Reduction of Inner Sulfonium Salts, Thioethers, and Sulfones Derived from *closo*-$[B_{12}H_{12}]^{2-}$ by Lithium in Methylamine: A New Route to Mercaptododecaborates

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Anions $[Me_2SB_{12}H_{11}]^-$ (**2**) and $[MeSB_{12}H_{11}]^{2-}$ (**3**) can be reduced by excess lithium in methylamine at −15 °C to yield $[HSB_{12}H_{11}]^{2-}$ (**1**) after workup. Such behavior toward this reducing system is similar to that of alkyl aryl sulfides. The sulfone $[MeSO_2B_{12}H_{11}]^{2-}$ (**12**) also yields **1** as a major boron product upon reduction, while alkyl aryl sulfones produce the corresponding arenes under the same conditions. Similarly, isomers of $(Me_2S)_2B_{12}H_{10}$ (**4**−**6**) are reduced by lithium in methylamine yielding dithiols $[(HS)_2B_{12}H_{10}]^{2-}$ (**7**−**9**). The tetrabutylammonium salts of **1** and **7**−**9** are obtained in 80−90% yields and characterized by multinuclear NMR and mass spectrometry, the latter three compounds being isolated and characterized for the first time. The reduction reaction provides access to dithiols **7**−**9** for biological evaluation and use in synthesis. Thus, **2** and **4**−**6** can be easily converted to $[R_2SB_{12}H_{11}]^-$ and $(R_2S)_2B_{12}H_{10}$ in a two-step reduction−alkylation procedure. 1,2-$(Bn_2S)_2B_{12}H_{10}$ (**13**) obtained by alkylation of the reduction product of **4** by benzyl chloride was characterized by single-crystal X-ray diffraction analysis. Crystal data for 1,2-$(Bn_2S)_2B_{12}H_{10}$·CD_3CN: *C*2/*c* (No. 15), $a = 13.666(1)$ Å, $b = 16.978(1)$ Å, $c = 14.667(1)$ Å, $\beta = 91.08(1)°$, $Z = 4$.

Introduction

A dodecaborate anion bearing a thiol group was first synthesized by Muetterties and co-workers from the reaction of $[B_{12}H_{12}]^{2-}$ with H_2S.[1] Since then, the product, $[HSB_{12}H_{11}]^{2-}$ (**1**), also known as BSH, was found to be a promising agent for boron neutron capture therapy (BNCT),[2] which spurred the development of new superior methods of its synthesis. Nakagawa and Nagai[3] and Tolpin and co-workers[4] used proton-assisted nucleophilic substitution on $[B_{12}H_{12}]^{2-}$ with *N*-methylthiopyrrolidone and *N*-methylbenzothiazole-2-thione, respectively, to obtain the intermediate thioethers which produced the desired thiolate upon alkaline hydrolysis. Electrophilic substitution as a method of sulfur introduction on the cage was also explored. Thus, Tolpin and co-workers[4] showed that acetylsulfenyl chloride reacts with $[B_{12}H_{12}]^{2-}$ yielding $[HSB_{12}H_{11}]^{2-}$, and Brattsev and Morris[5] used electrochemical oxidation of thiourea to generate the suitable electrophile to produce $[(H_2N)_2CSB_{12}H_{11}]^-$, which afforded thiolate after hydrolysis. On the other hand, dithiols received considerably less attention. Their formation was observed in reactions of $[B_{12}H_{12}]^{2-}$ with H_2S[1] and $ClSC(O)CH_3$,[4] and it was shown that they react with 5,5′-dithiobis(2-nitrobenzoic acid) to make mixed bis(disulfides).[4] No salt of $[(HS)_2B_{12}H_{10}]^{2-}$ either as a mixture of three possible isomers (**7**−**9**) or as an individual isomer was isolated.[6]

Studying the basic chemistry of the inner sulfonium salts derived from $[B_{12}H_{12}]^{2-}$, $[Me_2SB_{12}H_{11}]^-$ (**2**), and isomers of $(Me_2S)_2B_{12}H_{10}$ (**4**−**6**),[8,9] we found that they can be reduced to the corresponding methyl thioethers by excess sodium or potassium in liquid ammonia.[10] These thioethers are stable toward further cleavage to the corresponding thiolates and methane, a rather surprising fact considering the behavior of alkyl aryl sulfides, their organic counterparts.[11] On the other hand, Truce and co-workers[12] reported that lithium in methylamine reduces alkyl aryl sulfides to arylthiolates and alkanes, while the corresponding sulfones are reduced to aromatic hydrocarbons and alkylsulfinic acids (Scheme 1). Hoping to develop a new method of synthesis of dodecaboranethiolates as well as a method to remove a sulfur substituent from the cage, we studied the reduction of the inner sulfonium salts of dodecaborane and their derivatives by lithium in methylamine. The results are reported herein.

Results and Discussion

Reduction of $[MeSB_{12}H_{11}]^{2-}$ (3) and $[Me_2SB_{12}H_{11}]^-$ (2) and Synthesis of Derivatives of 1. The tetramethylammonium salt of thioether **3**, prepared from sulfonium salt **2** by reaction with NaSEt or sodium in liquid ammonia,[10] is reduced to the corresponding thiolate $[SB_{12}H_{11}]^{3-}$ by excess lithium in methylamine (Scheme 2) as expected from the behavior of alkyl aryl sulfides. Similarly, $[Me_3S][\mathbf{2}]$ is directly reduced to the above thiolate, apparently through the formation of intermediate

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(6) $[1,10\text{-}(HS)_2B_{10}Cl_8]^{2-}$, a closely related dimercaptane, was reported by Muetterties et al.[7] from the reaction of $1,10\text{-}(N_2)_2B_{10}Cl_8$ with H_2S.
(7) Knoth, W. H.; Sauer, J. C.; Miller, H. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 115.
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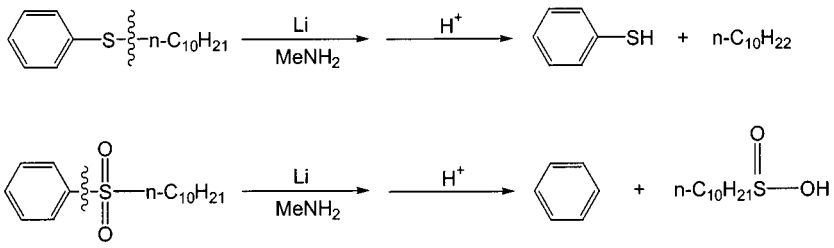
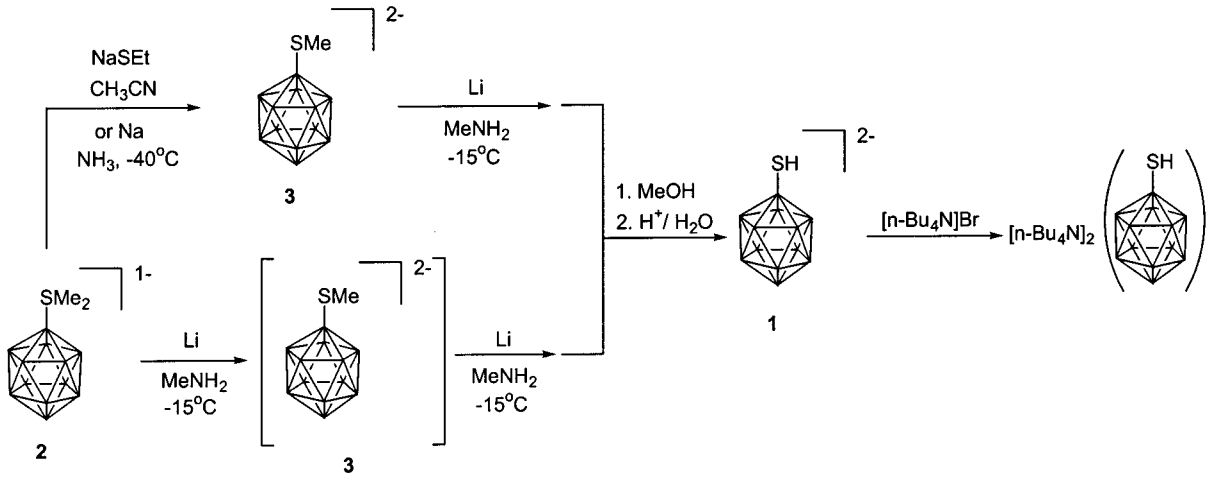
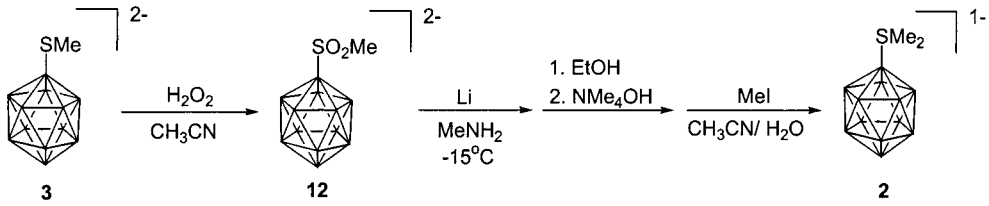
Scheme 1



Scheme 2



Scheme 3



thioether **3**. Under these conditions the tetramethylammonium and trimethylsulfonium cations are reduced as well providing the lithium salt soluble in water and alcohols. Attempts to isolate thiol **1** and dithiols **7**−**9** (see below) as their cesium salts in good yields were unsatisfactory since they are relatively soluble in water. Besides, $Cs_2[(HS)_2B_{12}H_{10}]$, which was precipitated by addition of CsCl to the aqueous acidified solution, was found to contain some CsCl by mass spectrometry (ESI). Therefore we used [*n*-Bu_4N]Br for metathesis purposes. This also allowed us to relate the integrals of the thiol protons to those of the cation. The reduction reaction makes various derivatives, $[R_2SB_{12}H_{11}]^-$ and $[RC(O)SB_{12}H_{11}]^{2-}$, easily accessible from **2**. For example, without isolation the reduction product was alkylated by allyl bromide. The ^{1}H NMR spectrum of the isolated tetramethylammonium salt of $[(C_3H_5)_2SB_{12}H_{11}]^-$ (**10**) agreed with the one reported earlier by Gabel and co-workers.[13] The isolated tetrabutylammonium salt of **1** was acylated by benzoyl chloride yielding the corresponding *S*-acyl derivative $[C_6H_5C(O)SB_{12}H_{11}]^{2-}$ (**11**), the tetramethylammonium salt of the latter dianion being reported by the same authors.[13]

Reduction of $[MeSO_2B_{12}H_{11}]^{2-}$ (12). The boron-cage analogue of the methyl phenyl sulfone was prepared by oxidation of **3** by hydrogen peroxide in acetonitrile. Upon reduction by lithium in methylamine this sulfone yielded, unexpectedly, the thiolate $[SB_{12}H_{11}]^{3-}$ as the main boron product instead of $[B_{12}H_{12}]^{2-}$ (Scheme 3). The failure of the analogy in this case might be attributed to the strength of the B(cage)−S bond. The product of reduction was isolated as the tetramethylammonium salt and reacted with methyl iodide, providing **2**, which was identified by its ^{11}B{^{1}H} NMR.[8,10] Since the reduction of sulfone **12** led to the same boron product as the reduction of sulfide **3** and sulfonium salt **2**, and sulfones are prepared from sulfides, the reduction of sulfones was not pursued any further.

Reduction of Isomers of $(Me_2S)_2B_{12}H_{10}$ (4−6) and Alkylation of Products. The early failure to isolate a salt of $[(HS)_2B_{12}H_{10}]^{2-}$ was presumably due to a mixture of isomers that formed.[4] We expected that starting from a pure isomer of $(Me_2S)_2B_{12}H_{10}$ (which are all available by chromatography followed by recrystallization) one can obtain the corresponding isomer of $[(HS)_2B_{12}H_{10}]^{2-}$ through reduction by lithium in methylamine. Indeed, reduction of each of the three isomers followed by acidification and metathesis with [*n*-Bu_4N]Br led to the tetrabutylammonium salt of the corresponding dithiol in 80−90% yields; one example of these reactions is presented in Scheme 4. In addition, all three reduction products were alkylated by benzyl chloride in the presence of NaI as a nucleophilic catalyst yielding the corresponding isomers of $(Bn_2S)_2B_{12}H_{10}$ (**13**−**15**). Thus, isomers of $(R_2S)_2B_{12}H_{10}$ can be prepared from **4**−**6** using the reduction by lithium in methyl-

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Scheme 4

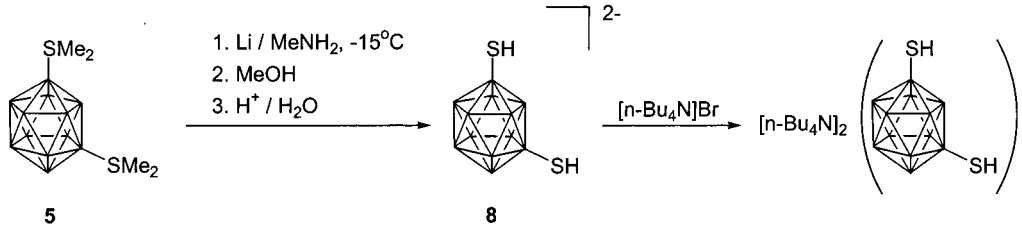

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Table 1. Crystallographic Data for 1,2-$(Bn_2S)_2B_{12}H_{10}$·CD_3CN (**13**·CD_3CN)

empirical formula	$C_{30}H_{38}D_3NB_{12}S_2$
fw	612.55
space group	*C*2/*c*
a, Å	13.6655(10)
b, Å	16.9782(10)
c, Å	14.6673(10)
β, deg	91.080(10)
vol, Å^3	3402.4(4)
Z	4
ρ (calcd), Mg m^{-3}	1.137
cryst size, mm	0.60 × 0.08 × 0.06
temp, K	150(2)
radiation (λ, Å)	0.71073
2θ limits, deg	4.70−50.02
μ, mm^{-1}	0.177
R1[a] [$I > 2\sigma(I)$]	0.0528
wR2[b] (all data)	0.1311

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1,2-$(Bn_2S)_2B_{12}H_{10}$·CD_3CN (**13**·CD_3CN)

Bond Lengths			
S(1)−C(1)	1.820(3)	B(4)−B(3)	1.777(4)
S(1)−C(8)	1.825(3)	B(4)−B(2)	1.795(4)
S(1)−B(1)	1.906(3)	B(4)−B(6)	1.798(4)
B(5)−B(6)	1.780(4)	B(1)−B(2)	1.751(4)
B(5)−B(4)	1.783(4)	B(1)−B(6)	1.774(4)
B(5)−B(3)	1.788(4)	B(3)−B(2)	1.779(4)
B(4)−B(1)	1.760(4)		
Angles			
C(1)−S(1)−C(8)	100.90(13)	B(2)−B(4)−B(6)	108.1(2)
C(1)−S(1)−B(1)	107.49(13)	B(2)−B(1)−B(4)	61.48(17)
C(8)−S(1)−B(1)	105.06(13)	B(2)−B(1)−B(6)	111.2(2)
C(2)−C(1)−S(1)	111.18(18)	B(4)−B(1)−B(6)	61.17(17)
C(9)−C(8)−S(1)	110.6(2)	B(2)−B(1)−S(1)	124.60(19)
B(6)−B(5)−B(4)	60.61(17)	B(4)−B(1)−S(1)	124.6(2)
B(6)−B(5)−B(3)	108.1(2)	B(6)−B(1)−S(1)	117.86(19)
B(4)−B(5)−B(3)	59.69(18)	B(1)−B(6)−B(5)	106.0(2)
B(1)−B(4)−B(3)	105.9(2)	B(1)−B(6)−B(4)	59.04(17)
B(1)−B(4)−B(5)	106.4(2)	B(5)−B(6)−B(4)	59.76(17)
B(3)−B(4)−B(5)	60.31(18)	B(4)−B(3)−B(2)	60.61(17)
B(1)−B(4)−B(2)	59.01(17)	B(4)−B(3)−B(5)	60.00(18)
B(3)−B(4)−B(2)	59.76(18)	B(2)−B(3)−B(5)	108.6(2)
B(5)−B(4)−B(2)	108.2(2)	B(1)−B(2)−B(3)	106.2(2)
B(1)−B(4)−B(6)	59.79(17)	B(1)−B(2)−B(4)	59.51(17)
B(3)−B(4)−B(6)	107.8(2)	B(3)−B(2)−B(4)	59.63(18)
B(5)−B(4)−B(6)	59.63(17)		

amine. 1,2-$(Bn_2S)_2B_{12}H_{10}$·CD_3CN (**13**·CD_3CN) was characterized by X-ray single-crystal diffraction. Tables 1 and 2 provide the crystallographic data and selected bond lengths and angles, respectively, for **13**·CD_3CN. The molecular structure of **13** (Figure 1) is very similar to the previously reported structure of 1,2-$(Me_2S)_2B_{12}H_{10}$[9] except that the sulfur−carbon bonds in **13** are 0.01−0.03 Å longer than those in 1,2-$(Me_2S)_2B_{12}H_{10}$. Compound **13** possesses crystallographically imposed C_2 symmetry in the solid state.

Oxidative Stability of Dithiols $[(HS)_2B_{12}H_{10}]^{2-}$ (7−9). Anion **1** is notorious for its tendency to undergo oxidation to disulfide and further.[14,15] In their attempt to isolate $[(HS)_2B_{12}H_{10}]^{2-}$ Tolpin and co-workers noticed that dithiols are similar in this respect.[4] Our results showed that the tetrabutylammonium salts of **7**−**9** turned blue within 1 min after precipitation from acidic aqueous solutions in air. The boron NMR spectra of these salts contained extra peaks. On the other hand, the white solids isolated under nitrogen turned blue slowly when exposed to air. The NMR samples of the white solids in acetonitrile and DMF showed new peaks upon standing in air and, if acidified with HCl, produced intensely blue colored solutions. This behavior is consistent with formation of disulfides upon oxidation by air and their ability to generate thiol or thiyl radicals, similar to that of **1**.[14]

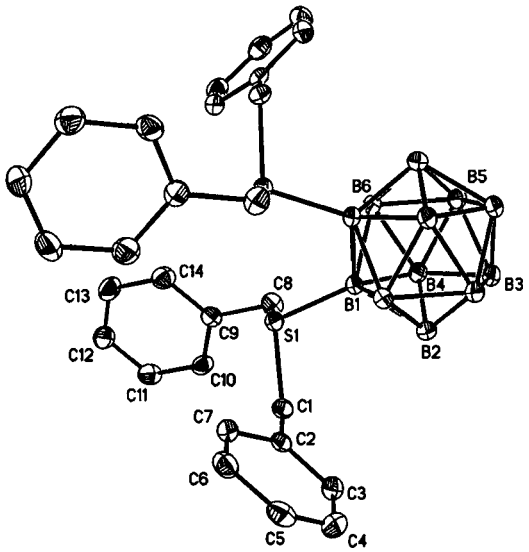

Figure 1. The molecular structure of 1,2-$(Bn_2S)_2B_{12}H_{10}$·CD_3CN showing the crystallographic numbering scheme. The solvent molecule and hydrogen atoms are omitted for clarity.

$^{11}B\{^1H\}$ NMR Spectra of $[HSB_{12}H_{11}]^{2-}$ (1), Isomers of $[(HS)_2B_{12}H_{10}]^{2-}$ (7−9), $[(C_3H_5)_2SB_{12}H_{11}]^-$ (10), and Isomers of $(Bn_2S)_2B_{12}H_{10}$ (13−15). The spectra of **1** and **7**−**9** are very similar to the corresponding spectra of $[MeSB_{12}H_{11}]^{2-}$ (**3**) and isomers of $[(MeS)_2B_{12}H_{10}]^{2-}$, respectively, except that the chemical shifts of the *ipso*-boron atoms in thiols are significantly moved upfield, presumably, due to the lower electron-withdrawing capacity of the SH substituent. Another difference is that the spectra of **7** and **8** (both anions have C_{2v} symmetry) look almost identical (Figure 2), while those of 1,2- and 1,7-$[(MeS)_2B_{12}H_{10}]^{2-}$ can be distinguished easily because the signals of B(3,6) and B(4,5,7,11) overlap in the spectrum of the former anion.[10] The assignment of the signals in all four spectra of thiols is the same as for the corresponding spectra of the methyl thioethers as it was shown by $^{11}B-^{11}B\{^1H\}$ 2D COSY experi-

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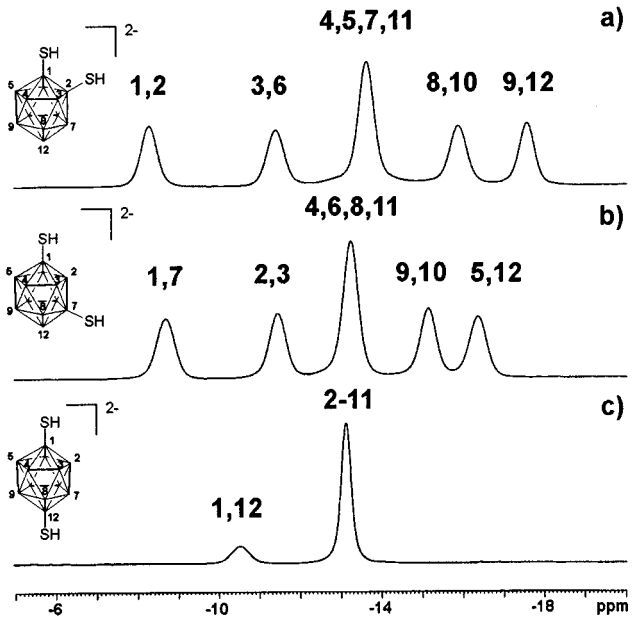

Figure 2. $^{11}B\{^1H\}$ NMR spectra (160.5 MHz) of $[1,2\text{-}(HS)_2B_{12}H_{10}]^{2-}$ (**7**) (a), $[1,7\text{-}(HS)_2B_{12}H_{10}]^{2-}$ (**8**) (b), and $[1,12\text{-}(HS)_2B_{12}H_{10}]^{2-}$ (**9**) (c) in CD_3CN (cation $[n\text{-}Bu_4N]^+$).

ments for thiols **1**, **7,** and **8** (see the Supporting Information). Thus, the SH substituent has nearly the same effect on the unsubstituted boron atoms as the SMe does. Spectra of **10** and **13**−**15** are very similar to those of **2** and **4**−**6**,[10] respectively; therefore we used the same assignments for their boron signals.

^1H and $^1H\{^{11}B\}$ NMR Spectra of $[HSB_{12}H_{11}]^{2-}$ (1), Isomers of $[(HS)_2B_{12}H_{10}]^{2-}$ (7−**9), and Isomers of $(Bn_2S)_2$-$B_{12}H_{10}$ (13**−**15).** Since we failed to locate any literature data on the chemical shift of the thiol proton in **1**, we were surprised to find this signal upfield from TMS at −0.42 ppm in CD_3CN (the usual range for the aliphatic thiols is 1.2−1.6 ppm and 2.8−3.6 ppm for aromatic ones[16]). On the other hand, such a low chemical shift correlates well with the observed low acidity of dianion **1**,[13] which is below that of the organic thiols. Similarly, the sulfhydryl protons of isomers of $[(HS)_2B_{12}H_{10}]^{2-}$ exhibit chemical shifts in the same region. These signals disappear upon addition of several drops of D_2O to NMR samples and shaking because of the H−D exchange. The chemical shift of the thiol protons in $[(HS)_2B_{12}H_{10}]^{2-}$ depends on the geometry of substitution, with the most upfield value for the 1,12-isomer and the least upfield (but still negative) value for the 1,2-isomer. The shielding of the thiol protons is in agreement with the donation of the electron density from a cage to a sulfur atom, as we suggested before for $[MeSB_{12}H_{11}]^{2-}$, $[(MeS)_2B_{12}H_{10}]^{2-}$, and $[(MeS)(Me_2S)B_{12}H_{10}]^-$.[10] On the basis of the values of the chemical shift, such donation is most important in the case of **9** and least important for **7**. $^1H\{^{11}B\}$-NMR spectra of the tetrabutylammonium salts of **1**, **7**, and **8** show the 5:1, 4:2:2, and 2:4:2 patterns, respectively, for the boron-attached protons. The second signal of intensity 5 in the spectrum of **1** is hidden under the triplet resulting from the cation. The same is true for the third signal of intensity 2 in the spectrum of **8**. The third signal of intensity 2 in the spectrum of **7** is covered by the triplet of quartets due to the cation. Two signals of intensity 4 (one of them is an overlap of two signals) and one of intensity 2 are found in the spectra of **13** and **14**, in agreement with their C_{2v} symmetry. Only one B−H signal can be seen in the spectra of **9** and **15**. The methylene hydrogens in **10** and **13**−**15** are diastereotopic and give rise to a pair of doublets in their ^1H NMR spectra.

Conclusion

Reduction of the inner methylsulfonium salts, thioethers, and sulfones derived from *closo*-$[B_{12}H_{12}]^{2-}$ by lithium in methylamine produces the corresponding thiols. Thus, **1** and **7**−**9** can be obtained essentially in a two-step synthesis involving pyrolysis of $BH_3{\cdot}SMe_2$ followed by reduction of $[Me_3S][\mathbf{2}]$ and **4**−**6**, respectively. Even though in our hands the yield of $[Me_3S]$-$[\mathbf{2}]$ after the pyrolysis never exceeded 50%, the reaction conditions are not optimized and the second step seems to proceed qualitatively. This two-step procedure might have an advantage over the previously known methods of synthesis of **1**. It is certainly valuable for the synthesis of dithiols **7**−**9**, which are isolated in pure form and characterized for the first time, making them available for biological evaluation and use in synthesis. Alternatively, the reduction reaction can be used for the synthesis of thiols in tandem with other known methods of synthesizing inner sulfonium salts[17] and thioethers[18] of *closo*-$[B_{12}H_{12}]^{2-}$. Our preliminary studies have also shown that the scope of the lithium reduction is not limited to *closo*-B_{12} system. Thus, 1,10-$(Me_2S)_2B_{10}H_8$ was reduced to $[1,10\text{-}(HS)_2B_{10}H_8]^{2-}$, which was isolated as the tetrabutylammonium salt and characterized by ^{11}B and ^1H NMR.[19]

Experimental Section

General Data. $[Me_3S][\mathbf{2}]$ and **4**−**6**, prepared by pyrolysis of $BH_3{\cdot}SMe_2$, were separated and purified as described earlier.[9,10] $BH_3{\cdot}SMe_2$ complex with 5−10% excess dimethyl sulfide and lithium powder (99.5%) were purchased from Aldrich Chemical Co. Methylamine was purchased from Matheson Tri-Gas, Inc., and dried over sodium prior to use. Chromatography was performed on Selecto silica gel (230−430 mesh) purchased from Fisher Scientific. ^{11}B and ^1H NMR spectra were obtained on a Bruker DRX-500 spectrometer at 160.5 and 500.1 MHz, respectively. Proton spectra were referenced to residual solvent protons. Boron spectra were referenced externally to $BF_3{\cdot}OEt_2$ in C_6D_6 ($\delta = 0.00$ ppm). ^{13}C NMR spectra were obtained on Bruker DRX-500 and DPX-400 spectrometers operating at 125.8 and 100.6 MHz, respectively, and referenced to deuterated solvent peaks. The ^1H NMR data for $[n\text{-}Bu_4N]^+$ cation are only listed once for $[n\text{-}Bu_4N]_2[\mathbf{1}]$ and omitted elsewhere. The mass spectra were recorded on the Micromass QTOF electrospray mass spectrometer. The elemental analysis was performed by Galbraith Laboratories, Inc.

X-ray Structure Determination. Single-crystal X-ray diffraction data were collected on an Enraf-Nonius KappaCCD diffraction system, which employs graphite-monochromated Mo Kα radiation. A single crystal of 1,2-$(Bn_2S)_2B_{12}H_{10}{\cdot}CD_3CN$ obtained by slow evaporation of CD_3CN from an NMR sample was mounted on the tip of a glass fiber coated with Parabar. Data were collected at 150 K. Unit cell parameters were obtained by indexing the peaks in the first 10 frames and refined employing the whole data set. All frames were integrated and corrected for Lorentz and polarization effects using DENZO.[20] The structure was solved by direct methods and refined using SHELXTL (difference electron density calculations, full least-squares refinements).[21] One molecule of solvent, CD_3CN, crystallizes with one molecule of 1,2-

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(19) NMR data for $[n\text{-}Bu_4N]_2[1,10\text{-}(HS)_2B_{10}H_8]$. ^1H NMR (CD_3CN): δ 0.32 (br s, 2H, S*H*). $^1H\{^{11}B\}$ NMR (CD_3CN): δ 0.26 (br s, 8H, B*H*). ^{11}B NMR (CD_3CN): δ 3.6 (s, B(1,10)), −26.0 (d, $J_{B-H} = 126$ MHz, B(2−9)).

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$(Bn_2S)_2B_{12}H_{10}$. The solvent molecule is disordered. Its center carbon resides on a 2-fold axis. The methyl group and nitrogen each occupy two separate off axis sites. Each pair of sites is related by the 2-fold axis. Occupancies of the sites are approximately 0.5.

Preparation of $[n\text{-}Bu_4N]_2[HSB_{12}H_{11}]$ ($[n\text{-}Bu_4N]_2$[1]). Method A. From $[NMe_4]_2[MeSB_{12}H_{11}]$. $[NMe_4]_2$[**3**] (0.2454 g, 0.730 mmol) was placed in a 50 mL round-bottom flask with a 9 mm solv-seal joint equipped with a stirbar. In a glovebox lithium powder (0.2122 g, 30. 57 mmol) was added and the flask was evacuated. Methylamine (25 mL) was condensed with liquid nitrogen, and the flask was warmed up to −15 °C by being placed in a cold ethanol−dry ice bath. The blue solution was stirred for 1 h at −15 ± 5 °C. Twice during this time the solution was frozen, and the noncondensable gas was pumped out. All volatiles were removed through a cold trap at −196 °C, and the residue was brought into a glovebag under nitrogen and dissolved in 30 mL of methanol to destroy excess lithium. The solvent was removed on a flash evaporator followed by pumping on the vacuum line through a cold trap. In the glovebag the residue was dissolved in 40 mL of distilled water, the pH was adjusted to about 1 with H_2SO_4 (1:1), and the solution was filtered into a 150 mL beaker. [*n*-Bu_4N]Br (0.6300 g, 1.956 mmol) was added to the filtrate, and the resulting white precipitate was filtered off. It was washed with 30 mL of distilled water followed by 30 mL of ether, scraped into a 50 mL round-bottom flask with a 15 mm solv-seal joint, attached to the vacuum line, and evacuated. The solid was kept under dynamic vacuum for 1.5 days at 70 °C (oil bath). The yield was 0.4068 g (81%).

Method B. From $[Me_3S][Me_2SB_{12}H_{11}]$. $[Me_3S]$[**2**] (0.9075 g, 3.240 mmol) was placed in a 150 mL round-bottom flask with a 15 mm solv-seal joint equipped with a stirbar. In the glovebox 0.5821 g (83.86 mmol) of lithium powder was added, the flask was evacuated, and 20 mL of methylamine was condensed by means of liquid nitrogen. Upon warming up to −15 °C in the cold bath, vigorous gas evolution occurred and the reaction mixture was cooled to −196 °C to pump out the noncondensable gas. After stirring at −15 ± 5 °C for 30 min the mixture was freeze−pumped again and stirred at the above temperature for another 30 min. After removing volatiles through a cold trap, a residue was brought into a glovebag under nitrogen and worked up similarly to method A. [*n*-Bu_4N]Br (2.60 g, 8.07 mmol) was used to precipitate the dianion from acidified aqueous solution. After washing with water and ether, the precipitate was placed into a 100 mL round-bottom flask with a 15 mm solv-seal joint, and the flask was evacuated on the vacuum line and kept under dynamic vacuum for 1.5 days at 60 °C; 1.9131 g of product was obtained (90% yield). The spectral characteristics of the products obtained by the two methods were identical. ^{1}H NMR (CD_3CN): δ 3.09 (m, 16H, NCH_2), 1.60 (m, 16H, NCH_2CH_2), 1.36 (tq, 16H, J = 7.4; 7.4 Hz, $NCH_2CH_2CH_2$), 0.97 (t, 24H, J = 7.4 Hz, $NCH_2CH_2CH_2CH_2$), −0.42 (br s, 1H, S*H*). ^{1}H{^{11}B} NMR (CD_3CN): δ 1.20 (br s, 5H, B*H*), 0.79 (br s, 1H, B*H*). ^{11}B NMR (CD_3CN): δ −8.8 (s, B(1)), −13.2 (d, J_{B-H} = 128 Hz, B(2−6)), −15.1 (d, J_{B-H} = 127 Hz, B(7−11)), −18.2 (d, J_{B-H} = 127 Hz, B(12)). MS (ESI): calcd for $C_{32}H_{84}N_2{}^{11}B_{12}SNa$, m/z = 683.742; obsd, m/z = 683.742 $(M + Na)^+$.

Preparation of $[Me_4N][(C_3H_5)_2SB_{12}H_{11}]$ ($[Me_4N]$[10]). $[Me_3S]$[**2**] (0.2753 g, 0.983 mmol) was placed in a 50 mL round-bottom flask with a 9 mm solv-seal joint and a stirbar. In the glovebox 0.2483 g (35.8 mmol) of lithium wire (small chunks) was added, the flask was evacuated, and 15 mL of methylamine was condensed by means of liquid nitrogen. The reduction was carried out at −15 ± 5 °C for 30 min, the mixture being freeze−pumped twice during this time. After solvent removal, EtOH (25 mL) was added carefully and the insoluble residue was filtered off. When ethanol was removed from the filtrate, acetonitrile (50 mL), water (10 mL), and 1 mL of allyl bromide were added to the residue, and the mixture was refluxed under nitrogen for 1 h. The volatile materials were removed on a flash evaporator followed by addition of water. Solid $[Me_4N]Cl$ was used to precipitate the anion. The resulting solid was washed with 60 mL of ether and dried at 70 °C. Mass of the crude product was 0.2370 g (73% yield). ^{1}H NMR (CD_3CN): δ 5.99−5.94 (m, 2H, C*H*═CH_2), 5.45−5.35 (m, 4H, CH═CH_2), 3.70 (dd, 2H, J = 13.6; 6.6 Hz, CH_aH$_b$), 3.54 (dd, 2H, J = 13.6; 7.9 Hz, CH$_a$H$_b$), 3.08 (s, 12H, NCH_3). ^{13}C{^{1}H} NMR (CD_3CN): δ 130.2, 123.3, 56.3 (t, J_{C-N} = 4 Hz), 43.6. ^{11}B NMR (CD_3CN): δ −10.1 (s, B(1)), −13.5 (d, B(12)), −14.1 (d, B(7−11)), −15.5 (d, B(2−6)).

Preparation of $[n\text{-}Bu_4N]_2[C_6H_5C(O)SB_{12}H_{11}]$ ($[n\text{-}Bu_4N]_2$[11]). This compound was prepared according to the procedure of Gabel and coworkers[13] for the synthesis of $[Me_4N]_2$[**11**] except that [*n*-$Bu_4N]_2$[**1**] was used as a starting material (0.4486 g, 0.681 mmol). The NMR pure [*n*-$Bu_4N]_2$[**11**] was obtained after drying of the material precipitated from ether under dynamic vacuum for 2 days at 80 °C (0.5195 g, 95% yield). ^{1}H NMR (CD_3CN): δ 7.96 (dd, 2H, J = 8.5; 1.3 Hz, C_6H_5), 7.45 (m, 1H, C_6H_5), 7.36 (m, 2H, C_6H_5). ^{13}C{^{1}H} NMR (CD_3CN): δ 195.1, 142.7, 132.1, 128.9, 128.0, 59.4 (t, J_{C-N} = 4 Hz), 24.5, 20.4, 14.0. ^{11}B NMR (CD_3CN): δ −9.5 (s, B(1)), −14.1 (d, B(2−6)), −15.2 (d, B(7−12)).

Preparation of $[NMe_4]_2[MeSO_2B_{12}H_{11}]$ ($[Me_4N]_2$[12]). $[Me_3S]$[**2**] (0.9274 g, 3.311 mmol) was converted into $[Me_4N]_2$[**3**] by reaction with sodium ethanethiolate.[10] The product was dissolved in 90 mL of acetonitrile, and 0.90 mL of 30% H_2O_2 was added. After stirring at room temperature for 42 h the ^{11}B NMR spectrum of the reaction mixture revealed that both sulfoxide and sulfone are present in an approximately 1:1 ratio (chemical shifts −5.0 and −6.0 ppm, respectively, for the *ipso*-boron atoms). Another portion of hydrogen peroxide (0.45 mL) was added, and stirring was continued for an additional 27 h. At this point the sulfoxide-to-sulfone ratio was about 1:2. The third portion of H_2O_2 (0.45 mL) was added, and reaction was carried on until no sulfoxide could be detected by ^{11}B NMR (67 h). Acetonitrile was removed on the flash evaporator, and ether (80 mL) was added to the oily residue in the flask. After trituration, white solid formed, which was filtered off, washed with 30 mL of ether and 30 mL of pentane, and dried under dynamic vacuum overnight at 95−100 °C. The yield of $[Me_4N]_2$[**12**] from $[Me_3S]$[**2**] was 90% (1.0980 g). ^{1}H NMR (CD_3CN): δ 3.10 (s, 24H, NCH_3), 2.55 (s, 3H, SO_2CH_3). ^{13}C{^{1}H} NMR (CD_3CN): δ 56.3 (t, J_{C-N} = 4 Hz), 45.7. ^{11}B NMR (CD_3CN): δ −6.0 (s, B(1)), − 14.8 (d, B(2−12)). Anal. Calcd: C, 29.36; H, 10.40; N, 7.61. Found: C, 29.55; H, 10.75; N, 7.46.

General Procedure for Preparation of $[n\text{-}Bu_4N]_2[(HS)_2B_{12}H_{10}]$. An isomer of $(Me_2S)_2B_{12}H_{10}$ (0.5−2.2 mmol) was placed in a 50 or 100 mL round-bottom flask with a 9 or 15 mm solv-seal joint and a stirbar, and lithium powder was added in the glovebox (typically the molar ratio of borane to metal was about 1:30). The flask was evacuated, and methylamine (20−25 mL) was condensed with liquid nitrogen. Upon warming up to −15 °C in a cold ethanol−dry ice bath, vigorous gas evolution took place, and the solution was frozen with liquid nitrogen to pump out the noncondensable gas. During the 1 h period of stirring at −15 ± 5 °C, the reaction mixture was freeze−pumped additionally 2−3 times. After solvent removal through a cold trap, the residue was dissolved carefully in methanol in a glovebag under nitrogen. Most of the methanol was removed on a flash evaporator, the residual solvent being removed on the vacuum line by pumping through a cold trap. A white solid was dissolved in 20−30 mL of distilled water in the glovebag, the pH of the solution was adjusted to about 1 with H_2SO_4 (1:1), and the solution was filtered into a 150 mL beaker followed by addition of solid [*n*-Bu_4N]Br (ratio of borane to salt about 1:2.6). The white precipitate was filtered off, washed with 30 mL of water and 30 mL of ether, placed in a 100 mL round-bottom flask with a 15 mm solv-seal joint, and pumped on the vacuum line with heating (70−80 °C) for 1.5−2 days. All salts have a good solubility in methanol and acetonitrile.

$[n\text{-}Bu_4N]_2[1,2\text{-}(HS)_2B_{12}H_{10}]$ ($[n\text{-}Bu_4N]_2$[7]). Starting from 0.1387 g of **4**, 0.2936 g of the product was isolated (81% yield). ^{1}H NMR (CD_3CN): δ −0.21 (br s, 2H, S*H*). ^{1}H{^{11}B} NMR (CD_3CN): δ 1.24 (br s, 4H, B*H*), 1.19 (br s, 2H, B*H*), 0.86 (br s, 2H, B*H*). ^{11}B NMR (CD_3CN): δ −8.3 (s, B(1,2)), −11.4 (d, J_{B-H} = 133 Hz, B(3,6)), −13.7 (d, J_{B-H} = 129 Hz, B(4,5,7,11)), −15.9 (d, J_{B-H} = 130 Hz, B(8,10)), −17.6 (d, J_{B-H} = 129 Hz, B(9,12)). MS (ESI): calcd for $C_{32}H_{84}N_2{}^{10}B_2{}^{11}B_{10}S_2Na$, m/z = 713.718; obsd, m/z = 713.717 $(M + Na)^+$.

$[n\text{-}Bu_4N]_2[1,7\text{-}(HS)_2B_{12}H_{10}]$ ($[n\text{-}Bu_4N]_2$[8]). Starting from 0.5635 g of **5**, 1.3316 g of the product was obtained (90% yield). ^{1}H NMR (CD_3CN): δ −0.38 (br s, 2H, S*H*). ^{1}H{^{11}B} NMR (CD_3CN): δ 1.43 (br s, 2H, B*H*), 1.22 (br s, 4H, B*H*), 1.01 (br s, 2H, B*H*). ^{11}B NMR (CD_3CN): δ −8.8 (s, B(1,7)), −11.5 (d, J_{B-H} = 132 Hz, B(2,3)), −13.3

(d, J_{B-H} = 130 Hz, B(4,6,8,11)), −15.2 (d, B(9,10)), −16.4 (d, B(5,12)). MS (ESI): calcd for $C_{32}H_{85}N_2{}^{10}B_2{}^{11}B_{10}S_2$, m/z = 691.734; obsd, m/z = 691.731 $(M + H)^+$.

[*n*-Bu$_4$N]$_2$[1,12-(HS)$_2$B$_{12}$H$_{10}$] ([*n*-Bu$_4$N]$_2$[9]). Starting from 0.4148 g of **6**, 0.9944 g of the product was isolated (92% yield). ^{1}H NMR (CD_3CN): δ −0.51 (br s, 2H, S*H*).^{1}H{^{11}B} NMR (CD_3CN): δ 1.24 (br s, 10H, B*H*). ^{11}B NMR (CD_3CN): δ −10.6 (s, B(1,12)), −13.2 (d, J_{B-H} = 128 Hz, B(2−11)). MS (ESI): calcd for $C_{32}H_{84}N_2{}^{10}B_2{}^{11}B_{10}S_2Na$, m/z = 713.718; obsd, m/z = 713.717 $(M + Na)^+$.

General Procedure for Preparation of (Bn$_2$S)$_2$B$_{12}$H$_{10}$. An isomer of $(Me_2S)_2B_{12}H_{10}$ (0.8−1.0 mmol) was placed in a 50 mL round-bottom flask with a 9 mm solv-seal joint and a stirbar. In a drybox, lithium wire cut into little pieces was added (molar ratio of borane to metal was about 1:30). The flask was evacuated, and 10 mL of methylamine was condensed by liquid nitrogen. Then the procedure was analogous to the one used for the synthesis of [*n*-Bu$_4$N]$_2$[(HS)$_2$B$_{12}$H$_{10}$], except that ethanol (95%) was used to destroy excess lithium. The precipitate, insoluble in ethanol, was filtered off and the solvent was removed on a flash evaporator. Acetonitrile (50 mL) was added to the residue followed by 1 mL of benzyl chloride and 0.25−0.30 g of sodium iodide, and the resulting mixture was refluxed for 2−3.5 h under nitrogen. The volatile materials were removed on the flash evaporator, the residue was partitioned between CH_2Cl_2 and water, and the organic phase was separated, dried with $MgSO_4$ and filtered. After solvent removal the crude product was chromatographed or recrystallized from an appropriate solvent.

Preparation of 1,2-(Bn$_2$S)$_2$B$_{12}$H$_{10}$ (13). Starting from 0.2210 g of 1,2-$(Me_2S)_2B_{12}H_{10}$, 0.2736 g of pure compound **13** (58%) was obtained after recrystallization of the crude product from acetone. ^{1}H NMR (CD_2Cl_2): δ 7.33−7.26 (m, 12H, C_6H_5), 7.05−7.03 (m, 8H, C_6H_5), 4.38 (d, 4H, J = 13.6 Hz, CH_aH$_b$), 4.06 (d, 4H, J = 13.6 Hz, CH$_a$H$_b$). ^{1}H{^{11}B} NMR (CD_2Cl_2): δ 1.84 (br s, 4H, B*H*), 1.65 (br s, 2H, B*H*), 1.60 (br s, 4H, B*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 131.3, 130.2, 129.6, 129.5, 47.1. ^{11}B NMR (CD_2Cl_2): δ −10.3 (s, B(1,2)), − 13.1 (d, B(9,12) and B(8,10)), −15.3 (d, J_{B-H} = 136 Hz, B(4,5,7,11)), −17.2 (d, J_{B-H} = 135 Hz, B(3,6)). MS (ESI): calcd for $C_{28}H_{39}{}^{11}B_{12}S_2$, m/z = 571.361; obsd, m/z = 571.363 $(M + H)^+$.

Preparation of 1,7-(Bn$_2$S)$_2$B$_{12}$H$_{10}$ (14). From 0.2506 g of 1,7-$(Me_2S)_2B_{12}H_{10}$, 0.4052 g of **14** (75%) was isolated after chromatography of the crude product (CH_2Cl_2−toluene, 1:1). The compound for characterization was recrystallized from toluene. ^{1}H NMR (CD_2Cl_2): δ 7.31−7.26 (m, 12H, C_6H_5), 7.14−7.12 (m, 8H, C_6H_5), 4.48 (d, 4H, J = 13.7 Hz, CH_aH$_b$), 4.02 (d, 4H, J = 13.6 Hz, CH$_a$H$_b$). ^{1}H{^{11}B} NMR (CD_2Cl_2): δ 1.80 (br s, 4H, B*H*), 1.74 (br s, 4H, B*H*), 1.58 (br s, 2H, B*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 131.8, 130.0, 129.4, 129.2, 46.9. ^{11}B NMR (CD_2Cl_2): δ −9.3 (s, B(1,7)), −13.9 (d, B(9,10)), −14.7 (d, B(5,12)), −15.4 (d, B(4,6,8,11)), −16.6 (d, B(2,3)). MS (ESI): calcd for $C_{28}H_{38}{}^{11}B_{12}S_2Na$, m/z = 593.343; obsd, m/z = 593.346 $(M + Na)^+$.

Preparation of 1,12-(Bn$_2$S)$_2$B$_{12}$H$_{10}$ (15). From 0.2638 g of 1,12-$(Me_2S)_2B_{12}H_{10}$, 0.4101 g of **15** (72%) was isolated after recrystallization of the crude product from acetonitrile−methanol. ^{1}H NMR (CD_2Cl_2): δ 7.30−7.24 (m, 12 H, C_6H_5), 7.12−7.10 (m, 8 H, C_6H_5), 4.48 (d, 4H, J_{H-H} = 13.7 Hz, CH_aH$_b$), 4.00 (d, 4H, J_{H-H} = 13.7 Hz, CH$_a$H$_b$). ^{1}H-{^{11}B} NMR (CD_2Cl_2): δ 1.73 (br s, 10H, B*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 132.0, 130.0, 129.4, 129.1, 46.9. ^{11}B NMR (CD_2Cl_2): δ −7.4 (s, B(1,12)), −15.4 (d, J_{B-H} = 137 Hz, B(2−11)). MS (ESI): calcd for $C_{28}H_{38}{}^{11}B_{12}S_2Na$, m/z = 593.343; obsd, m/z = 593.339 $(M + Na)^+$.

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Supporting Information Available: Tables of crystallographic data, positional parameters, bond lengths and bond angles, and anisotropic thermal parameters and ^{11}B−^{11}B{^{1}H} 2D COSY spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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