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Reactions of *nido*-6-SB_9H_{11} with Imines. Structural Characterization of *endo*-9-((*t*-Bu)MeC=NH)-*arachno*-6-SB_9H_{11}

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The reaction of *nido*-6-SB_9H_{11} with *N-tert*-butylformaldimine results in the formation of the unique zwitterionic compound 9-((*t*-Bu)$NH_2{}^+CH_2$)-*nido*-6-$SB_9H_9{}^-$ (1). The formation of 1 is consistent with a reaction sequence involving hydroboration of the imine at the B9 cage position accompanied by transfer of a proton from a cage-bridging site to the nitrogen atom. When 1 is then reacted with acetonitrile, a rearrangement occurs and the adduct *exo*-9-(CH_3CN)-*endo*-9-((*t*-Bu)$NHCH_2$)-*arachno*-6-SB_9H_{10} (2) is formed. The reaction of *nido*-6-SB_9H_{11} with *tert*-butylmethylketimine (4) gives the substituted imine product *endo*-9-((*t*-Bu)MeC=NH)-*arachno*-6-SB_9H_{11} (6). A single-crystal X-ray study of 6 confirmed that the imine adopts an endo position with regard to the *arachno*-6-SB_9H_{11} framework. Furthermore, the observed imine hydrogen to cage sulfur distance (2.712 (28) Å) is less than the sum of the van der Waals radii of hydrogen and sulfur, suggesting that the observed endo configuration may be stabilized by N–H- - -S hydrogen-bonding interactions. Thermolysis of 6 results in hydrogenation and rearrangement of the imine group to produce *exo*-9-((*t*-Bu)MeC(H)NH_2)-*arachno*-6-SB_9H_{11} (7).

Introduction

Upon thermolysis or photolysis, amine–borane adducts, such as $H_3B{\cdot}NH_3$, $B_3H_7{\cdot}NH_3$, and $B_9H_{13}{\cdot}NH_3$, have been shown to generate new boron–nitrogen compounds which may have higher boron–nitrogen bond orders (HB≡NH and $B_3N_3H_6$),[2] bridging amino groups (μ-(NH_2)B_2H_5),[3] or NH units incorporated into a borane cluster (*nido*-NB_9H_{13}).[4] The latter result in particular has prompted new investigations of the reactions of polyhedral boranes with both saturated and unsaturated nitrogen ligands as possible routes to new hybrid boron–nitrogen clusters.

The thiaborane *nido*-6-SB_9H_{11} is a strong Lewis acid and readily forms adducts of the formula 9-L-*arachno*-6-SB_9H_{11} with many σ-bases, including nitriles, ethers, dialkyl sulfides, and phosphines.[5] The compound also hydroborates both olefins and alkynes to give 9-R-*nido*-6-SB_9H_{10} compounds by a reaction sequence that has been proposed to involve initial π-coordination of the organic at the acidic 9-boron position.[6] Thus, we felt that *nido*-6-SB_9H_{11} should react with unsaturated nitrogen systems, such as imines, and that these reactions might then lead to a variety of products, including imine cage adducts and/or hydroborated or cage-insertion products. In this paper, we report our studies of the reactions of *nido*-6-SB_9H_{11} with two different imines, *N-tert*-butylformaldimine and *tert*-butylmethylketimine.

Experimental Section

All experimental manipulations were carried out using standard high-vacuum or inert-atmosphere techniques as described by Shriver.[7]

Materials. Me_4N^+-*arachno*-6-$SB_9H_{12}{}^-$ [8] and *N-tert*-butylformaldimine[9] were prepared as previously reported. Methylene chloride was dried over P_2O_5 and stored in vacuo until used. HCl/ether solutions were purchased from Aldrich and used as received. Degassed THF, toluene, xylene, pentane, and diethyl ether were stored over sodium–benzophenone ketyl until used. All other reagents were commercially obtained and used as received unless noted otherwise.

Physical Measurements. ^{11}B NMR spectra at 64.2 MHz, ^{13}C NMR spectra at 50.3 MHz, and ^1H NMR spectra at 200 MHz were obtained on a Bruker AF-200 spectrometer equipped with the appropriate decoupling accessories. All ^{11}B chemical shifts were referenced to $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm), with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to internal residual protons from the lock solvent (99.5% C_6D_6 or $CD_3C_6D_5$) and then referenced to $(CH_3)_4Si$ (0.0 ppm). Two-dimensional COSY ^{11}B–^{11}B experiments were performed at 64.2 MHz using the procedures described previously.[10] NMR data are summarized in Table I.

High- and low-resolution mass spectra were obtained on a VG-ZAB-E high-resolution mass spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1430 spectrophotometer. Elemental analyses were obtained from Robertson Microlit Laboratories Inc., Madison, NJ.

Synthesis of 9-((*t*-Bu)$NH_2{}^+CH_2$)-*nido*-6-$SB_9H_9{}^-$ (1). In a two-neck 50-mL flask, equipped with a stirbar, nitrogen inlet, and septum, a solution of *nido*-6-SB_9H_{11} in toluene was prepared from 1.08 g (5 mmol) of $Me_4N^+SB_9H_{12}{}^-$ and 0.63 g (2.5 mmol) of I_2. *N-tert*-Butylformaldimine, 0.43 g (5 mmol), was added by syringe at –78 °C. This solution was rapidly brought to room temperature. After all of the imine had dissolved, the mixture was quickly cooled to –78 °C. The mixture was stirred for 2 h at this temperature, while 1 precipitated. The solid was filtered off and washed with five portions (2 mL each) of toluene. Drying under high vacuum afforded 0.5 g (2.2 mmol, 43%) of 1, as a yellowish powder. Dec pt: 312 °C. Exact mass measured for $^{12}C_5{}^1H_{22}{}^{11}B_9{}^{14}N^{32}S$: calcd, 227.2310; found, 227.2321. IR (KBr pellet, cm^{-1}): 3190 (s), 3170 (s), 3120 (w), 2975 (w), 2560 (s), 2540 (s), 2510 (s), 2450 (s), 1580 (w), 1430 (m), 1380 (s), 1370 (s), 1355 (m), 1220 (m), 1190 (m), 1040 (m), 1030 (m), 1010 (m).

Synthesis of *exo*-9-(CH_3CN)-*endo*-9-((*t*-Bu)$NHCH_2$)-*arachno*-6-SB_9H_{10} (2). In a 50-mL two-neck flask equipped with a stirbar and a nitrogen inlet, 0.2 g (0.88 mmol) of 1 was dissolved in 10 mL of acetonitrile, and the solution was stirred for 2 h at room temperature. The solvent was vacuum-evaporated and the residue washed with five portions (2 mL

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Table I. NMR Data[a]

compound	nucleus	δ (multiplicity, *J* (Hz), assignment)
9-((*t*-Bu)$NH_2^+CH_2$)-*nido*-6-$SB_9H_9^-$ (**1**)	$^{11}B^b$	39.6 (s, B9), 18.0 (d, 144, 1B), 11.9 (d, 122, 1B), −1.1 (d, 138, 1B), −4.8 (br d, 1B), −8.3 (d, 138, 2B), −21.0 (d, 146, 1B), −32.0 (d, 153, 1B)
	$^1H^b$	7.60 (br s, 2H, NH), 3.08 (br s, 2H, CH_2), 1.59 (s, 9H, *t*-Bu), −3.4 (br m, 1H, μH)
	$^{13}C^b$	58.5 (s, C1–*t*-Bu), 38.2 (t, CH_2), 26.0 (q, C2–*t*-Bu)
nido-6-$SB_9H_{10}^-$	$^{11}B^d$	38.5 (d, 153, 1B), 16.7 (d, 157, 1B), 10.5 (d, 143, 1B), −1.1 (d, 132, 2B), −10.2 (d, 133, 2B), −20.2 (d, 152, 1B), −32.4 (d, 168, 1B)
exo-9-(CH_3CN)-*endo*-9-((*t*-Bu)$NHCH_2$)-*arachno*-6-SB_9H_{10} (**2**)	$^{11}B^b$	5.7 (s, B9), 2.5 (d, 122, B4), −4.2 (d, 154, B5,7), −13.9 (d, 165, B2), −30.7 (d, 135, B8,10), −36.2 (d, 143, B1,3)
	$^{11}B–^{11}B^b$	crosspeaks: B2–B1,3; B4–B1,3; B4–B9; B4–B8,10; B1,3–B5,7; B9–B8,10; B8,10–B1,3
	$^1H^b$	6.22 (br s, NH), 3.36 (s, 3H, CH_3), 2.31 (br s, 2H, CH_2), 1.45 (s, 9H, *t*-Bu), −2.15 (br m, 2H, μH)
	$^{13}C^b$	116.3 (br s, C1–CN), 58.3 (s, C1–*t*-Bu), 49.4 (br m, CH_2), 30.0 (s, C2–*t*-Bu), 18.4 (q, $NCCH_3$)
tert-butylmethylketimine (**4**)	$^1H^d$	9.2 (br s, 1H, NH)
N-(trimethylsilyl)-*tert*-butylmethylketimine (**5**)	$^1H^a$	1.86 (s, 3H, CH_3), 1.18 (s, 9H, *t*-Bu), 0.34 (s, 9H, $SiCH_3$)
	$^{13}C^b$	184.1 (s, N=C), 42.3 (s, C1–*t*-Bu), 27.9 (q, C2–*t*-Bu), 21.8 (q, $N{=}CCH_3$), 0.5 (q, $SiCH_3$)
endo-9-((*t*-Bu)MeC=NH)-*arachno*-6-SB_9H_{11} (**6**)	$^{11}B^c$	11.7 (d, 144, B4), 1.6 (d, 135, B9), −2.1 (d, 165, B5,7), −5.2 (d, 202, B2), −29.2 (d, 151, B8,10), −31.7 (d, 150, B1,3)
	$^{11}B–^{11}B^b$	crosspeaks: B2–B1,3; B1,3–B4; B1,3–B5,7; B1,3–B8,10; B4–B9; B4–B8,10; B9–B8,10
	$^1H^c$	8.54 (t, 50, NH), 2.48 (s, 3H, CH_3), 1.27 (s, 9H, *t*-Bu), −2.60 (br m, 2H, μH)
	$^{13}C^b$	195.6 (s, N=C), 42.7 (s, C1–*t*-Bu), 26.3 (q, C2–*t*-Bu), 18.0 (q, $N{=}C\mathit{C}H_3$)
exo-9-((*t*-Bu)MeC(H)NH_2)-*arachno*-6-SB_9H_{11} (**7**)	$^{11}B^b$	5.2 (d, 126, 1B), −8.2 (br m, 2B), −12.0 (br m, 2B), −33.3 (d/d, 135/31, B8,10), −37.9 (d, 147, B1,3)
	$^1H^b$	7.10 (br s, NH), 3.05 (q, 1H, CH), 1.39 (d, 3H, CH_3), 0.98 (s, 9H, *t*-Bu), −2.1 (br m, 2H, μH)
	$^{13}C^b$	65.2 (d, NCH), 33.6 (s, C1–*t*-Bu), 25.4 (q, C2–*t*-Bu), 13.1 (q, N–CCH_3)

[a] In C_6D_6. [b] In $CDCl_3$. [c] In CD_2Cl_2. [d] In THF.

each) of toluene. Drying under high vacuum yielded 0.2 g (0.75 mmol, 85%) of **2**, as a white powder. Dec pt: 246 °C. Exact mass measured for $^{12}C_7{}^1H_{25}{}^{11}B_9{}^{14}N_2{}^{32}S$: calcd, 268.2576; found, 268.2565. IR (KBr pellet, cm^{-1}): 3410 (s), 2980 (w), 2530 (s), 2500 (s), 2480 (s), 2160 (s), 1575 (m), 1520 (s), 1375 (m), 1205 (m), 1015 (m).

Synthesis of *N*-Lithio-*tert*-butylmethylketimine (3). A 100-mL two-neck round-bottom flask, equipped with a stirbar, nitrogen inlet, and septum, was charged with a solution of 15 mmol of MeLi in 50 mL of THF. Trimethylacetonitrile, 1.35 g (16.0 mmol), was rapidly added by syringe at room temperature, and the reaction mixture was stirred for 1 h. Solutions prepared in this manner were used for the synthesis of **4** and **5**, respectively.

Synthesis of *tert*-Butylmethylketimine (4). A solution of **3** prepared as described above was cooled at 0 °C and 13 mL of HCl/Et_2O (13 mmol) slowly added by syringe. The solution was stirred for 1 h and filtered, and the filtrate was vacuum-distilled to a second flask. The solution was then concentrated by vacuum evaporation up to 23 °C/100 Torr. Exact mass measured for $^{12}C_6{}^1H_{13}{}^{14}N$ (M + H): calcd, 100.1126; found, 100.1126. IR (in THF solution, cm^{-1}): 3220 (w), 1660 (s).

Synthesis of *N*-(Trimethylsilyl)-*tert*-Butylmethylketimine (5). A solution of **3** prepared as described above was cooled at 0 °C and 1.74 g (16 mmol) of trimethylsilyl chloride added dropwise by syringe. After 1 h, the ice bath was removed, the solution was filtered, and all volatiles were vacuum-evaporated to 23 °C/50 Torr. Distillation at 38 °C/40 Torr afforded 1.77 g (10.4 mmol, 69%) of **5**, as a colorless liquid. Exact mass measured for $^{12}C_9{}^1H_{21}{}^{14}N^{28}Si$: calcd, 171.1443; found, 171.1427. IR (neat, NaCl plates, cm^{-1}): 2960 (s), 1680 (s), 1365 (m), 1250 (s), 1130 (m), 870 (s), 835 (s).

Synthesis of *endo*-9-((*t*-Bu)MeC=NH)-*arachno*-6-SB_9H_{11} (6). In a two-neck 50-mL flask, equipped with a stirbar, nitrogen inlet, and septum, a solution of *nido*-6-SB_9H_{11} in toluene was prepared from 1.08 g (5 mmol) of $Me_4N^+SB_9H_{12}^-$ and 0.63 g (2.5 mmol) of I_2. An ether/thf solution containing excess **4** was added by syringe at −78 °C and the reaction mixture stirred for 1 h. After filtration, the volatiles were vacuum-evaporated and 0.63 g (2.6 mmol, 52.5%) of **6**, as colorless crystals, was obtained by crystallization from ether. Dec pt: 201 °C. Anal. Calcd for $C_6H_{24}B_9NS$: C, 30.08; H, 10.10; N, 5.85. Found: C, 29.87; H, 10.18; N, 5.55. Exact mass measured for $^{12}C_6{}^1H_{24}{}^{11}B_9{}^{14}N^{32}S$: calcd, 241.2467; found, 241.2444. IR (KBr pellet, cm^{-1}): 3370 (m), 2965 (w), 2930 (w), 2870 (w), 2560 (s), 2540 (s), 2530 (s), 1630 (m), 1440 (w), 1420 (w), 1370 (w), 1265 (w), 1010 (m).

Synthesis of *exo*-9-((*t*-Bu)MeC)(H)NH_2)-*arachno*-6-SB_9H_{11} (7). A 50-mL two-neck flask, equipped with a stirbar and reflux condenser, was charged with 0.31 g (1.27 mmol) of **6**. The solid was dissolved in 10 mL of xylene and the solution heated at 140 °C for 2 weeks. The solvent was vacuum-evaporated and the residue dissolved in 1 mL of ether. Precipitation of **7** by addition of 3 mL of pentane at −78 °C yielded 0.11 g (0.46 mmol, 36%) of **7**, as a colorless powder. Mp: 136 °C. Exact mass measured for $^{12}C_6{}^1H_{26}{}^{11}B_9{}^{14}N^{32}S$: calcd (M − H), 242.2545; found, 242.2566. IR (KBr pellet, cm^{-1}): 3300 (m), 3230 (m), 2960 (s), 2560 (s), 2520 (s), 1570 (m), 1470 (m), 1265 (m), 1090 (s), 1020 (s), 810 (w).

Crystallographic Data for 6. Single crystals of **6** were grown by crystallization from ether solutions. A suitably sized crystal was mounted and transferred to the diffractometer. Refined cell dimensions and their standard deviations were determined from a least-squares fit of the setting angles for 25 accurately centered reflections.

Collection and Reduction of the Data. Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer employing Cu Kα radiation from a highly oriented graphite-crystal monochromator. The intensities of three standard reflections measured at regular intervals showed no systematic change during data collection. The raw intensities were corrected for Lorentz and polarization effects but not for absorption.

Solution and Refinement of the Structure. All calculations were performed on a VAX 11/750 computer using the Enraf-Nonius structure package. The full-matrix least-squares refinement was phased on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights (w) were taken as $4F_o^2/(\sigma(F_o^2))^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The neutral-atom scattering factors and complex anomalous dispersion corrections are those stored in the SDP package. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as constant contributions to the structure factors and not refined.

Crystal and structure refinement data are summarized in Table II. Final positional parameters are given in Table III, and intramolecular bond distances are presented in Table IV.

Table II. Summary of the Structure Determination of *endo*-9-((*t*-Bu)MeC=NH)-*arachno*-6-SB_9H_{11} (**6**)

formula	$C_6H_{24}SB_9N$	μ(Cu Kα)	15.72 cm^{-1}
fw	239.63	D_{calcd}	1.050 g/cm^3
space group	$P2_1/n$	$F(000)$	512
Z	4	θ range	2.0–60.0°
a	11.624 (3) Å	no. of reflns, $F^2 > 3.0\sigma$	1327
b	10.285 (1) Å	no. of params	191
c	13.362 (2) Å	data/param ratio	6.9
β	108.34 (2)°	R,[a] R_w[b]	0.051, 0.061
V	1516.2 (9) $Å^3$		

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = (\sum(|F_o| - |F_c|)^2/\sum|F_o|^2)^{1/2}$.

Table III. Refined Positional Parameters for *endo*-9-((*t*-Bu)MeC=NH)-*arachno*-6-SB_9H_{11} (**6**)

atom	x	y	z	B_{eq}[a] ($Å^2$)
S	0.1177 (1)	0.0068 (1)	0.29725 (8)	5.59 (3)
B1	0.2740 (4)	0.2392 (4)	0.3876 (4)	5.5 (1)
B2	0.1344 (5)	0.1939 (5)	0.2999 (4)	5.5 (1)
B3	0.1369 (4)	0.2553 (4)	0.4213 (4)	4.8 (1)
B4	0.2738 (4)	0.2104 (4)	0.5172 (4)	4.7 (1)
B5	0.2733 (4)	0.0881 (5)	0.3291 (3)	5.6 (1)
B7	0.0537 (4)	0.1142 (5)	0.3848 (4)	5.0 (1)
B8	0.1437 (4)	0.1432 (4)	0.5236 (4)	5.0 (1)
B9	0.2974 (4)	0.0544 (4)	0.5707 (3)	4.6 (1)
B10	0.3666 (4)	0.1202 (4)	0.4668 (4)	5.1 (1)
C1	0.3074 (3)	–0.1942 (3)	0.5938 (2)	3.58 (8)
C2	0.3952 (4)	–0.1832 (4)	0.7017 (3)	6.2 (1)
C3	0.2679 (3)	–0.3267 (3)	0.5481 (3)	3.72 (8)
C4	0.1663 (4)	–0.3202 (4)	0.4436 (3)	5.7 (1)
C5	0.3758 (4)	–0.3937 (4)	0.5288 (3)	6.2 (1)
C6	0.2247 (4)	–0.4060 (4)	0.6252 (3)	6.6 (1)
N	0.2686 (2)	–0.0897 (3)	0.5415 (2)	3.61 (7)
H1	0.308 (3)	0.314 (3)	0.367 (2)	6.0[b]
H2	0.091 (3)	0.240 (3)	0.235 (2)	6.0[b]
H3	0.100 (3)	0.349 (3)	0.423 (2)	6.0[b]
H4	0.315 (3)	0.267 (3)	0.577 (2)	6.0[b]
H5	0.313 (3)	0.075 (3)	0.274 (2)	6.0[b]
H7	–0.035 (3)	0.109 (3)	0.366 (2)	6.0[b]
H8	0.101 (3)	0.182 (3)	0.575 (2)	6.0[b]
H9	0.346 (3)	0.063 (3)	0.651 (2)	6.0[b]
H10	0.459 (3)	0.136 (3)	0.483 (2)	6.0[b]
H510	0.340 (3)	0.026 (3)	0.417 (2)	6.0[b]
H78	0.097 (3)	0.048 (3)	0.478 (2)	6.0[b]
HN	0.228 (3)	–0.101 (3)	0.488 (2)	6.0[b]

[a] $B_{eq} = {}^4/_3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos \gamma + \beta_{13}ac \cos \beta + \beta_{23}bc \cos \alpha)$. [b] Thermal parameters were not refined.

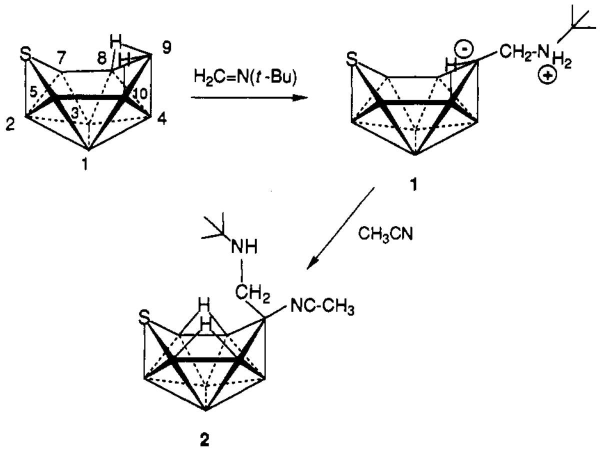
Table IV. Bond distances (Å) in *endo*-9-((*t*-Bu)MeC=NH)-*arachno*-6-SB_9H_{11} (**6**)

S–B2	1.933 (5)	B3–B7	1.727 (6)	B8–H8	1.049 (36)
S–B5	1.915 (5)	B3–B8	1.770 (7)	B8–H78	1.189 (29)
S–B7	1.920 (5)	B3–H3	1.061 (31)	B9–B10	1.932 (7)
B1–B2	1.740 (6)	B4–B8	1.689 (7)	B9–N	1.542 (5)
B1–B3	1.795 (8)	B4–B9	1.743 (6)	B9–B9	1.045 (28)
B1–B4	1.759 (7)	B4–B10	1.713 (7)	B10–H10	1.037 (31)
B1–B5	1.738 (7)	B4–H4	0.977 (29)	B10–H510	1.160 (30)
B1–B10	1.749 (6)	B5–B10	1.847 (6)	C1–C2	1.485 (4)
B1–H1	0.943 (33)	B5–H5	0.998 (35)	C1–C3	1.505 (4)
B2–B3	1.732 (7)	B5–H510	1.349 (29)	C1–N	1.284 (4)
B2–B5	1.883 (7)	B7–B8	1.845 (6)	C3–C4	1.521 (4)
B2–B7	1.872 (8)	B7–H7	0.984 (30)	C3–C5	1.523 (6)
B2–H2	0.979 (28)	B7–H78	1.373 (29)	C3–C6	1.518 (6)
B3–B4	1.761 (6)	B8–B9	1.927 (6)	N–HN	0.726 (26)

Results and Discussion

The reaction of *nido*-6-SB_9H_{11} with an imine would be expected to proceed with electrophilic attack at the nitrogen atom of the C=N bond and result in B—N bond formation. Such regiospecificity has previously been observed by both Paetzold[11] and Nöth[12] for the hydroboration of iminoboranes with tetrahydrofuran–borane. However, whether B–N or B–C products are obtained should also be affected by the other substituents present at the nitrogen and carbon positions. We, therefore, investigated the reactions of *nido*-6-SB_9H_{11} with two imines, *N*-*tert*-butylformaldimine and *tert*-butylmethylketimine, that have bulky *tert*-butyl groups substituted at the imine nitrogen and carbon atoms, respectively.

Scheme I. Synthesis of 9-((*t*-Bu)$NH_2^+CH_2$)-*nido*-6-$SB_9H_9^-$ (**1**) and *exo*-9-(CH_3CN)-*endo*-9-((*t*-Bu)$NHCH_2$)-*arachno*-6-SB_9H_{10} (**2**) from *nido*-6-SB_9H_{11}



The reaction (Scheme I) of *nido*-6-SB_9H_{11} with *N*-*tert*-butylformaldimine resulted in the formation of **1**, which was isolated as an air-sensitive, yellow powder. The unusual zwitterionic structure shown in the scheme is proposed on the basis of the spectroscopic data. Thus, the ^{11}B NMR spectrum of **1** shows eight resonances in a 1:1:1:1:1:2:1:1 ratio consistent with C_1 symmetry, and as shown in Table I, these resonances occur at chemical shifts comparable to those observed in the *nido*-6-$SB_9H_{10}^-$ anion. The signal at lowest field appears as a broad singlet, consistent with the presence of a substituent at this boron. The other resonances appeared as doublets. The ^1H NMR spectrum shows three signals with chemical shifts and integrals in agreement with NH_2, CH_2, and *t*-Bu groups. An intensity 1 resonance is observed at –3.4 ppm, which is consistent with the presence of a single cage-bridging proton. A resonance that can be attributed to the CH_2 group connecting the B9 and NH_2 units was found in the ^{13}C NMR spectrum as a broad multiplet, as expected for a methylene group bonded to boron. The IR spectrum of **1** shows the two characteristic bands for an NH_2 moiety at 3190 and 3170 cm^{-1}.

The formation of **1** may have resulted by at least two different types of reaction sequences. One sequence would be initially similar to that proposed for the hydroboration reactions of olefins by *nido*-6-SB_9H_{11}.[6] Thus, initial adduct formation at the electrophilic B9 boron site accompanied by hydroboration of the imine double bond by the B9–H group would yield an intermediate containing a saturated amine fragment, i.e. 9-((*t*-Bu)$NHCH_2$)-*nido*-6-SB_9H_{10}. Proton transfer from a cage-bridging site to the amine nitrogen could then yield the final zwitterionic product 9-((*t*-Bu)$NH_2^+CH_2$)-*nido*-6-$SB_9H_9^-$ (**1**). Given the imine C=N bond polarity and electron density distribution, an initial electrophilic attack should have been directed at the imine nitrogen atom and the final products should have been B–N rather than B–C bonded. However, the steric effects of the nitrogen *tert*-butyl group would be expected to favor carbon substitution. Similar reversed hydroborations have been observed for the reactions of aminoiminoboranes[3] with pentaborane(9), which yield B–B rather than B–N connected products.

An alternative reaction sequence leading to the formation of **1** might involve initial proton abstraction of a bridging hydrogen

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(11) (a) Küpper, S.; Englert, U.; Paetzold, P. *Heteroatom Chem.* **1990**, *1*, 479–484. (b) Bulak, E. Dissertation, RWTH, Aachen, Germany, 1990.

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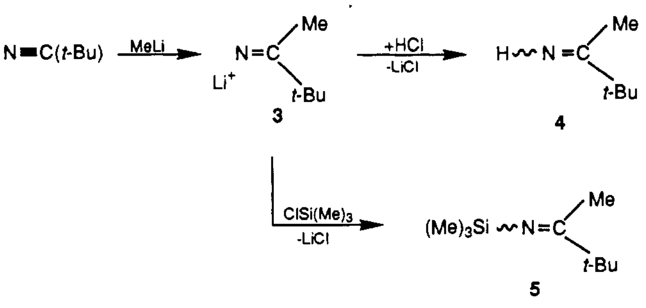
of *nido*-6-SB_9H_{11} by the imine, followed by electrophilic attack on the cage by the resulting $H_2C^+NH(t\text{-Bu})Me$ carbocation. The latter step could generate, for example a μ(8,9)-(aminomethyl)-thiaborane intermediate by attack at the vacated (B8–B9 or B10–B9) boron–boron edge, since such sites are highly nucleophilic. A subsequent bridge-to-B9-terminal position rearrangement could then produce the structure proposed for **1**. Reaction sequences related to both of those outlined above have been discussed for the reactions of pentaborane(9) with phosphaalkenes.[13]

Upon dissolution of **1** in acetonitrile, it immediately reacted (Scheme I) to form the new compound **2**, which could then be isolated as an air-stable, colorless powder. The formation of an acetonitrile adduct results in the donation of two additional electrons to the skeletal framework, and **2** should, therefore, adopt an arachno-type structure similar to those observed for the isoelectronic clusters *arachno*-6-$SB_9H_{12}^-$ and *exo*-9-(Et_3N)-*arachno*-6-SB_9H_{11}.[5] The gross cage geometries observed for 10-vertex nido and arachno cluster systems are similar but differ, for example, in the placement of the bridge hydrogens, with nido clusters such as *nido*-6-SB_9H_{11} having B8–B9 and B9–B10 hydrogen bridges, while arachno clusters favor hydrogens bridging the B5–B10 and B7–B8 edges.

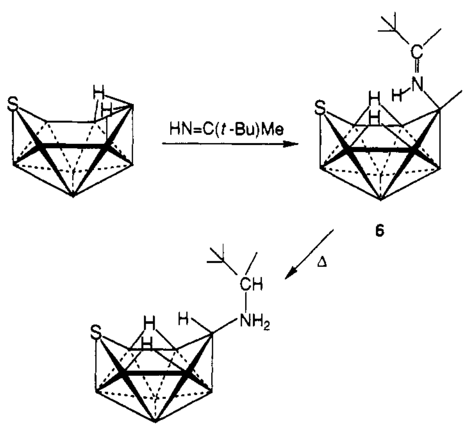
The composition and spectroscopic data for **2** are consistent with the arachno structure proposed in the scheme, in which both acetonitrile and *t*-BuN(H)CH_2– groups are substituted at the 9-boron. The ^{11}B NMR spectrum shows six signals in a 1:1:2:1:2:2 ratio, indicating that **2** has C_s symmetry. The chemical shifts of these resonances are characteristic of the *exo*-9-L-*arachno*-6-SB_9H_{11} framework,[14] and their assignments are further supported by 2D ^{11}B–^{11}B NMR COSY experiments. The signal at lowest field, 5.7 ppm, is found as a singlet, consistent with both the acetonitrile and the *t*-BuN(H)CH_2– groups substituted at the 9-boron. The ^1H NMR spectrum shows the resonances expected for the two bridging hydrogens, NH, CH_2, *t*-Bu, and $NCCH_3$ groups.

The IR spectrum obtained for **2** also supports the proposed structure since, in contrast to that observed for **1**, it has only one band in the NH region (3410 cm^{-1}). Thus, the formation of **2** from **1** involves both a nido to arachno cage transformation and a reverse proton transfer from the nitrogen to a cage-bridging site. The formation of the acetonitrile adduct apparently increases the basicity of the cage framework, enabling this proton transfer.

The ketimine **4** was prepared by addition of trimethylacetonitrile to methyllithium, followed by protonation of the resulting lithioimine **3** with HCl/OEt_2. Compound **4** was not isolated but was used in the form of its ether/thf solution. However, to confirm the structure of **3**, the *N*-(trimethylsilyl)ketimine **5** was prepared from the reaction of **3** with Me_3SiCl. Compound **5** was purified by distillation, isolated as a volatile, colorless liquid, and characterized by exact mass measurement, IR spectroscopy, and ^1H and ^{13}C NMR spectroscopy.



Scheme II. Syntheses of *endo*-9-((*t*-Bu)MeC=NH)-*arachno*-6-SB_9H_{11} (**6**) and *exo*-9-((*t*-Bu)MeC(H)NH_2)-*arachno*-6-SB_9H_{11} (**7**) from *nido*-6-SB_9H_{11}



The reaction (Scheme II) of the ketimine **4** with *nido*-6-SB_9H_{11} resulted in the formation of **6**, which was isolated as an air-stable, colorless crystalline product. As observed for **2**, the ^{11}B NMR spectrum of **6** shows six doublet resonances in a 1:1:2:1:2:2 ratio, indicating C_s symmetry. Significantly, the two resonances assigned, on the basis of a 2D ^{11}B–^{11}B NMR COSY experiment, to the B8,10 and B1,3 borons are shifted to lower field and have a smaller chemical shift difference than those found in the exo adducts[5] of *nido*-6-SB_9H_{11} (**6**: B1,3, –31.7 ppm; B8,10, –29.9 ppm. For example, *exo*-(*t*-Bu)$H_2N{\cdot}SB_9H_{11}$:[15] B1,3, –38.1 ppm; B8,10, –32.5 ppm). The ^1H NMR spectrum of **6** shows the signals expected for the two bridging hydrogens, *tert*-butyl, methyl, and NH groups. The NH resonance is found as a triplet with the magnitude of the observed coupling (J_{NH} = 50 Hz) in the range found for hydrogens bonded to sp^2-hybridized nitrogens.[16]

A single-crystal X-ray study of **6** established the structure shown in the ORTEP plot in Figure 1. The cage framework is consistent with those observed for other 10-vertex, 26-skeletal-electron systems, such as *exo*-9-(Et_3N)-*arachno*-6-SB_9H_{11}[5b] and μ(4,*exo*-9)-(1-$SiMe_3$-3-HN_3)-*arachno*-6-SB_9H_{10},[17] thus indicating that the ketimine is functioning as a two-skeletal-electron donor to the cage. The ketimine is bonded to B9 by a nitrogen–boron dative bond, and the group assumes the endo position with respect to the boron cluster. In most reported 9-L-*arachno*-6-SB_9H_{11} compounds, the base favors the exo position at the B9 boron. Only two other endo adducts have been proposed, *endo*-9-(HO)-*arachno*-6-$SB_9H_{11}^-$ [18] and *endo*-9-((*t*-Bu)N≡C)-*arachno*-6-SB_9H_{11},[19] but **6** is the first to be structurally characterized.

The B9–N1 distance in **6** (B9–N = 1.542 (5) Å) falls between the ranges normally observed for boron–nitrogen single (1.57–1.60 Å) and double bonds (1.30–1.43 Å)[20] and is shorter than the N–B9 distance observed[10b] in *exo*-9-(Et_3N)-*arachno*-6-SB_9H_{11} (1.600 (4) Å) but longer than that found in μ(4,*exo*-9)-(1-$SiMe_3$-3-H-N_3)-*arachno*-6-SB_9H_{10} (1.515 (10) Å).[17] The remaining intracage distances and angles are similar to those in both *exo*-9-(Et_3N)-*arachno*-6-SB_9H_{11} and μ(4,*exo*-9)-(1-$SiMe_3$-3-H-N_3)-*arachno*-6-SB_9H_{10}. Consistent with the structures found for other 10-vertex arachno cages, the two bridge hydrogens, H78 and

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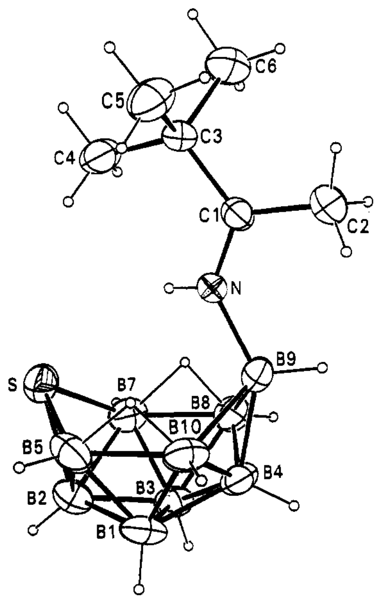

Figure 1. ORTEP drawing of the molecular structure of *endo*-9-((*t*-Bu)MeC═NH)-*arachno*-6-SB_9H_{11} (**6**).

H510, occupy positions on the B5–B10 and B7–B8 edges. Both bridging hydrogens are bonded in an asymmetrical fashion, being closer to B8 (B8–H78 = 1.189 (29) Å) and B10 (B10–H510 = 1.160 (30) Å) than to B7 (B7–H78 = 1.373 (29) Å) and B5 (B5–H510 = 1.349 (29) Å), respectively. This asymmetric configuration may result from the polarizing effect of the adjacent electronegative sulfur atom on the B5 and B7 atoms, thereby reducing their bonding interactions with H510 and H78.

The ketimine group is planar and the imine hydrogen is oriented toward the cage sulfur atom. The C1–N bond length (1.284 (4) Å) is within the normal CN double bond range,[21] and the angles about the N and C1 carbon atoms indicate formal sp^2 hybridizations: HN–N–B9 = 115.4 (24)°, HN–N–C1 = 113.6 (24)°, C1–N–B9 = 131.0 (2)°; C3–C1–C2 = 119.4 (3)°, C3–C1–N = 121.8 (2)°, C2–C1–N = 118.8 (3)°.

As mentioned above, in most 9-L-*arachno*-6-SB_9H_{11} adducts, the ligand favors the exo position at the B9 boron. That the imine group in **6** adopts the endo position may arise, as suggested for *endo*-9-(HO)-6-$SB_9H_{11}^-$,[18] because of hydrogen-bonding interactions between the imine hydrogen and the endo electron pair on the cage sulfur atom. The observed NH- - -S distance of 2.712 (28) Å is clearly compressed when compared to the sum of the van der Waals radii of sulfur and hydrogen (3.0 Å),[22] supporting a significant interaction of the imine hydrogen with the cage sulfur. The occurrence and importance of NH- - -S hydrogen-bonding, particularly in biological systems, have previously been noted, and the NH- - -S and N- - -S (3.333 (2) Å) distances and the S–H–N angle of 145.1 (30)° observed in **6** are consistent with previous examples.[23] The N- - -H510 (2.40 (4) Å) and N- - -H78 (2.37 (3) Å) distances also suggest the possibility of hydrogen-bonding interactions between these two bridge hydrogens and the imine nitrogen.

Todd proposed that *endo*-9-((*t*-Bu)N≡C)-6-SB_9H_{11} was the precursor to the carbon-inserted compound (*t*-Bu)NH_2–*nido*-CSB_9H_9.[19] This result suggested that upon thermolysis **6** might yield heteroatom cage-inserted products. Since the N–H and cage-bridging protons H78 and H510 are in close proximity (~2.1 Å), a process involving elimination of H_2 and insertion of the nitrogen atom into the cage framework to produce, for example, *μ*-((*t*-Bu)MeC═N)-*arachno*-6-SB_9H_{10} or (*t*-Bu)MeCH–*nido*-NSB_9H_9 might be expected to occur. Indeed, a similar type of nitrogen-insertion reaction has already been reported by Paetzold, who proposed that formation of the azaborane *nido*-$NB_{10}H_{13}$ in the reaction of HN_3 with $B_{10}H_{12}(SMe_2)_2$ proceeded through a *nido*-*μ*(5,6)-(NH_2)-6-(N_3)$B_{10}H_{12}$ intermediate.[4]

However, when **6** was refluxed in xylene for 2 weeks, no cage-inserted products were formed, but instead intermolecular hydrogenation of the imine and an endo to exo rearrangement was observed to produce *exo*-9-((*t*-Bu)MeC(H)NH_2)-*arachno*-6-SB_9H_{11} (**7**). **7** was isolated as a colorless powder in 38% yield, and its composition and spectroscopic data are consistent with structure shown in Scheme II. Thus, the ^{11}B NMR spectrum of **7**, like that of **6**, indicates C_s symmetry, showing five signals in a 1:2:2:2:2 ratio (one of the intensity 2 resonances arises from an overlap of two intensity 1 signals). The chemical shifts of these resonances are typical of those observed for the exo adducts of *exo*-9-L-*arachno*-6-SB_9H_{11}.[14] The ^1H and ^{13}C NMR spectra show the resonances expected for the 2,2-dimethylbutyl substituent. Also present in the ^1H NMR spectrum are the NH and bridging proton resonances. The IR spectrum has the characteristic double band for an NH_2 group at 3300 and 3230 cm^{-1}.

In summary, the results presented above clearly demonstrate that imines can react with polyhedral boranes to give, depending on the reaction conditions and the relative polarities and steric requirements of the nitrogen and carbon atoms in the C═N bond, a variety of new cluster types. We are now expanding our studies to include reactions of imines with other acidic polyhedral boranes with the aim of producing new nitrogen-inserted azaborane and azacarborane cage systems.

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Supplementary Material Available: Tables of anisotropic temperature factors, calculated hydrogen positions, bond angles, and least-squares planes (7 pages). Ordering information is given on any current masthead page.

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