Synthesis of the 1- and 2-$Me_2S{\cdot}B_{11}H_{13}$ Isomers. Crystal Structures of 2-$Me_2S{\cdot}B_{11}H_{13}$ and 7-$Me_2S{\cdot}B_{11}H_{13}$

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Treatment of $Me_3NH[B_{11}H_{14}]$ with excess H_2SO_4 and Me_2S formed 7-$Me_2S{\cdot}B_{11}H_{13}$ (**1**) in good yield. Thermal rearrangement of **1** at 110 °C in a sublimation apparatus formed a mixture of 1-$Me_2S{\cdot}B_{11}H_{13}$ (**2**) and 2-$Me_2S{\cdot}B_{11}H_{13}$ (**3**). Compound **1** was characterized by a single-crystal X-ray diffraction determination (space group $P2_1/c$, a = 7.194(1) Å, b = 12.240(3) Å, c = 13.520(3) Å, β = 102.60(1)°, Z = 4). Compound **3** was also characterized by a single-crystal X-ray diffraction determination (space group $P2_12_12_1$, a = 8.936(1) Å, b = 10.280(1) Å, c = 12.629(1) Å, Z = 2).

Introduction

Currently there is a renewed interest in the chemistry of the $B_{11}H_{14}^-$ ion due to its ready availability from the reaction of $NaBH_4$ with $BF_3{\cdot}OEt_2$ in diglyme.[1] Many icosahedral heteroborane molecules of the general type $B_{11}H_{11}E$ have been prepared employing the *nido*-$B_{11}H_{14}^-$ anion as the starting reagent. Thus, compounds containing Al,[2] Ge,[3] Sn,[3] Pb,[3] P,[4,5] As,[6] Sb,[7] Bi,[8] and Te[9] have been reported.

Protonation of $K[B_{11}H_{14}]$ with excess anhydrous HCl at −78 °C formed $B_{11}H_{15}$, which readily dissolved in toluene.[10] The proton and boron-11 NMR at low temperature of this neutral borane are consistent with a *nido* 11-vertex structure.

Some years ago it was reported that $B_{11}H_{14}^-$ reacted with acid at room temperature in dimethyl sulfide solution to form H_2 and a product with the composition $Me_2S{\cdot}B_{11}H_{13}$.[11] Even though this compound is a relatively stable substance, it has remained poorly characterized and its chemistry has not been further elucidated since this early publication.

In this report, we give further characterization data of the previously reported 7-$Me_2S{\cdot}B_{11}H_{13}$[11] and details about the thermal isomerization of this compound to a mixture of 1- and 2-$Me_2S{\cdot}B_{11}H_{13}$. Single-crystal X-ray diffraction studies of 2-$Me_2S{\cdot}B_{11}H_{13}$ and 7-$Me_2S{\cdot}B_{11}H_{13}$ are also reported.

Experimental Section

Physical Measurements. Boron (^{11}B) NMR spectra were obtained at 115.85 MHz with a Nicolet NT 360 spectrometer and were externally referenced to $BF_3{\cdot}O(C_2H_5)_2$ (positive values downfield). Proton NMR spectra were recorded on the same instrument at 361.1 MHz and were referenced to residual solvent protons. Proton chemical shift values were reported relative to tetramethylsilane. Infrared spectra were obtained on a Nicolet 510P FTIR spectrometer as KBr wafers. High-resolution mass spectra were obtained on a Kratos MS80 RFQQ spectrometer in electron-impact (30 eV), direct-probe mode. Melting points were obtained in sealed capillaries and are uncorrected.

Materials. All reactions were performed under an atmosphere of prepurified nitrogen, while workup and isolation of the products were performed in air. The $B_{11}H_{14}^-$ ion was prepared by the method of Dunks and co-workers[12] and was utilized as the trimethylammonium salt after recrystallization from ethanol. Flash chromatography was performed with 230–400-mesh silica gel (Aldrich, Merck, Grade 60, 60 Å). All other reagents were used as received.

Preparation of 7-$Me_2S{\cdot}B_{11}H_{13}$ (1). To a two-phase system consisting of Me_2S (15 mL) and concentrated H_2SO_4 (3 mL) was added $[Me_3NH][B_{11}H_{14}]$ (1.00 g, 5.18 mmol). The mixture was stirred vigorously with gas evolution (H_2) being observed. The two layers were separated, the H_2SO_4 layer was discarded, and the Me_2S layer was stripped *in vacuo*. The resulting pasty, light-yellow solid was recrystallized in CH_2Cl_2/*n*-pentane to give 0.64 g of 7-$Me_2S{\cdot}B_{11}H_{13}$ (64% yield). Compound **1** is a white, air- and moisture-sensitive solid: mp 145–147 °C; exact mass measured for $^{11}B_{10}{}^{10}B{}^1H_{18}{}^{12}C_2{}^{32}S$ $(M - 1H)^+$ 194.2178, calcd 194.2189; IR (cm^{-1}) 3021 (w), 2541 (s), 1422 (m), 1410 (m), 1402 (m), 1119 (w), 1040 (m), 1022 (m), 990 (m), 762 (w).

Thermal Rearrangement of 7-$Me_2S{\cdot}B_{11}H_{13}$ to 1- and 2-$Me_2S{\cdot}B_{11}H_{13}$ (Compounds 2 and 3, Respectively). To a sublimer equipped with a water-cooled cold finger was added 0.420 g (2.16 mmol) of **1**. With vacuum applied, the sublimer was immersed in an oil bath preheated to 110 °C. After about 3 h, **1** changed to a hard, glassy, yellow residue in the bottom of the sublimer and 0.168 g of white solid had collected on the cold finger. The white solid was dissolved in a minimum amount of benzene, loaded onto a 22 cm × 1 cm silica gel column and eluted with a 50:50 (vol/vol) benzene/hexanes mixture to give two bands. The two bands were identified as follows: band 1, 1-$Me_2S{\cdot}B_{11}H_{13}$ (**2**) [R_f = 0.67 (C_6H_6); 0.024 g (0.12 mmol), 5.6% (based on starting **1**); white, air- and moisture-sensitive solid; mp 166–168 °C; precise mass determined for $^{11}B_{11}{}^1H_{17}{}^{12}C_2{}^{32}S^+$ $(M - 2H)^+$ 194.2072, calcd 194.2075; IR (cm^{-1}) 3025 (w), 2963 (m), 2919 (w), 2851 (w), 2544 (s), 1424 (m), 1412 (m), 1262 (s), 1096 (s), 1022 (s), 843 (m), 802 (s)]; band 2, 2-$Me_2S{\cdot}B_{11}H_{13}$ (**3**) [R_f = 0.51 (C_6H_6); 0.078 g (0.40 mmol); 19% (based on starting **1**), yellow-white, air- and moisture-sensitive solid; mp 131–132 °C; precise mass determined for $(M - 2H)^+$ as $^{11}B_{11}{}^1H_{17}{}^{12}C_2{}^{32}S^+$ 194.2078, calcd 194.2075; IR (cm^{-1}) 3030 (w), 3018 (w), 3009 (w), 2963 (w), 2938 (w), 2926 (w), 2546 (s), 1426 (s), 1410 (m), 1401 (m), 1262 (w), 1113 (m), 1098 (m), 804 (w)].

X-ray Structure Determination for 7-$Me_2S{\cdot}B_{11}H_{13}$ (1). Compound **1** was crystallized from a mixture of methylene chloride and *n*-pentane. A small, well-formed crystal was cleaved from a larger sample and affixed to the end of a glass fiber using silicone grease, and the mounted sample was then transferred to the goniostat where it was cooled to −169 °C for characterization and data collection.[13] Standard inert-atmosphere handling techniques were used throughout the investigation. A systematic search of a limited hemisphere of reciprocal space located a set of reflections with monoclinic symmetry and systematic absences corre-

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Table I. Crystallographic Data for 7-$Me_2S{\cdot}B_{11}H_{13}$ (**1**)

empirical formula	$C_2H_{19}B_{11}S$
color of crystal	colorless
crystal dimens	0.25 × 0.25 × 0.45 mm
space group	$P2_1/c$
cell dimens (–169 °C; 54 reflns)	
	a = 7.194(1) Å
	b = 12.240(3) Å
	c = 13.520(3) Å
	β = 102.60(1)°
Z	4 molecules/cell
V	1161.91 Å^3
ρ_{calcd}	1.110 g cm^{-3}
wavelength	0.71069 Å
mol wt	194.14
linear abs coeff	2.113 cm^{-1}
detector-to-sample dist	22.5 cm
sample-to-source dist	23.5 cm
takeoff angle	2.0°
av ω-scan width at half-height	0.25°
scan speed	8.0°/min
scan width	(2.0 + dispersion)°
single bkgd time at extremes of scan	4 s
aperture size	3.0 × 4.0 mm
limits of data collection	
min 2θ	6°
max 2θ	45°
tot. no. of reflns collected	2259
no. of unique intensities	1518
no. with $F > 0.0$	1411
no. with $F > 2.33\sigma(F)$	1274
R for averaging	0.033
final residuals	
$R(F)$	0.0392
$R_w(F)$	0.0381
goodness of fit for the last cycle	1.210
max Δ/σ for last cycle	0.03

sponding to the unique space group $P2_1/c$. Subsequent solution and refinement of the structure confirmed this to be the proper space group. Data were collected using a standard moving crystal, moving detector technique with fixed background counts at each extreme of the scan. Data were corrected for Lorentz and polarization terms and equivalent data averaged. The structure was solved by direct methods (MULTAN78) and Fourier techniques. A difference Fourier phase on the non-hydrogen atoms clearly located all hydrogen atoms, and these were refined anisotropically in the subsequent least-squares refinement. A final difference Fourier map was essentially featureless, the largest peak being 0.14 e/Å^3.

X-ray Structure Determination for 2-$Me_2S{\cdot}B_{11}H_{13}$ (3). Crystals of **3** were obtained by crystallization from benzene and *n*-pentane. A suitable small, clear crystal was selected and transferred to the goniostat where it was cooled to –174 °C for characterization and data collection.[13] All handling was performed in a dry nitrogen atmosphere. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with orthorhombic symmetry and systematic absences corresponding to the unique orthorhombic space group $P2_12_12_1$. Subsequent solution and refinement confirmed this choice. Data were collected using a standard moving crystal, moving detector scan with fixed background at each extreme of the scan. Data were collected for $\pm h,+k,\pm l$ in the range $6 > 2\theta > 50°$. All data were corrected for Lorentz, polarization, and absorption effects, and a final data set obtained by averaging equivalent data. The structure was readily solved by direct methods (MULTAN78) and Fourier techniques. All hydrogen atoms were readily located and refined isotropically. A final difference Fourier map revealed numerous peaks of maximum intensity 0.34 e/Å^3 in the boron cage as well as near the sulfur atom. The bridging hydrogen atoms are asymmetric as expected, to accommodate for the H···H interactions.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for 7-$Me_2S{\cdot}B_{11}H_{13}$[a]

atom	x	y	z	B_{iso} (Å^2)
B(1)	1290(4)	9695(3)	2595(2)	16
B(2)	1189(4)	10484(3)	3680(2)	15
B(3)	2921(4)	10782(3)	2920(2)	14
B(4)	1830(5)	10552(3)	1630(2)	16
B(5)	–555(4)	10173(3)	1601(2)	15
B(6)	–966(4)	10068(3)	2855(2)	16
B(7)	1861(4)	11838(3)	3492(2)	13
B(8)	2211(4)	11904(3)	2108(2)	14
B(9)	–56(4)	11501(3)	1254(2)	15
B(10)	–1906(5)	11173(3)	2052(2)	15
B(11)	–761(4)	11390(3)	3408(2)	15
S(12)	3389(1)	12545(1)	4647.2(5)	14
C(13)	4991(4)	13359(3)	4104(2)	19
C(14)	4988(5)	11539(3)	5313(2)	19
H(1)	176(4)	885(2)	266(2)	18(5)
H(2)	161(3)	1017(2)	444(2)	14(5)
H(3)	446(4)	1062(2)	321(2)	18(5)
H(4)	262(4)	1024(2)	112(2)	25(6)
H(5)	–131(3)	968(2)	100(2)	7(5)
H(6)	–188(4)	947(2)	307(2)	16(5)
H(7)	319(3)	1253(2)	194(2)	16(5)
H(8)	–50(3)	1181(2)	50(2)	8(5)
H(9)	–344(4)	1124(2)	174(2)	21(6)
H(10)	–144(3)	1169(2)	397(2)	11(5)
H(11)	54(4)	1233(2)	175(2)	21(6)
H(12)	–146(4)	1194(2)	260(2)	21(6)
H(13)	97(4)	1251(3)	319(2)	29(6)
H(14)	426(4)	1387(2)	366(2)	20(6)
H(15)	562(4)	1293(2)	376(2)	17(6)
H(16)	578(4)	1369(2)	464(2)	18(6)
H(17)	582(4)	1189(2)	578(2)	14(6)
H(18)	557(4)	1112(2)	484(2)	29(7)
H(19)	427(4)	1106(2)	566(2)	26(6)

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. B_{iso} values are ×10. Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table III. Bond Distances (Å) for 7-$Me_2S{\cdot}B_{11}H_{13}$

S(12)–C(13)	1.797(3)	B(8)–B(9)	1.848(4)
S(12)–C(14)	1.788(3)	B(9)–B(10)	1.930(4)
S(12)–B(7)	1.910(3)	B(10)–B(11)	1.858(4)
B(1)–B(2)	1.770(4)	C(13)–H(14)	0.94(3)
B(1)–B(3)	1.776(4)	C(13)–H(15)	0.89(3)
B(1)–B(4)	1.783(4)	C(13)–H(16)	0.91(3)
B(1)–B(5)	1.770(4)	C(14)–H(17)	0.881(28)
B(1)–B(6)	1.793(4)	C(14)–H(18)	0.99(3)
B(2)–B(3)	1.816(4)	C(14)–H(19)	0.97(3)
B(2)–B(6)	1.776(4)	B(1)–H(1)	1.085(27)
B(2)–B(7)	1.760(4)	B(2)–H(2)	1.071(24)
B(2)–B(11)	1.763(4)	B(3)–H(3)	1.109(25)
B(3)–B(4)	1.773(4)	B(4)–H(4)	1.06(3)
B(3)–B(7)	1.762(4)	B(5)–H(5)	1.064(23)
B(3)–B(8)	1.762(4)	B(6)–H(6)	1.068(27)
B(4)–B(5)	1.769(4)	B(7)–H(13)	1.06(3)
B(4)–B(8)	1.776(4)	B(8)–H(7)	1.097(26)
B(4)–B(9)	1.774(4)	B(8)–H(11)	1.308(25)
B(5)–B(6)	1.789(4)	B(9)–H(8)	1.063(23)
B(5)–B(9)	1.750(5)	B(9)–H(11)	1.244(26)
B(5)–B(10)	1.754(4)	B(10)–H(9)	1.097(27)
B(6)–B(10)	1.774(5)	B(10)–H(12)	1.195(27)
B(6)–B(11)	1.776(5)	B(11)–H(10)	1.055(24)
B(7)–B(8)	1.943(4)	B(11)–H(12)	1.286(26)
B(7)–B(11)	1.943(4)		

Results and Discussion

We have used the two-phase system Me_2S/H_2SO_4 to produce 7-$Me_2S{\cdot}B_{11}H_{13}$ in 64% yield from $B_{11}H_{14}^-$ according to the equation

$$B_{11}H_{14}^- + H^+ + SMe_2 \rightarrow 7\text{-}Me_2S{\cdot}B_{11}H_{13} + H_2$$

A similar procedure has been used previously to form 9-$Me_2S{\cdot}$7,8-$C_2B_9H_{11}$ from 7,8-$C_2H_9H_{12}^-$, employing dimethyl sulfoxide and sulfuric acid.[14] More recently, 7-$HCB_{10}H_{12}^-$, a carborane ion isoelectronic with $B_{11}H_{14}^-$, was converted to 8-$Me_2S{\cdot}$7-$HCB_{10}H_{11}$ by the Me_2S/H_2SO_4 method.[15] The boron framework of 7-$Me_2S{\cdot}B_{11}H_{13}$ is an icosahedral structure with one vertex

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Table IV. Crystallographic Data for 2-$Me_2S\cdot B_{11}H_{13}$ (3)

empirical formula	$C_2H_{19}B_{11}S$
color of crystal	colorless
crystal dimens	0.44 × 0.37 × 0.50 mm
space group	$P2_12_12_1$
cell dimens (−174 °C; 156 reflns)	
	a = 8.936(1) Å
	b = 10.280(1) Å
	c = 12.629(1) Å
Z	2 molecules/cell
V	1160.16 Å^3
ρ_{calcd}	1.112
wavelength	0.71069 Å
mol wt	194.14
linear abs coeff	2.116
min/max abs	0.82/0.88
detector-to-sample dist	22.5 cm
sample-to-source dist	23.5 cm
takeoff angle	2.0°
av ω-scan width at half-height	0.25°
scan speed	4.0°/min
scan width	(2.0 + dispersion)°
single bkdg time at extremes of scan	0 s
aperture size	3.0 × 4.0 mm
limits of data collection	
min 2θ	6°
max 2θ	45°
tot. no. of reflns collected	5631
no. of unique intensities	4210
no. with $F > 0.0$	4092
no. with $F > 2.33\sigma(F)$	3748
R for averaging	0.019
final residuals	
$R(F)$	0.0314
$R_w(F)$	0.0321
goodness of fit for last cycle	1.247
max Δ/σ for last cycle	0.02

removed. The ^{11}B NMR spectrum of **1** contains a 2:1:1:4:1:2 pattern of resonances which is consistent with this *nido* 11-vertex structure. The area 1 signal at −27.6 ppm (see Tables VII and VIII for ^{11}B and ^1H NMR data, respectively) is a singlet and is due to the boron atom bonded to the dimethyl sulfide ligand. The proton NMR spectrum (360 MHz) of **1** with ^{11}B decoupling at room temperature contains a 2:2:2:2:2 pattern of resonances in the terminal region (3.58–1.77 ppm) and an area 3 signal at −2.91 ppm for the bridge protons. The low-field resonance at 3.58 ppm appears to be two overlapping signals of area 1 each.

A single-crystal X-ray diffraction study of **1** gave the structure illustrated in Figure 1.

The boron–boron distances about the open face of the cage of **1** range from 1.848 to 1.943 Å, with an average of 1.904 Å (see Table III), which is similar to the corresponding distances of $B_{11}H_{14}^-$ (average 1.886 Å).[10] The boron–boron distances within the cage of **1** range from 1.750 to 1.816 Å, with an average of 1.772 Å. These distances are also similar to the boron–boron distances with the $B_{11}H_{14}^-$ cage (average 1.762 Å). The exo terminal boron–hydrogen bond distances of **1** range from 1.05 to 1.10 Å, with an average of 1.07 Å. The endo terminal boron–hydrogen distance is 1.06 Å. The bridge hydrogen to boron distances range from 1.19 to 1.30 Å. These distances are all quite similar to the respective distances for $B_{11}H_{14}^-$.[10] Thus, it is found that compound **1** has a molecular structure which is quite similar to that of the isoelectronic $B_{11}H_{14}^-$ ion.

Table V. Fractional Coordinates and Isotropic Thermal Parameters for 2-$Me_2S\cdot B_{11}H_{13}$[a]

atom	x	y	z	B_{iso} (Å^2)
B(1)	8804(2)	4175(1)	9437(1)	11
B(2)	7611(1)	5145(1)	8631(1)	10
B(3)	8272(1)	5767(1)	9842(1)	10
B(4)	10150(1)	5214(2)	10025(1)	11
B(5)	10639(2)	4252(1)	8898(1)	12
B(6)	9059(2)	4234(1)	8042(1)	12
B(7)	8119(2)	6812(1)	8727(1)	10
B(8)	9759(1)	6859(1)	9683(1)	10
B(9)	11296(2)	5904(1)	8996(1)	12
B(10)	10623(2)	5183(1)	7705(1)	13
B(11)	8599(2)	5796(1)	7546(1)	11
S(12)	5552.8(3)	4720.5(3)	8452.1(2)	11
C(13)	4913(1)	4331(1)	9766(1)	14
C(14)	5557(2)	3123(1)	7863(1)	20
H(1)	838(2)	332(2)	981(2)	20(4)
H(2)	757(2)	597(2)	1048(1)	15(4)
H(3)	1060(2)	503(2)	1077(1)	19(3)
H(4)	1138(2)	343(2)	898(1)	16(4)
H(5)	884(2)	346(2)	752(2)	18(4)
H(6)	730(2)	756(2)	869(1)	15(3)
H(7)	990(2)	756(2)	1026(1)	16(4)
H(8)	1240(2)	614(2)	912(1)	18(4)
H(9)	1131(2)	489(2)	704(1)	18(4)
H(10)	803(2)	591(2)	678(2)	18(4)
H(11)	893(2)	687(2)	788(2)	22(4)
H(12)	1044(3)	719(2)	902(2)	38(5)
H(13)	1096(3)	625(2)	794(2)	38(5)
H(14)	495(2)	507(2)	1014(1)	20(4)
H(15)	395(2)	406(2)	971(1)	15(4)
H(16)	554(2)	367(2)	1006(1)	13(3)
H(17)	462(2)	282(2)	786(2)	24(4)
H(18)	598(2)	316(2)	714(2)	27(4)
H(19)	615(2)	260(2)	826(2)	21(4)

[a] Fractional coordinates are $\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms. Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table VI. Bond Distances (Å) for 2-$Me_2S\cdot B_{11}H_{13}$

S(12)–C(13)	1.8008(14)	B(8)–B(9)	1.8973(19)
S(12)–C(14)	1.8028(14)	B(9)–B(10)	1.8892(20)
S(12)–B(2)	1.9039(13)	B(10)–B(11)	1.9260(20)
B(1)–B(2)	1.7792(19)	C(13)–H(14)	0.897(21)
B(1)–B(3)	1.7795(20)	C(13)–H(15)	0.904(18)
B(1)–B(4)	1.7717(20)	C(13)–H(16)	0.954(18)
B(1)–B(5)	1.7771(21)	C(14)–H(17)	0.895(22)
B(1)–B(6)	1.7771(20)	C(14)–H(18)	0.990(21)
B(2)–B(3)	1.7593(19)	C(14)–H(19)	0.911(20)
B(2)–B(6)	1.7618(19)	B(1)–H(1)	1.069(20)
B(2)–B(7)	1.7771(19)	B(3)–H(2)	1.042(18)
B(2)–B(11)	1.7624(19)	B(4)–H(3)	1.037(17)
B(3)–B(4)	1.7873(19)	B(5)–H(4)	1.076(18)
B(3)–B(7)	1.7763(19)	B(6)–H(5)	1.051(19)
B(3)–B(8)	1.7511(19)	B(7)–H(6)	1.068(17)
B(4)–B(5)	1.7863(20)	B(7)–H(11)	1.290(19)
B(4)–B(8)	1.7797(21)	B(8)–H(7)	1.031(18)
B(4)–B(9)	1.7994(20)	B(8)–H(12)	1.089(23)
B(5)–B(6)	1.7793(20)	B(9)–H(8)	1.031(18)
B(5)–B(9)	1.8006(19)	B(9)–H(12)	1.530(23)
B(5)–B(10)	1.7853(20)	B(9)–H(13)	1.415(23)
B(6)–B(10)	1.7571(21)	B(10)–H(9)	1.084(17)
B(6)–B(11)	1.7717(20)	B(10)–H(13)	1.171(23)
B(7)–B(8)	1.8998(19)	B(11)–H(10)	1.097(19)
B(7)–B(11)	1.8716(19)	B(11)–H(11)	1.218(20)

When **1** was heated at 110 °C in a sublimer under vacuum for 3 h, 40% by weight of the material was collected on the water-cooled sublimer probe. Boron-11 NMR of the sublimate suggested that it consisted of two new substances and that 7-$Me_2S\cdot B_{11}H_{13}$ was not a component of the sublimate. The two new compounds were separated by chromatography on silica gel with a benzene/hexanes mixture as eluent. The first substance to be eluted from the column (designated compound **2**) had a rather simple ^{11}B NMR spectrum consisting of an area 1 singlet at low field and two area 5 doublets. The high-resolution mass spectrum of **2** indicated that it was an isomer of the starting 7-$Me_2S\cdot B_{11}H_{13}$. The ^{11}B and ^1H NMR spectral data (see Tables VII and VIII, respectively) suggest that **2** is 1-$Me_2S\cdot B_{11}H_{13}$, in which bridge-hydrogen exchange is occurring at room temperature to effectively give a 5-fold axis of symmetry to the molecule. The second component obtained by column chromatography proved to be the remaining positional isomer, 2-$Me_2S\cdot B_{11}H_{13}$ (compound **3**). The ^{11}B spectrum of **3** contained six resonances with the relative areas 1:2:2:1:3:2. The unit area signal at −15.6 ppm was

Table VII. Boron-11 NMR Data for the $Me_2S{\cdot}B_{11}H_{13}$ Isomers

compd	chem shift^a (ppm), rel intens, J_{B-H} (Hz)
1-$Me_2S{\cdot}B_{11}H_{13}$ (**2**)	−4.2, 1B, singlet; −14.8, 5B, 147; −18.0, 5B, 144
2-$Me_2S{\cdot}B_{11}H_{13}$ (**3**)	−5.7, 1B, 148; −10.4, 2B, 143; −13.9, 2B, 153; −15.6, 1B;^{b} −18.0, 3B, 153; −22.6, 2B, 146
7-$Me_2S{\cdot}B_{11}H_{13}$ (**1**)	1.7, 2B, 149; 0.5, 1B, 137; −7.2, 1B, 145; −12.8, 4B, 137; −25.6, 1B, singlet; −27.6, 2B, 149

^{a} C_6D_6 solvent. ^{b} $J_{^{11}B-^{1}H}$ coupling unresolved.

Table VIII. $^1H/^1H\{^{11}B\}$ NMR Data for the 1-, 2-, and 7-$Me_2S{\cdot}B_{11}H_{13}$ Isomer^a

compd	chem shift (ppm),^{b} rel intens, assignt
1-$Me_2S{\cdot}B_{11}H_{13}$ (**2**)	2.43, 5H, BH_t; 1.76, 5H, BH_t; 1.07, 6H, Me_2S; −3.31, 3H, BH_b
2-$Me_2S{\cdot}B_{11}H_{13}$ (**3**)	3.23, 1H, BH_t; 2.48, 1H, BH_t; 2.43, 2H, BH_t; 2.39, 2H, BH_t; 2.21, 2H, BH_t; 2.14, 2H, BH_t; 1.08, 6H, Me_2S; −3.36, 3H, BH_b
7-$Me_2S{\cdot}B_{11}H_{13}$ (**1**)	3.58, 2H, BH_t; 3.23, 2H, BH_t; 2.82, 2H, BH_t; 1.99, 2H, BH_t; 1.77, 2H, BH_t;1.03, 6H, Me_2S; −2.91, 3H, BH_b

^{a} BH_t = boron hydrogen terminal. BH_b = boron hydrogen bridge. ^{b} C_6D_6 solvent.

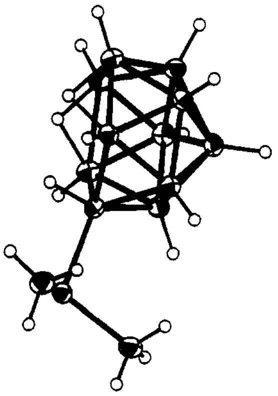


Figure 1. ORTEP diagram of 7-$Me_2S{\cdot}B_{11}H_{13}$.

a doublet but the J_{B-H} coupling constant could not be resolved due to overlapping peaks. The singlet due to the Me_2S-substituted boron atom lies as a shoulder in the area 3 peak at −18.0 ppm. The $^1H\{^1B\}$ NMR spectrum of **3** contains six resonances with relative areas of 1:1:2:2:2:2 for the B–H terminal cage positions. The three bridge hydrogen signals appear as one broad signal at −3.36 ppm. This NMR data suggest that compound **3** is an 11-vertex icosahedral fragment with C_s symmetry.

The configuration of the initial thermal rearrangement experiments in a vacuum sublimator strongly suggest that dimethyl sulfide does not dissociate from $Me_2S{\cdot}B_{11}H_{13}$ and that this is an intramolecular process. Sealed, evacuated capillary tubes containing solid 7-$Me_2S{\cdot}B_{11}H_{13}$ were heated for 10 min at 5 °C intervals in the 130–160 °C range. Analysis of the products by ^{11}B NMR and thin-layer chromatography indicated that **1** begins to rearrange to **2** and **3** at 140 °C and that conversion is complete by 155 °C. Further sealed-tube thermal studies may improve the yields of the 1- and 2-isomers and demonstrate which isomer is the most thermodynamically-stable.

There have been few studies of thermal polyhedral rearrangements of *nido* cage compounds reported to date. Previously, we had reported that when certain icosahedral metallacarbaboranes were converted to *nido* derivatives by reduction with sodium amalgam, they could be thermally isomerized at much lower temperatures.[16] Relatively low-temperature isomerization of *nido* cage compounds may prove to be a general method to obtain new positional isomers in many other cage systems.

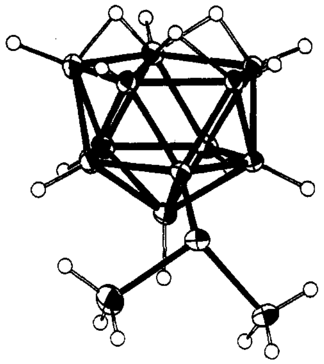
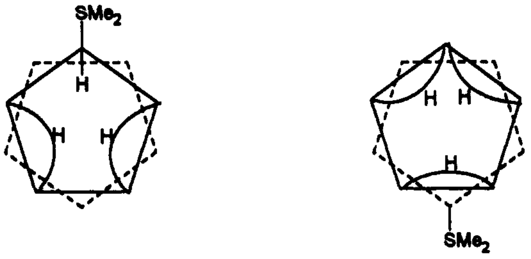


Figure 2. ORTEP diagram of 2-$Me_2S{\cdot}B_{11}H_{13}$.



7-Isomer 2-Isomer

Figure 3. Location of the bridging and endo terminal hydrogen atoms relative to the dimethyl sulfide substituent in the 11-vertex cage isomers.

The molecular structure of 2-$Me_2S{\cdot}B_{11}H_{13}$ was determined from single-crystal X-ray diffraction data. The boron framework of this molecular is based on a slightly distorted icosahedral structure with one boron atom removed (see Figure 2). The boron–boron distances about the open face of 2-$Me_2S{\cdot}B_{11}H_{13}$ range from 1.871 to 1.899 Å (see Table VI), and the boron–boron distances within the cage range from 1.757 to 1.800 Å, which are similar to the corresponding distances of 7-$Me_2S{\cdot}B_{11}H_{13}$. The bridge hydrogen-to-boron distances range from 1.171 to 1.530 Å. This large variation is due to the unsymmetrical B–H–B arrangement of the two bridge hydrogens on adjacent edges of the open face. Interesting features of the structure of the 2-isomer are the three bridge hydrogen atoms on the open face of the cage and the location of the bridging hydrogen atoms relative to the dimethyl sulfide substituent. As illustrated in Figure 3, there is a distinct difference in the location of the bridging and endo terminal hydrogens on these isomeric cage structures relative to the dimethyl sulfide substituent. The energy difference between these two alternate bridge/endo hydrogen arrangements on the open face is probably fairly small.

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Supplementary Material Available: Tables of anisotropic thermal parameters and bond angles (13 pages). Ordering information is given on any current masthead page.

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(16) Hanusa, T. P.; Todd, L. J. *Polyhedron* **1985**, *4*, 2063.