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S-Alkylation and S-Amination of Methyl Thioethers − Derivatives of *closo*-$[B_{12}H_{12}]^{2-}$. Synthesis of a Boronated Phosphonate, *gem*-Bisphosphonates, and Dodecaborane-*ortho*-carborane Oligomers

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Abstract: A variety of S-alkylated products was prepared by alkylation of methyl thioethers $[MeSB_{12}H_{11}]^{2-}$ (**5**), [1-(MeS)-2(7,12)-$(Me_2S)B_{12}H_{10}]^-$ (**6**−**8**), and [1,2(7,12)-$(MeS)_2B_{12}H_{10}]^{2-}$ (**9**−**11**) with alkyl halides and tosylates in acetonitrile. Since these methyl thioethers can be prepared easily in B-10-enriched form on a large scale and due to their chemical versatility, they are potentially very attractive boron entities for the design and synthesis of therapeutics for boron neutron capture therapy of cancer. It was found that alkylation of **6**−**8** can be complicated by an equilibrium which establishes between, on the one hand, one of the former species and, on the other hand, 1,2(7,12)-$(Me_2S)_2B_{12}H_{10}$ (**2**−**4**) and [1,2(7,12)-$(MeS)_2B_{12}H_{10}]^{2-}$ (**9**−**11**). A boronated phosphonate 1-$(MeS(CH_2)_4P(O)(OEt)_2)$-7-$(Me_2S)B_{12}H_{10}$ (**14g**) and a *gem*-bisphosphonate 1-$(MeS(CH_2)_3CH[P(O)(OEt)_2]_2)$-7-$(Me_2S)B_{12}H_{10}$ (**14h**) were prepared from thioether **7** and the corresponding iodide and tosylate, respectively, and subsequently converted to their sodium salts. The propargyl sulfonium salts obtained by alkylation of thioethers **7**, **8**, **10**, and **11** with propargyl bromide have been further converted to two- and three-cage oligomers containing both *ortho*-carborane and dodecaborane moieties. Methyl thioethers derived from *closo*-$[B_{12}H_{12}]^{2-}$ are excellent participants in Michael addition reactions in the presence of a strong acid. The sulfonium salts with tertiary alkyl and vinyl substituents have been prepared by this method. Methyl thioethers **5**−**11** react with hydroxylamine-*O*-sulfonate yielding the corresponding aminosulfonium salts, albeit in lower yields as compared to those in the alkylation reactions. Several derivatives of methyl thioethers **5**−**11** have been characterized by single-crystal X-ray diffraction.

Introduction

Interest in the chemistry of the icosahedral *closo*-$[B_{12}H_{12}]^{2-}$ anion has been rekindled, with increasing recognition of its versatility in forming exopolyhedral derivatives that have the potential for a wide range of applications. Hawthorne and co-workers,[1] for example, have recently reported on a series of seminal investigations that have produced and characterized several closomeric derivatives of *closo*-$[B_{12}H_{12}]^{2-}$ that are not only extremely interesting but also, as they have indicated, possess the potential for a wide range of applications, from materials to medicine. Other groups[2] have also reported on recent derivative chemistry of this ion in general, with a particular emphasis upon derivatives that might have medical applications.

Our interests are centered around the chemistry of dimethyl sulfide derivatives of *closo*-$[B_{12}H_{12}]^{2-}$: $[Me_2SB_{12}H_{11}]^-$ (**1**), 1,2-$(Me_2S)_2B_{12}H_{10}$ (**2**), 1,7-$(Me_2S)_2B_{12}H_{10}$ (**3**), and 1,12-$(Me_2S)_2$-$B_{12}H_{10}$ (**4**), most of which are readily produced from neat BH_3-SMe_2.[3] This presents, of course, the possibility for feasible large-scale syntheses of these compounds which offer many possibilities for applications. In a sense, **2**, **3**, and **4** can be viewed as exopolyhedral analogues of 1,2-, 1,7-, and 1,12-isomers of

† College of Pharmacy.

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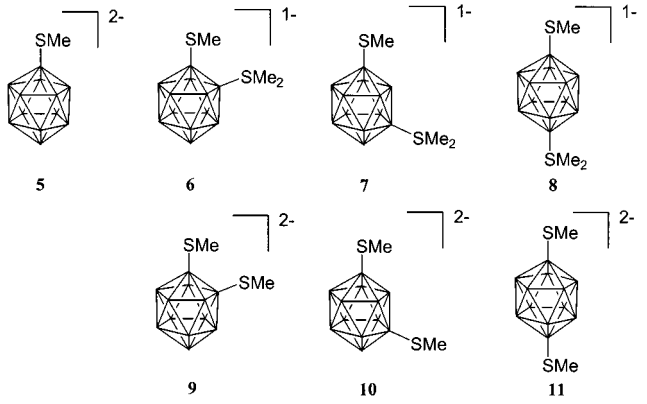
Chart 1



carborane, $C_2B_{10}H_{12}$. The derivative chemistry of sulfur, in principle, can parallel some of the rich organic chemistry observed[29] on the carbon atoms of the carborane isomers without disrupting the boron−sulfur bonds. Furthermore, the B−H vertexes are also accessible. Boron-10-enriched compounds, which are a crucial factor in the design and synthesis of boron neutron capture therapy (BNCT) agents,[4] could be produced from the relatively easily prepared isomers **2**, **3**, and **4**. In principle, analogues of many of the new systems outlined by Hawthorne[1] including their possible applications can be visualized. It should be recognized that the key precursor to icosahedral carboranes is the relatively expensive $B_{10}H_{14}$, while that for the dimethyl sulfide derivatives of $[B_{12}H_{12}]^{2-}$ is the much cheaper $NaBH_4$.

The excellent nucleophilicity of methyl thioethers derived from *closo*-$[B_{12}H_{12}]^{2-}$ was first observed by Muetterties and co-workers who obtained sulfonium salts **1** and $(Me_2S)_2B_{12}H_{10}$ (a mixture of isomers **2**−**4**) by alkylation of $[MeSB_{12}H_{11}]^{2-}$ (**5**) and $[(MeS)_2B_{12}H_{10}]^{2-}$ (a mixture of isomers **9**−**11**, Chart 1), with trimethylsulfonium iodide.[5] S-Alkylation of the methyl thioether $[(MeS)(Me_2S)B_{12}H_{10}]^-$ (a mixture of isomers **6**−**8**) by RX, where X is a halogen and R = *m*-$CH_2C_6H_4COOH$, *p*-$CH_2C_6H_4NO_2$, and *p*-$CH_2C_6H_4NH_2$, was used later by Soloway and co-workers in the synthesis of protein-binding boranes.[6]

In this paper, we report the results of extended alkylation studies using recently characterized methyl thioethers **5**−**11**[7] and a variety of alkylating reagents. In particular, tertiary alkyl and vinyl substituents can be easily introduced onto a thioether sulfur atom of **5**−**11** in Michael addition-type reactions. Obviously, the high reactivity of these methyl thioethers would allow for the facile introduction of these boron clusters into therapeutic structures either directly or through linkers such as alkyl-, vinyl-, allenyl-, propargyl-, or other groups. Indeed, using S-alkylation reactions, a phosphonate, *gem*-bisphosphonates, and dodecaborane-*ortho*-carborane oligomers have been prepared with the eventual goal of evaluation for BNCT. S-Amination of methyl thioethers with hydroxylamine-*O*-sulfonate yielded aminosulfonium salts. Although this reaction is formally analogous to the reaction of methyl thioethers with alkyl halides, apparently other processes are competing, and the yields are significantly lower.

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Results and Discussion

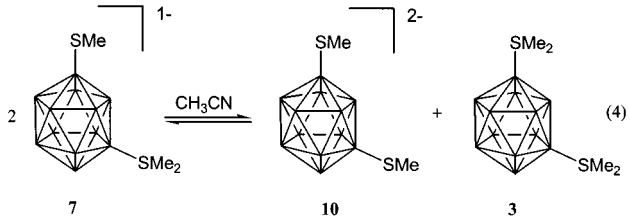
Alkylation of Methyl Thioethers 5−11 by Alkyl Halides. Primary alkyl iodides as well as allyl, benzyl, and propargyl bromides are excellent alkylating agents for thioethers **5**−**11** (eqs 1−3, Table 1). Addition of one of these reagents to a

$$\underset{\mathbf{5}}{[MeSB_{12}H_{11}]^{2-}} + RX \xrightarrow{CH_3CN} \underset{\mathbf{12a-c}}{[(MeSR)B_{12}H_{11}]^-} + X^- \quad (1)$$

$$\underset{\mathbf{6-8}}{[1\text{-}(MeS)\text{-}2(7,12)\text{-}(Me_2S)B_{12}H_{10}]^-} + RX \xrightarrow{CH_3CN} \underset{\mathbf{13},\ \mathbf{14a-l},\ \mathbf{15a}}{1\text{-}(MeSR)\text{-}2(7,12)\text{-}(Me_2S)B_{12}H_{10}} + X^- \quad (2)$$

$$\underset{\mathbf{9-11}}{[1,2(7,12)\text{-}(MeS)_2B_{12}H_{10}]^{2-}} + 2RX \xrightarrow{CH_3CN} \underset{\mathbf{16},\ \mathbf{17a-c},\ \mathbf{18a}}{1,2(7,12)\text{-}(MeSR)_2B_{12}H_{10}} + 2X^- \quad (3)$$

solution of any thioether **5**−**11** as a tetramethyl ammonium salt in acetonitrile at room temperature results in almost immediate precipitation of the corresponding halide. As expected, secondary alkyl iodides and primary alkyl bromides react considerably more slowly. We were surprised to discover that a product of alkylation of **6**−**8** was always accompanied by formation of a parent sulfonium salt $(Me_2S)_2B_{12}H_{10}$ in small quantities, when a reaction mixture was heated. However, by studying demethylation of isomers of $(Me_2S)_2B_{12}H_{10}$ by nucleophiles in DMF and CH_3CN, we noticed that the reaction of 1 equiv of a nucleophile with $(Me_2S)_2B_{12}H_{10}$ produces not only a monothioether, but also a dithioether and a starting bissulfonium salt in lesser amounts, the ratio of the last two being approximately 1:1. Considering these experimental facts, we proposed that in these solvents a thioether-sulfonium species is in equilibrium with dithioether and bissulfonium species as pictured below for the 1,7-isomer (eq 4). To prove the existence of equilibrium 4,



equimolar amounts of **3** and $[Me_4N]_2$[**10**] were placed in an NMR tube and dissolved in acetonitrile-d_3. The solution was allowed to stand at room temperature while being occasionally monitored by $^{11}B\{^1H\}$ NMR. New signals that could be attributed to thioether **7** being formed were clearly observed on the fifth day after mixing. Since the appearance of the spectrum was changing very slowly at room temperature, the solution was heated at 70° C to allow for the equilibrium to establish faster. After heating for 5 days, no further change in the spectrum, which at this point primarily featured the signals due to **7**, was observed. A similar experiment was run in acetonitrile with **4** and $[Me_4N]_2$[**11**]. At room temperature this

Table 1. Alkylation of Methyl Thioethers **5**−**11** by Alkyl Halides and Tosylates in CH_3CN

entry	thioether	alkyl halide or tosylate	alkylation product	yield (%)[a]
1	**5**	C_2H_5I	$[(MeSC_2H_5)B_{12}H_{11}]^-$, **12a**	93/77
2	**5**	CH_2I_2	$[(MeSCH_2I)B_{12}H_{11}]^-$, **12b**	80
3	**5**	$CH_3S(O)(CH_2)_2Cl$	$[(MeS(CH_2)_2S(O)Me)B_{12}H_{11}]^-$, **12c**	75/63
4	**6**	$HC{\equiv}CCH_2Br$	1-$(MeSC_3H_3)$-2-$(Me_2S)B_{12}H_{10}$, **13**	95
5	**7**	C_2H_5I	1-$(MeSC_2H_5)$-7-$(Me_2S)B_{12}H_{10}$, **14a**	99
6	**7**	CH_2I_2	1-$(MeSCH_2I)$-7-$(Me_2S)B_{12}H_{10}$, **14b**	94/88
7	**7**	$I(CH_2)_3I$	1-$(MeS(CH_2)_3I)$-7-$(Me_2S)B_{12}H_{10}$, **14c** $(\mu\text{-}CH_2)[1\text{-}(MeSCH_2)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]_2$, **14d**	80
8	**7**	$HO(CH_2)_3Br$	1-$(MeS(CH_2)_3OH)$-7-$(Me_2S)B_{12}H_{10}$, **14e**	97
9	**7**	$CH_3OC(O)(CH_2)_2Br$	1-$(MeS(CH_2)_2C(O)OMe)$-7-$(Me_2S)B_{12}H_{10}$, **14f**	97
10	**7**	$(EtO)_2P(O)(CH_2)_4I$	1-$(MeS(CH_2)_4P(O)(OEt)_2)$-7-$(Me_2S)B_{12}H_{10}$, **14g**	93
11	**7**	$[(EtO)_2P(O)]_2CH(CH_2)_3OTs$ $[(EtO)_2P(O)]_2CH(CH_2)_3OMs$	1-$(MeS(CH_2)_3CH[P(O)(OEt)_2]_2)$-7-$(Me_2S)B_{12}H_{10}$, **14h**	85 95
12	**7**	*i*-PrI	1-(*i*-PrSMe)-7-$(Me_2S)B_{12}H_{10}$, **14i**	89
13	**7**	$PhCH_2Cl$	1-(MeSBn)-7-$(Me_2S)B_{12}H_{10}$, **14j**	94
14	**7**	$H_2C{=}CHCH_2Br$	1-$(MeSC_3H_5)$-7-$(Me_2S)B_{12}H_{10}$, **14k**	99/94
15	**7**	$HC{\equiv}CCH_2Br$	1-$(MeSC_3H_3)$-7-$(Me_2S)B_{12}H_{10}$, **14l**	96
16	**8**	$HC{\equiv}CCH_2Br$	1-$(MeSC_3H_3)$-12-$(Me_2S)B_{12}H_{10}$, **15a**	94
17	**9**	$H_2C{\equiv}CCH_2Br$	1,2-$(MeSC_3H_3)_2B_{12}H_{10}$, **16**	
18	**10**	*i*-PrI	1,7-(*i*-PrSMe)$_2B_{12}H_{10}$, **17a**	99/76
19	**10**	$PhCH_2Cl$	1,7-(MeSBn)$_2B_{12}H_{10}$, **17b**	95/90
20	**10**	$HC{\equiv}CCH_2Br$	1,7-$(MeSC_3H_3)_2B_{12}H_{10}$, **17c**	92
21	**11**	$HC{\equiv}CCH_2Br$	1,12-$(MeSC_3H_3)_2B_{12}H_{10}$, **18a**	93

[a] Crude yield/yield after recrystallization.

equilibrium established even more slowly. Thus, **8** was still a minor component 139 days after mixing. However, heating at 70° C for 6 days resulted in **8** as a major component of the mixture (see Supporting Information). Thus, mixtures of similar composition, where the monoanion predominates, can be obtained from $(Me_2S)_2B_{12}H_{10}$ and $[(MeS)_2B_{12}H_{10}]^{2-}$, on the one hand, and $[(MeS)(Me_2S)B_{12}H_{10}]^-$ (demonstrated by demethylation reactions of **2**−**4**, 1:1 ratio), on the other hand, proving the existence of the proposed equilibria. Since they establish very slowly at room temperature, isomers of $(Me_2S)_2B_{12}H_{10}$ are not usually observed among the products of alkylation of **6**−**8** by primary alkyl iodides as well as allyl, benzyl, and propargyl iodides and bromides which react very rapidly. Heating a reaction mixture to increase the rate of alkylation in the case of the less reactive alkyl tosylates and chlorides also increases the rate of establishment of equilibrium 4 or similar to it, producing $(Me_2S)_2B_{12}H_{10}$ and the dialkylated product, $(MeSR)_2B_{12}H_{10}$. As a matter of fact, these equilibria can be used for the synthesis of **6**−**8** from **2**−**4** and **9**−**11**. Thus, $[Me_4N][\mathbf{7}]$ was isolated in 75% yield after reflux of a mixture of **3** and $[Me_4N]_2[\mathbf{10}]$ (1 mmol of each) in acetonitrile for 75 h. $[Me_4N][\mathbf{8}]$ was obtained in comparable yield (73%) in a similar reaction after 135 h of reflux. These yields are close to those obtained from reactions of **3** and **4** with nucleophiles (phthalimide, ethanethiolate),[7] and the simplicity of the preparation may overcome the fact that these reactions require longer times.

Interestingly, when either **5** or **7** is alkylated by CH_2I_2 (Table 1, entries 2 and 6), only the product of monosubstitution is formed, even if the reaction mixture containing excess borane is refluxed. The carbon atom is presumably too hindered for the substitution of the second iodide by the bulky sulfur nucleophile. However, the smaller ethanethiolate anion displaces iodide from $[(MeSCH_2I)B_{12}H_{11}]^-$ (**12b**) yielding $[(MeSCH_2SEt)\text{-}B_{12}H_{11}]^-$ (**12d**) upon reflux. As expected, a small amount of disubstitution product **14d** (a mixture of *meso*- and D,L-diastereomers) is formed in the reaction of thioether **7** with excess 1,3-diiodopropane (Table 1, entry 7).

Similar to allyl bromide, propargyl bromide is an excellent alkylating agent for methyl thioethers **5**−**11**. Reaction takes place almost instantly in acetonitrile. Interestingly, upon recrystallization from ethanol, 1-$(MeSC_3H_3)$-7-$(Me_2S)B_{12}H_{10}$ (**14l**) partially isomerized to its allenyl isomer (ratio propargyl:allenyl 3.9:1). Surprisingly, under similar conditions the corresponding 1,12-isomer (**15a**) did not isomerize. The conversion of a propargyl to a more stable allenyl isomer is known to occur for prop-2-ynyl sulfones and sulfonium salts.[8a] This process is catalyzed by bases. Similarly, addition of a drop of triethylamine to NMR samples of **13**, **14l**, and **15a** in CD_3CN resulted in almost complete propargyl−allenyl isomerization in a few days. Reaction of dithioether **10** with excess propargyl bromide in the presence of potassium phthalimide resulted in a mixture containing dipropargyl, diallenyl, and mixed propargyl−allenyl isomers. This mixture was separated by medium-pressure column chromatography (MPLC) using EtOAc−hexane (1:1) as an eluent yielding 14% of dipropargyl, 37% of diallenyl, and 43% of the mixed propargyl-allenyl isomer. When heated in ethanol, the propargyl−allenyl isomer produced a mixture of all three isomers. Isomerization of propargyl or allenyl groups of these sulfonium salts to a 1-methylethynyl ($CH_3{-}CC{-}$) group was never observed, although the allenyl to 1-methylethynyl isomerization has been reported previously by Zakharkin and co-workers[8b] for *ortho*- and *meta*-allenylcarboranes in the presence of a stronger base, *t*-BuOK.

Stereochemistry of Alkylation. When R is not a methyl group (eqs 1−3), prochiral methyl thioethers **5** and **6**−**8** yield racemic sulfonium salts $[(MeSR)B_{12}H_{11}]^-$ and $(MeSR)(Me_2S)\text{-}B_{12}H_{10}$. Thus, the X-ray structures of 1-(MeSR)-7-$(Me_2S)B_{12}H_{10}$ (**14i**, R = *i*-Pr, Figure 1; **14j**, R = Bn, see Supporting Information) determined by single-crystal X-ray diffraction reveal that every molecule in a unit cell is related to its

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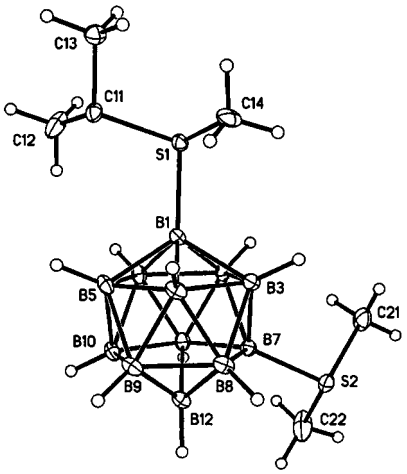
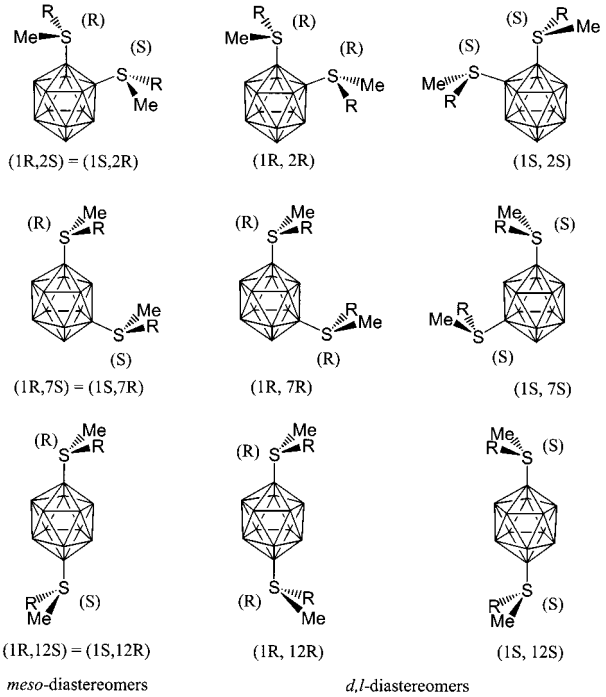


Figure 1. The molecular structure of 1-(*i*-PrSMe)-7-(Me_2S)$B_{12}H_{10}$ (**14i**) with 25% thermal ellipsoids.

Chart 2



enantiomer via a center of symmetry. Prochiral methyl dithioethers **9**−**11** produce racemic $[(MeSR)(MeS)B_{12}H_{10}]^-$ upon reaction with 1 equiv of RX. Addition of a second equivalent of RX should lead to formation of diastereomers (Chart 2). In the case of **9** and **10**, which have the same symmetry (C_{2v}), these would be a racemic mixture of (*R*,*R*)- and (*S*,*S*)-1,2(7)-$(MeSR)_2B_{12}H_{10}$ (both C_2) and achiral diastereomer *meso*-(*R*,*S*)-1,2(7)-$(MeSR)_2B_{12}H_{10}$ (C_s) possessing a mirror plane. Similarly, dialkylation of **11** would result in a racemic mixture of (*R*,*R*)- and (*S*,*S*)-1,12-$(MeSR)_2B_{12}H_{10}$ (both C_2) and *meso*-(*R*,*S*)-1,12-$(MeSR)_2B_{12}H_{10}$ (C_i), the latter compound being achiral by virtue of a center of symmetry. The presence of diastereomers is not supported by ^{1}H NMR for either 1,7- or 1,12-$(MeSR)_2B_{12}H_{10}$, as only one set of signals is observed, regardless of the identity of R. A possible explanation is that the asymmetric centers in the 1,7- and 1,12-isomers are too far from each other, which renders the environment of the corresponding protons in two diastereomers to be very similar and thus indistinguishable by

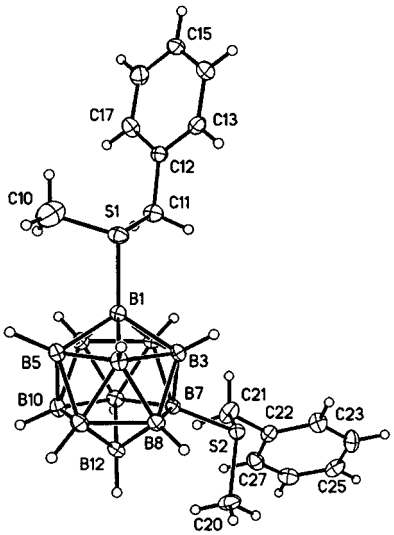


Figure 2. The molecular structure of *meso*-1,7-$(MeSBn)_2B_{12}H_{10}$ (**17b**) with 25% thermal ellipsoids.

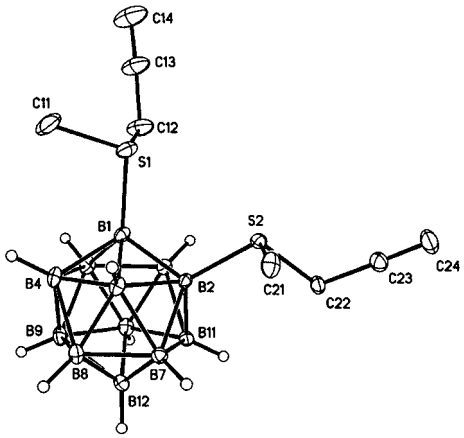
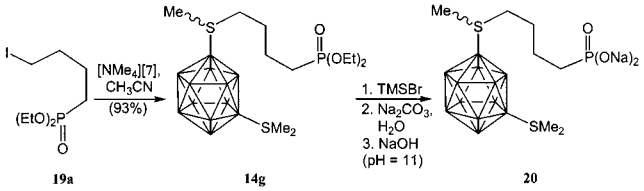


Figure 3. The molecular structure of *meso*-1,2-$(MeSC_3H_3)_2B_{12}H_{10}$ (**16**) with 25% thermal ellipsoids. Hydrogen atoms on carbons are omitted for clarity.

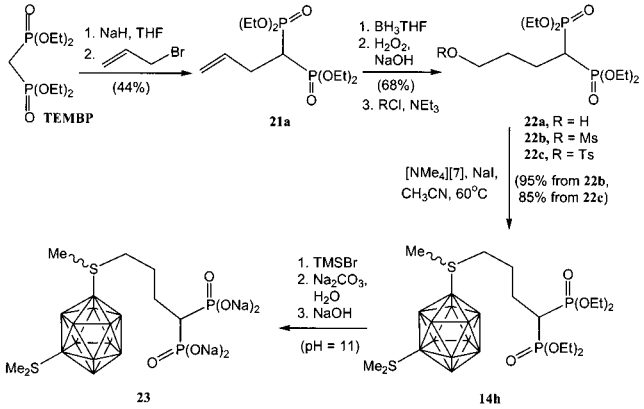
NMR. The molecular structure of 1,7-$(MeSBn)_2B_{12}H_{10}$ (**17b**) (Figure 2) revealed that the chosen crystal was of the *meso*-diastereomer, but other crystals were not examined for the presence of the D,L-diastereomer. However, the asymmetric centers in 1,2-$(MeSR)_2B_{12}H_{10}$ are close to each other; therefore, the ^{1}H NMR spectrum of **16** displays two sets of signals, one for the *meso*- and another for the D,L-diastereomer. Unfortunately, only the *meso*-diastereomer of **16** produced X-ray quality crystals from a dichloromethane solution of the mixture of diastereomers (Figure 3).

Synthesis of Boronated Phosphonate and *gem*-Bisphosphonates by Alkylation of 7 with Primary Alkyl Iodides and Tosylates. A phosphonate and a *gem*-bisphosphonate containing an icosahedral borane cage were synthesized for potential use as BNCT agents. The rationale for their syntheses stems from previous biological studies indicating that certain phosphorus-containing boron clusters are selectively taken up to a high extent in tumor/rodent models.[9a] Also, due to their selective uptake in primary and metastatic bone tumors, bis- and polyphosphonates have found wide application in the diagnosis and therapy of these cancers.[9b−e] Recently, targeted radiotherapy of bone tumors with α-emitter-containing phosphonates has been proposed.[9f,g] Thus, boronated derivatives of bisphosphonates

Scheme 1. Synthesis of Boronated Phosphonate **14g** and Its Sodium Salt **20**



Scheme 2. Synthesis of *gem*-Bisphosphonate **14h** and Its Sodium Salt **23**



may have potential for the palliative and possibly curative treatment of primary and metastatic bone tumors by BNCT.

Taking advantage of the excellent reactivity of methyl thioether **7** toward primary alkyl iodides and the hydrolytic stability of the resulting S−C linkage, a boronated diethyl butylphosphonate **14g** was synthesized according to Scheme 1. Synthesis of a similar compound containing a terminal *gem*-bisphosphonate group presented a greater challenge. Tetraethyl 1-iodo-4,4-bisphosphonobutane (**19b**) is not available via the alkylation of tetraethyl methylene bisphosphonate (TEMBP) by 1,3-diiodopropane (Scheme 2). From the reaction in THF only the elimination product, tetraethyl 1,1-bisphosphonobut-3-ene (**21a**), was isolated, while the reaction in toluene produced tetraethyl cyclobutane-1,1-bisphosphonate (**21b**) and **21a**. Ebetino et al.[10] isolated tetraisopropyl cyclobutane-1,1-bisphosphonate in 70% yield from the reaction of tetraisopropyl methylenebisphosphonate with propane-1,3-ditosylate under similar conditions. An attempt to alkylate TEMBP with a sulfonium salt bearing a terminal iodide (**14c**) was also unsuccessful as iodide was mostly eliminated under the reaction conditions yielding **14k**, identified by comparison with the spectrum of the authentic sample prepared according to eq 2. The desired bisphosphonate **14h** was obtained in only 19% yield; therefore, it was decided to return to a synthetic scheme where **14h** is obtained by alkylation of thioether **7** by a halide or tosylate already bearing the bisphosphonate moiety. Keeping in mind that **21a** formed easily in the alkylation of TEMBP by 1,3-diiodopropane, we prepared **21a** using allylbromide as an alkylating reagent. Since the resulting mixtures containing the monoalkylated product along with some dialkylated product and TEMBP were difficult to separate, the entire mixture was usually subjected to the hydroboration-oxidation procedure.[11] Tosylation or mesylation of a residue consisting of monoalcohol and TEMBP (diol is lost in the workup) afforded a mixture of sulfonate ester **22b** (**22c**) and TEMBP, which was easier to separate. Reaction of a sulfonate ester with the tetramethylammonium salt of **7** in acetonitrile is sluggish even upon heating; however, addition of dry NaI dramatically improves the rate of conversion. An alternative procedure for the preparation of **22a** has been recently reported by Sturtz and co-workers.[13] Ethyl esters **14g** and **14h** were converted into the sodium salts of the corresponding phosphonic and bisphosphonic acids, respectively, by treatment with excess bromotrimethylsilane (TMSBr) followed by the carbonate-buffered hydrolysis of the resulting trimethylsilyl esters and adjusting the pH of solutions to 11 with aqueous NaOH.[14] Ethyl esters **14g** and **14h** are the first examples of compounds containing both a *closo*-B_{12} moiety and a phosphonate or bisphosphonate group, although similar compounds based on *ortho*-carborane have been reported.[15] The sodium salts **20** and **23** were subjected to in vivo evaluation for BNCT using various tumor/rodent models.[16] In particular, **23** showed very promising results in an osteosarcoma/mouse model.

Nucleophilic Addition of Methyl Thioethers to Activated Alkenes and Alkynes. Alkylation of methyl thioethers by alkyl halides and tosylates has its usual limitations. Only primary and secondary alkyl groups can be introduced. However, addition of a nucleophile to an electron-deficient alkene (Michael addition) is not affected by steric problems nearly as much since the carbon to be attacked is sp^2-hybridized. Organic thioethers are known to form sulfonium salts upon reaction with activated alkenes.[17] Similarly, thioethers **5**−**11** react with a variety of α,β-unsaturated substrates (Table 2, Scheme 3) in the presence of a strong acid, such as HCl. As expected, tertiary substituents can be introduced easily by this method. When an electron-deficient alkyne was used (propiolic acid), vinyl sulfonium salts **25a**,**b** were produced, a result not available by a simple alkylation. The presence of a strong acid is absolutely necessary to drive the reaction to completion by trapping the intermediate carbanion, which is in equilibrium with the starting materials. The reaction of methyl thioethers with acrylonitrile under acidic conditions reported here is a reverse of the retro-Michael reaction reported by Gabel and co-workers[18] in which $[(RSCH_2CH_2CN)B_{12}H_{11}]^-$ and $[Me_4N]OH$ yielded acrylonitrile and

(9) (a) Bechtold, R. A.; Kaczmarczyk, A.; Messer, J. R. *J. Med. Chem.* **1975**, *18*, 371−376. (b) Brown, D. L.; Robbins, R. *J. Clin. Pharmacol.* **1999**, *39*, 651−660. (c) Bruland, O. S.; Aas, M.; Solheim, O. P.; Vindern, M.; Hoie, J. *Bone Miner*. **1994**, *25*, 497−499. (d) Bruland, O. S.; Skretting, A.; Solheim, O. P.; Aas, M. *Acta Oncol*. **1996**, *35*, 380−384. (e) Lattimer, J. C.; Corwin, L. A. J.; Stapleton, J.; Volkert, W. A.; Ehrhardt, G. J.; Ketring, A. L.; Anderson, S. K.; Simon, J.; Goeckler, W. F. *J. Nucl. Med.* **1990**, *31*, 1316−1325. (f) Hassfjell, S. P.; Hoff, P.; Bruland, O. S.; Alstad, J. *J. Labelled Compd. Radiopharm.* **1994**, *34*, 717−734. (g) Hassfjell, S. P.; Bruland, O. S.; Hoff, P. *Nucl. Med. Biol.* **1997**, *24*, 231−237.

(10) Ebetino, F. H.; Degenhardt, C. R.; Jamieson, L. A.; Burdsall, D. C. *Heterocycles* **1990**, *30*, 855−862.

(11) The alternative preparation of **21a** by phosphonylation of diethyl phosphonobut-3-ene[12] did not produce a higher yield of the desired bisphosphonate in our hands.

(12) Dufau, C.; Sturtz, G. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *69*, 93−102.

(13) Gourves, J.-P.; Couthon, H.; Sturtz, G. *Phosphorus, Sulfur Silicon Relat. Elem.* **1998**, *132*, 219−229.

(14) Gross, H.; Keitel, I.; Costisella, B.; McKenna, C. E. *Phosphorus, Sulfur Silicon Relat. Elem.* **1991**, *61*, 177−181.

(15) (a) Semioshkin, A.; Lemmen, P.; Inyushin, S.; Ermanson, L. In *Advances In Boron Chemistry*; Siebert, W., Ed.; The Royal Society of Chemistry: Cambridge, 1997; pp 311−314. (b) Komagata, T.; Kawanabe, T.; Matsushita, T. Japanese Patent 11080177 A2 990326 Heisei, 1999.

(16) (a) Kultyshev, R. G.; Tjarks, W.; Adams, D. M.; Rotaru, J.; Barth, R. F.; Soloway, A. H.; Shore, S. G. Abstracts of ACS 31st Central Regional Meeting; The Ohio State University, Columbus, Ohio, June 21−23, 1999. (b) Tjarks, W.; Barth, R. F.; Rotaru, J.; Adams, D. M.; Yang, W.; Kultyshev, R. G.; Forrester, J.; Barnum, B. A.; Soloway, A. H.; Shore, S. G. *Anticancer Res.* **2001**, *21*, 841−846.

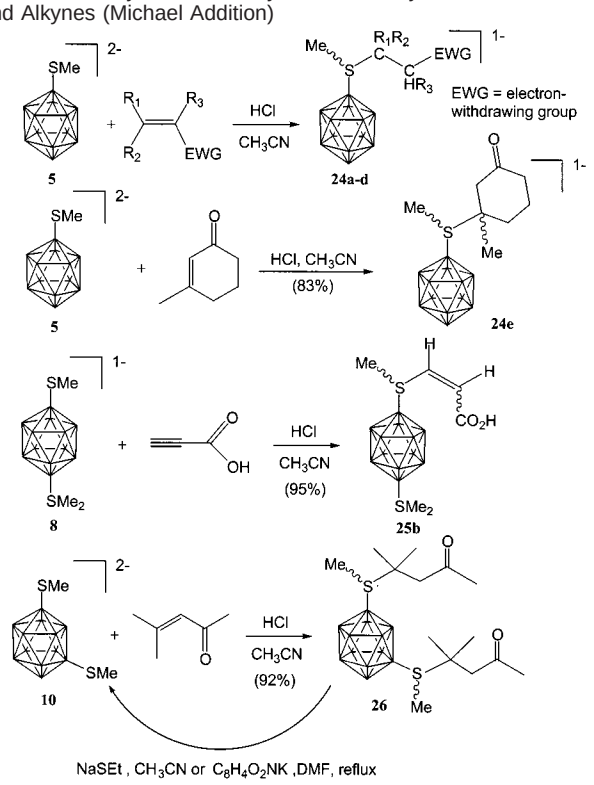
(17) Stirling, C. J. M. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum Press: New York, 1977; pp 473−525.

Table 2. Alkylation of Methyl Thioethers **5** and **10** by Activated Alkenes (Michael Addition)

entry	thioether	R_1	R_2	R_3	EWG[a]	product	yield, %[b]
1	**5**	H	H	H	CN	$[(MeSCH_2CH_2CN)B_{12}H_{11}]^-$, **24a**	85/70[c]
2	**5**	Ph	H	H	Ac	$[(MeSCHPhCH_2C(O)Me)B_{12}H_{11}]^-$, **24b**	93[c]
3	**5**	H	H	$P(O)(OEt_2)_2$	$P(O)(OEt_2)_2$	$[(MeSCH_2CH[P(O)(OEt)_2]_2)B_{12}H_{11}]^-$, **24c**	89[c]
4	**5**	Me	Me	H	Ac	$[(MeSCMe_2CH_2C(O)Me)B_{12}H_{11}]^-$, **24d**	88/52[c]
5	**10**	Me	Me	H	Ac	1,7-$(MeSCMe_2CH_2C(O)Me)_2B_{12}H_{10}$, **26**	92

[a] Electron-withdrawing group. [b] Crude yield/yield after recrystallization. [c] Isolated as tetramethylammonium salt.

Scheme 3. Alkylation of Methyl Thioethers by Activated Alkenes and Alkynes (Michael Addition)



$[RSB_{12}H_{11}]^{2-}$ (a leaving group) via β-hydrogen abstraction. Although we did not attempt similar retro-Michael reactions using $[Me_4N]OH$, the same result was obtained when we tried to remove both methyl groups in **26** by excess NaSEt or potassium phthalimide. Instead of the expected dithioether featuring tertiary substituents on each sulfur atom, dithioether **10** was obtained as the only boron product (Scheme 3). This was confirmed by methylation of the reaction product with methyl iodide and isolation of **3**.

A modest degree of diastereoselectivity was observed in the conjugate addition reactions of substrates possessing two different substituents at the β-carbon. Thus, for *trans*-4-phenyl-3-butene-2-one and **5** the ratio of diastereomeric products is 4.4:1, as calculated from the integration data of the ^{1}H NMR spectrum. Unfortunately, it was not possible to determine whether the major product has a syn or anti relative stereochemistry. A lower degree of diastereoselectivity (approximately 3:2 ratio) was observed when the same thioether reacted with 3-methyl-2-cyclohexen-1-one. The *Z*/*E* product ratio for the reaction of thioethers **7** and **8** with an excess of propiolic acid seems to depend on the time of stirring and favors the more stable *E*-isomer at longer reaction times. Thus, for **7** it was 1.8:1

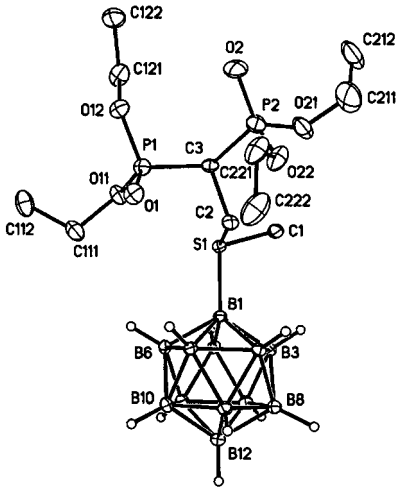


Figure 4. The molecular structure of $[(MeSCH_2CH[P(O)(OEt)_2]_2)B_{12}H_{11}]^-$ (**24c**) with 25% thermal ellipsoids. Hydrogen atoms on carbons are omitted for clarity.

after 45 min and 1:1.15 after 20 h. Similarly, when **8** was used as a nucleophile, the *Z*/*E* product ratio also decreased as the reaction time increased from 40 min to 24 h (1.7:1 vs 1.3:1, respectively). The *E*- and *Z*-proton signals were assigned from the values of the coupling constants of the vicinal vinyl protons.[19]

Hutchinson and Thornton[20] have shown that tetraalkyl ethenylidene bisphosphonates can participate in Michael addition reactions with various nucleophiles, giving especially good results with thiols. Keeping in mind that methyl thioethers **5**−**11** are excellent nucleophiles, Michael addition was used as an alternative route to the boronated *gem*-bisphosphonates. Reaction of the readily available tetraethyl ethenylidene bisphosphonate[21] with thioether **5** afforded **24c** (Figure 4), a charged homologue of bisphosphonobutane **14h** having one less Me_2S substituent, in 89% yield.

NMR Spectra of the Alkylation Products. When R is a primary alkyl group, the $^{11}B\{^1H\}$ NMR spectra of $[(MeSR)B_{12}H_{11}]^-$, $(MeSR)(Me_2S)B_{12}H_{10}$, and $(MeSR)_2B_{12}H_{10}$ are not very different from those of $[Me_2SB_{12}H_{11}]^-$ and $(Me_2S)_2B_{12}H_{10}$ and therefore are not reported in the Experimental Section. However, replacing R with a secondary or tertiary alkyl group significantly modifies the appearance of the spectrum. Thus, while the signals due to the B(5,12) and B(4,6,8,11) overlap in the spectra of 1,7-$(Me_2S)_2B_{12}H_{10}$ and 1-(MeSR)-7-$(Me_2S)B_{12}H_{10}$ (R = Et, CH_2I, $(CH_2)_3I$) even at 160.5 MHz, all signals are resolved in the spectra of **14i** (R = *i*-Pr) and 1,7-(*i*-$PrSMe)_2B_{12}H_{10}$ (**17a**) because of the shift of the peak of intensity

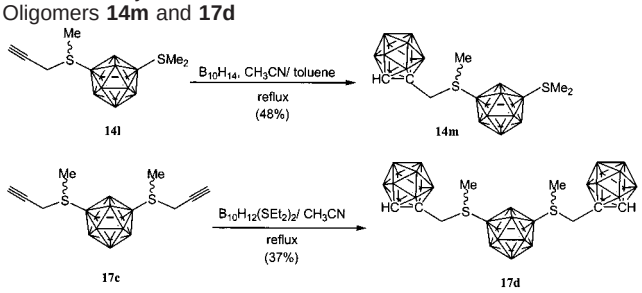
(18) Gabel, D.; Moller, D.; Harfst, S.; Rosler, J.; Ketz, H. *Inorg. Chem.* **1993**, *32*, 2276−2278.

(19) Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1998.

(20) Hutchinson, D. W.; Thornton, D. M. *J. Organomet. Chem.* **1988**, *346*, 341−348.

(21) Degenhardt, C. R.; Burdsall, D. C. *J. Org. Chem.* **1986**, *51*, 3488−3490.

Scheme 4. Synthesis of *ortho*-Carborane-dodecaborane Oligomers **14m** and **17d**



2 downfield. In the case of compound **26**, this signal moves downfield even further and overlaps with another signal of intensity 2 due to B(9,10) (see Supporting Information). The presence of the vinyl substituent on a sulfur atom (**25a**,**b**) does not lead to any significant changes in the $^{11}B\{^1H\}$ NMR spectra of these compounds as compared to those of **3** and **4**. The characteristic feature of ^1H NMR spectra of alkylated products is the presence of two diastereotopic methylene hydrogens (or any other identical groups attached to the carbon atom next to asymmetric sulfur atom). These hydrogens usually appear downfield from the Me_2S singlet as an "AB quartet". For $(MeSR)(Me_2S)B_{12}H_{10}$ the MeS signal is upfield from the Me_2S when R is an alkyl group such as Et, *i*-Pr, Bn, or allyl. The presence of an electron-withdrawing group in R causes this order to reverse (R = CH_2I (**12b**), $(CH_2)_2C(O)OMe$ (**14f**), C_3H_3 (**13**, **14l**, and **15a**)). When an electron-withdrawing group is attached to a γ-carbon and further, the Me_2S and MeS resonances have almost the same chemical shifts as in **14c**, **14e**, **14g**, and **14h**.

Synthesis of Dodecaborane-*ortho*-carborane Oligomers. A number of open-chain and macrocyclic compounds containing several carborane nuclei have been reported.[22] In these compounds the cages are linked either by vertexes (C−C, C−B) or some spacer like $-(CH_2)_3-$ or a disubstituted benzene ring. Recently, oligomeric structures containing a number of *nido*-*o*-carboranyl clusters have received considerable attention as potential BNCT agents.[23a] However, similar systems incorporating the *closo*-B_{12} cage, which may also serve as valuable boron moieties in BNCT agents, have been less well studied.[23b] The use of boron cluster entities containing different types of boron cages has been proposed as an innovative strategy in the synthesis of BNCT agents.[2d,23c] We used propargyl sulfonium salts **14l**, **15a**, **17c**, and **18a** as starting materials in the synthesis of two- and three-cage compounds **14m**, **15b**, **17d**, and **18b**, respectively, containing both *o*-carborane and dodecaborane cages linked together via $-CH_2-S(Me)-$ units as shown in Scheme 4 for **14l** and **17c**. The isolated yields are moderate in the case of two-cage compounds (40−50%) and even lower for three-cage compounds (25−40%). Both $B_{10}H_{12}(SEt_2)_2$ and $B_{10}H_{12}(CH_3CN)_2$ complexes were used as starting materials to form the *o*-carborane nucleus, and neither was of particular advantage. Since the presence of allenyl isomers was never detected after these reactions, it seems unlikely that the partial isomerization of propargyl sulfonium salts is responsible for these moderate yields. The yields can be definitely improved if a better way of separation of the two- and three-cage products from the unreacted propargyl starting materials can be found. The molecular structures of both **14m** and **15b** were determined; the latter is shown in Figure 5 (see Supporting Information for the structure of **14m**). The $^{11}B\{^1H\}$ NMR spectrum of a two- or three-cage compound appears to be a sum of the spectra of the corresponding sulfonium salt (**3** or **4**) and monoalkyl C-substituted *ortho*-carborane, 1-R-1,2-$C_2B_{10}H_{11}$, taken with a coefficient 1 or 2 depending on the number of the *ortho*-carborane units present. Ten signals can be found in the spectra of **14m** and **17d** (see Supporting Information). Among those, five belong to the 1,7-disubstituted dodecaborane unit, and the other six can be assigned to the *ortho*-carborane unit(s), with the overall number of signals being reduced to 10 due to the overlap of the borane B(1,7) singlet and one of the *ortho*-carborane signals at −8.5 ppm. There is no such overlap in the spectra of **15b** and **18b**; therefore, the expected number of signals (eight) is observed, two of which are due to the 1,12-disubstituted dodecaborane unit. The $^1H\{^{11}B\}$ NMR spectra of these compounds are also sums of the spectra of the appropriately substituted $B_{12}H_{10}$ and 1,2-$C_2B_{10}H_{11}$ units. Structure **17d** in Scheme 4 can be considered as a model building block for the possible preparation of novel boron oligomers and polymers composed of different types of boron clusters. Variation of length and type of the spacer arms as well as specific removal of some or all *S*-methyl groups in such oligopolymers could potentially produce "custom-tailored" boron trailers for various types of receptor-targeting approaches in BNCT.

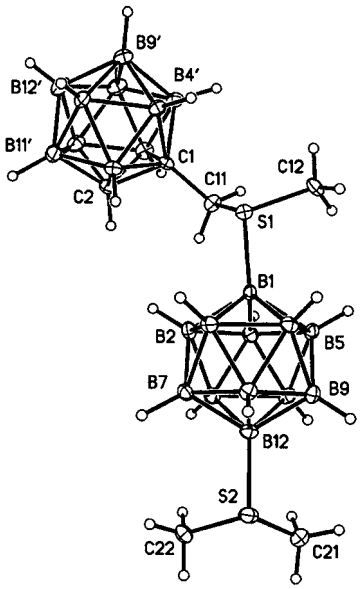


Figure 5. The molecular structure of 1-(1′,2′-$C_2B_{10}H_{11}CH_2SMe$)-12-(Me_2S)$B_{12}H_{10}$ (**15b**) with 25% thermal ellipsoids.

Amination of Methyl Thioethers with Hydroxylamine-*O*-sulfonate. Hertler and Raasch reported[24] that *closo*-$[B_{12}H_{12}]^{2-}$ and $[Me_3NB_{12}H_{11}]^-$ react with potassium hydroxylamine-*O*-sulfonate to yield B-substituted products, $(H_3N)_2B_{12}H_{10}$ and $(Me_3N)(H_3N)B_{12}H_{10}$, believed to be mostly 1,7-isomers.

(22) (a) Chizhevsky, I. T.; Johnson, S. E.; Knobler, C. B.; Gomez, F. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1993**, *115*, 6981−6982. (b) Clegg, W.; Gill, W. R.; MacBride, J. A. H.; Wade, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1328−1329.

(23) (a) Nakanishi, A.; Guan, L.; Kane, R. R.; Kasamatsu, H.; Hawthorne, M. F. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 238−241. (b) Gula, M.; Perleberg, O.; Gabel, D. In *Contemporary Boron Chemistry*; Davidson, M., Hughes, A. K., Marder, T. B., Wade, K., Eds.; The Royal Society of Chemistry: Cambridge, 2000; pp 115−119. (c) Hosmane, N. S.; Franken, A.; Zhang, G.; Srivastava, R. R.; Smith, R. Y.; Spielvogel, B. F. *Main Group Met. Chem.* **1998**, *21*, 319−324.

(24) Hertler, W. R.; Raasch, M. S. *J. Am. Chem. Soc.* **1964**, *86*, 3661−3668.

$[1\text{-}(Me_2S)B_{10}H_9]^-$ produced $1\text{-}(Me_2S)\text{-}6\text{-}(H_3N)B_{10}H_8$. Since the directive effect of the electron-rich methylthio group might be the opposite of that of the dimethyl sulfide substituent, it was hoped that methyl thioethers would react with substitution on the boron adjacent to the already substituted boron atom. Thus, $[Me_2SB_{12}H_{11}]^-$ would form $1\text{-}(Me_2S)\text{-}2\text{-}(H_3N)B_{12}H_{10}$, which may be envisioned as a precursor for an interesting *S*,*N*-bidentate ligand $[1\text{-}(MeS)\text{-}2\text{-}(H_2N)B_{12}H_{10}]^{2-}$. Unfortunately, the sulfur atoms in methyl thioethers are too nucleophilic for the amination to occur at a boron site, and aminosulfonium salts are produced instead (eqs 5−7) in a reaction similar to S-alkylation by alkyl

$$\underset{\mathbf{5}}{[MeSB_{12}H_{11}]^{2-}} + [H_2NOSO_3]^- \xrightarrow{CH_3CN,\ H_2O} \underset{\mathbf{27}}{[(MeSNH_2)B_{12}H_{11}]^-} + SO_4^{2-} \quad (5)$$

$$\underset{\mathbf{7-8}}{[1\text{-}(MeS)\text{-}7(12)\text{-}(Me_2S)B_{12}H_{10}]^-} + [H_2NOSO_3]^- \xrightarrow{CH_3CN,\ H_2O} \underset{\mathbf{28-29}}{1\text{-}(MeSNH_2)\text{-}7(12)\text{-}(Me_2S)B_{12}H_{10}} + SO_4^{2-} \quad (6)$$

$$\underset{\mathbf{10-11}}{[1,7(12)\text{-}(MeS)_2B_{12}H_{10}]^{2-}} + 2[H_2NOSO_3]^- \xrightarrow{CH_3CN,\ H_2O} \underset{\mathbf{30-31}}{1,7(12)\text{-}(MeSNH_2)_2B_{12}H_{10}} + 2SO_4^{2-} \quad (7)$$

halides or tosylates. Despite this similarity, the yields of S-aminated products are generally lower than those of the sulfonium salts, and their isolation always requires chromatography due to the presence of unidentified side products.

The $^{11}B\{^1H\}$ NMR spectra of **27** and **30**−**31** are very similar to those of their parent sulfonium salts, except that the substituted boron atoms resonate at a slightly lower field in the former case. The *ipso*-boron atoms in **28** and **29** give rise to two distinct singlets in a 1:1 ratio due to the $MeSNH_2$ and Me_2S substituents. Presumably, the most downfield signal is due to the boron bearing the $MeSNH_2$ group. S-Amination results in a downfield shift of methyl resonances in ^1H NMR spectra of the aminosulfonium salts as compared to those of the parent sulfonium compounds. All resonances in the spectra of compounds with the 1,7-substitution pattern are located slightly downfield from the corresponding resonances of the 1,12-substituted aminosulfonium salts, as was the case with parent sulfonium salts **3** and **4**. The molecular structure of *meso*-1,12-$(H_2NSMe)_2B_{12}H_{10}$ (**31**) was determined by single-crystal X-ray diffraction (Figure 6).

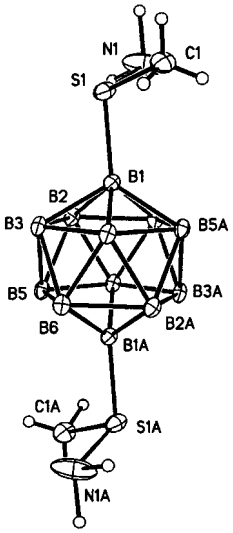


Figure 6. The molecular structure of *meso*-1,2-$(MeSNH_2)_2B_{12}H_{10}$ (**31**) with 25% thermal ellipsoids.

Experimental Section

General Methods. Tetramethylammonium salts of methyl thioethers **5**−**11** were prepared according to the previously published methods.[7] Diethyl 1-iodo-4-phosphonobutane (**19a**) was obtained according to the procedure of Kim et al.[25] All alkylating reagents except mesityl oxide (Acros Organics) were purchased from Aldrich. Chromatography was performed on Selecto silica gel (230−430 mesh). Radial chromatography was performed on Chromatotron (model 8924, Harrison Research). For separation of boron compounds, fractions obtained after chromatography were analyzed by TLC using the palladium dichloride stain. ^1H NMR spectra were obtained on Bruker DRX-500, DPX-400, and AM-250 spectrometers at 500.1, 400.1, and 250.1 MHz, respectively, and referenced to residual solvent protons. ^{13}C NMR spectra were obtained on Bruker DRX-500, DPX-400, and AM-250 spectrometers operating at 125.8, 100.6, and 62.9 MHz, respectively, and referenced to deuterated solvent signals. ^{11}B spectra were obtained on the Bruker DRX-500 spectrometer at 160.5 MHz and referenced externally to $BF_3{\cdot}OEt_2$ in C_6D_6 ($\delta = 0.00$ ppm). ^{31}P NMR spectra were obtained on Bruker DRX-500 and AM-250 spectrometers operating at 202.5 and 101.3 MHz, respectively, and referenced externally to 85% H_3PO_4. Coupling constants are reported in Hertz. The mass spectra were recorded either on the Micromass QTOF Electrospray (ESI) or on the VG-70 (EI) mass spectrometers. Elemental analyses were performed by Galbraith Laboratories, Inc., of Knoxville, TN. Complete syntheses are described in Supporting Information.

General Procedure for the Synthesis of $[(MeSR)B_{12}H_{11}]^-$ by Reaction of 5 with Alkyl Halides. To a solution of $[Me_4N]_2$[**5**] (1−2 mmol) in acetonitrile (15−20 mL) was added an excess of alkyl halide, and the resulting mixture was stirred overnight at room temperature. The volatile materials were removed in vacuo leaving behind a residue, which was washed with water, cold ethanol, and pentane and was dried overnight at 70 °C.

General Procedure for the Synthesis of $[(MeSR)B_{12}H_{11}]^-$ by Reaction of 5 with Activated Alkenes (Michael Addition). Concentrated HCl (0.3−0.5 mL) was added to a solution containing 0.8−1.0 mmol of $[Me_4N]_2$[**5**] and an excess of an activated alkene in 20−30 mL of acetonitrile. The resulting mixture was stirred overnight and concentrated in vacuo. The residue was washed with water, cold ethanol, and pentane and was dried overnight at 70 °C.

General Procedure for the Synthesis of $(MeSR)(Me_2S)B_{12}H_{10}$ and $(MeSR)_2B_{12}H_{10}$. In a typical experiment, 0.5−1.0 mmol of $[Me_4N]$-$[(MeS)(Me_2S)B_{12}H_{10}]$ or $[Me_4N]_2$ $[(MeS)_2B_{12}H_{10}]$ in a 100 mL round-bottom flask is dissolved in 15−25 mL of acetonitrile, and excess alkyl halide is added. After overnight stirring, volatiles are removed on a flash evaporator, and a residue is partitioned between dichloromethane and water. After phase separation, an aqueous phase is extracted with a fresh portion of CH_2Cl_2, and the organic phases are combined and dried over $MgSO_4$. The crude products are obtained after solvent removal under reduced pressure and purified by chromatography and/or recrystallization.

$[Me_4N][(MeSCH_2SEt)B_{12}H_{11}]$ ($[Me_4N][12d]$). A 50 mL three-neck round-bottom flask equipped with a condenser, stirbar, and rubber

(25) Kim, C. U.; Luh, B. Y.; Misco, P. F.; Bronson, J. J.; Hitchcock, M. J. M.; Ghazzouli, I.; Martin, J. C. *J. Med. Chem.* **1990**, *33*, 1207−1213.

septum was charged in a drybox with 0.0406 g of sodium (1.76 mmol) followed by addition of 5 mL of ethanol. When gas evolution ceased, 0.13 mL of ethanethiol (1.703 mmol) was added by syringe followed by a solution of 0.6401 g of [Me_4N][**12b**] (1.588 mmol) in 10 mL of acetonitrile. The resulting mixture was refluxed for 2.5 h, the volatile materials were removed under reduced pressure, and the residue was recrystallized from water providing the title compound as a white solid (0.3947 g, 74%). ^{1}H NMR (CD_3CN, 500 MHz): δ 4.17 (d, 1H, $^2J_{HH}$ = 13.9, SCH_aH$_b$S), 3.87 (d, 1H, $^2J_{HH}$ = 13.9, SCH$_a$$H_b$S), 3.08 (s, 12H, N(C$H_3$)$_4$), 2.73−2.67 (m, 2H, SC$H_2CH_3$), 2.54 (s, 3H, SC$H_3$), 1.26 (t, 3H, $^3J_{HH}$ = 7.4, CH$_2$CH_3). ^{13}C{^{1}H} NMR (CD_3CN): δ 56.3 (t, J_{CN} = 4), 47.1, 27.2, 23.3, 14.6. MS (ESI): calcd for $C_4H_{21}{}^{10}B_2{}^{11}B_{10}S_2$, *m*/*z* = 263.2278. Obsd, *m*/*z* = 263.2290 (M^-).

1-(MeS(CH$_2$)$_4$P(O)(OEt)$_2$)-7-(Me$_2$S)B$_{12}$H$_{10}$ (14g). A solution of [Me_4N][**7**] (0.9605 g, 2.972 mmol) and **19a** (1.0366 g, 3.24 mmol) in 20 mL of acetonitrile was stirred for 22.5 h. After a standard workup procedure the crude product was chromatographed using a EtOAc−MeOH mixture (9:1) as an eluent. The product free of solvents was obtained as a colorless oil (1.2202 g, 93%) after 2 days of heating on the vacuum line at 100 °C (oil bath). ^{1}H NMR ($CDCl_3$): δ 4.14−4.04 (m, 4H, OCH_2CH$_3$), 3.10−3.02 (m, 1H, SCH_aH$_b$), 2.81−2.74 (m, 1H, SCH$_a$$H_b$), 2.53 (s, 6H, S(C$H_3$)$_2$), 2.52 (s, 3H, SC$H_3$), 1.94−1.68 (m, 6H, C$H_2CH_2CH_2$P), 1.33 (t, 6H, OCH$_2CH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 61.8 (d, $^2J_{CP}$ = 6.3, OCH_2), 42.4 (s, SCH_2), 26.7 (d, *J* = 14.8), 25.8 (s, S(CH_3)$_2$), 25.0 (d, $^1J_{CP}$ = 141.9, CH_2P), 23.6 (s, SCH_3), 21.7 (d, *J* = 4.5), 16.6 (d, $^3J_{CP}$ = 5.8). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 31.2. Anal. Calcd: C, 29.87; H, 8.43. Found: C, 29.61; H, 8.74.

1-(MeS(CH$_2$)$_4$P(O)(ONa)$_2$)-7-(Me$_2$S)B$_{12}$H$_{10}$·*x*H$_2$O (20). Dry dichloromethane (15 mL) was condensed on the vacuum line into a 100 mL round-bottom flask containing 1.0139 g of diethyl ester **14g** and a stirbar. In the drybox, 1.22 mL of 97% TMSBr (8.97 mmol) was added by syringe. After the solution was stirred in the sealed flask for 24 h, the ^{31}P{^{1}H} NMR spectrum of the solution indicated the complete conversion of the diethyl ester to the bis(trimethylsilyl) ester having a single signal at 15.3 ppm. The volatile materials were removed under reduced pressure, and the solution of sodium carbonate (0.302 g, 2.85 mmol) in 6 mL of water was added to the residue causing a white solid to precipitate. A small amount of acetone was added to dissolve the precipitate, and the resulting solution was stirred overnight in a beaker. After filtration, 1 mL of aqueous 3M NaOH was added to the solution to adjust the pH approximately to 11. The solution was transferred into a 250 mL round-bottom flask followed by removal of water on the rotary evaporator with heating. The off-white residue was redissolved in 10 mL of water and transferred into a 500 mL Erlenmeyer flask followed by addition of 350 mL of 2-propanol. The white precipitate was filtered off, washed with 10 mL of ethanol (95%) and pentane, and dried overnight at 70 °C. The product (0.7459 g, 76%) is hygroscopic; therefore, the yield is only approximate. ^{1}H NMR (CD_3-OD, 500 MHz): δ 3.05−2.99 (m, 1H, SCH_aH$_b$), 2.88−2.82 (m, 1H, SCH$_a$$H_b$), 2.511 (s, 6H, S(C$H_3$)$_2$), 2.508 (s, 3H, SC$H_3$), 1.85−1.65 (m, 4H, S(Me)CH_2CH_2), 1.50−1.44 (m, 2H, CH_2P(O)(ONa)$_2$). ^{13}C{^{1}H} NMR (CD_3OD, 125.8 MHz): δ 44.0, 30.8 (d, $^1J_{CP}$ = 130), 29.1 (d, $^2J_{CP}$ = 17), 26.0, 25.2 (d, $^3J_{CP}$ = 3.4), 23.7. ^{31}P{^{1}H} NMR (CD_3OD, 202.5 MHz): δ 22.7. MS (ESI): calcd for $C_7H_{28}O_3{}^{10}B_2{}^{11}B_{10}PS_2Na_2$, *m*/*z* = 431.2203. Obsd, *m*/*z* = 431.2205 ($M + H)^+$.

HO(CH$_2$)$_3$CH[P(O)(OEt)$_2$]$_2$ (22a). Dry THF (5 mL) was condensed into a 25 mL three-neck round-bottom flask containing 0.6004 g of **21a** (1.829 mmol) and a stirbar. The flask was placed into an ice-water bath for 30 min followed by the addition of 3.0 mL of a 1.0 M solution of BH_3THF in THF under nitrogen. After stirring for 1.5 h, the reaction mixture was quenched with methanol followed by the addition of 1.0 mL of aqueous 3M NaOH and 1.0 mL of 30% H_2O_2 and heating at 50 °C for 1 h. Aqueous potassium chloride solution was added, and the product was extracted with 40 mL of chloroform. After the second extraction with a fresh portion of chloroform, the extracts were combined, and the solvent was removed under reduced pressure leaving behind the desired alcohol as a colorless oil (0.428 g, 68%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 4.17 and 4.15 (2 quintets, 8H, $^3J_{HP}$ = $^3J_{HH}$ = 7.1, OCH_2CH$_3$), 3.65 (t, 2H, $^3J_{HH}$ = 5.9, CH_2OH), 3.17 (br s, 1H, O*H*), 2.36 (tt, 1H, $^2J_{HP}$ = 24.3, $^3J_{HH}$ = 5.5; C*H*[P(O)(OEt)$_2$]$_2$), 2.15−1.93 (m, 2H, CH_2CH), 1.80 (quintet, $^3J_{HH}$ = 6.6, CH_2CH$_2$OH), 1.33 (t, 12H, $^3J_{HH}$ = 7.1, OCH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 63.0 and 62.8 (2d, $^2J_{CP}$ = 6.6; OCH_2), 61.6 (s, CH_2OH), 36.0 (t, $^1J_{CP}$ = 133.5, C*H*[P(O)(OEt)$_2$]$_2$), 31.9 (t, $^2J_{CP}$ = 6.1, CH_2CH), 21.9 (t, $^3J_{CP}$ = 4.8, CH$_2$CH_2CH$_2$), 16.4 (d, $^3J_{CP}$ = 6.1, OCH$_2$CH_3). ^{31}P{^{1}H} NMR ($CHCl_3$): δ 25.4.

MsO(CH$_2$)$_3$CH[P(O)(OEt)$_2$]$_2$ (22b). The general procedure for mesylation of alcohols by Grossland and Servis[26] was used. In a typical experiment, 0.3 mL of triethylamine and 8 mL of dry dichloromethane were condensed onto 0.428 g of alcohol **22a** (1.236 mmol) in a three-neck 50 mL round-bottom flask equipped with a stirbar and rubber septum. The flask was placed in an ice-water bath, and the solution was stirred for 1 h under nitrogen. Mesyl chloride (0.12 mL) was added slowly by syringe (within 15 min). After appearance of precipitate, the solution was stirred for an additional 1 h followed by the standard workup procedure. The title compound, a colorless liquid, was held on the vacuum line overnight to remove the residual solvent (0.450 g, 86%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.20 (t, 2H, $^3J_{HH}$ = 5.8, CH_2-OMs), 4.18−4.10 (m, 8H, OCH_2CH$_3$), 2.98 (s, 3H, CH_3SO$_2$), 2.28 (tt, 1H, $^2J_{HP}$ = 24.0, $^3J_{HH}$ = 5.5; C*H*[P(O)(OEt)$_2$]$_2$), 2.05−1.98 (m, 4H, CH_2CH_2), 1.31 (t, 12H, $^3J_{HH}$ = 7.0, OCH$_2$CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 202.5 MHz): δ 24.3.

1-(MeS(CH$_2$)$_3$CH[P(O)(OEt)$_2$]$_2$)-7-(Me$_2$S)B$_{12}$H$_{10}$ (14h). A. From 22c. In a drybox, 0.304 g of NaI (2.03 mmol) was added to a 100 mL round-bottom flask containing 0.9229 g of tosylate (1.837 mmol) and a stirbar. Dry acetonitrile (10 mL) was condensed, and the resulting solution was stirred at room temperature for 1.5 h. To the cloudy yellowish solution was added [Me_4N][**7**] (0.564 g, 1.745 mmol), and the resulting mixture was heated at 70 °C under nitrogen with a condenser for 7 h. The solvent was removed under reduced pressure, and a residue was partitioned between dichloromethane and water. The organic phase was separated and dried with sodium sulfate. The crude yellowish oil obtained after the solvent removal was purified by radial chromatography on a 4 mm layer plate using a EtOAc−MeOH mixture (4:1) as an eluent. The mixture was introduced as a solution in dichloromethane. After combining the appropriate fractions and removing solvents on a flash evaporator, the residual solvents were removed on the vacuum line by heating at 80 °C for 36 h providing 0.8627 g of **14h** (85%) as a thick white oil.

B. From 22b. In a procedure similar to the one described above for tosylate, 0.9933 g of mesylate (2.341 mmol), 0.330 g of NaI (2.20 mmol), and 0.6680 g of [Me_4N][**7**] (2.067 mmol) afforded 1.1414 g of **14h** (95%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.17−4.05 (m, 8H, OCH_2-CH$_3$), 3.02−2.92 (m, 1H, SCH_aH$_b$), 2.81−2.72 (m, 1H, SCH$_a$$H_b$), 2.49 (s, 6H, S(C$H_3$)$_2$), 2.47 (s, 3H, SC$H_3$), 2.23 (tt, 1H, $^2J_{HP}$ = 24.0, $^3J_{HH}$ = 5.3; C*H*[P(O)(OEt)$_2$]$_2$), 2.10−1.90 (m, 4H, SCH$_2$CH_2CH_2), 1.29 (t, 12H, $^3J_{HH}$ = 7.0, OCH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 62.9 and 62.7 (2d, $^2J_{CP}$ = 6.7, 6.8; OCH_2), 42.4 (s, SCH_2), 36.1 (t, $^1J_{CP}$ = 134.0, C*H*-[P(O)(OEt)$_2$]$_2$), 25.7 (s, S(CH_3)$_2$), 25.0 (t, $^3J_{CP}$ = 6.7, CH$_2$CH_2), 24.5 (t, $^2J_{CP}$ = 5.1, SCH$_2$CH_2CH_2), 23.2 (s, SCH_3), 16.4 (d, $^3J_{CP}$ = 6.1, OCH$_2$CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 23.1.

1-(MeS(CH$_2$)$_3$CH[P(O)(ONa)$_2$]$_2$)-7-(Me$_2$S)B$_{12}$H$_{10}$·*x*H$_2$O (23). In a drybox, 1.20 mL of 97% TMSBr (8.82 mmol) was added to a solution of 0.8627 g of **14h** (1.487 mmol) in 10 mL of dry dichloromethane, and the resulting solution was stirred under nitrogen for 40 h. The volatile materials were removed under reduced pressure followed by addition of 0.68 g of anhydrous sodium carbonate in 5 mL of water. A white precipitate appeared that was dissolved upon addition of acetone. After standing overnight, the solution was filtered, and its pH was adjusted approximately to 11 by addition of aqueous 3M NaOH. After

(26) Grossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195−3196.

water removal on the flash evaporator, the yellowish solid residue was dissolved in 10 mL of water and filtered. To the filtrate in a 500 mL Erlenmeyer flask was added 300 mL of 2-propanol causing a white solid to precipitate. It was extracted with 120 mL of the boiling methanol−water mixture (5:1), washed with pentane, and dried for 2 days at 70 °C. The resulting sodium salt is a white solid very soluble in water (0.6941 g, 88% estimated yield assuming no water of crystallization). ^{1}H NMR (D_2O, 500 MHz): δ 3.06−3.01 (m, 1H, SCH_aH$_b$), 2.94−2.89 (m, 1H, SCH$_a$$H_b$), 2.54 (s, 3H, SC$H_3$), 2.52 (s, 6H, S(C$H_3$)$_2$), 2.03−1.76 (m, 4H, C$H_2CH_2$), 1.68 (tt, 1H, $^2J_{HP}$ = 21.5, $^3J_{HH}$ = 6.2, CH[P(O)(ONa)$_2$]). ^{13}C{^{1}H} NMR (D_2O, 100.6 MHz): δ 42.8, 41.0 (t, $^1J_{CP}$ = 116), 27.2 (t, J_{CP} = 7.3), 26.9 (br s), 25.2, 22.6. ^{11}B{^{1}H} NMR (D_2O, 128.4 MHz): δ −5.7 (s, B(1,7)), −12.3 (d, all other borons). ^{31}P{^{1}H} NMR (D_2O, 202.5 MHz): δ 21.0. MS (ESI): calcd for $C_7H_{26}O_6{}^{10}B_2{}^{11}B_{10}P_2S_2Na_4$, m/z = 555.1506. Obsd, m/z = 555.1512 $(M + H)^+$.

1-(*E*/*Z*-MeSCHCHCOOH)-7-(Me$_2$S)B$_{12}$H$_{10}$ (25a). Concentrated HCl (0.4 mL) was added to a solution of [Me$_4$N][**7**] (0.2425 g, 0.750 mmol) and 0.06 mL of propiolic acid (0.94 mmol) in 20 mL of acetonitrile, and the resulting solution was stirred for 40 min. The volatile materials were removed in vacuo, and an oily residue was partitioned between CH_2Cl_2 and water. The organic phase was washed with a fresh portion of water and dried over $MgSO_4$. The solvent was removed under reduced pressure providing the title compound as a fluffy white hygroscopic material (0.1820 g, 76%). ^{1}H NMR (CD_3CN, 500 MHz): δ 7.15* (d, 1H, $^3J_{HH}$ = 15.2, CHSMe), 6.70 (d, 1H, $^3J_{HH}$ = 9.6, CHSMe), 6.63 (d, 1H, $^3J_{HH}$ = 9.6, CHCOOH), 6.44* (d, 1H, $^3J_{HH}$ = 15.2, CHCOOH), 2.74* and 2.68 (2s, 3H, SCH_3), 2.483* and 2.479 (2s, 6H, S(CH_3)$_2$) (*E-isomer). ^{13}C{^{1}H} NMR (CD_3CN): δ 164.5, 164.1, 135.8, 135.0, 132.5, 131.7, 27.8, 26.0, 25.2.

1-(1′,2′-C$_2$B$_{10}$H$_{11}$CH$_2$SMe)-7-(Me$_2$S)B$_{12}$H$_{10}$ (14m). A 25 mL three-neck round-bottom flask was charged with 0.1717 g of **14l** (0.596 mmol), 0.0729 g of $B_{10}H_{14}$ (0.596 mmol), and a stirbar. Dry acetonitrile (10 mL) was condensed onto the reagents, and the resulting solution was refluxed overnight under continuous nitrogen flow. The volatile materials were removed under reduced pressure, and the residue was extracted with CH_2Cl_2. The dichloromethane solution was filtered, concentrated, and chromatographed using CH_2Cl_2 as an eluent. The pure title compound was obtained as a white powder (0.1168 g, 48%). ^{1}H NMR (CD_3CN, 250 MHz): δ 4.45 (br s, 1H, CH), 3.90 (d, 1H, J = 15.7, SCH_aH$_b$), 3.84 (d, 1H, J = 15.7, SCH$_a$$H_b$), 2.72 (s, 3H, SC$H_3$), 2.50 (s, 6H, S(C$H_3$)$_2$). ^{13}C{^{1}H} NMR ($CD_3CN$, 125.8 M): δ 71.1, 64.5, 48.9, 27.2, 26.0. ^{11}B NMR (CD_3CN, 160.5 MHz): δ −2.1 (d, J_{BH} = 149, 1B), −4.3 (d, J_{BH} = 148, 1B), −8.6 (d, J_{BH} = 128, 2B), −8.6 (s, B(1,7)), −11.2 (d, 2B), −11.8 (d, 2B), −12.2 (d, 2B), −13.3 (d, B(9,10)), −14.3 (d, B(5,12)), −15.0 (d, J_{BH} = 135, B(4,6,8,11)), −16.4 (d, B(2,3)). MS (EI): calcd for $C_6H_{32}{}^{10}B_4{}^{11}B_{18}S_2$, m/z = 406.4140. Obsd, m/z = 406.4149 (M^+).

1,7-(1′,2′-C$_2$B$_{10}$H$_{11}$CH$_2$SMe)$_2$B$_{12}$H$_{10}$ (17d). A 25 mL three-neck round-bottom flask was charged with 0.2285 g of **17c** (0.732 mmol), 0.4602 g of $B_{10}H_{12}(SEt_2)_2$ (1.531 mmol), and a stirbar. Dry acetonitrile (10 mL) was condensed onto the reagents, and the resulting solution was refluxed under nitrogen for 16 h. The volatile materials were removed under reduced pressure, and acetone was added to the residue. The solution was allowed to evaporate to dryness in a hood. The residue was partitioned between dichloromethane and water, and the organic phase was separated and dried over $MgSO_4$. After the solvent removal, the crude product was chromatographed using a CH_2Cl_2−toluene mixture (2:3) as an eluent. The title compound was isolated as a white powder (0.1504 g, 37%). ^{1}H NMR ($(CD_3)_2CO$, 500 MHz): δ 5.06 (br s, 2H, CH), 4.18 (d, 2H, $^2J_{HH}$ = 15.7, SCH_aH$_b$), 4.03 (d, 2H, $^2J_{HH}$ = 15.7, SCH$_a$$H_b$), 2.86 (s, 6H, SC$H_3$). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$): δ 71.2, 64.5, 49.0, 26.9. ^{11}B NMR ($(CD_3)_2CO$, 160.5 MHz): δ −1.9 (d, J_{BH} = 149, 2B), −4.1 (d, J_{BH} = 148, 2B), −8.4 (d, J_{BH} = 142, 4B), −8.4 (s, B(1,7)), −10.9 (d, 4B), −11.6 (d, 4B), −12.0 (d, 4B), −12.6 (d, B(9,10)), −14.0 (d, B(5,12)), −14.7 (d, J_{BH} = 132, B(4,6,8,11)), −16.3 (d, J_{BH} = 146, B(2,3)). MS (ESI): calcd for $C_8H_{42}{}^{10}B_4{}^{11}B_{28}S_2Na$, m/z = 573.5762. Obsd, m/z = 573.5778 $(M + Na)^+$.

Table 3. Crystallographic Data for 1-(*i*-PrSMe)-7-(Me$_2$S)B$_{12}$H$_{10}$ (**14i**), *meso*-1,2-(MeSC$_3$H$_3$)$_2$B$_{12}$H$_{10}$ (**16**), and *meso*-1,7-(MeSBn)$_2$B$_{12}$H$_{10}$ (**17b**)

	14i	**16**	**17b**
empirical formula	$C_6H_{25}B_{12}S_2$	$C_8H_{22}B_{12}S_2$	$C_{16}H_{30}B_{12}S_2$
formula weight	291.10	312.10	416.24
crystal color	colorless	colorless	colorless
cryst size, mm	0.31 × 0.31 × 0.15	0.42 × 0.31 × 0.15	0.50 × 0.15 × 0.08
space group	$P2_1/c$	$Pbca$	$P\bar{1}$
a, Å	11.593(1)	16.579(3)	7.266(2)
b, Å	12.754(1)	11.322(2)	11.976(4)
c, Å	11.543(1)	19.758(4)	14.488(4)
α, deg	90	90	93.65(3)
β, deg	91.95(1)	90	104.41(2)
γ, deg	90	90	105.43(3)
vol, Å^3	1705.7(2)	3708.8(1)	1165.6(6)
Z	4	8	2
ρ (calcd), Mg m^{-3}	1.134	1.118	1.186
temp, K	150	150	293
radiation (λ, Å)	0.71073	0.71073	0.71073
2θ limits, deg	4.74−50.06	4.80−50.06	4.28−44.96
μ, mm^{-1}	0.288	0.269	0.231
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0394	0.0416	0.0631
w$R_2{}^b$ (all data)	0.1260	0.1302	0.1962
GOF on F^2	1.041	1.078	1.073

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} w$R_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$.

Table 4. Crystallographic Data for [Me$_4$N][(MeSCH$_2$CH[P(O)(OEt)$_2$]$_2$)B$_{12}$H$_{11}$] ([Me$_4$N][**24c**]), 1-(1′,2′-C$_2$B$_{10}$H$_{11}$CH$_2$SMe)-12-(Me$_2$S)B$_{12}$H$_{10}$ (**15b**), and *meso*-1,12-(MeSNH$_2$)$_2$B$_{12}$H$_{10}$ (**31**)

	[Me$_4$N][**24c**]	**15b**	**31**
empirical formula	$C_{15}H_{49}B_{12}NO_6P_2S$	$C_6H_{32}B_{22}S_2$	$C_2H_{20}B_{12}N_2S_2$
formula weight	563.27	406.26	226.04
crystal color	colorless	colorless	colorless
cryst size, mm	0.23 × 0.15 × 0.15	0.53 × 0.31 × 0.15	0.38 × 0.31 × 0.12
space group	$P2_12_12_1$	Cc	$P2_1/n$
a, Å	8.955(1)	7.481(1)	7.933(1)
b, Å	14.566(1)	29.578(1)	8.780(1)
c, Å	24.271(1)	10.573(1)	10.925(1)
α, deg	90	90	90
β, deg	90	90.21(1)	108.45(1)
γ, deg	90	90	90
vol, Å^3	3166.0(4)	2339.4(4)	721.8(1)
Z	4	4	2
ρ (calcd), Mg m^{-3}	1.182	1.153	1.224
temp, K	150	150	173
radiation (λ, Å)	0.71073	0.71073	0.71073
2θ limits, deg	4.84−50.02	4.74−50.10	5.60−50.04
μ, mm^{-1}	0.234	0.222	0.337
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0477	0.0430	0.0480
w$R_2{}^b$ (all data)	0.1047	0.1074	0.1301
GOF on F^2	1.028	1.071	1.030

^{a} $R_1 = \sum| |F_o| - |F_c||/\sum|F_o|$. ^{b} w$R_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$.

[Me$_4$N][(MeSNH$_2$)B$_{12}$H$_{11}$] ([Me$_4$N][27]). A solution of [Me$_4$N]$_2$-[**5**] (0.2120 g, 0.631 mmol) in 10 mL of acetonitrile water (1:1) was added to a solution of H_2NOSO_3K obtained by mixing 0.0805 g of hydroxylamine-*O*-sulfonic acid (0.690 mmol) and 0.0498 g of K_2CO_3 (0.360 mmol) in 5 mL of water. The resulting solution was stirred overnight, and most of the acetonitrile was removed on a flash evaporator. The precipitate was filtered off, washed with cold ethanol (2−3 mL) and pentane, and dried at 70 °C for 2 h. The title compound was obtained as a white powder (0.1391 g, 79%). ^{1}H NMR (CD_3CN, 400 MHz): δ 3.47 (br s, 2H, SNH_2), 3.08 (s, 12H, N(CH_3)$_4$), 2.59 (s, 3H, SCH_3). ^{13}C{^{1}H} NMR (CD_3CN): δ 56.1 (t, J_{CN} = 4), 33.8. ^{11}B NMR (CD_3CN): δ −7.9 (s), −14.1 (d), −15.8 (d). MS (ESI): calcd for $CH_{16}N^{10}B_2{}^{11}B_{10}S$, m/z = 204.2193. Obsd, m/z = 204.2203 (M^-).

General Procedure for the Synthesis of (MeSNH$_2$)(Me$_2$S)B$_{12}$H$_{10}$ and (MeSNH$_2$)$_2$B$_{12}$H$_{10}$. A solution of potassium hydroxylamine-*O*-sulfonate obtained by mixing H_2NOSO_3H and potassium carbonate (2:

1) in water was added to a solution of the tetramethylammonium salt of the corresponding thioether in water (**10**, **11**) or acetonitrile (**7**, **8**). The mixture was stirred at room temperature and concentrated in vacuo. The resulting solution was extracted with dichloromethane, the organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Aminosulfonium salt products were purified by column chromatography.

Single-Crystal X-ray Diffraction Analyses. Single-crystal X-ray diffraction data were collected on an Enraf-Nonius CAD4 (**14j**, **17b**) and Enraf-Nonius KappaCCD (**14i**, **15b**, **16**, [Me_4N][**24**], **31**). Crystal data are given in Tables 3 and 4. A Bruker SMART 1000 CCD diffractometer was employed for compound **14m**. Crystal data for this compound are given in Supporting Information. All instruments employ graphite-monochromated Mo Kα radiation. When the Enraf-Nonius CAD4 diffractometer was used, a single crystal was mounted inside a glass capillary. Unit cell parameters were obtained by a least-squares refinement of the angular settings from 25 reflections, well distributed in reciprocal space and lying in the 2θ range of 24−30°. Diffraction data were corrected for Lorentz and polarization effects. With the Enraf-Nonius KappaCCD diffraction system, a single crystal was mounted on the tip of a glass fiber coated with Parabar. 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.[27] The structures were solved by the direct method and refined using SHELXTL (difference electron density calculations, full least-squares refinements).[28] After all non-hydrogen atoms were located and refined anisotropically, H atoms on organic groups (alkyl, phenyl groups) were calculated assuming standard −CH geometries. All other hydrogen atoms were located and refined isotropically. In the case of **14m**, frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The final structural refinement required application of a pseudo-orthorhombic twinning law with a twinning parameter of 0.223.

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Supporting Information Available: Complete synthetic procedures and characterization of compounds, time-evolved $^{11}B\{^1H\}$ NMR spectra of the equimolar mixture of **4** and [Me_4N]$_2$[**11**], ^1H NMR spectra of 1,7-$(MeSR)_2B_{12}H_{10}$ (R = CH═C═CH_2, CH_2CCH) and 1-(MeSCH═C═CH_2)-7-($MeSCH_2CCH$)-$B_{12}H_{10}$, $^{11}B\{^1H\}$ NMR spectra of **3**, **17a**, **26**, **14m**, and **17d**, X-ray molecular structures of **14j** and **14m**, tables of crystallographic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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