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Azatricarbaborane 7-*t*-Bu-*arachno*-7,1,5,12-$NC_3B_8H_{12}$ and Parent Tricarbaboranes *nido*-[5,6,9-$C_3B_7H_{10}]^-$ and -5,6,9-$C_3B_7H_{11}$

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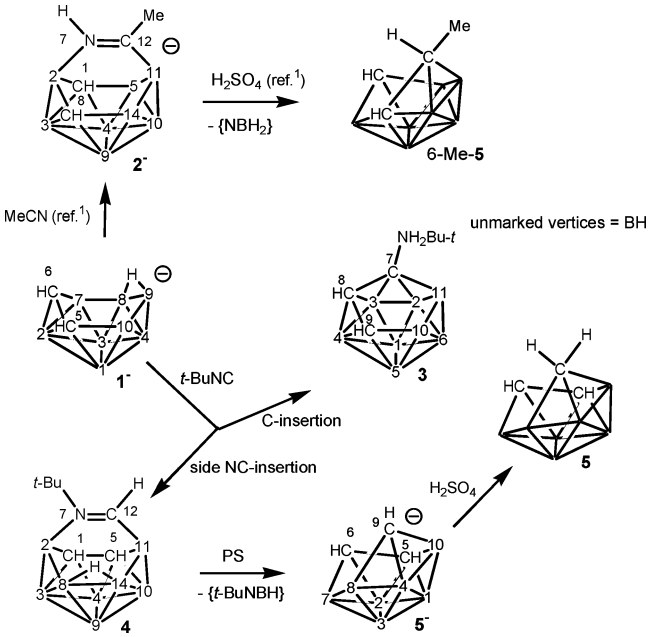
The neutral azatricarbaborane 7-*t*-Bu-*arachno*-7,1,5,12-$NC_3B_8H_{12}$, isolated as a side product (yield 2%) from the new synthesis of 7-*t*-$BuNH_2$-*nido*-7,8,9-$C_3B_8H_{10}$ (yield 70%), can be easily converted to the first parent representatives of the 10-vertex *nido* family of tricarbaboranes, [5,6,9-$C_3B_7H_{10}]^-$ and 5,6,9-$C_3B_7H_{11}$.

As shown in Scheme 1 (upper part), Sneddon's group reported[1] that prolonged reaction between MeCN and the [*nido*-5,6-$C_2B_8H_{11}]^-$ anion (**1**$^-$)[2] produced so far a single representative of the azatricarbaborane family, the 12-vertex [12-Me-*arachno*-7,1,8,12-$NC_3B_8H_{12}]^-$anion (**2**$^-$), as a result of complete CN insertion into the cluster area. Interestingly, protonation of anion **2**$^-$ with concentrated sulfuric acid (Scheme 1, upper part) did not lead to the expected neutral species Me-*arachno*-$NC_3B_8H_{12}$ but to the net loss of a {NBH_2} group and the formation of the C-methylated 10-vertex tricarbaborane 6-Me-*nido*-5,6,9-$C_3B_7H_{10}$.[1]

Herein we report on the isolation of the first neutral representative of the azatricarbaborane series, 7-*t*-Bu-*arachno*-7,1,5,12-$NC_3B_8H_{12}$, and the formation of the first two parent members of the 10-vertex *nido* family of tricababoranes, [5,6,9-$C_3B_7H_{10}]^-$ and 5,6,9-$C_3B_7H_{11}$. The last two compounds can be used as a source of further compounds of the tricarbaborane series and building blocks for the generation of metallatricarbaborane complexes.

As shown in Scheme 1 (middle part), treatment of the dicarbaborane *nido*-5,6-$C_2B_8H_{12}$ (**1**)[2] with proton sponge [PS = 1,8-(dimethylamino)naphthalene] (in situ generation of anion **1**$^-$) and *t*-BuNC in CH_2Cl_2 gave rise to the main product, 7-*t*-$BuNH_2$-*nido*-7,8,9-$C_3B_8H_{10}$ (**3**),[3] in 70% yield (C insertion of the isocyanide carbon). This reaction is, however, accompanied by the low-yield (2%) formation of a neutral species, which was characterized as the 12-vertex 7-*t*-Bu-*arachno*-7,1,5,12-$NC_3B_8H_{12}$ (**4**) by NMR spectroscopy and X-ray diffraction analysis.[4] This side reaction is consistent with complete NC insertion of the isocyanide carbon into the cage of anion **1**$^-$ associated with the rearrangement of cage carbon vertices.

Scheme 1



Treatment of azacarborane **4** with PS led, in turn, to almost quantitative formation of the parent [*nido*-5,6,9-$C_3B_7H_{10}]^-$ anion (**5**$^-$) under formal elimination of the {*t*-BuNBH} group from the cluster (see Scheme 1, bottom part). The fate of this group was not further traced because of small amounts of the material. In this respect, the conversion of **4** into **5**$^-$ shows some parallels to the formation of 6-Me-*nido*-5,6,9-$C_3B_7H_{10}$ (6-Me-**5**) via acidification of anion **2**$^-$ outlined in Scheme 1.[1]

It can be inferred from Scheme 1 that the formation of **5**$^-$ is consistent with the removal of the N7 and B2 vertices in **4**, followed by the formation of two new B8−C12 and

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C12−B14 bonds. The C9 vertex in $\mathbf{5}^-$ thus originates from the "imine" C12 carbon atom in **4**. As expected, anion $\mathbf{5}^-$ can be smoothly acidified with concentrated H_2SO_4 to produce the neutral carborane *nido*-5,6,9-$C_3B_7H_{11}$ (**5**).

An X-ray diffraction study on **4** (see Figure 1) reveals that the 12-vertex *arachno* geometry featured by Sneddon's compound $\mathbf{2}^-$,[1] except that **4** is neutral, contains one bridging B−H−B hydrogen and differs in the positioning of the CH cluster units. The N−C bond distance is at 1.2946(16) Å, consistent with a double bond [cf. 1.310(3) Å in $\mathbf{2}^-$],[1] which is also reflected by the bond angles around the "bridging" N═C unit that all approximate to 120°. The structures of compounds **4**, $\mathbf{5}^-$, and **5** were finally optimized at the RMP2-(fc)/6-31G* level (analytical frequency calculations at RHF/6-31G* confirmed these arrangements to be minima on the respective potential hypersurfaces), and the results are depicted in Figures 2−4, respectively. The calculated data were used for GIAO-MP2/II (Huzinaga type II basis set, i.e., TZP, employed) calculation of theoretical ^{11}B and ^{13}C NMR shifts, of which, namely, the ^{11}B NMR shifts agree remarkably well with the experimental data (the use of II failed for **4** because of vast requirements on computer memory and scratch disk space; II′ was the same as II but DZ on H was employed instead).[5]

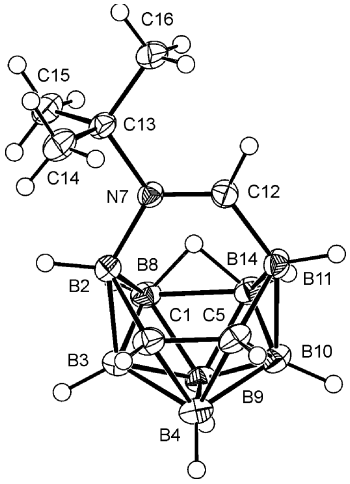

Figure 1. ORTEP drawing in the crystal structure of **4**. Ellipsoids were at the 50% probability level. Selected bond lengths (Å) and angles (deg): N7−C12 1.295(2), C12−B11 1.553(2), C1−B3 1.682(2), B8−B14 1.814-(2), C1−B2 1.675(2), C1−B4 1.692(2), C1−C5 1.503(2), N7−C12−B11 124.91(13), C12−N7−B2 120.21(12).

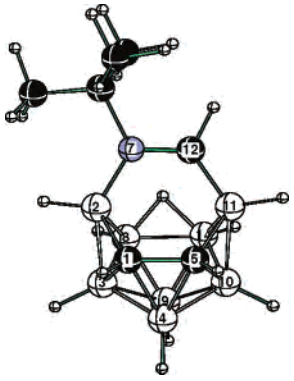

Figure 2. Structure of **4** optimized at the RMP2(fc)/6-31G* level (cluster numbering). Selected bond lengths (Å) and angles (deg): C1−C5 1.497, C1−B4 1.697, C1−B2 1.683, C1−B3 1.679, B8−B14 1.804, other B−B (mean) 1.762, B−Hb (mean) 1.302, B−Ht (mean) 1.190, C(cluster)−H (mean) 1.088, C12−N7 1.316, B2−N7 1.527, C1−B2−N7 108.8, B2−N7−C12 120.0, C5−B11−C12 105.4, N7−C12−B11 125.9.

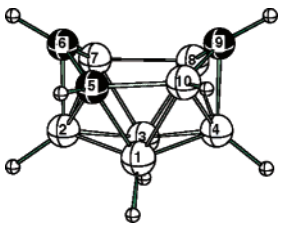

Figure 3. Structure of the [*nido*-5,6,9-$C_3B_7H_{10}$]$^-$ anion ($\mathbf{5}^-$) optimized at the RMP2(fc)/6-31G* level. Selected bond lengths (Å) and angles (deg): C5−C6 1.464, C5−B10 1.723, C6−B7 1.516, B7−B8 1.899, B8−C9 1.526, C9−B10 1.536, mean B−B 1.785, mean B−H 1.200, mean C−H 1.090, B10−C5−C6 116.9, C5−C6−B7 113.8, B7−B8−C9 110.8, B8−C9−B10 115.9, C9−B10−C5 113.3. Calculated [GIAO-MP2/II′//RMP2(fc)/6-31G*] vs experimental NMR chemical shifts: $\delta(^{11}B)_{calcd}/\delta(^{11}B)_{exp}$ (assignment) 5.4/6.9 (B8), 3.9/5.1 (B7), −4.5/−4.4 (B1), −10.4/−10.2 (B3), −13.3/−13.1 (B10), −29.6/−28.1 (B2), −29.4/−29.7 (B4); $\delta(^{13}C)_{calcd}/\delta(^{13}C)_{exp}$ (assignment) 113.6/116.7 (C6), 123.3/116.7 (C9), 58.9/55.5 (C5).

(4) (a) **3** and **4**: A solution of **1** (2 g, 16.3 mmol) in CH_2Cl_2 (200 mL) was treated with PS (10.7 g, 50 mmol) and *t*-BuNC (g, 100 mmol) under stirring and intensive cooling to 0 °C. The stirring was continued for an additional 2 h at room temperature, and the mixture was treated with 10% aqueous HCl (50 mL) under shaking at 0 °C. The organic (bottom) layer was separated, the volatile materials were evaporated, and the residual material was washed with hexane and then recrystallized from aqueous ethanol to give 2.35 g (70%) of **3**. The hexane washings were reduced in volume and mounted onto the top of a silica gel column (30 × 2.5 cm), and the column was eluted with hexane to collect the main fraction of R_f = ca. 0.1, from which **4** (67 mg, 2%) was isolated by evaporation and crystallization from hexane. **4**: mp 132 °C; ^{11}B NMR ($CDCl_3$, all doublets) δ 0.5 (ca. 160, 2B, B3,14), −1.4 (ca. 160, 2B, B8,10), −14.8 (ca. 140, 1B, B2), −15.6 (ca. 130, 1B, B4), −25.3 (125, 1B, B11), −33.9 (d, 146, 1B, B9); ^{1}H{^{11}B}-NMR ($CDCl_3$, all singlets) δ 9.20 (1H, H12), 3.02 (1H, H2), 2.77 (1H, H8 or H10), 2.69 (1H, H8 or H10), 2.67 (1H, H3 or H14), 2.54 (2H, H3 or H14 and H4), 2.43 (1H, H1 or H5), 2.12 (2H, H1 or H5 and H11), 1.44 (9H, *t*-Bu), 0.51 (1H, H9), −6.04 (1H, μ-H8,14); ^{13}C-{^{1}H}NMR ($CDCl_3$, all singlets) δ 193.0 (1C, C12), 66.5 (1C, *t*-Bu), 52.0 (1C, C1 or C5), 42.8 (1C, C1 or C5), 30.1 (3C, *t*-Bu); MS *m/z* 207 (2%, M^+), 204 (20%). Anal. Calcd (%) for $C_7H_{21}B_8N$ (205.73): C, 40.86; H, 10.29. Found: C, 40.91; H, 9.89. Crystal data for **4**: $C_7H_{21}B_8N$, fw = 205.73, triclinic, $P\bar{1}$ (No. 2), a = 9.7720(3) Å, b = 12.6770(3) Å, c = 12.7240(4) Å, α = 61.5680(15)°, β = 68.1640-(15)°, γ = 78.9350(19)°, V = 1286.46(6) Å^3, Z = 4, λ = 0.710 73 Å, μ = 0.052 mm^{-1}, D_{calcd} = 1.062 Mg m^{-3}, T = 150(2) K, R1 = 0.0448 for 4566 reflections with $I > 2\sigma(I)$, wR(F^2) = 0.1187 for all 5920 independent data, and S = 1.03. (b) ($PSH^+\mathbf{5}^-$): A solution of **4** (50 mg, 0.24 mmol) in CH_2Cl_2 (10 mL) was treated with PS (54 mg, 0.25 mmol) under stirring at room temperature for 2 h. A layer of hexanes (20 mL) was then carefully added by syringe onto the surface of the solution, and the mixture was left standing for 2 days. The deposited white crystals were removed by filtration and vacuum dried to obtain $PSH^+\mathbf{5}^-$ (79 mg, 97%). $PSH^+\mathbf{5}^-$: mp 147 °C; ^{11}B NMR (CD_3CN, all doublets, 1B) δ 6.9 (134, B8), 5.1 (134, B7), −4.4 (140, B1), −10.2 (129, B3), −13.1 (134, B10), −28.1 (ca. 175, B2), −29.7 (ca. 140, B4); ^{1}H{^{11}B}NMR (CD_3CN, all singlets) δ 4.94 (1H, H6), 4.68 (1H, H5), 3.13 (1H, H8), 2.64 (1H, H7), 2.60 (1H, H1), 2.16 (1H, H9), 1.92 (2H, H3,10), 0.90 (1H, H2), 0.27 (1H, H4); ^{13}C{^{1}H}NMR (CD_3-CN, all singlets) δ 116.7 (2C, C5,9), 55.5 (1C, C5). Anal. Calcd (%) for $C_{17}H_{33}B_7N_2$ (341.13): C, 59.85; H, 9.75. Found: C, 58.48; H, 9.65. (c) *nido*-5,6,9-$C_3B_7H_{11}$ (**5**): A solution of $PSH^+\mathbf{5}^-$ (50 mg, 0.15 mmol) in CH_2Cl_2 (10 mL) was treated with concentrated H_2SO_4 (2 mL) under shaking at 0 °C for 1 h. The CH_2Cl_2 layer was removed and subjected to trap-to-trap fractionation as in ref 1 to obtain 9 mg (48%) of **5**. **5**: mp 115 °C; ^{11}B NMR ($CDCl_3$, all doublets, 1B) δ 23.1 (154, B8), 4.5 (153, B7), −0.8 (ca. 155, B10), −1.6 (ca. 155, B1), −9.4 (140, B3), −14.6 (177, B2), −36.2 (165, B4); ^{1}H{^{11}B}-NMR ($CDCl_3$, all singlets, 1H) δ 6.35 (H6), 4.32 (H8), 4.23 (H5), 3.57 (H7), 3.20 (H1), 3.04 (H10), 2.62 (*exo*-H9), 2.45 (H3), 1.83 (H2), 1.07 (H4), −1.24 (t, J_{HH} = 13 Hz, *endo*-H9); ^{13}C{^{1}H}NMR ($CDCl_3$, all singlets, 1C) δ 139.3 (C6), 51.0 (C5), 30.0 (C9); MS *m/z* 124 (60%, M^+), 123 (100%).

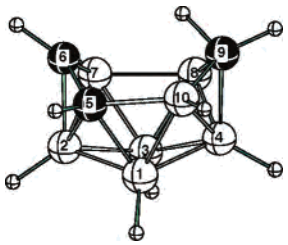

Figure 4. Structure of **5** optimized at the RMP2(fc)/6-31G* level. Selected bond lengths (Å) and angles (deg): C5−C6 1.464, C5−B10 1.717, C6−B7 1.520, B7−B8 1.907, B8−C9 1.692, C9−B10 1.566, mean B−B 1.774, mean 1.189, mean C−H 1.100, B10−C5−C6 115.6, C5−C6−B7 115.8, B7−B8−C9 109.9, B8−C9−B10 112.3, C9−B10−C5 112.6. Calculated [GIAO-MP2/II′//RMP2(fc)/6-31G*] vs experimental NMR chemical shifts: $\delta(^{11}B)_{calcd}$/ $\delta(^{11}B)_{exp}$ (assignment) 20.0/23.1 (B8), 4.3/4.5 (B7), 0.5/−1.6 (B1), 0.0/−0.8 (B10), −7.9/−9.4 (B3), −15.4/−14.6 (B2), −37.9/−36.2 (B4); $\delta(^{13}C)_{calcd}/\delta(^{13}C)_{exp}$ (assignment) 139.3/135.5 (C6), 65.4/51.0 (C5), 44.8/30.0 (C9).

In accordance with the absence of symmetry, the ^{11}B NMR spectrum[4] of **4** consists of eight doublets, while the spectra of **5**$^-$ and **5** reveal seven different boron environments. The spectra of the last two compounds are very similar to those of their 6-methyl analogues,[1,6] with the most remarkable differences being downfield shifts of the B2 resonance due to methyl substitution.

The ^{1}H{^{11}B} NMR spectrum of **4** exhibits three different singlets of the cage CH units together with eight BH singlets and one high-field singlet resonance due to the μ-H8,14 bridging hydrogen, all of intensity 1. The singlet of intensity 9 was attributed to the *t*-Bu hydrogen atoms. The ^{13}C{^{1}H}-NMR spectrum[4] of **4** shows a broad downfield CH═N singlet, two sharper cage CH singlets, and two resonances of relative intensities 1 and 3 due to the *t*-Bu substituent.

The ^{1}H{^{11}B} NMR spectrum[4] of **5**$^-$ exhibits singlets of the three different cage CH units together with seven BH singlets, and the corresponding ^{13}C{^{1}H} NMR spectrum[4] exhibits two closely related C6,9 singlets and one C5 singlet. The ^{1}H{^{11}B} NMR spectrum[4] of the neutral congener **5** exhibits two downfield CH6 and CH5 singlets together with two higher field singlets attributed to exo and endo components of the $CH_2$9 unit and seven BH singlets. The ^{13}C{^{1}H} NMR spectrum[4] of **5** shows one downfield C6 singlet and two C5 and C9 singlets.

In summary, we realized the synthesis of the first neutral azatricarbaborane **4**, which is, together with anion **2**$^-$,[1] a second representative of the azatricarbaborane series. It was also demonstrated that compound **4** can be easily converted to the 10-vertex *nido* family of tricarbaboranes **5**$^-$ and **5**. The last two compounds are the first parent (unsubstituted) members of the 10-vertex *nido* family of tricarbaboranes. Although their 6-methylated analogues have been known for a longer time,[1,6] the parent compounds featuring this cluster series have not yet been isolated. A more efficient synthetic route to these tricarbaboranes and their substituted derivatives is ongoing in our laboratories and will be reported in due course.

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Supporting Information Available: Crystal data and details of the structure determination, final coordinates and equivalent isotropic displacement parameters of the non-hydrogen atoms, hydrogen atom positions and anisotropic and isotropic displacement parameters, bond distances and angles, torsion angles, contact distances, and hydrogen bonds for compound **4**. This material is available free of charge via Internet at http://pubs.acs.org.

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(5) Geometry optimizations (without symmetry restrictions first at RHF/6-31G*, in the final step including correlation energy at MP2), analytical frequencies, and magnetic property calculations were carried out with *Gaussian 03* on a PC Fujitsu Siemens: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.03; Gaussian, Inc.: Wallingford, CT, 2003.

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