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One-Step Preparation of Dimethyl Sulfide Substituted Icosahedral Boranes: The Crystal and Molecular Structures of 1,7-$(SMe_2)_2B_{12}H_{10}$, 1,12-$(SMe_2)_2B_{12}H_{10}$, and $[SMe_3][B_{12}H_{11}(SMe_2)]\cdot MeCN$

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1,7-$(SMe_2)_2B_{12}H_{10}$, 1,12-$(SMe_2)_2B_{12}H_{10}$, and $[SMe_3][B_{12}H_{11}(SMe_2)]$ were prepared and isolated from the self-condensation reaction of $BH_3\cdot SMe_2$ in the absence of a solvent. At 150 °C the reaction yields, primarily, two isomers: 1,7-$(SMe_2)_2B_{12}H_{10}$, the major component, and 1,12-$(SMe_2)_2B_{12}H_{10}$ the minor component, that are separated by thin layer chromatography. Single-crystal X-ray structure determinations were performed for both isomers, confirming the structures inferred from ^1H, ^{11}B, and $^{11}B\{^1H\}$-$^{11}B\{^1H\}$ (COSY) NMR spectra. Crystal data for 1,7-$(SMe_2)_2B_{12}H_{10}$: trigonal $P3_221$, $a = 12.901(10)$ Å, $b = 12.901(10)$ Å, $c = 23.73(2)$ Å, $\gamma = 120°$, $Z = 9$. Crystal data for 1,12-$(SMe_2)_2B_{12}H_{10}$: orthorhombic $Pbca$, $a = 10.101(2)$ Å, $b = 11.220(2)$ Å, $c = 13.464(2)$ Å, $Z = 4$. At 60 °C, the self-condensation of $BH_3\cdot SMe_2$ is very slow, but yields $[SMe_3][B_{12}H_{11}(SMe_2)]$ as the major product. Multinuclear and 2-dimensional NMR spectra are in full accord with the structure determined by X-ray methods. Crystal data for $[SMe_3][B_{12}H_{11}(SMe_2)]\cdot MeCN$: monoclinic $P2_1$, $a = 8.904(10)$ Å, $b = 9.08(2)$ Å, $c = 12.39(3)$Å, $\beta = 93.82°$, $Z = 2$.

Introduction

Previous work by Muetterties *et al.*[1,2] showed that mixtures of diborane and dimethyl sulfide in a 1.75:1 ratio heated at 70 °C for 10 h led to the isolation (in low yields) of $B_9H_{13}(SMe_2)$ and $[B_{11}H_{14}]^-$ as the only nonvolatile polyboron species. However, when the temperature was raised to 150 °C, it was found that 12-vertex polyboranes of icosahedral architecture were obtained, chiefly $B_{12}H_{10}(SMe_2)_2$ and $[B_{12}H_{11}(SMe_2)]^-$. Additionally, $[B_{12}H_{12}]^{2-}$ was obtained in 1% yield, and the $[BH_2(SMe_2)_2]^+$ cation was reported in 2% yield. Reaction of $[H_3O]_2[B_{12}H_{12}]$ with dimethyl sulfide has been shown to result in the anions $B_{12}H_{11}(SMe)^{2-}$ and $B_{12}H_{10}(SMe)_2{}^{2-}$. $B_{12}H_{11}(SMe_2)^-$ and $B_{12}H_{10}(SMe_2)_2$ were obtained by transmethylation using trimethylsulfonium iodide.[3] $B_{12}H_{10}(SMe_2)_2$ and the $[B_{12}H_{11}(SMe_2)]^-$ anion have also been produced from $[B_{12}H_{12}]^{2-}$ using a mixture of dimethyl sulfoxide and acetic anhydride.[4] However, full spectral and structural characterization appears to have never been performed. More importantly, in the case of the neutral disubstituted compound, the isomeric nature of the product(s) does not seem to have been addressed.

Here, we present a simple, one-step procedure using $BH_3\cdot SMe_2$ which yields predominantly the neutral 12-vertex 1,7-$(SMe_2)_2B_{12}H_{10}$ isomer, along with a small quantity of the 1,12-disubstituted compound. Upon minor modification of the reaction conditions, $[SMe_3][B_{12}H_{11}(SMe_2)]$ may be isolated in moderate yield. While this reaction is very slow, minimal workup procedures are required to obtain pure $[SMe_3][B_{12}H_{11}(SMe_2)]$.

Results and Discussion

1,7-$(SMe_2)_2B_{12}H_{10}$ and 1,12-$(SMe_2)_2B_{12}H_{10}$. Dimethyl sulfide−borane,[5] $BH_3\cdot SMe_2$, was converted to an isomeric mixture of $B_{12}H_{10}(SMe_2)_2$ by heating it at 150 °C for 10 h in a steel pressure vessel. With removal of volatile components (unreacted $BH_3\cdot SMe_2$ and liberated H_2 and SMe_2) there remained an off-white glassy material, the bulk of which was extracted into 1,2-dichloroethane. The ^{11}B NMR spectrum of the extracted product was consistent with that of 1,2- or 1,7-$(SMe_2)_2B_{12}H_{10}$, but showed slight impurities. Attempts to crystallize the product at this stage by various solvent diffusion and slow evaporation experiments yielded only oily materials or amorphous solids. The product was purified by preparative TLC using SiO_2/1,2-dichloroethane. While this method enabled isolation of a pure product, it also resulted in significant diminution of yield. The major band occurred around R_f 0.73, with a minor mobile band around R_f 0.79. This is consistent with the earlier report of Wright and Kaczmarczyk, who reported two mobile bands, but infrared spectra and elemental analyses were obtained on the material prior to the TLC separation.[4]

The major band from the TLC separation in the present study yielded diffraction quality crystals of 1,7-$(SMe_2)_2B_{12}H_{10}$. They were grown by slow solvent evaporation from a 1,2-dichloroethane solution at room temperature. Crystal data are presented in Table 1. The 1,7-$(SMe_2)_2B_{12}H_{10}$ isomer crystallizes in the trigonal space group $P3_221$, with two crystallographically independent molecules. One of the molecules (molecule X, Figure 1a) sits in a general position, while the second (molecule Y, Figure 1b) resides on a 2-fold axis.

The second half of molecule Y is generated from the first through this 2-fold axis. Atomic coordinates and equivalent isotropic thermal parameters are presented in Table 2, and selected bond lengths and angles are given in Table 3. The individual molecules consist of icosahedral boron frameworks, with average B−B distance of 1.78 Å. Angles between the connectivities in an ideal icosahedron are defined as 60°. The effect of substitution on the boron framework appears to be small, although the B2−B1−B3 (B2−B1−B2′ for molecule Y) and B2−B7−B3 (B2−B1′−B2′ for molecule Y) angles are consistently wider than 60°. Conversely, the obtuse angles

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(1) Miller, H. C.; Miller, N. E.; Muetterties, E. L. *J. Am. Chem. Soc.* **1963**, *85*, 3885.

(2) Miller, H. C.; Miller, N. E.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 1456.

(3) Knoth, W. H.; Sauer, J. C.; England, D. C.; Hertler, W. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 3973.

(4) Wright, J.; Kaczmarczyk, A. *Inorg. Chem.* **1973**, *12,* 1453.

(5) Dimethyl sulfide−borane was purchased from Aldrich Chemical Co., Milwaukee, WI, and contains 5−10% excess dimethylsulfide to stabilize the complex. The reagent was used as supplied.

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Table 1. Crystallographic Data for 1,7-$(SMe_2)_2B_{12}H_{10}$ (**1**), 1,12-$(SMe_2)_2B_{12}H_{10}$ (**2**), and $[SMe_3][B_{12}H_{11}(SMe_2)]\cdot MeCN$ (**3**)

	1	**2**	**3**
chemical formula	$C_4H_{22}B_{12}S_2$	$C_4H_{22}B_{12}S_2$	$C_7H_{29}B_{12}NS_2$
mol wt	264.08	264.08	321.16
cryst system	trigonal	orthorhombic	monoclinic
space group	$P3_221$ (No. 154)	*Pbca* (No. 61)	*P*21 (No. 4)
a, Å	12.901(10)	10.101(2)	8.904(10)
b, Å	12.901(10)	11.220(2)	9.08(2)
c, Å	23.73(2)	13.464(2)	12.39(3)
unique angle, deg	$\gamma = 120$		$\beta = 93.82(1)$
V, Å^3	3421(5)	1525.9(5)	999(4)
Z	9	4	2
temp, °C	−60	−60	−60
Mo Kα radiation (λ), Å	0.710 73	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.154	1.149	1.068
μ, cm^{-1}	3.2	3.0	2.5
R_F[a]	0.0366	0.050	0.0609
R_{wF}	0.0709[b]	0.035[c]	0.1137[b]

[a] $R_F = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] Refined on F^2: $R_{wF} = wR_2 = [\sum w(|F_o^2 - F_c^2|)^2/\sum w(F_o^2)^2]^{1/2}$. [c] Refined on *F*: $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

between the substituted boron sites, B1−B2−B7 (B1−B2−B1′ for molecule Y) and B1−B3−B7 (B1−B2′−B1′ for molecule Y), are observed to be narrower than the 108° expected for a regular icosahedron. In molecule X, which occupies a general position, the methyl groups of the pendant dimethyl sulfide ligands are in an eclipsed conformation whereas in molecule Y, which sits on a crystallographic 2-fold axis, they are staggered.

The ^{11}B NMR spectrum of 1,7-$(SMe_2)_2B_{12}H_{10}$ consists of a singlet at −8.9 ppm that is assigned to the two B−S bonded boron atoms and three doublet peaks at −13.5, −15.1, −16.4 ppm that account for the remaining 10 boron atoms. Figure 2 shows the $^{11}B\{^1H\}-^{11}B\{^1H\}$ (COSY) spectrum, which allows assignment of all boron positions, on the basis of the structure of the 1,7-$(SMe_2)_2B_{12}H_{10}$.

The ^1H NMR spectrum of 1,7-$(SMe_2)_2B_{12}H_{10}$ is consistent with that published previously for what was reported to be an isomeric mixture;[4] it is also very similar to the ^1H NMR spectrum of the mixture of the 1,7 and 1,12 isomers obtained in the present study before they were separated. In the present case this is due to the fact that the 1,12 isomer is a very minor component of the mixture and also that its ^1H and ^{11}B resonances are overlapped by those of the 1,7 isomer. A major singlet resonance, assignable to CH_3 protons, occurs at 2.49 ppm in the ^1H NMR spectrum of 1,7-$(SMe_2)_2B_{12}H_{10}$. A broad quartet centered around 1.6 ppm, assignable to several overlapping boron-bonded hydrogen signals, is resolved into four singlets between δ 1.7 and 1.4 ppm, of relative intensity 1:1:2:1, upon broadband ^{11}B decoupling of the ^1H spectrum. This is consistent with the structure of 1,7-$(SMe_2)_2B_{12}H_{10}$. Selective decoupling of the sulfur-bonded boron atoms has, as expected, minimal effect on the appearance of the proton spectrum. The $^{13}C\{^1H\}$ spectrum of 1,7-$(SMe_2)_2B_{12}H_{10}$, showed only the expected singlet from the carbon atoms of the methyl groups on sulfur, all four of which are equivalent, at δ = 25.98 ppm.

Diffraction quality crystals of 1,12-$(SMe_2)_2B_{12}H_{10}$ were grown from the minor band of the TLC separation by slow solvent evaporation from a 1,2-dichloroethane solution. The molecular structure is shown in Figure 3. Crystal data are given in Table 1. Table 4 lists positional and equivalent isotropic thermal parameters. Selected bond distances and angles are presented in Table 5. The 1,12-$(SMe_2)_2B_{12}H_{10}$ isomer possesses a crystallographically imposed center of symmetry about the centroid of the $\{B_{12}\}$ cage in the solid state, resulting in the observed perfectly staggered conformation of the dimethyl sulfide ligands.

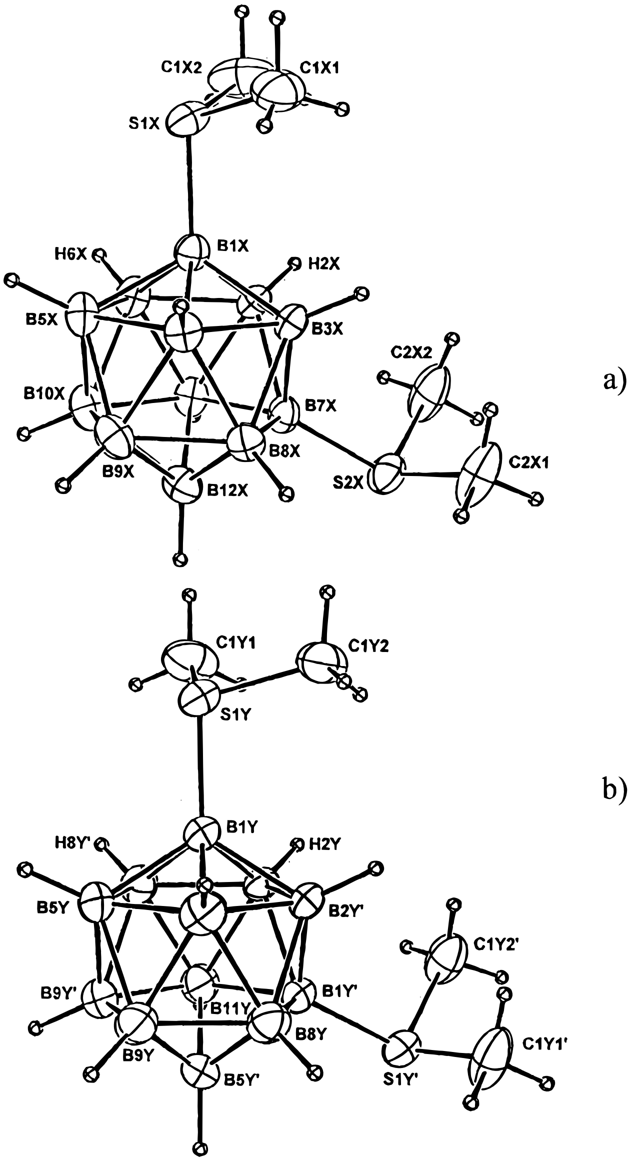

Figure 1. (a) ORTEP plot of molecule X of 1,7-$(SMe_2)_2B_{12}H_{10}$, showing eclipsed conformation of the two SMe_2 units. (b) ORTEP plot of molecule Y of 1,7-$(SMe_2)_2B_{12}H_{10}$, showing the staggered conformation of the SMe_2 substituents. Atoms labeled (with a prime) were generated *via* a crystallographic 2-fold axis connecting the midpoints of the B2Y−B2Y′ and B9Y−B9Y′ connectivities.

The ^{11}B NMR spectrum of 1,12-$(SMe_2)_2B_{12}H_{10}$. consists of a singlet at −8.1 ppm that is assigned to borons bonded to sulfur and a doublet at −13.9 ppm that is assigned to borons bonded to hydrogen. The ^1H spectrum consists of the singlet signal from CH_3 hydrogens at 2.50 ppm and a quartet at 1.2 ppm produced by the B−H protons, all of which are equivalent. The spectra are consistent with the solid state structure.

Isomerization of 1,7-$(SMe_2)_2B_{12}H_{10}$ into 1,12-$(SMe_2)_2B_{12}H_{10}$ could not be achieved by thermal means. A sample was heated to 250 °C for 12 h, resulting in significant H_2 loss and the formation of a beige microcrystalline solid that was insoluble in common organic solvents and water. This is consistent with the work of Muetterties,[2] who reported decomposition of (presumably an isomeric mixture of) $B_{12}H_{10}(SMe_2)_2$ when attempting to determine its melting point.

$[SMe_3][B_{12}H_{11}(SMe_2)]$. The salt $[SMe_3][B_{12}H_{11}(SMe_2)]$ was prepared by heating $BH_3\cdot SMe_2$ at 60 °C with stirring for a period

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 1,7-$(SMe_2)_2B_{12}H_{10}$

	x	*y*	*z*	*B*,[a] Å^2
S1X	0.9867(1)	0.4002(1)	1.1857(1)	2.6(1)
S2X	0.5370(1)	0.0415(1)	1.3127(1)	2.7(1)
S1Y	1.0830(1)	1.2688(1)	0.9069(1)	2.8(1)
C1X1	1.0746(2)	0.4198(3)	1.2470(1)	4.0(1)
C1X2	0.9821(3)	0.2721(3)	1.1546(2)	5.1(1)
C2X1	0.6150(3)	0.0668(3)	1.3779(1)	4.3(1)
C2X2	0.5709(3)	−0.0619(2)	1.2804(1)	4.2(1)
C1Y1	1.1792(3)	1.2668(3)	0.8537(1)	4.3(1)
C1Y2	1.1853(3)	1.4040(3)	0.9422(1)	3.7(1)
B1X	0.8306(3)	0.3473(2)	1.2135(1)	2.1(1)
B2X	0.7193(2)	0.1954(2)	1.2147(1)	2.0(1)
B3X	0.7807(2)	0.2774(2)	1.2789(1)	1.8(1)
B4X	0.8109(3)	0.4271(3)	1.2684(1)	2.0(1)
B5X	0.7685(3)	0.4386(3)	1.1982(1)	2.2(1)
B6X	0.7121(3)	0.2955(3)	1.1648(1)	2.2(1)
B7X	0.6262(3)	0.1850(2)	1.2710(1)	2.0(1)
B8X	0.6800(3)	0.3235(2)	1.3052(1)	2.1(1)
B9X	0.6721(3)	0.4222(3)	1.2552(1)	2.4(1)
B10X	0.6114(3)	0.3402(3)	1.1917(1)	2.4(1)
B11X	0.5803(3)	0.1908(3)	1.2017(1)	2.1(1)
B12X	0.5557(3)	0.2698(3)	1.2573(1)	2.4(1)
B1Y	1.0593(3)	1.1436(3)	0.9570(1)	2.3(1)
B2Y	1.1758(3)	1.1167(3)	0.9740(1)	2.1(1)
B5Y	0.9202(3)	1.0078(3)	0.9558(1)	3.0(1)
B8Y	1.0138(3)	1.0541(3)	1.0690(1)	2.7(1)
B9Y	0.8935(3)	0.9512(3)	1.0256(1)	3.3(1)
B11Y	0.9602(3)	1.1088(3)	1.0142(1)	2.8(1)

[a] Values are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 1,7-$(SMe_2)_2B_{12}H_{10}$[a]

S1X−C1X1	1.783(3)	S1X−C1X2	1.784(3)
S1X−B1X	1.892(3)	S2X−C2X2	1.774(3)
S2X−C2X1	1.784(3)	S2X−B7X	1.897(3)
S1Y−C1Y1	1.779(3)	S1Y−C1Y2	1.784(3)
S1Y−B1Y	1.902(3)	B1X−B3X	1.749(4)
B1X−B4X	1.756(4)	B1X−B2X	1.758(4)
B1X−B6X	1.761(4)	B1X−B5X	1.762(4)
B2X−B7X	1.756(4)	B2X−B6X	1.790(4)
B2X−B11X	1.792(4)	B2X−B3X	1.797(4)
B3X−B7X	1.748(4)	B3X−B4X	1.786(4)
B3X−B8X	1.789(4)	B4X−B8X	1.773(4)
B4X−B5X	1.783(4)	B4X−B9X	1.788(4)
B5X−B9X	1.777(4)	B5X−B10X	1.780(4)
B5X−B6X	1.796(4)	B6X−B10X	1.782(4)
B6X−B11X	1.785(4)	B7X−B8X	1.758(4)
B7X−B11X	1.763(4)	B7X−B12X	1.768(4)
B8X−B9X	1.781(4)	B8X−B12X	1.797(4)
B9X−B12X	1.781(4)	B9X−B10X	1.782(4)
B10X−B12X	1.765(5)	B10X−B11X	1.778(4)
B11X−B12X	1.790(4)	B1Y−B2Y	1.751(4)
B1Y−B8Y′	1.754(4)	B1Y−B2Y′	1.758(4)
B1Y−B11Y	1.762(4)	B1Y−B5Y	1.774(4)
B2Y−B1Y′	1.758(4)	B2Y−B11Y′	1.777(4)
B2Y−B8Y′	1.785(4)	B2Y−B2Y′	1.807(6)
B5Y−B9Y′	1.766(5)	B5Y−B9Y	1.774(5)
B5Y−B8Y′	1.790(5)	B5Y−B11Y	1.793(5)
B8Y−B1Y′	1.754(4)	B8Y−B11Y	1.777(4)
B8Y−B9Y	1.781(5)	B8Y−B2Y′	1.785(4)
B8Y−B5Y′	1.790(5)	B9Y−B5Y′	1.766(5)
B9Y−B9Y′	1.773(7)	B9Y−B11Y	1.788(5)
B11Y−B2Y′	1.777(4)		

C1X1−S1X−C1X2	101.1(2)	C1X1−S1X−B1X	104.68(14)
C1X2−S1X−B1X	105.89(14)	C2X2−S2X−C2X1	100.5(2)
C2X2−S2X−B7X	104.54(14)	C2X1−S2X−B7X	105.2(2)
C1Y1−S1Y−C1Y2	99.6(2)	C1Y1−S1Y−B1Y	104.4(2)
C1Y2−S1Y−B1Y	105.28(14)	B3X−B1X−B4X	61.3(2)
B3X−B1X−B2X	61.7(2)	B4X−B1X−B2X	111.4(2)
B3X−B1X−B6X	111.2(2)	B4X−B1X−B6X	110.9(2)
B2X−B1X−B6X	61.2(2)	B3X−B1X−B5X	110.8(2)
B4X−B1X−B5X	60.9(2)	B2X−B1X−B5X	111.0(2)
B6X−B1X−B5X	61.3(2)	B3X−B1X−S1X	123.1(2)
B4X−B1X−S1X	119.2(2)	B2X−B1X−S1X	122.4(2)
B6X−B1X−S1X	118.3(2)	B5X−B1X−S1X	116.4(2)
B7X−B2X−B1X	104.1(2)	B7X−B3X−B1X	104.9(2)
B2X−B7X−B8X	111.4(2)	B3X−B7X−B11X	111.4(2)
B2X−B7X−B11X	61.2(2)	B8X−B7X−B11X	110.9(2)
B3X−B7X−B12X	111.2(2)	B2X−B7X−B12X	110.9(2)
B8X−B7X−B12X	61.3(2)	B11X−B7X−B12X	60.9(2)
B3X−B7X−S2X	122.6(2)	B2X−B7X−S2X	122.0(2)
B8X−B7X−S2X	119.3(2)	B11X−B7X−S2X	118.4(2)
B12X−B7X−S2X	116.8(2)	B2Y−B1Y−B8Y′	61.2(2)
B2Y−B1Y−B2Y′	62.0(2)	B8Y′−B1Y−B2Y′	111.3(2)
B2Y−B1Y−B11Y	111.0(2)	B8Y′−B1Y−B11Y	110.6(2)
B2Y′−B1Y−B11Y	60.6(2)	B2Y−B1Y−B5Y	110.7(2)
B8Y′−B1Y−B5Y	61.0(2)	B2Y′−B1Y−B5Y	110.3(2)
B11Y−B1Y−B5Y	61.0(2)	B2Y−B1Y−S1Y	121.5(2)
B8Y′−B1Y−S1Y	120.2(2)	B2Y′−B1Y−S1Y	120.7(2)
B11Y−B1Y−S1Y	119.1(2)	B5Y−B1Y−S1Y	118.8(2)
B1Y−B2Y−B1Y′	104.6(2)		

[a] Symmetry transformations used to generate equivalent atoms (′): *y*, *x*, −*z* + 2.

of approximately 4 months, with liberated H_2 gas being removed periodically. After removal of the volatile components, the reaction mixture was extracted with Et_2O. The small quantity of product obtained from this extract was chiefly $B_9H_{13}(SMe_2)$, identified from its ^{11}B NMR spectrum.[6] The remainder of the product was extracted with THF. A small quantity of material was obtained from this extraction. From its ^{11}B NMR spectrum it appears to be a mixture of several species, one of which may be the $[B_{12}H_{11}(SMe_2)]^-$ anion.

The product which was washed with THF was then extracted with acetone. After removal of the acetone, the product was dissolved in acetonitrile and crystalline material was obtained by slow evaporation at room temperature of solvent from the solution. Crystals were mounted in capillaries in a glovebag saturated with CH_3CN vapor, a drop of CH_3CN added to each of the capillaries. The crystals were found to be stable under these conditions.

A single-crystal X-ray analysis revealed the product to crystallize as $[SMe_3][B_{12}H_{11}(SMe_2)]\cdot MeCN$. No displacement of the dimethyl sulfide ligand by acetonitrile was observed at room temperature, even after significant periods of time. $B_{10}H_{12}(SMe_2)_2$ is quantitatively converted to $B_{10}H_{12}(MeCN)_2$ after only a few minutes in refluxing acetonitrile.[7]

Crystal data for $[SMe_3][B_{12}H_{11}(SMe_2)]\cdot MeCN$ are given in Table 1. Positional and equivalent isotropic thermal parameters of $[B_{12}H_{11}(SMe_2)]^-$ are presented in Table 6. Selected bond lengths and bond angles are given in Table 7. Figure 4 shows an ORTEP plot of the $[B_{12}H_{11}(SMe_2)]^-$ anion.

Atoms C2A, C2B, B3, B4, B8, and B11 could only be refined isotropically. The thinness of the platelike crystal (smallest dimension 0.15 mm) and its tendency to lose solvent, which necessitated mounting the crystal in a capillary along with a drop of acetonitrile, may have led to these difficulties in refinement.

The SMe_2 substituent appears to be slightly tilted away from the B4−B5 connectivity, as the B4−B1−S2 and B5−B1−S2 angles are 122.6(8) and 124.5(2)°, respectively, whereas the other three angles at B1 (B2−B1−S2, B3−B1−S2, and B6−B1−S2) average 117.1(6)°.

In addition to the single-crystal X-ray analysis, $[SMe_3]$-$[B_{12}H_{11}(SMe_2)]$ was identified by IR and multinuclear NMR

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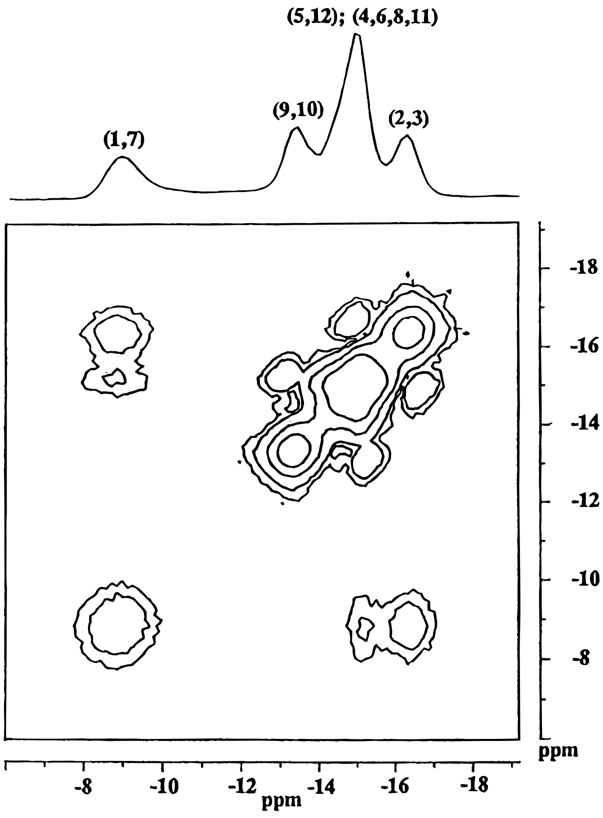

Figure 2. $^{11}B\{^1H\}-^{11}B\{^1H\}$ (COSY) spectrum of 1,7-$(SMe_2)_2B_{12}H_{10}$ showing all peak assignments.

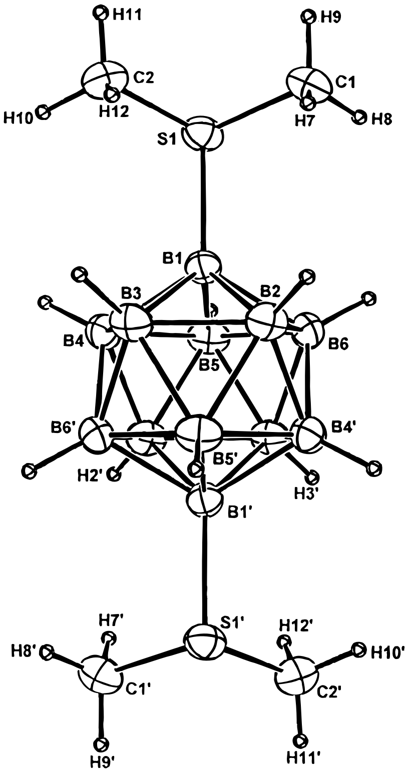

Figure 3. ORTEP plot of 1,12-$(SMe_2)_2B_{12}H_{10}$.

spectra and elemental analyses. When the workup procedure is carried out after an arbitrary 4 month period, it was found that the major product contains approximately 15% of the boron initially present in the dimethyl sulfide−borane starting material. Presumably, even longer reaction times would lead to greater yields of the product.

Table 4. Positional and Equivalent Isotropic Thermal Parameters for 1,12-$(SMe_2)_2B_{12}H_{10}$

	x	*y*	*z*	*B*, [a] Å^2
S1	0.97423(6)	0.22304(6)	0.68338(5)	2.28(1)
C1	0.8058(3)	0.2188(2)	0.7249(2)	3.04(6)
C2	0.9798(3)	0.3636(2)	0.6201(2)	3.21(6)
B1	0.9832(3)	0.1055(2)	0.5813(2)	1.90(5)
B2	0.8449(3)	0.0558(3)	0.5144(2)	2.19(6)
B3	0.9728(3)	0.1395(2)	0.4540(2)	2.15(6)
B4	1.1277(3)	0.0965(3)	0.5099(2)	2.09(6)
B5	1.0948(3)	−0.0117(3)	0.6024(2)	2.20(6)
B6	0.9202(3)	−0.0374(3)	0.6053(2)	2.16(6)
H2	0.750(2)	0.094(2)	0.526(1)	1.6(4)*
H3	0.963(2)	0.234(2)	0.433(1)	2.2(5)*
H4	1.208(2)	0.154(2)	0.518(1)	1.3(4)*
H5	1.152(2)	−0.017(2)	0.665(1)	3.2(5)*
H6	0.873(2)	−0.059(2)	0.672(1)	2.0(5)*
H7	0.752(2)	0.228(2)	0.664(2)	4.5(6)*
H8	0.800(2)	0.141(2)	0.755(2)	5.0(6)*
H9	0.797(3)	0.281(2)	0.774(2)	5.4(7)*
H10	1.066(2)	0.368(2)	0.584(2)	4.7(6)*
H11	0.969(2)	0.428(2)	0.662(2)	5.0(6)*
H12	0.909(2)	0.366(2)	0.567(2)	4.5(6)*

[a] Starred values are for atoms that were refined isotropically. Values of anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) [$a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)$].

Table 5. Selected Bond Distances (Å) and Angles (deg) for 1,12-$(SMe_2)_2B_{12}H_{10}$

S1−C1	1.791(3)	B2−B6	1.781(4)
S1−C2	1.793(3)	B2−H2	1.07(2)
S1−B1	1.907(3)	B3−B4	1.802(5)
C1−H7	0.99(3)	B3−H3	1.10(2)
C1−H8	0.97(3)	B4−B5	1.770(5)
C1−H9	0.97(3)	B4−H4	1.04(2)
C2−H10	1.00(3)	B5−B6	1.787(4)
C2−H11	0.92(3)	B5−H5	1.03(2)
C2−H12	1.01(3)	B6−H6	1.04(2)
B1−B2	1.752(4)	H7−H8	1.64(4)
B1−B3	1.758(4)	H7−H9	1.66(4)
B1−B4	1.751(4)	H8−H9	1.60(4)
B1−B5	1.755(4)	H10−H11	1.59(4)
B1−B6	1.755(4)	H10−H12	1.61(4)
B2−B3	1.792(5)	H11−H12	1.57(4)
C1−S1−C2	101.6(2)	B2−B1−B5	110.9(2)
C1−S1−B1	104.6(2)	B2−B1−B6	61.0(2)
C2−S1−B1	105.3(1)	B3−B1−B4	61.8(2)
S1−C1−H7	105(2)	B3−B1−B5	111.0(2)
S1−C1−H8	102(2)	B3−B1−B6	110.9(2)
S1−C1−H9	106(2)	B4−B1−B5	60.7(2)
H7−C1−H8	114(3)	B4−B1−B6	110.6(2)
H7−C1−H9	117(2)	B5−B1−B6	61.2(2)
H8−C1−H9	111(2)	S1−C2−H10	107(2)
S1−C2−H11	113(2)	S1−C2−H12	110(2)
H10−C2−H11	111(2)	H10−C2−H12	106(2)
H11−C2−H12	109(2)	S1−B1−B2	123.5(2)
S1−B1−B3	123.3(2)	S1−B1−B4	118.3(2)
S1−B1−B5	115.6(2)	S1−B1−B6	118.8(2)
B2−B1−B3	61.4(2)	B2−B1−B4	111.4(2)

Both the ^1H and $^{13}C\{^1H\}$ NMR spectra of $[SMe_3][B_{12}H_{11}(SMe_2)]$ display two resonances in the ratio 3:2, in accord with the number of methyl groups in the $[SMe_3]^+$ cation and SMe_2 substituent respectively. The $^{11}B\{^1H\}$ spectrum of $[SMe_3][B_{12}H_{11}(SMe_2)]$ displays three signals in the ratio 1:6:5. The resonance of relative area 1 at −6.3 ppm is assigned to the sulfur-substituted atom, B1. This resonance retains its singlet character in the undecoupled ^{11}B spectrum. The 2-dimensional $^{11}B\{^1H\}$-$^{11}B\{^1H\}$ spectrum, shown in Figure 5, indicates that the next highest frequency peak (relative area 6), −10.9 ppm, corresponds to the B7−B11 belt of borons, in coincidence with the B12 signal. Resonating at lowest frequency are the B2−

Table 6. Positional and Equivalent Isotropic Thermal Parameters for $[B_{12}H_{11}SMe_2]^-$

	x	y	z	B,[a] Å^2
S2	−0.1552(1)	−0.1256(5)	0.1847(1)	2.4(1)
C2A	−0.2099(6)	−0.2974(7)	0.1235(5)	3.8(2)*
C2B	−0.2094(8)	−0.0033(7)	0.0761(5)	5.1(2)*
B1	0.0580(4)	−0.1279(17)	0.1968(3)	1.9(1)
B2	0.1431(11)	−0.0304(11)	0.3078(7)	1.6(2)
B3	0.1421(13)	−0.2264(13)	0.3076(8)	2.3(2)*
B4	0.1629(12)	−0.2860(12)	0.1714(8)	2.4(3)*
B5	0.1721(4)	−0.1294(17)	0.0865(3)	2.0(1)
B6	0.1591(11)	0.0345(11)	0.1712(7)	1.7(2)
B7	0.3082(4)	−0.1280(16)	0.3505(3)	2.1(1)
B8	0.3198(10)	−0.2891(9)	0.2663(6)	1.4(2)*
B9	0.3308(13)	−0.2210(13)	0.1306(9)	2.9(2)
B10	0.3433(10)	−0.0265(11)	0.1309(7)	1.4(2)
B11	0.3185(13)	0.0273(12)	0.2674(8)	2.9(2)*
B12	0.4273(4)	−0.1212(17)	0.2411(3)	2.3(1)

[a] Starred values are for atoms that were refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:$(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table 7. Selected Bond Distances (Å) and Angles (deg) for $[B_{12}H_{11}SMe_2]^-$

S2−C2B	1.785(7)	S2−C2A	1.787(7)
S2−B1	1.894(4)	B1−B4	1.75(2)
B1−B5	1.756(6)	B1−B3	1.762(14)
B1−B2	1.764(13)	B1−B6	1.77(2)
B2−B11	1.75(2)	B2−B7	1.767(12)
B2−B3	1.779(7)	B2−B6	1.806(13)
B3−B7	1.778(14)	B3−B8	1.787(14)
B3−B4	1.793(14)	B4−B9	1.71(2)
B4−B8	1.765(13)	B4−B5	1.77(2)
B5−B9	1.699(14)	B5−B6	1.83(2)
B5−B10	1.841(12)	B6−B11	1.79(2)
B6−B10	1.832(13)	B7−B11	1.75(2)
B7−B12	1.776(6)	B7−B8	1.803(14)
B8−B9	1.800(14)	B8−B12	1.84(2)
B9−B10	1.769(7)	B9−B12	1.810(14)
B10−B12	1.740(13)	B10−B11	1.787(13)
B11−B12	1.70(2)		
C2B−S2−C2A	99.8(4)	C2B−S2−B1	106.6(4)
C2A−S2−B1	105.5(5)	B4−B1−B5	60.7(6)
B4−B1−B3	61.4(6)	B5−B1−B3	111.4(6)
B4−B1−B2	110.2(6)	B5−B1−B2	111.7(6)
B3−B1−B2	60.6(3)	B4−B1−B6	111.5(3)
B5−B1−B6	62.5(6)	B3−B1−B6	111.6(6)
B2−B1−B6	61.5(6)	B4−B1−S2	122.6(8)
B5−B1−S2	124.5(3)	B3−B1−S2	116.0(6)
B2−B1−S2	115.6(5)	B6−B1−S2	119.8(8)

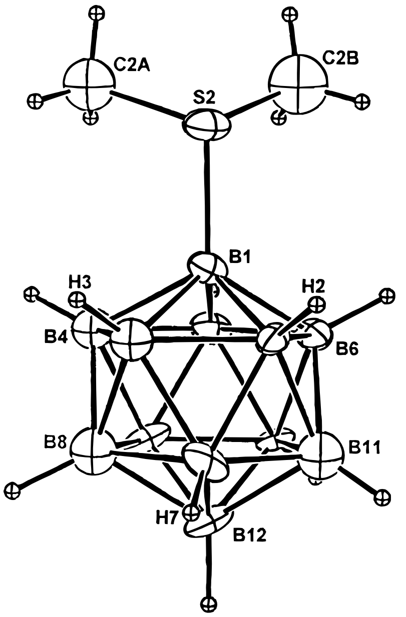

Figure 4. ORTEP plot of the $[B_{12}H_{11}(SMe_2)]^-$ anion.

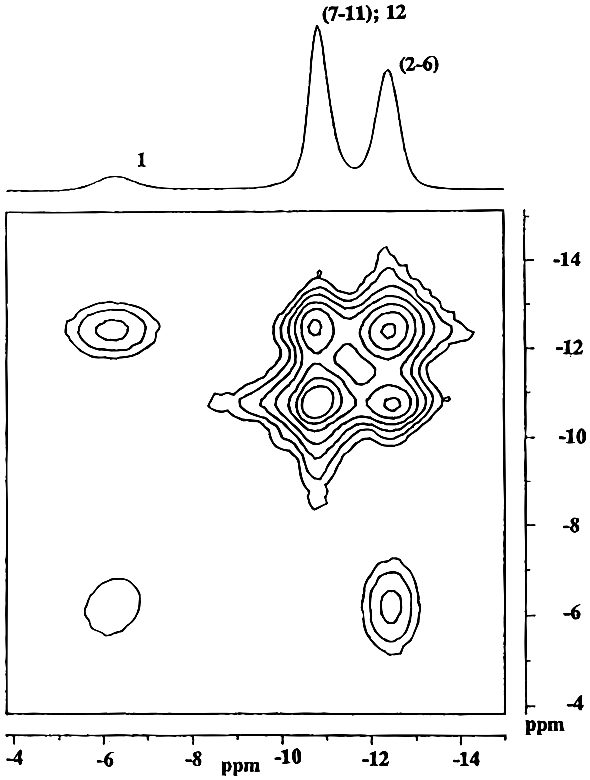

Figure 5. $^{11}B\{^1H\}-^{11}B\{^1H\}$ (COSY) spectrum of $[SMe_3][B_{12}H_{11}(SMe_2)]$ showing all peak assignments.

B6 nuclei at −12.5 ppm. The ^{11}B signals for this type of compound[7] are typically observed as shown, in descending order of frequency: B1, B2−B6, B7−B11, B12. The only other examples of which we are aware[8,9] in which the boron atom (B12) opposite the site of substitution (B1) in a monosubstituted *closo*-$\{B_{12}\}$ anion does not resonate at the lowest frequency are in the complexes $[B_{12}H_{11}(HgSCN)]^{2-}$ and $[B_{12}H_{11}I]^{2-}$.

It is of interest that the major product of the self-condensation reaction of $BH_3{\cdot}SMe_2$ at 60 °C is the monosubstituted $[B_{12}H_{11}(SMe_2)]^-$ anion, where the reaction at 150 °C using commercial $BH_3{\cdot}SMe_2$ yields primarily 1,7-$(SMe_2)_2B_{12}H_{10}$. Additionally, the earlier reaction of 1.75 equiv of B_2H_6 and SMe_2 at 150 °C described by Muetterties *et al.*,[1,2] was reported to give chiefly $B_{12}H_{10}(SMe_2)_2$. Furthermore, the previous work[2] proposed that the monosubstituted $[B_{12}H_{11}(SMe_2)]^-$ anion is formed as a result of "base displacement" from the disubstituted neutral compound, but the apparent predominance of the $[B_{12}H_{11}(SMe_2)]^-$ anion at lower temperatures and $B_{12}H_{10}(SMe_2)_2$ at higher temperatures implies that the reverse may be the case, where an $\{SMe_2\}$ function is picked up by a monosubstituted moiety to produce the disubstituted species.

It was initially hoped that we might be able to isolate $\{B_{10}\}$ species from the self-condensation of $BH_3{\cdot}SMe_2$, or from the reaction at low temperatures of $B_9H_{13}(SMe_2)$ with $BH_3{\cdot}SMe_2$. The reaction temperature was kept low as it is known that $B_9H_{13}(SMe_2)$ decomposes at elevated temperatures to give principally $B_{10}H_{14}$ and n-$B_{18}H_{22}$.[10] If the heating of $BH_3{\cdot}SMe_2$ at 60 °C is halted after a relatively short time (*ca.* 1 week) then the only

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isolable nonvolatile products are $B_9H_{13}(SMe_2)$ and $[SMe_3][B_{11}H_{14}]$, with no *closo*-icosahedral species present. Both are obtained in very low yield at this stage, in accord with previous observations,[1,2] and were identified by their ^1H and ^{11}B NMR spectra.[6,11] The quantities of the $\{B_9\}$ and $\{B_{11}\}$ species obtained after 4 months were not proportionately greater than those obtained after 1 week. This, along with the fact that no species with less than 12 boron atoms were isolated from the reaction of $BH_3{\cdot}SMe_2$ at 150 °C, suggests that these are intermediates on the way to the stable icosahedral species.

Experimental Section

General Information. Materials were handled by standard vacuum line and inert atmosphere techniques.[12] The dimethyl sulfide−borane complex with 5−10% excess dimethyl sulfide as stabilizing agent (Aldrich Chemical Co.) was used as received. Diethyl ether and tetrahydrofuran (THF) were dried by distillation from sodium benzophenone ketyl and were stored in bulbs containing sodium benzophenone ketyl. Acetone was dried with, distilled from, and stored over type 4A Linde molecular sieves. Acetonitrile was dried for 2−3 days over P_4O_{10} with stirring and then transferred by distillation to a storage bulb. 1,2-Dichloroethane was also dried over P_4O_{10} and distilled into a storage bulb for use.

^{11}B ($\delta(BF_3{\cdot}OEt_2) = 0.00$ ppm) and ^1H (δ(TMS) = 0.00 ppm) NMR spectra were obtained on a Bruker 250 NMR spectrometer operating at 80.25 and 250 MHz respectively. $^{11}B\{^1H\}-^{11}B\{^1H\}$ (COSY) data were obtained at 90.30 MHz on a Bruker 300 MHz instrument. $^{13}C\{^1H\}$ spectra (δ(TMS) = 0.00 ppm) were recorded at 62.90 and 125.76 MHz on Bruker 250 and 500 spectrometers, respectively. Fourier transform infrared (FTIR) spectra were measured on a Mattson Polaris Infrared spectrometer. Elemental analyses were performed by Mikroanalitische Labor Pascher, Remagen, Germany.

1,7-$(SMe_2)_2B_{12}H_{10}$ and 1,12-$(SMe_2)_2B_{12}H_{10}$. In a controlled atmosphere glovebox, $BH_3{\cdot}SMe_2$ (neat, with 5−10% excess SMe_2) (5.0 mL, ∼50 mmol) was syringed into the glass liner of a 300-mL stainless steel pressure vessel (Parr Instruments). The reactor was sealed, removed from the drybox, and connected to a high vacuum line. The lower part of the vessel was cooled to −78 °C and the pressure was reduced to *ca.* 5 Torr. The reactor was again sealed, and heated to 150 °C behind a safety shield. The pressure in the reactor rose to *ca.* 200 psi within a few hours, the temperature being held at 150 °C for a total of 10 h. After the vessel had returned to room temperature, it was again cooled to −78 °C and purged with N_2 in an efficient hood, to remove the hydrogen gas which was liberated in the reaction. The vessel was then attached to the high vacuum line, and the volatile components were distilled away. The reactor was then opened to the air and the off-white glassy solid product was transferred to a flask fitted with a vacuum extractor.

The product was dissolved in 1,2-dichloroethane (25 mL) and filtered, and then solvent was removed *in vacuo*. Mass of crude product = 0.60 g (2.27 mmol, 54% based on boron content of starting $BH_3{\cdot}SMe_2$ assuming the $B_{12}H_{10}(SMe_2)_2$ formulation).

Thin layer chromatography was performed using SiO_2 plates with 1,2−dichloroethane as eluent. The major mobile band appeared at R_f 0.73, and the minor mobile component at R_f 0.79. Both bands were collected from silica using 1,2−dichloroethane. Removal of solvent from the major band gave pure 1,7-$(SMe_2)_2B_{12}H_{10}$, 0.198 g, 0.75 mmol, 18%. The minor band, 1,12-$(SMe_2)_2B_{12}H_{10}$, was collected in only very small quantities.

Characterization of 1,7-$(SMe_2)_2B_{12}H_{10}$. NMR data (ppm, CD_2Cl_2): $\delta(^1H)$ 2.49 (s, $-S(CH_3)_2$), 1.6 (q, br, B−*H*); $\delta(^{11}B)$ −8.9 (s, 1, *B*−S), −13.5 (d*, 1), −15.1 (d*, 3), −16.4 (d*, 1). The three doublets marked with an asterisk overlap to give an apparent quartet. Average J_{BH} = 135 Hz. $\delta(^{11}B\{^1H\}-^{11}B\{^1H\}$, COSY) −8.9 (s; B1,7), −13.5 (d; B9,10), −15.1 (d; B5,12; B4,6,8,11), −16.4 (d; B2,3); δ $^{13}C\{^1H\}$ 25.98 (s, $-S(CH_3)_2$). IR data (KBr Pellet, cm^{-1}): 3015 (m), 2930 (m), 2510 (vs), 1424 (s), 1410 (s), 1330 (m), 1305 (w), 1052 (m), 1035 (s), 1002 (s), 965 (s), 940 (m, sh), 920 (w), 896 (w), 870 (w, sh), 854 (m), 835 (w, sh), 808 (s), 724 (m), 680 (w), 668 (w). Anal. Calcd for $C_4H_{22}B_{12}S_2$: C, 18.19; H, 8.40; B, 49.1; S, 24.3; Found: C, 18.57; H, 8.54; B, 48.0; S, 22.4%.

Characterization of 1,12-$(SMe_2)_2B_{12}H_{10}$. NMR data (ppm, CD_2Cl_2): $\delta(^1H)$ 2.50 (s, $-S(CH_3)_2$), 1.2 (q, br, B−*H*); $\delta(^{11}B)$ −8.1 (s, *B*−S), −13.9 (d, J_{BH} = 136 Hz).

$[SMe_3][B_{12}H_{11}(SMe_2)]$. In a controlled-atmosphere glovebox, $BH_3{\cdot}SMe_2$ (5.0 mL, ∼50 mmol) was syringed into a flask of 50 mL volume, containing a Teflon-coated magnetic stir bar. The flask was attached to a vacuum line, and its contents was cooled to −196 °C. The N_2 atmosphere was then pumped away, the flask re-sealed and its contents allowed to return to ambient temperature. The flask was then placed in a stirred oil bath at 60 °C behind a safety shield. Liberated H_2 was measured by a calibrated Toepler system, at intervals of approximately 1 week. After a few weeks, a small quantity of colorless solid material began to be observed in the mixture. After approximately 4 months, *ca.* 25 mmol of H_2 gas had been collected. At this stage, the volatile components of the mixture were distilled away into another vessel held at −196 °C, and the reaction flask containing a quantity of colorless solid material was taken into the glovebox, where it was connected to a vacuum extractor.

The crude product was extracted several times with a small quantity (*ca.* 20 mL) of diethyl ether. Upon removal of the diethyl ether from the filtrate, a small quantity of an oily solid was left, and this was shown by its ^{11}B NMR spectrum to be principally $B_9H_{13}(SMe_2)$.[6] Subsequent similar extraction of the product with tetrahydrofuran (THF) led to the isolation of a small amount of a waxy colorless material. NMR studies showed this to be a complex mixture, possibly containing the $[B_{12}H_{11}(SMe_2)]^-$ anion.

The bulk of the product remained undissolved by diethyl ether or THF. The product was then dissolved in acetone (20 mL). Upon filtration, only a trace of insoluble material was left behind on the frit. Removal of solvent from the acetone solution *in vacuo* gave a colorless solid, $[SMe_3][B_{12}H_{11}(SMe_2)]$, 0.172 g, 0.61 mmol, 15% yield based on boron content of the starting material. NMR data (ppm, CD_3CN): $\delta(^1H)$ 2.81 (s, 3, $[S(CH_3)_3]^+$), 2.44 (s, 2, $-S(CH_3)_2$); $\delta(^{11}B)$ −6.3 (s, 1, *B*−S), −10.9 (d*, 6), −12.5 (d*, 5). Doublets overlap to give an apparent triplet; average J_{BH} = 127 Hz. $\delta(^{11}B\{^1H\}-^{11}B\{^1H\}$, COSY) −6.2 (1, B1), −10.5 (6, B7-B11, B12), −12.5 (5, B2-B6); $\delta(^{13}C\{^1H\})$ 27.3 (s, 3, $[S(CH_3)_3]^+$), 25.9 (s, 2, $-S(CH_3)_2$). IR data (KBr pellet, cm^{-1}): 3009 (m), 2922 (w), 2498 (vs), 1419 (m), 1353 (w), 1330 (vw), 1045 (m), 998 (vw), 960 (w), 827 (vw), 719 (vw). Anal. Calcd for $C_5H_{26}B_{12}S_2$: C, 21.44; H, 9.36; B, 46.3; S, 22.9. Found: C, 20.40; H, 9.42; B, 46.0; S, 22.0%.

X-ray Data Collection and Reduction for 1,7-$(SMe_2)_2B_{12}H_{10}$, 1,12-$(SMe_2)_2B_{12}H_{10}$, and $[SMe_3][B_{12}H_{11}(SMe_2)]{\cdot}MeCN$. X-ray data were collected with a Enraf-Nonius CAD4 diffractometer on single crystals in sealed glass capillaries and examined with graphite-monochromated Mo Kα radiation. All of the crystals examined were colorless. The crystal of $[SMe_3][B_{12}H_{11}(SMe_2)]{\cdot}MeCN$ was placed in a glovebag that was saturated with acetonitrile vapor and loaded in a capillary that contained a drop of MeCN to prevent solvent loss from the crystal. Cell dimensions were obtained from 25 reflections measured in the range $24° < 2\theta < 30°$. Intensity data were collected in the $\omega/2\theta$ scan mode. For 1,7-$(SMe_2)_2B_{12}H_{10}$ and $[SMe_3][B_{12}H_{11}(SMe_2)]{\cdot}MeCN$ the intensities of four standard reflections and for 1,12-$(SMe_2)_2B_{12}H_{10}$ the intensities of five standard reflections were measured periodically during the data collection. They showed no significant decay. All data were corrected for Lorentz and polarization effects but not for absorption.

For 1,7-$(SMe_2)_2B_{12}H_{10}$ data for one hemisphere of reciprocal space were collected ($4° < 2\theta < 45°$; $+h$, $\pm k$, $\pm l$) and systematic absences were observed only for $(00l)$ reflections, with $l \neq 3n$. The structure was solved in the trigonal space group $P3_221$ (No. 154) by direct methods using SHELXS86 and refined using SHELXL93 (difference electron density calculations, full-matrix least-squares refinements,

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(12) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; John Wiley and Sons: New York, 1986.

sulfur, carbon, and boron anisotropic, and hydrogen atoms placed in calculated positions, riding on the atoms to which they are bonded).

For 1,12-$(SMe_2)_2B_{12}H_{10}$ data for one hemisphere of reciprocal space were collected ($4° < 2\theta < 45°$; $+h$, $\pm k$, $\pm l$). The structure was solved in the orthorhombic space group *Pbca* (No. 61) by a combination of direct methods (MULTAN 11/82) and difference Fourier syntheses. The structure was refined using full-matrix least-squares methods (sulfur, carbon, and boron anisotropic; hydrogen isotropic).

For $[SMe_3][B_{12}H_{11}(SMe_2)]\cdot MeCN$ data for one hemisphere of reciprocal space were collected ($4° < 2\theta < 45°$; $+h$, $\pm k$, $\pm l$). The structure was solved in the monoclinic space group $P2_1$ (No. 4) by direct methods using SHELXS86 and refined using SHELXL93 (difference electron density calculations, full-matrix least-squares refinements, sulfur, nitrogen, four carbons, and eight borons anisotropic; three carbons and four borons isotropic; hydrogen atoms placed in calculated positions, riding on the atoms to which they are bonded).

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Supporting Information Available: Listings of crystallographic data, for **1**−**3**, hydrogen atom parameters, anisotropic thermal parameters, bond distances, and bond angles for 1,7-$(SMe_2)_2B_{12}H_{10}$ and $[SMe_3]$-$[B_{12}H_{11}(SMe_2)]\cdot MeCN$, and anisotropic thermal parameters for 1,12-$(SMe_2)_2B_{12}H_{10}$ (19 pages). Ordering information is given on any current masthead page.

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