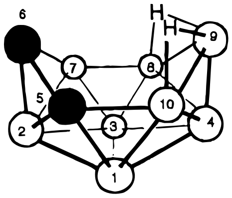
cipitated as $[PPh_4]^+$ salts from the original aqueous portion and then separated by chromatography. Treatment of the aforementioned aqueous layer with NaOH and Me_2SO_4 generates directly 7-Me_3N-*nido*-7,8,9-$C_3B_8H_{10}$ (**3c**) in yields approaching 30% as a consequence of the methylation of the exopolyhedral nitrogen atom in **3a**, whereby anion **4** remains intact to be precipitated by a suitable countercation.

We observed a straightforward, but low-yield, formation of a compound of the tricarbollide type for the second time upon treatment of the neutral carborane **1** with Bu^tNC. From this experiment we isolated, among other still not clearly identified unstable products, a zwitterionic species formulated as 7-(Bu^tNH_2)-7,8,9-$C_3B_8H_{10}$ (**3b**). From many experiments, the best yield (15%) has been isolated using benzene as the solvent at room temperature:

$$Bu^tNC + nido\text{-}C_2B_8H_{12} \rightarrow Bu^tNH_2\text{-}nido\text{-}C_3B_8H_{10} \quad (6)$$

Compound **3b** was isolated in its pure state by preparative TLC, followed by high-temperature vacuum sublimation as a white solid.



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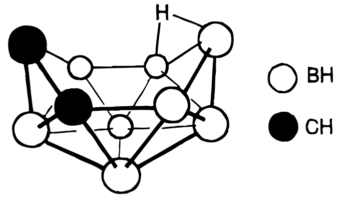

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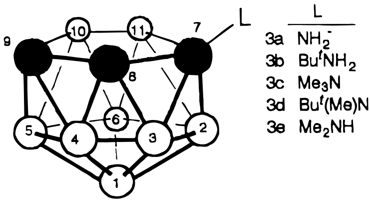

3

The yield of **3b** was significantly improved when the [5,6-$C_2B_8H_{11}]^-$ anion (**2**)[7] (generated in situ from the neutral carborane **1** and excess NaH in glyme) was employed in place of the neutral dicarbaborane **1** as the dicarbaborane source. Addition of Bu^tNC to the resulting solution of **2** and stirring for 2−4 days at room temperature, followed by acidification with diluted hydrochloric acid, resulted in the isolation of the $BuNH_2$ derivative **3b**. This was obtained as the main component of the reaction mixture by preparative TLC or column chromatography on silica gel in yields varying between 45% and 60% in many experiments. When the room-temperature reaction between anion **2** and Bu^tNC in glyme (RT, 2 days) was folloved by the addition of Me_2SO_4, the N-methylated derivative, 7-[Bu^t(Me)NH]-7,8,9-$C_3B_8H_{10}$ (**3d**), was isolated as the main product upon preparative TLC separation in CH_2Cl_2. The same product can be also prepared in 96% yield by the methylation of the Bu^tNH_2 compound **3b** with dimethyl sulfate in an alkaline ethanolic solution.

Both of the Bu^tNH_2 and Bu^t(Me)NH derivatives **3b** and **3d** were found to be convertible into the Me_3N compound **3c** by methylation with use of excess methyl iodide and NaH in refluxing glyme. A typical yield of **3c** from several experiments was about 35% after its chromatographical isolation. Although there is no direct evidence for the reaction mechanism, this transmethylation reaction seems to be consistent with an interesting elimination of isobutylene from the [7-(Bu^t*N*Me)-7,8,9-$C_3B_8H_{10}]^-$ anion ($\mathbf{3d}^-$) formed via deprotonation of the neutral **3d** by NaH:

$$(CH_3)_3C{-}(CH_3)NH{-}C_3B_8H_{10} + H^- \rightarrow [(CH_3)_3C{-}(CH_3)N{-}C_3B_8H_{10}]^- + H_2 \quad (7)$$

$$[(CH_3)_3C{-}(CH_3)N{-}C_3B_8H_{10}]^- \rightarrow (CH_3)_2C{=}CH_2 + [CH_3NH{-}C_3B_8H_{10}]^- \quad (8)$$

$$[CH_3NH{-}C_3B_8H_{10}]^- + H^- + 2CH_3I \rightarrow (CH_3)_3NC_3B_8H_{10} + 2I^- \quad (9)$$

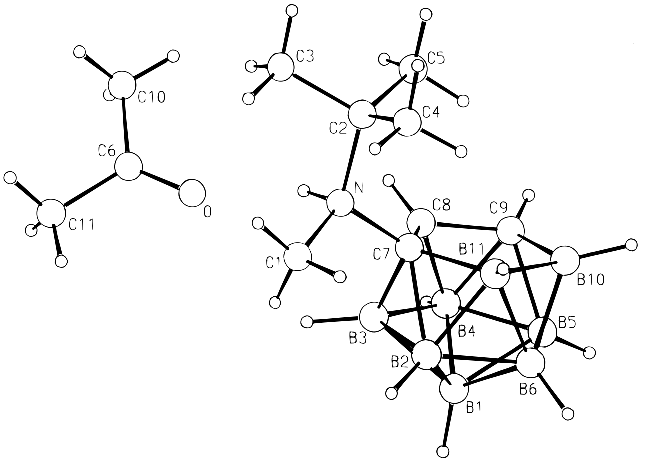

Figure 1. PLUTO representation of the molecular structure of 7-[Bu^t(Me)NH]-*nido*-7,8,9-$C_3B_8H_{10}\cdot Me_2CO$ (**3d**).

Another zwitterionic compound of the **3** type, the Me_2NH derivative **3e**, was obtained in 9% yield as a side product from the room-temperature reaction between **3c** and sodium metal in THF in the presence of naphthalene, as a result of a competitive demethylation[17] of the Me_3N functionality in **3c**. The main products obtained from this reaction, 7,8,9-*nido*-$C_3B_8H_{12}$ and 8-Me-7,8,9-*nido*-$C_3B_8H_{11}$, will be reported in a separate paper.[18]

Structural and NMR Studies. The constitution of the zwitterionic compounds of type **3** was established by an X-ray diffraction analysis of the Bu^t(Me)NH derivative **3d**, which crystallizes as acetone solvate $\mathbf{3d}\cdot Me_2CO$ by slow evaporation from acetone solution at room temperature. This study, as shown in Figure 1, has revealed the characteristic adjacent disposition of the three cluster carbons with no extra hydrogen within the open pentagonal face of the molecule. This geometry

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(17) For demethylation reactions see, for example: (a) Plešek, J.; Jelínek, T.; Drdáková, E.; Heřmánek, S.; Štíbr, B. *Colect. Czech. Chem. Commun.* **1984**, *49*, 1559−1562. (b) Plešek, J.; Jelínek, T.; Štíbr, B. *Polyhedron* **1984**, *3*, 1351−1355.

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Table 2. Positional Parameters for Non-hydrogen Atoms in 7-[Bu^t(Me)NH]-*nido*-7,8,9-$C_3B_8H_{10}$·Me_2CO (**3d**)

atom	*x*	*y*	*z*	*U*(eq)^a
B(1)	7044(2)	1186(2)	9014(2)	49(1)
B(2)	6024(2)	893(2)	9283(2)	44(1)
B(3)	5325(2)	1581(2)	7979(2)	44(1)
B(4)	6544(2)	2612(2)	8293(2)	48(1)
B(5)	7989(2)	2572(2)	9785(2)	47(1)
B(6)	7658(2)	1521(2)	10390(2)	45(1)
C(7)	5026(2)	2255(2)	8767(1)	33(1)
C(8)	5340(2)	3148(2)	8262(1)	37(1)
C(9)	6755(2)	3686(2)	9198(1)	42(1)
B(10)	7470(2)	3168(2)	10444(2)	42(1)
B(11)	6282(2)	2155(2)	10149(1)	38(1)
N	3545(1)	2195(1)	8127(1)	39(1)
C(1)	3128(2)	910(2)	8152(2)	60(1)
C(2)	3063(2)	3254(2)	8439(1)	44(1)
C(3)	1518(2)	3340(3)	7442(2)	74(1)
C(4)	3459(3)	2949(2)	9547(2)	59(1)
C(5)	3685(2)	4484(2)	8543(2)	51(1)
O	1724(2)	2020(2)	5669(1)	90(1)
C(6)	732(2)	2160(2)	4670(2)	54(1)
C(10)	191(3)	3413(3)	4128(2)	95(1)
C(11)	−48(3)	1064(2)	3905(2)	83(1)

^{a} Defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Interatomic Distances (Å) for 7-[Bu^t(Me)NH]-*nido*-7,8,9-$C_3B_8H_{10}$·Me_2CO (**3d**)

(a) Cluster			
B(1)−B(2)	1.779(3)	B(4)−H(4B)	1.13(2)
B(1)−B(3)	1.742(3)	B(5)−B(6)	1.758(3)
B(1)−B(4)	1.741(3)	B(5)−C(9)	1.713(3)
B(1)−B(5)	1.777(3)	B(5)−B(10)	1.785(3)
B(1)−B(6)	1.806(3)	B(5)−H(5B)	1.11(2)
B(1)−H(1B)	1.10(2)	B(6)−B(10)	1.782(3)
B(2)−B(3)	1.774(3)	B(6)−B(11)	1.781(3)
B(2)−B(6)	1.755(3)	B(6)−H(6B)	1.13(2)
B(2)−C(7)	1.755(2)	C(7)−N	1.509(2)
B(2)−B(11)	1.799(3)	C(7)−C(8)	1.513(2)
B(2)−H(2B)	1.13(2)	C(7)−B(11)	1.624(2)
B(3)−B(4)	1.758(3)	C(8)−C(9)	1.513(2)
B(3)−C(7)	1.765(2)	C(8)−H(8C)	0.93(2)
B(3)−C(8)	1.727(3)	C(9)−B(10)	1.620(3)
B(3)−H(3B)	1.10(2)	C(9)−H(9C)	0.93(2)
B(4)−B(5)	1.765(3)	B(10)−B(11)	1.725(3)
B4)−C(8)	1.728(3)	B(10)−H(10B)	1.11(2)
B(4)−C(9)	1.731(3)	B(11)−H(11B)	1.11(2)
(b) Ligand			
N−C(1)	1.495(3)	C(2)−C(3)	1.528(3)
N−C(2)	1.569(2)	C(2)−C(4)	1.522(3)
N−H	0.86(2)	C(2)−C(5)	1.509(3)

is in agreement with the expected 26-electron *nido* count[19] and was also predicted on the basis of chemical arguments, multinuclear NMR spectroscopy, and mass spectrometry.[7] The crystal data, coordinates, selected bond distances, and angles for compound **3c** are given in Tables 1−4.

Table 4. Selected Angles (deg) for 7-[Bu^t(Me)NH]-*nido*-7,8,9-$C_3B_8H_{10}$·Me_2CO (**3d**)

(a) Cluster			
B(2)−B(1)−B(6)	58.63(11)	C(9)−B(5)−B(4)	59.68(11)
B(3)−B(1)−B(2)	60.50(11)	C(9)−B(5)−B(6)	101.85(13)
B(3)−B(1)−B(5)	108.1(2)	C(9)−B(5)−B(10)	55.14(10)
B(3)−B(1)−B(6)	106.92(13)	B(2)−B(6)−B(1)	59.93(12)
B(4)−B(1)−B(2)	108.52(14)	B(2)−B(6)−B(5)	108.31(13)
B(4)−B(1)−B(3)	60.65(12)	B(2)−B(6)−B(10)	107.41(13)
B(4)−B(1)−B(5)	60.21(12)	B(2)−B(6)−B(11)	61.16(11)
B(4)−B(1)−B(6)	107.0(2)	B(5)−B(6)−B(1)	59.79(12)
B(5)−B(1)−B(2)	106.42(14)	B(5)−B(6)−B(10)	60.55(12)
B(5)−B(1)−B(6)	58.75(12)	B(5)−B(6)−B(11)	107.25(13)
B(1)−B(2)−B(11)	108.3(2)	B(10)−B(6)−B(1)	107.44(14)
B(3)−B(2)−B(1)	58.70(11)	B(11)−B(6)−B(1)	107.96(13)
B(3)−B(2)−B(11)	106.47(13)	B(11)−B(6)−B(10)	57.92(11)
B(6)−B(2)−B(1)	61.44(12)	N−C(7)−B(2)	121.50(13)
B(6)−B(2)−B(3)	107.7(2)	N−C(7)−B(3)	112.11(12)
B(6)−B(2)−B(11)	60.13(11)	N−C(7)−C(8)	114.74(12)
C(7)−B(2)−B(1)	103.13(14)	N−C(7)−B(11)	124.35(13)
C(7)−B(2)−B(3)	60.03(10)	B(2)−C(7)−B(3)	60.53(10)
C(7)−B(2)−B(6)	100.86(13)	C(8)−C(7)−B(2)	110.60(13)
C(7)−B(2)−B(11)	54.35(9)	C(8)−C(7)−B(3)	63.03(11)
B(1)−B(3)−B(2)	60.80(12)	C(8)−C(7)−B(11)	111.76(13)
B(1)−B(3)−B(4)	59.64(12)	B(11)−C(7)−B(2)	64.22(10)
B(1)−B(3)−C(7)	104.25(12)	B(11)−C(7)−B(3)	115.21(13)
B(4)−B(3)−B(2)	107.97(14)	B(3)−C(8)−B(4)	61.18(12)
B(4)−B(3)−C(7)	101.74(13)	C(7)−C(8)−B(3)	65.64(11)
C(7)−B(3)−B(2)	59.44(10)	C(7)−C(8)−B(4)	114.83(13)
C(8)−B(3)−B(1)	102.75(14)	C(7)−C(8)−C(9)	110.18(13)
C(8)−B(3)−B(2)	100.40(12)	C(9)−C(8)−B(3)	113.63(13)
C(8)−B(3)−B(4)	59.44(11)	C(9)−C(8)−B(4)	64.16(12)
C(8)−B(3)−C(7)	51.33(9)	B(5)−C(9)−B(4)	61.63(11)
B(1)−B(4)−B(3)	59.71(12)	C(8)−C(9)−B(4)	63.95(12)
B(1)−B(4)−B(5)	60.91(12)	C(8)−C(9)−B(5)	112.0(2)
B(3)−B(4)−B(5)	107.89(14)	C(8)−C(9)−B(10)	111.07(14)
C(8)−B(4)−B(1)	102.75(14)	B(10)−C(9)−B(4)	116.4(2)
C(8)−B(4)−B(3)	59.38(11)	B(10)−C(9)−B(5)	64.67(11)
C(8)−B(4)−B(5)	100.08(13)	B(6)−B(10)−B(5)	59.04(11)
C(8)−B(4)−C(9)	51.89(10)	C(9)−B(10)−B(5)	60.19(11)
C(9)−B(4)−B(1)	104.13(13)	C(9)−B(10)−B(6)	104.63(14)
C(9)−B(4)−B(3)	102.13(13)	C(9)−B(10)−B(11)	104.07(13)
C(9)−B(4)−B(5)	58.69(11)	B(11)−B(10)−B(5)	108.51(14)
B(1)−B(5)−B(10)	108.6(2)	B(11)−B(10)−B(6)	61.01(12)
B(4)−B(5)−B(1)	58.88(12)	B(6)−B(11)−B(2)	58.72(11)
B(4)−B(5)−B(10)	106.79(13)	C(7)−B(11)−B(2)	61.42(10)
B(6)−B(5)−B(1)	61.46(12)	C(7)−B(11)−B(6)	105.16(12)
B(6)−B(5)−B(4)	108.1(2)	C(7)−B(11)−B(10)	102.89(13)
B(6)−B(5)−B(10)	60.41(11)	B(10)−B(11)−B(2)	107.98(14)
C(9)−B(5)−B(1)	103.35(14)	B(10)−B(11)−B(6)	61.08(12)
(b) Ligand			
C(1)−N−HN	107.2(12)	C(3)−C(2)−N	106.7(2)
C(1)−N−C(2)	112.8(2)	C(4)−C(2)−N	111.1(2)
C(1)−N−C(7)	112.4(2)	C(4)−C(2)−C(3)	110.5(2)
C(2)−N−HN	102.6(12)	C(5)−C(2)−N	108.70(14)
C(7)−N−HN	105.8(12)	C(5)−C(2)−C(3)	109.0(2)
C(7)−N−C(2)	115.03(12)	C(5)−C(2)−C(4)	110.7(2)

Inspection of Table 3 clearly suggests that the intracluster C−C, C−B, and B−B distances in **3d** are comparable to the equivalent atom separations in the isoelectronic, but not isostructural, dicarbaborane analogue [*nido*-7,8-$C_2B_9H_{12}$]$^-$ (5).[20] The identical C(7)−C(8) and C(8)−C(9) distances, approaching at 1.513 Å a single C−C bond, are slightly shorter than the C(7)−C(8) distance in **5**. The open-face B−B distances in **5** (mean 1.823 Å) are remarkably longer than the B(10)−B(11) separation in **3d** (1.725 Å) due to the presence of one bridging hydrogen in **5** oscillating between the B(9)−B(10) and B(10)−B(11) positions. Other interatomic separations and angles are otherwise very similar to those in **5**. As expected from the generally shorter C−B interbelt distances (mean 1.737 Å) in comparison to the equivalent B−B separations (mean 1.782 Å), the open pentagonal face in **3d** is not planar but is folded to an envelope conformation about the C(7)−C(9) vector such that the C(7)−C(8)−C(9) area dips toward the B(2)−B(3)−B(4)−B(5)−B(6) lower pentagonal belt. The lower belt is essentially planar (σ = 0.004 Å), and with respect to it, the aforementioned three- and four-atom [C(9)−B(10)−B(11)−C(7)] portions of the upper pentagonal face make fold angles (φ and θ)[21] of 1.10(14)° and 1.60(12)° respectively.

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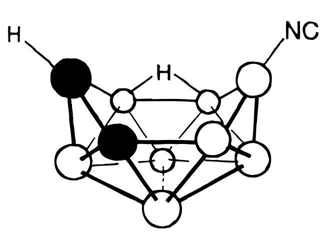

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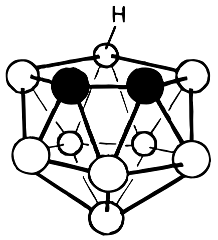

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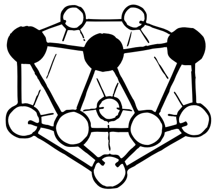

6

The structure determined is entirely in agreement with the results of high-field NMR spectroscopy of the zwitterionic compounds of type **3** (see Table 5 and Figure 2). As demonstrated graphically in Figure 2, the ^{11}B and ^{1}H NMR spectra of all compounds of type **3** exhibit eight different resonances for individual {BH} cluster units, in agreement with the absence of any element of symmetry due to the asymmetrical positioning of the ligand group at the C(7) site. The ^{1}H NMR spectra also show all resonances expected for the ligand N-alkyl groups and two nonequivalent cage {CH} units, with no evidence for the presence of extra hydrogen. Intercomparison of boron and proton NMR shifts for individual compounds in Figure 2 shows a very similar shielding behavior with a typical grouping of seven closely spaced lower-field {BH} resonances along with a single high-field {B(1)H} resonance. As expected, the parent anion **6**[7] exhibits a very similar shielding behavior, except that the number of resonaces is reduced to five of relative intensities 1:2:2:2:1, as expected from its C_s symmetry. Unfortunately, the absence of the corresponding NMR data for the isoelectronic and isostructural dicarbollide dianions 7,8- and 7,9-$[nido\text{-}C_2B_9H_{11}]^{2-}$ does not permit straightforward comparison of the associated NMR patterns, which are expected to be very similar.

All cluster {BH} and {CH} resonances were assigned by $[^{11}B-^{11}B]$-COSY[22] and in some cases by $[^{1}H-^{1}H]$-COSY[23] experiments, which allows for the assessement of substituent effects exerted by the asymmetrically positioned L group in compounds of type **3**. Of these, the most remarkable is the antipodal shielding[24] of the {B(5)H} resonances, increasing in the order of ligands (relative shielding constants[25] in parentheses): NH_2^- (0.6) < Me_3N (1.3) < Bu^tNH_2 (1.4) < $Bu^t(Me)NH$ (2.5) = Me_2NH (2.5) on the ^{11}B shielding scale and Me_3N (−0.63) < Me_2NH (−0.50) < Bu^tNH_2 (−0.51) = $Bu^t(Me)NH$ (−0.51) < NH_2^- (−0.35) on the ^{1}H shielding scale.

We failed to grow suitable crystals of anion **4**, but its [9-CN-*arachno*-5,6-$C_2B_8H_{12}]^-$ constitution can be derived unambiguously by comparison of the shielding patterns with those of the structurally analogous compounds of the [9-L-*arachno*-5,6-$C_2B_8H_{12}$ series.[26] From the magnitude of σ_{rel} at the substituted B(9)H site, approaching that of MeCN,[27] we strongly prefer the isocyano constitution to the cyano form. This is also in agreement with the assumption that **4** is formed by competitive *exo* N-attack by the CN^- anion at the B(9) site of **2** under the reaction conditions employed (see Discussion below).

Discussion

The results presented above clearly demonstrate that the cyanide anion and isonitriles react with cluster borane anions and lead to straightforward monocarbon insertion reactions as do those of nitriles[4] and polarized alkynes.[5a] Of synthetic importance is that, in contrast to polarized alkynes, the reactions with 10-vertex *nido* dicarbaborane compounds lead to tricarbaboranes. This family of carbaboranes has been a rarity in comparison with the numerous mono- and dicarbaboranes[28] since only a few tricarbaboranes have previously been reported. Among the known compounds of this class, alkylated species such as 2,3,4-R_2-*nido*-$C_3B_3H_5$[29] (see also the recent revision),[30] 2,3,5-R_5-*nido*-C_3B_3H[31] (R = alkyl or H), 6-Me-*nido*-5,6,9-$C_3B_7H_{10}$,[4,5a] and 6-R-*arachno*-5,6,7-$C_3B_7H_{12}$ (R = $NCCH_2$, $MeOCOCH_2$, and $MeCOCH_2$)[5a] and the [1-($NCCH_2$)-*hypho*-1,2,5-$C_3B_6H_{12}]^-$ anion prevail.[5a] Of particular importance is that the cyanide and isonitrile reactions lead in turn to parent, unsubstituted tricarbaboranes,[7] of which only two, the peculiarly structured *closo*-$C_3B_5H_7$[32] together with *hypho*-$C_3B_4H_{12}$,[33] have so far been reported. The latter species, however, has recently been found to be 1-Me-*arachno*-2,5-μ-CH_2-1-CB_4H_7.[34] Moreover, these synthetic approaches yield the first reported examples of tricarbollides,[7] the long anticipated compounds of the 11-vertex *nido* class of tricarbaboranes.

Although the mechanisms of the CN^- and RNC cage insertion reactions have not yet been studied in detail, several steps in the reaction sequences as in stoichiometric eqs 4 and 6 may be significant, apart from the fact that all cluster-insertion processes apparently start by *endo* attack by the insertion agent. The CN^- anion and/or Bu^tNC moieties are thought to be strongly polarized with the terminal carbon in each compound having a *negative* charge, in contrast to the positively charged terminal carbon in polarized alkynes.[5a] As suggested in Scheme 1, an *endo* attack by the negative $R-N\equiv C$ carbon at the positively charged C(6) site of anion **2**, followed by the transfer of the B(8)−H−B(9)

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Table 5. NMR Data

compound	nucleus	δ (multiplicity, assignment, J_{BH} (Hz))
NMe_4^+[7-H_2N-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ (**3a**)	^{11}B[a]	−16.1 (d, B(6), ...[b]), −16.8 (d, B(10,11), ...[b]), −17.3 (d, B(5), ...[b]), −19.8 (d, B(4), 161), −24.1 (d, B(2,3), 165), −47.0 (d, B(1), 140)
	^{11}B−^{11}B	crosspeaks: B(6)−B(10,11);[c] B(6)−B(5);[c] B(6)−B(2,3), B(6)−B(1); B(10,11)−B(2);[c] B(10,11)-B(2,3); B(5)−B(4);[c] B(4)−B(2,3); B(4)−B(1); B(2,3)−B(1)
	^{1}H[d]	3.50 (NMe_4^+), 3.02 (H_2N), 2.51 (H(9)), 1.60 (H(8)), 1.58(H(4)), 1.49 (H(3)), 1.44 (H(5)), 1.26 (H(10)), 1.11 (H(11)), 0.99 (H(6)), 0.91 (H(2)), 0.08 (H(1))
7-(Bu^tNH_2)-*nido*-7,8,9-$C_3B_8H_{10}$ (**3b**)	^{11}B[a,e]	−14.0 (d, B(6), 139), −14.9 (d, (B10), 142), −18.1 (d, (B5), 132), −18.5 (d, B(11), 132), −20.2 (d, B(4), 167), −22.5 (d, B(2), 154), −22.9 (d, B(3), 165), −46.9 (d, B(1), 147)
	^{11}B−^{11}B	crosspeaks: B(6)−B(10);[c] B(6)−B(5); B(6)−B(11); B(6)−B(2), B(6)−B(1); B(10)−B(5); B(10)-B(11); B(5)−B(4); B(5)-B(1); B(11)−B(2); B(3)−B(2);[c] B(4)−B(3); B(4)−B(1); B(2)−B(1); B(3)−B(1)
	^{1}H[d]	7.6 (NH_2), 2.82 (H(9)), 1.78 (H(8)), 1.66 (H(4)), 1.62 (Bu^t), ∼1.60 (H(3,5)), 1.50 (H(10,11)), 1.29 (H(6)), 1.14 (H(2)), 0.26 (H(1))
7-(Me_3N)-*nido*-7,8,9-$C_3B_8H_{10}$, (**3c**)	^{11}Ba	−16.2 (d, B(6,11), ∼140), −18.0 (d, B(5), ∼164), −19.2 (d, B(10), ∼138), −21.9 (d, B(2,4) ∼158), −23.7 (d, B(3), 165), −47.2 (d, B(1), 147)
	^{11}B−^{11}B	crosspeaks: B(6,11)−B(5); B(6,11)−B(10); B(6,11)−B(2); B(6,11)−B(1); B(5)−B(10); B(5)−B(2,4); B(5)−B(1); B(2,4)−B(3); B(2,4)−B(1)
	^{1}H[d]	3.09 (Me_3N), 2.70 (H(9)), 1.90 (H(4)), 1.79 (H(8)),1.72 (H(5)), 1.60 (H(3)), 1.42 (H(10)), 1.32 (H(11)), 1.17 (H(2)), 1.09 (H(6)), 0.18 (H(1))
7-[Bu^t(Me)NH]-*nido*-7,8,9-$C_3B_8H_{10}$ (**3d**)	^{11}B[a]	−15.2 (d, B(6,11), ∼132), −19.2 (d, B(5), ∼153), −20.1 (d, B(10), ∼150), −21.5 (d, B(4)), −22.4 (d, B(2,3), ∼149), −46.5 (d, B(1), 143)
	^{11}B−^{11}B	crosspeaks: B(6,11)−B(5), B(6,11)−B(10); B(6,11)−B(5), B(6,11)−B(1); B(5)−B(10);[c] B(2)−B(3);[c] B(5)−B(1); B(4)−B(2,3); B(4)−B(1); B(2,3)−B1
	^{1}H[d]	4.31 [Bu^t(Me)N*H*], 2.69 (H(9)), 2.60 [Bu^t(*Me*)NH, 3H], 1.78 (H(8)), 1.66 (H(4)), 1.63 (H(3)), ∼1.60 (H(5)),[b] 1.54 [Bu^t(*Me*)NH, 9 H], ∼1.45 (H(10)),[b] 1.35 (H(11)), 1.12 (H(6)), 1.10 (H(2)), 0.23 (H(1))
7-(Me_2NH)-*nido*-7,8,9-$C_3B_8H_{10}$ (**3e**)	^{11}B[a,e]	−15.6 (d, B(11), 125), −16.4 (d, B(6), 135), −19.2 (d, B(5), 149), −20.5 (d, B(10), 126), −21.3 (d, B(4), 164), −22.5 (d, B(2), 148), −23.9 (d, B(3), 164), −47.2 (d, B(1), 143)
	^{11}B−^{11}B	crosspeaks: B(11)−B(6);[c] B(11)−B(10); B(6)−B(5), B(6)−B(10);[c] B(6)−B(2); B(6)−B(1); B(5)−B(10);[c] B(5)−B(4); B(5)−B(1); B(4)−B(3); B(4)−B(1); B(2)−B(3); B(2)−B(1) B(3)−B(1)
	^{1}H[d]	5.30 (s, br, Me_2N*H*), 2.81 (t, *Me*$_2$NH, 6 H, *J* ∼20 Hz) 2.59 (H(9)), 1.79 (H(8)), 1.69 (H(4)), 1.59 (H(5)), 1.57 (H(3)), 1.29 (H(10,11)), 1.09 (H(2), 1.06 (H(6)), 0.18 (H(1))
	^{1}H−^{1}H	crosspeaks to cage {CH}: H(9)−H(8); H(9)−H(4); H(9)−H(5); H(9)−H(10); H(8)−H(4);[c] H(8)−H(3)[c]
[PPh_4]$^+$[9-CN-*arachno* -5,6-$C_2B_8H_{12}$]$^-$ (**4**)	^{11}Ba	2.1 (d, B(4), 140), −2.6 (d, B(2), 166), −11.3 (d, B(7), 142), −15.0 (d, B(10), 132), −21.6 (d, B(8), 140), −32.6 (d, B(1), 154), −37.9 (d, B(9), 115), −45.5 (d, B(3), 142)
	^{11}B−^{11}B	B(4)−B(10); B(4)−B(8); B(4)−B(1); B(4)−B(9); B(4)−B(3); B(2)−B(7); B(2)−B(1); B(2)−B(3); B(7)−B(3); B(10)−B(1); B(10)−B(9); B(8)−B(9); B(8)−B(3); B(1)−B(3)
	^{1}H[d]	2.75 (H(2)), 2.31 (H(7)), 2.27 (H(4)), 1.86 (H(5)), 1.57 (H(10)), 1.12 (H(8)), 0.89 (H(1)), 0.89 (*exo*-H(6)), 0.78 (*endo*-H(6)), 0.64 (H(9)), 0.03 (H(3)), −3.68 (μH(7,8))

[a] $\delta(^{11}B)$ values in CD_3CN determined from $^{11}B\{^1H$(broadband)$\}$ measurements with assignments by [^{11}B−^{11}B]-COSY NMR spectroscopy and by graphical intercomparison of the ^{11}B NMR patterns of compounds of type 3. [b] Value uncertain due to peak overlap. [c] Uncertain crosspeaks due to close proximity of resonances. [d] Assignments by $^1H\{^{11}B$(broadband)$\}$ and $^1H\{^{11}B$(selective)$\}$ NMR spectroscopy; unless stated otherwise, all signals are singlets of relative intensity 1 in the $^1H\{^{11}B$(broadband)$\}$ NMR spectrum. [e] J_{BH} coupling constants determined by [^{1}H−^{11}B] correlation spectroscopy.

bridging proton onto the N-atom, leads to an intermediate imino derivative [*endo*-6-(Bu^{t}NH═C)-*nido*-5,6-$C_2B_8H_{10}$]$^-$. The unsaturated and highly positive sp^2 arrangement with an empty orbital on the imine carbon is then removed by electron attack from the B(8)−B(9) area of enhanced electron density,[5b] followed by C-cluster insertion with the formation of the [7-(RNH)-*nido*-7,8,9-$C_3B_8H_{10}$]$^-$ anion (3^-), which is in turn protonated to give compound **3**.

Another interesting aspect of the cluster insertion is the sequential hydrogenation of the original isonitrile N≡C bond, the net result of which is the formation of the exopolyhedral N−C bond in the resulting zwitterion 3 with concomitant generation of a 26-electron {*nido*-C_3B_8} cage system. This hydrogenation requires four electrons which are supplied by the starting *nido* anion **2**. Two more electrons are then required to completely interrupt the N−C bond and form the unsubstituted *nido* anion **6**. In this particular case, these must be supplied by additional reaction with sodium,[7] while in the case of Sneddon's nitrile reaction in eq 1[4] the two additional electrons are supplied by the [*arachno*-$C_2B_7H_{12}$]$^-$ moiety, in which they are inherently contained, to achieve a complete N−C bond cleavage. Con-

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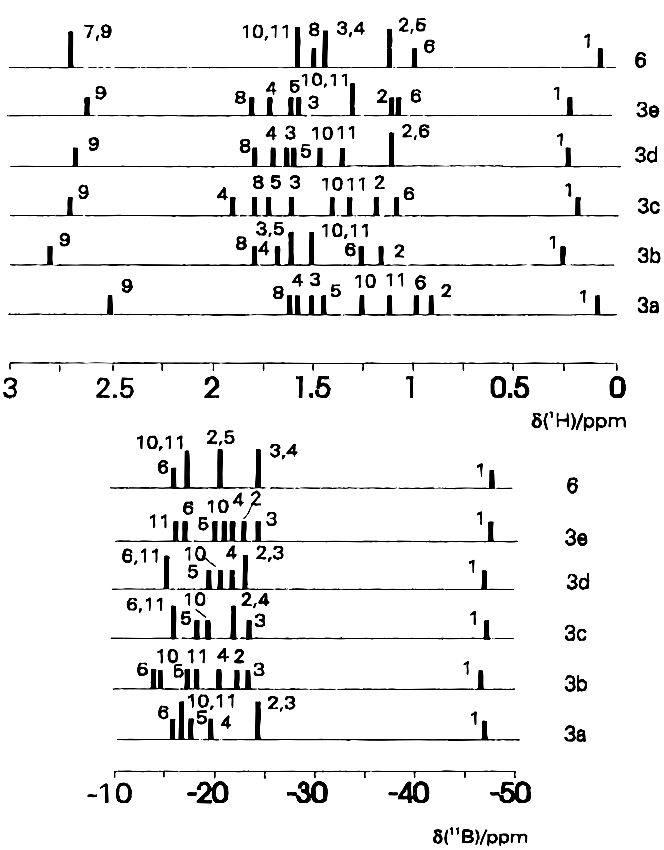
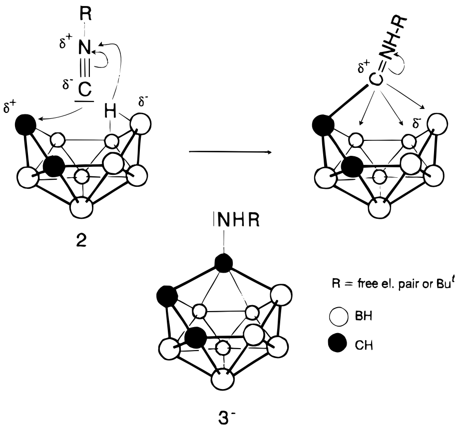


Figure 2. Stick representation and intercomparison of ^{1}H (upper diagram) and ^{11}B chemical shifts and relative intensities for compounds 7-L-*nido*-7,8,9-$C_3B_8H_{10}$ (**3**) with those of the parent anion [*nido*-7,8,9-$C_3B_8H_{11}$]$^-$ (**6**) (data from ref 7).

Scheme 1



sequently, we are currently investigating viable variations of tricarbollide syntheses based on reactions between {*arachno*-C_2B_8} substrates[26,35] and isonitriles or cyanides.

The disadvantage of the otherwise high-yield nitrile synthesis[4] is that this inevitably leads to C-methyl substituted tricarbaboranes, in contrast to reaction sequences of the isonitrile/cyanide synthesis (see eqs 4 and 6) that generate ultimately[7] *unsubstituted* tricarbollides. Neverthless, one of the drawbacks of the latter method is lower yields (35%) of the CN$^-$ insertion reaction as in eq 4 due to the competitive formation of anion **4** that seems to result from an *exo* attack by the cyanide nitrogen at the B(9) site of the anionic substrate **2**. As far as we have found to date, the only viable starting material for the isocyanide synthesis is Bu^{t}NC, giving up to 60% yields of compounds of type **3**, in contrast to the isocyanides MeNC and PhCH$_2$NC that generate complex reaction mixtures containing only small amounts of the desired tricarbaboranes of structure **3**.

In conclusion, the results described in this paper have demonstrated that a merger between the traditional cyanide/isonitrile synthesis[1,2] and the new "anionic" approach to monocarbon insertion reactions[4,5] can engender structurally flexible series of the long-anticipated tricarbollide compounds of the 11-vertex 7-L-*nido*-7,8,9-$C_3B_8H_{10}$ cluster constitution. These can be converted to the parent anion **6**,[7] and the most recent results have clearly shown that both the Me_3N derivative **3c** or anion **6** can be rearranged smoothly to the isomeric counterparts of the {*nido*-7,8,10-C_3B_8} series[8,36] via clean thermal rearrangement. Also Sneddon's group has recently reported on the synthesis of the substituted derivatives [10-R-*nido*-7,8,10-$C_3B_8H_{10}$]$^-$ (R = Me and $PhCH_2$) via cluster-expansion of the corresponding [9-R-*nido*-5,6,9-$C_3B_8H_{10}$]$^-$ anions.[9] This now rapidly expanding area of tricarbollide chemistry is of particular importance for the synthesis of the recently reported[37] 12-vertex metallatricarbollides of the {*closo*-$MC_3B_8H_{10}$} type which are expected to enormously enrich the so far scarcely represented area of metallatricarbaboranes.[4b,29,38] Besides this metallatricarbollide area, we have been currently investigating new reactions leading to new types of nonmetallic tricarbaborane species. Also ongoing are experiments leading to boron-elimination reactions in the tricarbollide series, as documented by the recent synthesis of the first unsubstituted 10-vertex tricarbaborane *arachno*-5,6,9-$C_3B_7H_{13}$.[8]

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Supporting Information Available: Tables of calculated hydrogen positional parameters, bond distances and bond angles for **3d**·Me_2CO (22 pages). Ordering information is given on any current masthead page.

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