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Synthesis and Characterization of Sulfide, Sulfide−Sulfonium, and Bissulfide Derivatives of $[B_{12}H_{12}]^{2-}$. Additivity of Me_2S and MeS^- Substituent Effects in ^{11}B NMR Spectra of Disubstituted Icosahedral Boron Clusters[†]

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The 1,2-, 1,7-, and 1,12-isomers of $(Me_2S)_2B_{12}H_{10}$ (**O**, **M**, and **P**) react with potassium phthalimide in DMF or EtSNa in CH_3CN/EtOH upon reflux producing the corresponding isomers of $[(MeS)(Me_2S)B_{12}H_{10}]^-$ ($\mathbf{O^{1-}}$, $\mathbf{M^{1-}}$, $\mathbf{P^{1-}}$). If excess of either nucleophile is used, $[Me_2SB_{12}H_{11}]^-$ (**1**) and **O** , **M** , **P** can be converted into dianions $[MeSB_{12}H_{11}]^{2-}$ (**2**) and $[(MeS)_2B_{12}H_{10}]^{2-}$ ($\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, $\mathbf{P^{2-}}$). The use of EtSNa is recommended since it facilitates the isolation of products compared to the potassium phthalimide method. When **1** or **O**, **M**, **P** are treated with an excess of an alkali metal (Na, K) in liquid ammonia at −40 °C, sulfide **2** or bissulfide dianions $\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, $\mathbf{P^{2-}}$ are obtained cleanly and almost instantly. While both the nucleophilic substitution and alkali metal reduction methods are useful for the synthesis of dianions **2**, $\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, and $\mathbf{P^{2-}}$, only the former method is suitable for the synthesis of the sulfide−sulfonium anions $\mathbf{O^{1-}}$, $\mathbf{M^{1-}}$, $\mathbf{P^{1-}}$. The analysis of the ^{11}B NMR spectra of **1**, **O**, **M**, **P** and anions derived from them demonstrated that the spectra of the disubstituted species can be predicted qualitatively, keeping in mind the simple substituent effects obtained from the spectra of monosubstituted anions **1** and **2**. Some evidence is found for small partial double bond character of the B−SMe bonds in anions. $[MePPh_3]^+$ salts of $[MeSB_{12}H_{11}]^{2-}$ (**2**) and $[1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]^-$ ($\mathbf{M^{1-}}$) are structurally characterized by single-crystal X-ray diffraction analysis. Crystal data: $[MePPh_3]_2[MeSB_{12}H_{11}]$, $P2_1$ (No. 4), $a = 9.243(1)$ Å, $b = 18.272(1)$ Å, $c = 12.548(1)$ Å, $\beta = 103.17(1)°$, $Z = 2$; $[MePPh_3][1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]$, $P\bar{1}$ (No. 2), $a = 9.278(2)$ Å, $b = 12.003(5)$ Å, $c = 14.819(7)$ Å, $\alpha = 112.18(4)°$, $\beta = 105.61(3)°$, $\gamma = 92.91(3)°$, $Z = 2$.

Introduction

The inner sulfonium salts[1] $[Me_2SB_{12}H_{11}]^-$ (**1**) and $(Me_2S)_2B_{12}H_{10}$ have been known for over 30 years,[5−7] but only recently have **1** and all isomers of $(Me_2S)_2B_{12}H_{10}$ been characterized by multinuclear NMR and X-ray diffraction techniques.[8−10] Muetterties et al.[2] observed that carbon atoms in the related compounds $(Me_2S)_2B_{10}H_8$ and $(Me_2S)_2B_{10}H_2Cl_6$ are sufficiently electrophilic to be attacked by nucleophiles such as phthalimide ion and tributylphosphine. These reactions yielded $[(MeS)(Me_2S)B_{10}H_8]^-$ and $[(MeS)_2B_{10}H_2Cl_6]^{2-}$, respectively. Similarly, Soloway et al.[12] used potassium phthalimide in DMF to synthesize $[(MeS)(Me_2S)B_{12}H_{10}]^-$ from a mixture of isomers of $(Me_2S)_2B_{12}H_{10}$. Although dianions $[MeSB_{12}H_{11}]^{2-}$ (**2**) and $[(MeS)_2B_{12}H_{10}]^{2-}$ were not obtained by nucleophilic substitution reaction, they were synthesized earlier from $[B_{12}H_{12}]^{2-}$ and dimethyl disulfide.[7] Since the isomers of monoanions $[(MeS)(Me_2S)B_{12}H_{10}]^-$ and dianions $[(MeS)_2B_{12}H_{10}]^{2-}$ were never characterized, our initial goal was their synthesis from pure isomers of $(Me_2S)_2B_{12}H_{10}$ (referred to below as **O**, **M**, and **P** to emphasize the ortho, meta, and para relationship between substituents in 1,2-, 1,7-, and 1,12-$(Me_2S)_2B_{12}H_{10}$, see Chart 1). In this process we found the procedure utilizing potassium phthalimide in DMF to be tedious with respect to workup. Therefore, the additional goal of the work presented here was to find alternative ways of synthesis of anions $\mathbf{O^{1-}}$, $\mathbf{M^{1-}}$, $\mathbf{P^{1-}}$ and $\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, $\mathbf{P^{2-}}$. Having obtained the ^{11}B NMR spectra of **1**, **2**, **O**, **M**, **P** and anions derived from them, we attempted their thorough analysis. The results are also reported below.

Results and Discussion

Preparation of $[1\text{-}(MeS)\text{-}2(7,12)\text{-}(Me_2S)B_{12}H_{10}]^-$ ($\mathbf{O^{1-}}$, $\mathbf{M^{1-}}$, $\mathbf{P^{1-}}$) by Nucleophilic Substitution. Potassium Phthalimide Method. A slight excess of potassium phthalimide was used to convert the individual isomers of $(Me_2S)_2B_{12}H_{10}$ into the corresponding sulfide−sulfonium anions (eq 1). The reaction was usually stopped after 3 h of reflux, at which point some

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[†] Dedicated to the memory of Dr. Stanislav Hermanek.

(1) The term “inner -onium salt” was used by Muetterties and Knoth[2, 3] for partially or fully charge-compensated[4] *closo*-borane polyhedrons substituted with one or two molecules of a neutral two-electron donor such as R_2S, R_3N, N_2.

(2) Knoth, W. H.; Hertler, W. R.; Muetterties, E. L. *Inorg. Chem.* **1965**, *4*, 280.

(3) Knoth, W. H. *J. Am. Chem. Soc.* **1966**, *88*, 935.

(4) Kang, H. C.; Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2024.

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

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

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

(8) Jasper, S. A., Jr.; Jones, R. B.; Mattern, J.; Huffman, J. C.; Todd, L. J. *Inorg. Chem.* **1994**, *33*, 5620.

(9) Hamilton, E. J. M.; Jordan, G. T., IV; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1996**, *35*, 5335.

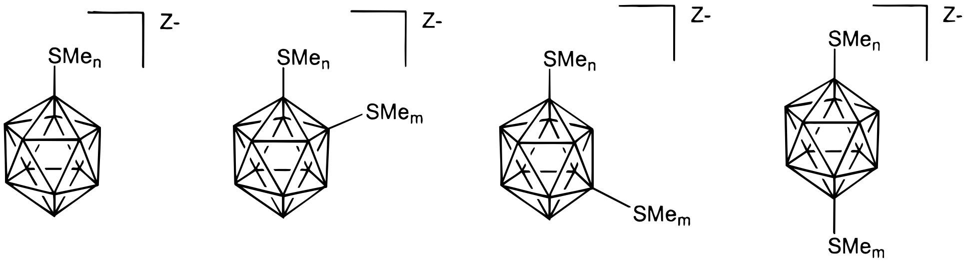
(10) Kultyshev, R. G.; Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1999**, *38*, 4913.

(11) Preliminary studies showed that a similar compound, 1,10-$(Me_2S)_2B_{10}H_8$, also reacts with *n*-BuLi in THF, yielding primarily the corresponding monoanion. After a metathesis reaction, $[NMe_4][1\text{-}(MeS)\text{-}10\text{-}(Me_2S)B_{10}H_8]$ was obtained in 75% yield.

(12) Sneath, R. L., Jr.; Soloway, A. H.; Dey, A. S. *J. Med. Chem.* **1974**, *17*, 796.

10.1021/ic000198o CCC: $19.00

Chart 1. Structures of **1**, **2**, Isomers of $(Me_2S)_2B_{12}H_{10}$, and Anions Derived from Them



1, n = 2, Z = 1

2, n = 1, Z = 2

O, n = m = 2, Z = 0

$\mathbf{O^{1-}}$, n = 1, m = 2, Z = 1

$\mathbf{O^{2-}}$, n = m = 1, Z = 2

M, n = m = 2, Z = 0

$\mathbf{M^{1-}}$, n = 1, m = 2, Z = 1

$\mathbf{M^{2-}}$, n = m = 1, Z = 2

P, n = m = 2, Z = 0

$\mathbf{P^{1-}}$, n = 1, m = 2, Z = 1

$\mathbf{P^{2-}}$, n = m = 1, Z = 2

$$1,2(7,12)\text{-}(Me_2S)_2B_{12}H_{10} \xrightarrow[\text{DMF, reflux}]{C_8H_4O_2NK} K[1\text{-}(MeS)\text{-}2(7,12)\text{-}(Me_2S)B_{12}H_{10}] + C_8H_4O_2NMe \quad (1)$$

starting material was still present, as well as dianions $\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, $\mathbf{P^{2-}}$. The molar ratios of the nucleophile to borane higher than 2:1 and longer reflux time lead to dianions $\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, and $\mathbf{P^{2-}}$. The recovery of the unreacted starting material in the potassium phthalimide method requires its separation from *N*-methylphthalimide. Also, the use of DMF as a solvent makes this method a bit tedious due to the slowness of its removal. On the other hand, DMF seems to be necessary since potassium phthalimide in, for example, acetonitrile is ineffective. A nucleophile to be used instead of the phthalimide ion should be more reactive toward methyl carbon than phthalimide ion and possibly produce low-boiling methylated byproducts, which are easy to remove. Among the plethora of possible candidates we tried *n*-BuLi and EtSNa.

***n*-BuLi method.** It was reported[2] that *n*-BuLi in hexane added to a mixture of isomers of the related compound $(Me_2S)_2B_{10}H_8$ in ether acts as a base removing a proton from a methyl group. However, we found that *n*-BuLi in pentane added to a suspension of **M** or **P** in THF acts primarily as a nucleophile yielding $\mathbf{M^{1-}}$ and $\mathbf{P^{1-}}$, respectively (eq 2). Results of several

$$1,7(12)\text{-}(Me_2S)_2B_{12}H_{10} \xrightarrow[\text{THF, rt}]{n\text{-BuLi}} Li[1\text{-}(MeS)\text{-}7(12)\text{-}(Me_2S)B_{12}H_{10}] + C_5H_{12} \quad (2)$$

runs showed that yields of $\mathbf{M^{1-}}$ comparable with those obtained by the potassium phthalimide method can be achieved if the reaction is run for 3−3.5 h. However, the yields of $\mathbf{P^{1-}}$ were substantially lower.[11] The use of *n*-BuLi was abandoned in favor of sodium ethanethiolate as described below.

Sodium Ethanethiolate Method. Sodium ethanethiolate generated in situ from EtSH and EtONa reacts with **M** and **P** upon reflux according to eq 3. This is an analogue of a syn-

$$1,7(12)\text{-}(Me_2S)_2B_{12}H_{10} \xrightarrow[\text{CH}_3\text{CH/EtOH, reflux}]{\text{EtSNa}} Na[1\text{-}(MeS)\text{-}7(12)\text{-}(Me_2S)B_{12}H_{10}] + EtSMe \quad (3)$$

proportionation reaction between thiolate $[SB_{12}H_{11}]^{3-}$ and sulfonium salt $[(NCCH_2)_2SB_{12}H_{11}]^-$ observed by Gabel and coworkers,[13] except that two different sulfides are produced instead of one. The yields of $\mathbf{M^{1-}}$ and $\mathbf{P^{1-}}$ (as their tetramethylammonium salts) are similar to the yields obtained by the potassium phthalimide method and better than those obtained by the *n*-BuLi method. It seems that the ethoxide ion by itself does not affect the demethylation of the sulfonium sulfur; therefore an excess of NaH used to generate EtONa can be tolerated. On the other hand, an excess of EtS^- results in demethylation of the second sulfur atom and formation of $\mathbf{M^{2-}}$ and $\mathbf{P^{2-}}$, respectively. We did not check this method for the synthesis of $\mathbf{O^{1-}}$ or $\mathbf{O^{2-}}$ from **O** because of the relative unavailability of the starting material, but it is expected to work as well.

Preparation of $[MeSB_{12}H_{11}]^{2-}$ (2) by Nucleophilic Substitution. Gabel and co-workers[13] observed that the alkylation of $[HSB_{12}H_{11}]^{2-}$ with primary alkyl halides always produced mixtures of mono- and dialkylated products. For the purpose of conversion of dialkylated products into monoalkylated ones it was of interest to determine if potassium phthalimide in DMF or EtSNa in CH_3CN/ EtOH is capable of transforming **1** into **2**. Since the trimethylsulfonium salt of **1** is one of the major products of the pyrolysis of $BH_3{\cdot}SMe_2$,[9,10] it was used as a starting material. A 3:1 and 4.7:1 molar ratio of nucleophile to borane salt was used with phthalimide and ethanethiolate, respectively, to ensure that the trimethylsulfonium cation also reacted completely (eqs 4 and 5). With phthalimide ion 50%

$$[Me_3S][Me_2SB_{12}H_{11}] \xrightarrow[\text{DMF, reflux}]{C_8H_4O_2NK\text{ (excess)}} K_2[MeSB_{12}H_{11}] + Me_2S + 2C_8H_4O_2NMe \quad (4)$$

$$[Me_3S][Me_2SB_{12}H_{11}] \xrightarrow[\text{CH}_3\text{CN/EtOH, reflux}]{\text{EtSNa (excess)}} Na_2[MeSB_{12}H_{11}] + Me_2S + 2EtSMe \quad (5)$$

conversion was achieved after 2 h, as judged by ^{11}B NMR. The complete conversion was reached after 18 h of reflux. When sodium ethanethiolate was used, the reaction was complete after overnight reflux. Both $[MePPh_3]^+$ and $[NMe_4]^+$ salts of anion **2** were isolated. Interestingly, anion **1** failed to produce dianion **2** with *n*-BuLi in THF.

Preparation of $[MeSB_{12}H_{11}]^-$ (2) and $[(MeS)_2B_{12}H_{10}]^{2-}$ (O^{2-}, M^{2-}, P^{2-}) by Reduction of 1 and O, M, P with Alkali Metals. Although both the potassium phthalimide and sodium ethanethiolate methods can be used for the synthesis of **2**, $\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, and $\mathbf{P^{2-}}$, we also suggest an alternative method. Dianions **2**, $\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, and $\mathbf{P^{2-}}$ can be synthesized by reduction of **1**, **O**, **M**, and **P** with an alkali metal in liquid ammonia (eqs 6 and 7). The reaction takes place almost instantly and gives exclusively

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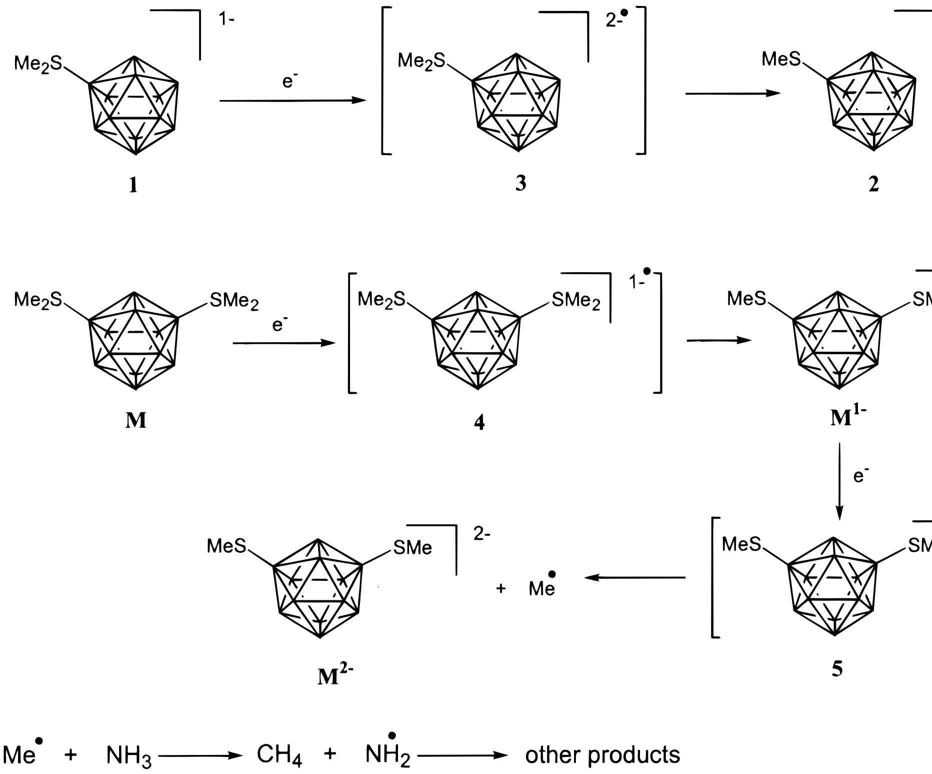
(13) Gabel, D.; Moller, D.; Harfst, S.; Rosler, J.; Ketz, H. *Inorg. Chem.* **1993**, *32*, 2276.

Chart 2. Mechanism of the Alkali Metal Reduction of the Inner Sulfonium Salts **1** and **M**



$$[Me_3S][Me_2SB_{12}H_{11}] \xrightarrow[\substack{-40\ ^\circ C \\ M = Na, K}]{M,\ NH_3(liq)} M_2[MeSB_{12}H_{11}] + Me_2S + CH_4 + \text{other products} \quad (6)$$

$$1,2(7,12)\text{-}(Me_2S)_2B_{12}H_{10} \xrightarrow[\substack{-40\ ^\circ C \\ M = Na, K}]{M,\ NH_3(liq)} M_2[1,2(7,12)\text{-}(MeS)_2B_{12}H_{10}] + CH_4 + \text{other products} \quad (7)$$

dianions if an excess of an alkali metal is used. Since methane was identified by mass-spectrometric analysis of the noncondensable gas collected by a Toepler pump, reduction of **1**, **O**, **M**, and **P** probably occurs through radical pathways illustrated by Chart 2 where compound **M** also represents the identical behavior of **O** and **P**. It is remarkable that sulfide dianions **2**, $\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, and $\mathbf{P^{2-}}$ are stable toward further cleavage to the corresponding dodecaboranethiolates and methane. This would be the expected pathway if we assume their behavior to be analogous to that of the aryl alkyl sulfides.[14] An attempt to use a 1:1 molar ratio of borane **M** to sodium to synthesize monoanion $\mathbf{M^{1-}}$ failed, resulting in a mixture of the unreacted borane, $\mathbf{M^{1-}}$, and dianion $\mathbf{M^{2-}}$.

$^{11}B\{^1H\}$ NMR Spectra of 1, 2, Isomers of $(Me_2S)_2B_{12}H_{10}$ and Anions Derived from Them. The understanding of ways in which a substituent influences the chemical shift of a boron atom requires the unambiguous assignment of all signals in the spectrum of the cluster molecule. This was done earlier for **1**, **O**, and **M** from consideration of the corresponding $^{11}B-^{11}B-\{^1H\}$ 2D COSY, $^{11}B\{^1H\}$, and ^{11}B NMR spectra.[9,10] All the signals in the spectra of $\mathbf{O^{1-}}$, $\mathbf{M^{1-}}$, $\mathbf{P^{1-}}$, $\mathbf{O^{2-}}$, and $\mathbf{M^{2-}}$ were assigned similarly. The 2D spectra can be found in the Supporting Information. The spectra of **P** and $\mathbf{P^{2-}}$ are simple and unambiguous.

Table 1. ^{11}B Chemical Shifts and Signal Assignments of $[Me_3S][Me_2SB_{12}H_{11}]$ and $[NMe_4]_2[MeSB_{12}H_{11}]$ in CD_3CN

	B(1), α	B(2−6), β	B(7−11), γ	B(12), δ
$[Me_2SB_{12}H_{11}]^-$, **1**	−9.5	−15.7	−14.2	−14.2
$[MeSB_{12}H_{11}]^{2-}$, **2**	−5.6	−14.3	−15.4	−17.5

The substituent effects on the NMR shifts of boron atoms in the *closo*-B_{12} cage are discussed here using Hermanek's notation: the substituted boron atoms are called α, atoms ortho to them are called β, and so on.[15] If upon substitution a signal of a boron atom α, β, γ, or δ to this substituent is found downfield from the signal of $[B_{12}H_{12}]^{2-}$ in CD_3CN (chemical shift −15.05 ppm), we refer to it as a result of a downfield α-, β-, γ-, or δ-effect of this substituent and vice versa. **1** and **2** can be considered as results of substitution of H^- in $[B_{12}H_{12}]^{2-}$ by Me_2S and MeS^- moieties, respectively. Compounds **O**, **M**, **P**, and anions $\mathbf{O^{1-}}$, $\mathbf{M^{1-}}$, $\mathbf{P^{1-}}$, $\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, and $\mathbf{P^{2-}}$ can be treated similarly. Below we refer to the substituents as Me_2S ("dimethyl sulfide") and MeS^- ("methylthio"). Apparently, α-boron atoms are the most sensitive to the introduction of a substituent (Table 1). Both substituents manifest large downfield α-effects, that of MeS^- being larger than that of Me_2S. Both substituents show significant δ-effects (antipodal effects), but their signs are different: while the signal of the boron atom δ to MeS^- is moved upfield, that of the atom δ to Me_2S is moved downfield. Similar to the α-effect, the magnitude of the δ-effect is larger for MeS^- than for Me_2S. β-MeS^- has a downfield effect while β-Me_2S moves the signal upfield. On the other hand, γ-MeS^- seems to have a small upfield effect while γ-Me_2S moves the signal downfield as much as δ-Me_2S. As Table 1 clearly shows, methylthio and dimethyl sulfide substituents affect the chemical shifts of the unsubstituted boron atoms in the opposite directions. These effects are not necessarily of the same magnitude; therefore, the spectra of **1** and **2** in the unsubstituted region can

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(14) Wardell, J. L. In *The Chemistry Of The Thiol Group, part 1*; Patai, S., Ed; Wiley: London, 1974; pp 235−238.

(15) Hermanek, S. *Chem. Rev.* **1992**, *92*, 325.

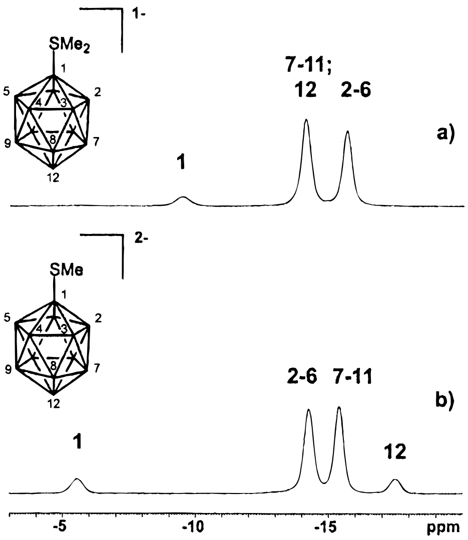


Figure 1. $^{11}B\{^1H\}$ NMR spectra (160.5 MHz) of $[Me_2SB_{12}H_{11}]^-$ (a) and $[MeSB_{12}H_{11}]^{2-}$ (b) in CD_3CN.

Table 2. ^{11}B Chemical Shifts and Signal Assignments for Isomers of $(Me_2S)_2B_{12}H_{10}$ in CD_3CN

isomer	α	δ	γ,γ	β,γ	β,β
$1,2\text{-}(Me_2S)_2B_{12}H_{10}$, **O**	−10.5 B(1,2) β	−13.9 B(9,12) γ	−14.3 B(8,10)	−15.9 B(4,5,7,11)	−17.4 B(3,6)
$1,7\text{-}(Me_2S)_2B_{12}H_{10}$, **M**	−8.7 B(1,7) γ	−14.5 B(5,12) β	−13.5 B(9,10)	−15.0 B(4,6,8,11)	−16.4 B(2,3)
$1,12\text{-}(Me_2S)_2B_{12}H_{10}$, **P**	−7.4 B(1,12) δ			−15.2 B(2−11)	

be regarded as approximate mirror images of each other (Figure 1). The "plane of reflection" is located at the position of the chemical shift of boron atoms in $[B_{12}H_{12}]^{2-}$ (−15.05 ppm).

Now it is of interest to examine the spectra of the disubstituted species possessing the substituents of the same type (Me_2S in **O**, **M**, **P** or MeS^- in $\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, $\mathbf{P^{2-}}$) or of mixed type (Me_2S and MeS^- in $\mathbf{O^{1-}}$, $\mathbf{M^{1-}}$, $\mathbf{P^{1-}}$) and find out if the above effects correlate with the position of the peaks in their observed spectra. Let us first consider the spectra of **O**, **M**, **P** which were discussed briefly earlier.[10] As Table 2 suggests, the lowest field signal is always due to α-borons. This signal moves downfield from **O** to **P** as the upfield effect of β-Me_2S in **O** is replaced by the downfield γ-Me_2S effect in **M** and, finally, by the downfield δ-Me_2S effect in **P**. Since the lower chemical shift of α-borons in **P** compared to that of the α-borons in **M** is not expected from the equal γ- and δ-Me_2S downfield effects (Table 1), other factors are most likely to be involved. Among the unsubstituted boron atoms the lowest downfield are δ,γ-borons in **O** (two downfield effects) and γ,γ-borons in **M** (two downfield effects). δ,β-Borons in **M** are not as deshielded as δ,γ-borons in **O** because of the upfield β-Me_2S effect. β,γ-Borons are almost at the chemical shift of $[B_{12}H_{12}]^{2-}$ or slightly above because of the partial cancellation of the γ-downfield and β-upfield Me_2S effects. The most upfield signal is always due to β,β-boron atoms in accordance with the upfield effect of β-Me_2S.

Let us now consider the spectra of dianions $\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, $\mathbf{P^{2-}}$ where two MeS^- substituents affect the chemical shifts (Table 3). As for **1**, **2** and **O**, **M**, **P**, the most downfield signal always corresponds to α-boron atoms. This signal moves upfield as the downfield β-effect of the second MeS^- in $\mathbf{O^{2-}}$ is replaced initially with the small upfield γ-effect in $\mathbf{M^{2-}}$ and then with the larger upfield δ-effect in $\mathbf{P^{2-}}$. As expected from the behavior of MeS^- opposite to Me_2S, among the unsubstituted atoms those β to both substituents are the most downfield and those δ to one of them are the most upfield. Since δ,γ-atoms in $\mathbf{O^{2-}}$ and δ,β-atoms in $\mathbf{M^{2-}}$ have almost equal chemical shifts, the antipodal effect apparently prevails over the β-effect (this is not the case with two Me_2S substituents and δ,β-borons are not the lowest downfield among the unsubstituted atoms in **M**, Table 2). β,γ-Boron atoms are not as deshielded as β,β according to the contribution of the small upfield effect of the γ-MeS^- substituent. γ,γ-Borons appear on the right from $[B_{12}H_{12}]^{2-}$ because of the double contribution of the upfield γ-MeS^- effect. The spectra of **O**, **M**, **P** and $\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, $\mathbf{P^{2-}}$ are another example of MeS^- and Me_2S substituents affecting the chemical shifts of the unsubstituted boron atoms in the opposite directions. That is why the spectra of **O** and $\mathbf{O^{2-}}$, and **P** and $\mathbf{P^{2-}}$ in the unsubstituted region are also the "mirror images" of each other with the position of the "reflection plane" approximately at the chemical shift of $[B_{12}H_{12}]^{2-}$ (Figure 2a,c and Figure 4a,c). A similar reflection relationship is not exact for the spectra of **M** and $\mathbf{M^{2-}}$ (Figure 3a,c) where the order of (9,10) and (5,12) signals is not the same upon reflection because, as noted above, the δ-MeS^- effect overrides the β-MeS^- effect while the δ- and β-Me_2S effects are comparable.

The dependence of the chemical shift on the position of a given atom with respect to both methylthio and dimethyl sulfide substituents in the $^{11}B\{^1H\}$ NMR spectra of $\mathbf{O^{1-}}$, $\mathbf{M^{1-}}$, $\mathbf{P^{1-}}$ is

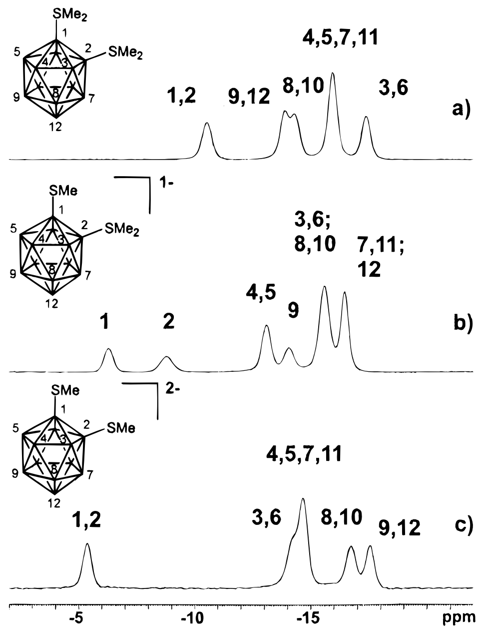


Figure 2. $^{11}B\{^1H\}$ NMR spectra (160.5 MHz) of $1,2\text{-}(Me_2S)_2B_{12}H_{10}$ (a), $[1\text{-}(MeS)\text{-}2\text{-}(Me_2S)B_{12}H_{10}]^-$ (b), and $[1,2\text{-}(MeS)_2B_{12}H_{10}]^{2-}$ (c) in CD_3CN.

Table 3. ^{11}B Chemical Shifts and Signal Assignments for Isomers of $[NMe_4]_2[(MeS)_2B_{12}H_{10}]$ in CD_3CN

isomer	α	β,β	β,γ	γ,γ	δ
$[1,2\text{-}(MeS)_2B_{12}H_{10}]^{2-}$, $\mathbf{O^{2-}}$	−5.4 B(1,2) β	−14.3 B(3,6)	−14.7 B(4,5,7,11)	−16.7 B(8,10)	−17.5 B(9,12) γ
$[1,7\text{-}(MeS)_2B_{12}H_{10}]^{2-}$, $\mathbf{M^{2-}}$	−5.8 B(1,7) γ	−13.6 B(2,3)	−14.6 B(4,6,8,11)	−15.8 B(9,10)	−16.8 B(5,12) β
$[1,12\text{-}(MeS)_2B_{12}H_{10}]^{2-}$, $\mathbf{P^{2-}}$	−6.9 B(1,12) δ		−14.5 B(2−11)		

Table 4. ^{11}B Chemical Shifts and Signal Assignments for Isomers of $[NMe_4][(MeS)(Me_2S)B_{12}H_{10}]$ in CD_3CN

isomer	α-MeS^-	α-Me_2S	δ-Me_2S	β-MeS^-, γ-Me_2S	β,β	γ,γ	γ-MeS^-, β-Me_2S	δ-MeS^-
$[1\text{-}(MeS)\text{-}2\text{-}(Me_2S)B_{12}H_{10}]^-$,	−6.3	−8.8	−14.1	−13.1	−15.6	−15.6	−16.5	−16.5
O^{1-}	B(1)	B(2)	B(9)	B(4,5)	B(3,6)	B(8,10)	B(7,11)	B(12)
	β-Me_2S	β-MeS^-	γ-MeS^-					γ-Me_2S
$[1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]^-$,	−4.5	−9.9	−13.1	−13.7	−15.2	−14.8	−16.3	−18.4
M^{1-}	B(1)	B(7)	B(5)	B(4,6)	B(2,3)	B(9,10)	B(8,11)	B(12)
	γ-Me_2S	γ-MeS^-	β-MeS^-					β-Me_2S
$[1\text{-}(MeS)\text{-}12\text{-}(Me_2S)B_{12}H_{10}]^-$,	−3.4	−10.4	−3.4	−13.6			−16.2	−10.4
P^{1-}	B(1)	B(12)	B(1)	B(2−6)			B(7−11)	B(12)
	δ-Me_2S	δ-MeS^-	α-MeS^-					α-Me_2S

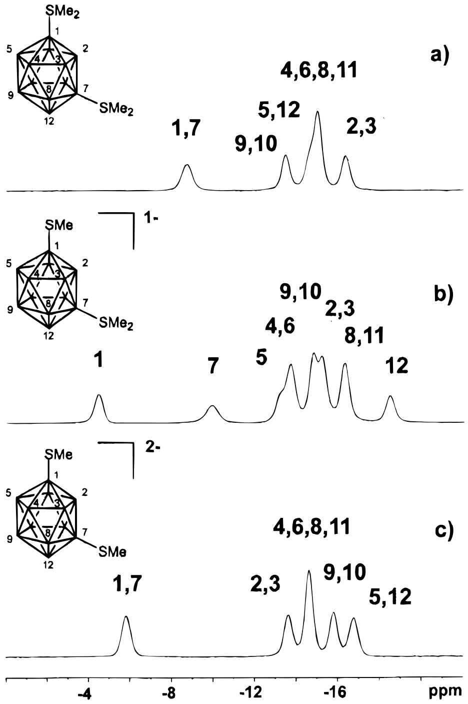


Figure 3. $^{11}B\{^1H\}$ NMR spectra (160.5 MHz) of $1,7\text{-}(Me_2S)_2B_{12}H_{10}$ (a), $[1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]^-$ (b), and $[1,7\text{-}(MeS)_2B_{12}H_{10}]^{2-}$ (c) in CD_3CN.

shown in Table 4. As with **1** and **2**, the lowest field signal in the spectra of **O**$^{1-}$, **M**$^{1-}$, **P**$^{1-}$ is always due to a boron atom α to a MeS^- substituent and the next lowest to boron atoms α to Me_2S. Among the unsubstituted boron atoms, signals on the left from $[B_{12}H_{12}]^{2-}$ are always due to boron atoms δ to Me_2S (downfield effect) or atoms β to MeS^- and γ to Me_2S (two downfield effects). On the other hand, the signals on the right from $[B_{12}H_{12}]^{2-}$ are due to boron atoms δ to MeS^- (upfield effect) or those γ to MeS^- and β to Me_2S (two upfield effects). The observed chemical shifts of the atoms δ to Me_2S and δ to MeS^- nicely fit the general picture. In the first series the signal moves downfield as we proceed from γ-MeS^- (small upfield effect) in **O**$^{1-}$ to β-MeS^- (downfield effect) in **M**$^{1-}$ and, finally, to α-MeS^- (large downfield effect) in **P**$^{1-}$. In the second series the signal moves upfield as we go from α-Me_2S (large downfield effect) in **P**$^{1-}$ to γ-Me_2S (downfield effect) in **O**$^{1-}$ and β-Me_2S (upfield effect) in **M**$^{1-}$. Not surprisingly, when the upfield and downfield effects of different substituents cancel each other, the signal of the corresponding boron atom can be found close to that in $[B_{12}H_{12}]^{2-}$. This is exactly the situation when an atom is either β or γ to both substituents. Because of the opposite effects of dimethyl sulfide and methylthio substituents, the spectra of the monoanions in the unsubstituted region themselves are approximately symmetric with respect to the chemical shift of $[B_{12}H_{12}]^{2-}$ (Figures 2b−4b).

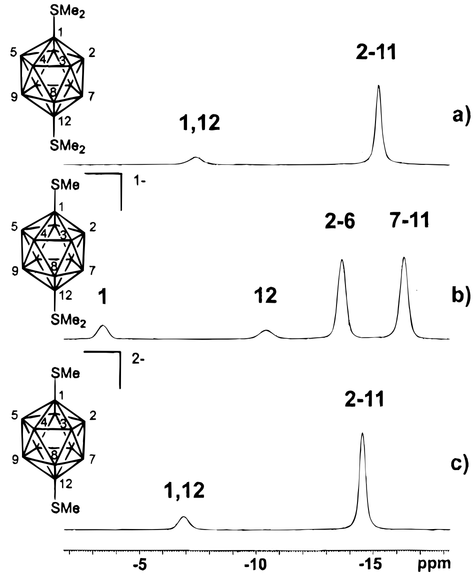
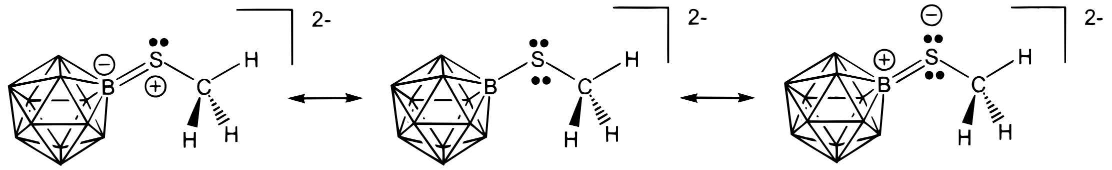


Figure 4. $^{11}B\{^1H\}$ NMR spectra1(160.5 MHz) of $1,12\text{-}(Me_2S)_2B_{12}H_{10}$ (a), $[1\text{-}(MeS)\text{-}12\text{-}(Me_2S)B_{12}H_{10}]^-$ (b), and $[1,12\text{-}(MeS)_2B_{12}H_{10}]^{2-}$ (c) in CD_3CN.

In conclusion, the above results indicate that the effects of MeS^- and Me_2S substituents obtained from the comparison of the spectra of **1** and **2** (Table 1) and applied to the various disubstituted species based on $[B_{12}H_{12}]^{2-}$ are mostly in agreement with the experimental spectra of the disubstituted species. In other words, these substituent effects are additive. We understand that this additivity is only approximate since, for example, it does not account for the chemical shifts of boron atoms of the same type but belonging to different isomers being sufficiently different (for example, the shifts of the β,β-borons in **O** and **M**, Table 2). On the other hand, it still allows us to predict the positions of the boron signals relative to $[B_{12}H_{12}]^{2-}$ and each other correctly in most of the cases. It would be of interest to test the additivity further by analysis of the NMR spectra of the compounds possessing three or more substituents of the above types, e.g., $(MeS)(Me_2S)_2B_{12}H_9$, if such compounds are synthesized. Finally, comparing the spectral data obtained by Hermanek and co-workers[15] for 1,2- and $1,7\text{-}X_2B_{12}H_{10}{}^{2-}$ (X = Cl, Br, I, in d_6-acetone) with our spectra of **O**$^{2-}$ and **M**$^{2-}$ (in CD_3CN) and neglecting the differences between these solvents, it appears as if the MeS^- substituent is very close to the Br^- substituent in its ability to affect the chemical shifts of boron atoms in a *closo*-B_{12} cage.

^1H NMR Spectra of 1, 2, Isomers of $(Me_2S)_2B_{12}H_{10}$, and Anions Derived from Them. In the room temperature ^1H NMR spectrum of **2** a broad quartet is observed due to the methyl hydrogens coupled to the nearest boron atom. Upon broad-band boron decoupling the signal turns into a sharp singlet. No coupling of the methyl hydrogens to boron atoms is observed in the ^1H NMR spectrum of the parent sulfonium anion **1**. As

Chart 3. Resonance Structures of Sulfide Anion **2**



6 **2** **7**

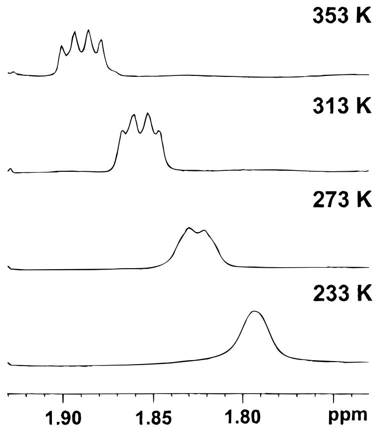


Figure 5. Variable-temperature behavior of the MeS signal in 500 MHz ^1H NMR spectra of $[1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]^-$ in CD_3CN.

for **2**, a broad quartet is observed in the ^1H NMR spectra of $\mathbf{O^{1-}}$, $\mathbf{M^{1-}}$, $\mathbf{P^{1-}}$ due to a methylthio hydrogen coupled to the nearest boron atom, B1 (upon selective boron decoupling at the frequency of B1 this quartet collapses into a singlet). The coupling becomes more resolved at higher temperatures. Thus, the MeS^- signal appears almost like the expected 1:1:1:1 quartet in the ^1H NMR spectrum of $\mathbf{M^{1-}}$ at 80 °C while the coupling is completely wiped out at −40 °C (Figure 5). This is an example of "thermal decoupling".[16] In the room temperature ^1H NMR spectra of $\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, $\mathbf{P^{2-}}$ the methyl signals appear as broad doublets rather than quartets. In fact, for $\mathbf{O^{2-}}$ the corresponding signal is so broad that we could not determine the value of the coupling constant. Nevertheless, the shape of the signals becomes more "quartet-like" at higher temperature, and they all turn into sharp singlets upon broad-band boron decoupling. The presence of H−B coupling via three bonds for methylthio hydrogens in species **2**, $\mathbf{O^{1-}}$, $\mathbf{M^{1-}}$, $\mathbf{P^{1-}}$, $\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, and $\mathbf{P^{2-}}$ vs its absence for dimethyl sulfide hydrogens in **1**, **O**, **M**, **P** , $\mathbf{O^{1-}}$, $\mathbf{M^{1-}}$, and $\mathbf{P^{1-}}$ might suggest a partial double bond character of the B−SMe bonds resulting either from donation of electron density from sulfur atom to the cage or from the negatively charged cage to the sulfur atom, as illustrated by resonance structures **6** and **7** in Chart 3. Some contribution from one of the resonance structures with B−SMe double bonds[17] is supported by the X-ray studies of **2** and $\mathbf{M^{1-}}$ (see below). Of course, the proposed partial double bond character of the B−SMe bonds in anions is very small, because the observed B−S distance in the case of the true boron−sulfur double bond, such as in compound F−B═S, is much shorter (1.606 Å as determined by microwave spectroscopy).[18]

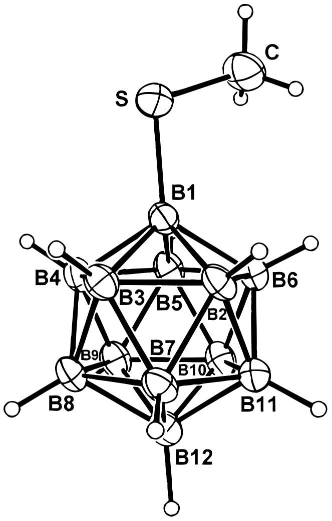


Figure 6. Molecular structure of $[MeSB_{12}H_{11}]^{2-}$.

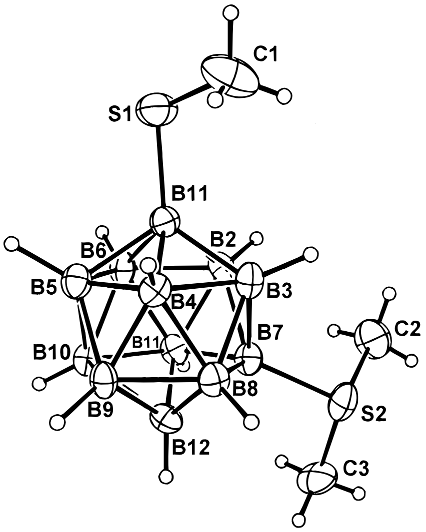


Figure 7. Molecular structure of $[1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]^-$.

The Molecular Structures of $[MePPh_3]_2[MeSB_{12}H_{11}]$ ($[MePPh_3]_2$[2]) and $[MePPh_3][1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]$ ($[MePPh_3][\mathbf{M^{1-}}]$). The molecular structures of anions **2** and $\mathbf{M^{1-}}$ determined by single-crystal X-ray analysis are shown in Figures 6 and 7, respectively. Table 5 gives crystallographic data, and Tables 6 and 7 give selected bond lengths and angles for the anions of $[MePPh_3]_2$[**2**] and $[MePPh_3][\mathbf{M^{-1}}]$.

The molecular structures of anions **2** and $\mathbf{M^{1-}}$ are very similar to those of their parent compounds, **1** and **M**, except that the B−S bonds linking the methylthio substituent to a cage seem to be consistently shorter than those for the dimethyl sulfide substituent. Thus, in **2** the B(1)−S bond length is 1.872(2) Å (Table 6) vs 1.894(4) Å in **1**.[9] Similarly, two B−S bonds in

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[16] Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

[17] The chemical evidence available so far supports the donation of the electron density from cage to sulfur atom. First, sulfide dianions **2**, $\mathbf{O^{2-}}$, $\mathbf{M^{2-}}$, and $\mathbf{P^{2-}}$ can be methylated by trimethylsulfonium iodide,[7] which suggests that a sulfur atom of the methylthio group on the negatively charged cage is more nucleophilic than that in a regular organic methyl sulfide. Second, the preliminary studies showed that under the conditions of electrophilic substitution the sulfide anions derived from $[B_{12}H_{12}]^{2-}$ react on sulfur rather than boron.

[18] Cooper, T. A.; Firth, S.; Kroto, H. W. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1499.

Table 5. Crystallographic Data for $[MePPh_3]_2[MeSB_{12}H_{11}]$ ($[MePPh_3]_2$[**2**]) and $[MePPh_3][1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]$ ($[MePPh_3]$[$\mathbf{M}^{1-}$])

	$[MePPh_3]_2$[**2**]	$[MePPh_3]$[$\mathbf{M}^{1-}$]
empirical formula	$C_{39}H_{50}B_{12}P_2S$	$C_{22}H_{37}B_{12}PS_2$
fw, amu	742.51	526.33
space group	$P2_1$	$P\bar{1}$
a, Å	9.243(1)	9.278(2)
b, Å	18.272(1)	12.003(5)
c, Å	12.548(1)	14.819(7)
α, deg	90	112.18(4)
β, deg	103.17(1)	105.61(3)
γ, deg	90	92.91(3)
vol, Å^3	2063.6(3)	1450(1)
Z	2	2
ρ(calcd), Mg m^{-3}	1.195	1.205
cryst size, mm	0.38 × 0.27 × 0.19	0.38 × 0.20 × 0.10
T, °C	−100	−60
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
μ, mm^{-1}	0.185	0.252
R1[a] [$I \geq 2.0\sigma(I)$]	0.0363	0.064
wR2[b] (all data)	0.0975	0.163

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

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $[MeSB_{12}H_{11}]^{2-}$ (**2**)

Bond Lengths			
S−C	1.804(2)	B(4)−B(9)	1.788(4)
S−B(1)	1.872(2)	B(5)−B(9)	1.765(4)
B(1)−B(6)	1.769(3)	B(5)−B(10)	1.768(3)
B(1)−B(4)	1.770(3)	B(5)−B(6)	1.787(3)
B(1)−B(5)	1.771(3)	B(6)−B(10)	1.782(3)
B(1)−B(3)	1.771(3)	B(6)−B(11)	1.790(3)
B(1)−B(2)	1.781(3)	B(7)−B(11)	1.776(4)
B(2)−B(3)	1.778(3)	B(7)−B(8)	1.779(4)
B(2)−B(7)	1.781(4)	B(7)−B(12)	1.782(3)
B(2)−B(6)	1.784(3)	B(8)−B(12)	1.783(4)
B(2)−B(11)	1.785(3)	B(8)−B(9)	1.794(4)
B(3)−B(4)	1.784(3)	B(9)−B(10)	1.779(3)
B(3)−B(8)	1.787(4)	B(9)−B(12)	1.781(4)
B(3)−B(7)	1.793(3)	B(10)−B(11)	1.785(3)
B(4)−B(5)	1.781(3)	B(10)−B(12)	1.791(4)
B(4)−B(8)	1.783(4)	B(11)−B(12)	1.786(4)
Angles			
C−S−B(1)	102.35(12)	B(5)−B(1)−S	118.09(15)
B(6)−B(1)−S	117.72(15)	B(3)−B(1)−S	125.07(15)
B(4)−B(1)−S	122.21(16)	B(2)−B(1)−S	122.53(15)

Table 7. Selected Bond Lengths (Å) and Angles (deg) for $[1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]^-$ ($\mathbf{M}^{1-}$)

Bond Lengths			
S(1)−C(1)	1.793(6)	B(4)−B(8)	1.769(8)
S(1)−B(1)	1.870(6)	B(4)−B(5)	1.777(7)
S(2)−C(3)	1.798(6)	B(5)−B(10)	1.761(8)
S(2)−C(2)	1.799(6)	B(5)−B(9)	1.778(8)
S(2)−B(7)	1.911(6)	B(5)−B(6)	1.794(8)
B(1)−B(3)	1.780(7)	B(6)−B(10)	1.775(8)
B(1)−B(5)	1.784(8)	B(6)−B(11)	1.783(8)
B(1)−B(2)	1.784(8)	B(7)−B(11)	1.750(7)
B(1)−B(4)	1.791(7)	B(7)−B(12)	1.752(7)
B(1)−B(6)	1.793(7)	B(7)−B(8)	1.767(7)
B(2)−B(7)	1.758(8)	B(8)−B(9)	1.783(8)
B(2)−B(6)	1.778(7)	B(8)−B(12)	1.788(7)
B(2)−B(11)	1.791(7)	B(9)−B(12)	1.768(8)
B(2)−B(3)	1.799(7)	B(9)−B(10)	1.795(7)
B(3)−B(7)	1.758(8)	B(10)−B(12)	1.769(8)
B(3)−B(8)	1.775(8)	B(10)−B(11)	1.770(8)
B(3)−B(4)	1.795(8)	B(11)−B(12)	1.785(8)
B(4)−B(9)	1.768(8)		
Angles			
C(1)−S(1)−B(1)	103.3(3)	B(4)−B(1)−S(1)	122.5(4)
C(3)−S(2)−C(2)	100.1(3)	B(6)−B(1)−S(1)	118.4(3)
C(3)−S(2)−B(7)	105.6(3)	B(11)−B(7)−S(2)	123.0(3)
C(2)−S(2)−B(7)	104.8(3)	B(12)−B(7)−S(2)	120.9(4)
B(3)−B(1)−S(1)	125.4(3)	B(3)−B(7)−S(2)	117.7(3)
B(5)−B(1)−S(1)	118.8(4)	B(2)−B(7)−S(2)	121.4(3)
B(2)−B(1)−S(1)	122.7(3)	B(8)−B(7)−S(2)	117.1(3)

sulfide−sulfonium anion $\mathbf{M}^{1-}$ are distinctly different. The B(1)−S(1) bond length is 1.870(6) Å while the B(7)−S(2) bond is 0.04 Å longer (Table 7). For comparison, the B−S bonds in sulfonium compounds **O**, **M**, and **P** range from 1.889(4) to 1.907(3) Å.[9,10] These differences are statistically significant.[19] The B−B bond lengths and B−B−B angles in **2** range from 1.765(4) to 1.794(3) Å and from 59.3(1)° to 60.7(1)°, respectively. The methyl group is located over a region defined by B2, B5, and B6; therefore, the boron−sulfur bond is tilted away from this side of the cage to reduce the steric interaction between methyl hydrogen atoms and hydrogen atoms on boron atoms. Consequently, the angles of B2−B1−S (122.5(2)°), B5−B1−S (122.2(2)°), and B6−B1−S (125.1(2)°) are larger than those of B3−B1−S (117.7(2)°) and B4−B1−S (118.1(2)°). The B−B bond lengths and B−B−B angles in $\mathbf{M}^{1-}$ are in the ranges 1.750(7)−1.799(7) Å and 59.0(3)−61.5(3)°, respectively. Supposedly due to the steric interaction between boron hydrogens and methyl group, both B−SMe and B−SMe_2 bonds are tilted away from three boron atoms of the adjacent pentagonal faces as discussed above for **2**.

Experimental Section

General Data. $[Me_3S][Me_2SB_{12}H_{11}]$ and isomers **O**, **M**, **P** were prepared by pyrolysis of $BH_3 \cdot SMe_2$ and separated as described earlier.[10] The trimethylsulfonium salt was additionally purified by extraction with hot water and washing with ethanol and pentane followed by extraction with CH_2Cl_2. **M** and **P** were recrystallized from toluene and acetonitrile, respectively. Potassium phthalimide (98%), 2.0 M solution of *n*-BuLi in pentane, ethanethiol (97%), and sodium hydride (95%) were purchased from Aldrich Chemical Co. and used as received. THF and ammonia were dried over sodium and distilled. DMF was distilled from barium oxide. ^{11}B and ^{1}H NMR spectra were obtained on a Bruker DRX-500 spectrometer at 160.5 and 500.1 MHz, respectively. 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 AM-250 and DPX-400 spectrometers operating at 62.9 and 100.6 MHz, respectively. The infrared spectra were recorded on a Mattson Polaris FTIR spectrometer. The elemental analyses were performed by Galbraith Laboratories, Inc.

X-ray Structure Determination. Single-crystal X-ray diffraction data were collected on either an Enraf-Nonius CAD4 diffractometer or an Enraf-Nonius KappaCCD diffraction system. Both instruments employ graphite-monochromated Mo Kα radiation. When the Enraf-Nonius CAD4 diffractometer was used, a single crystal of $[MePPh_3][1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]$ was mounted and sealed inside a glass capillary under nitrogen. 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 2 Å range of 24−30°. Diffraction data were corrected for Lorentz and polarization effects. With the Enraf-Nonius KappaCCD diffraction system, a single crystal of $[MePPh_3]_2[MeSB_{12}H_{11}]$ 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

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(19) The unweighted average of $n = 14$ recent determinations of the distance d_{2i} (B−SMe_2) is $D_2 = 1.900$ Å. Using a standard method,[20] this value was compared with the average d_{1i} (B−SMe), $D_2 = 1.871$ Å, from $m = 2$ determinations. With $S_w = \sum_{i=1}^{14}(d_{2i} - D_2)^2 + \sum_{j=1}^{2}(d_{1i} - D_1)^2 = 6.08 \times 10^{-4}$ Å^2, $s = (S_w/(n + m - 2))^{1/2} = 6.59 \times 10^{-3}$, Student's t is calculated as $(|D_2 - D_1|)/(s(1/n + 1/m)^{1/2}) = 5.82$, which is greater than $t_{14,0.005} = 3.326$. The 95% confidence limits for the difference in bond distances are 0.018 and 0.040 Å.

using DENZO.[21] The structures were solved by direct methods and refined using SHELXTL (difference electron density calculations, full least-squares refinements).[22]

Preparation of [MePPh$_3$]$_2$[MeSB$_{12}$H$_{11}$] ([MePPh$_3$]$_2$[2]). Potassium Phthalimide Method. [Me$_3$S][Me$_2$SB$_{12}$H$_{11}$] (0.2087 g, 0.745 mmol) was placed in a 25 mL three-necked round-bottom flask equipped with a stirbar followed by 0.4172 g of 98% potassium phthalimide (2.207 mmol) and 10−15 mL of DMF. The solution was refluxed under nitrogen for 18 h, and DMF was removed. Distilled water (25 mL) was added to the yellowish residue and stirred. The resulting precipitate was filtered off and a solution of [MePPh$_3$]Br in methanol added to the filtrate until complete precipitation was achieved. White solid was filtered off, washed with 5 mL of ethanol followed by 30 mL of pentane, and dried at 70 °C overnight, yielding 0.5370 g of salt (97%). ^{1}H and ^{11}B NMR spectra of this material were identical to those of the salt synthesized by the alkali metal reduction method (see below).

Alkali Metal Reduction Method. [Me$_3$S][Me$_2$SB$_{12}$H$_{11}$] (0.9408 g, 3.358 mmol) was placed in a 100 mL round-bottom flask equipped with a stirbar. Sodium (0.5451 g, 23.71 mmol) was added, and the flask was attached to a vacuum line and evacuated. Ammonia (8−10 mL) was condensed in the flask with liquid nitrogen, and the flask was immersed in an ethanol−dry ice cold bath at −40 °C. Upon melting of ammonia, a blue color appeared and a noncondensable gas evolved (***CAUTION!*** Pressure in the system should be monitored closely to release gas if necessary). After stirring for 15 min at -40 ± 5 °C ammonia was evaporated and methanol added carefully to the residue to destroy excess sodium. The solvent was removed, the residue was redissolved in water, and the anion was precipitated by addition of [MePPh$_3$]Br in methanol. Pure [MePPh$_3$]$_2$[**2**] was obtained after recrystallization from water−acetonitrile (2.1361 g, 86%). ^{1}H NMR (CD$_3$CN): δ 7.62−7.89 (m, 30H, P(C$_6$$H_5$)$_3$), 2.83 (d, 6H, $J_{H-P} = 14$ Hz, PCH_3), 1.78 (bq, 3H, $J_{H-B} = 4.1$ Hz, SCH_3). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 136.1 (d, $J_{C-P} = 3$ Hz), 134.3 (d, $J_{C-P} = 11$ Hz), 131.2 (d, $J_{C-P} = 13$ Hz), 120.45 (d, $J_{C-P} = 89$ Hz), 15.8 (s), 9.5 (d, $J_{C-P} = 58$ Hz). ^{11}B NMR (CD$_3$CN): δ −5.6 (s, B(1)), −14.3 (d, $J_{B-H} = 126$ Hz, B(2−6)), −15.4 (d, $J_{B-H} = 158$ Hz, B(7−11)), −17.5 (d, $J_{B-H} = 147$ Hz, B(12)). IR (KBr): 3057 (w), 2988 (w), 2919 (m), 2868 (w), 2473 (vs), 1591(w), 1483 (w), 1440 (s), 1335 (w), 1119 (s), 1049 (m), 1000 (w), 900 (s), 844 (m), 798 (m), 766 (m), 740 (m), 721 (m), 690 (s). Anal. Calcd: B, 17.47; S, 4.32; C, 63.08; H, 6.79. Found: B, 17.50; S, 4.49; C, 63.00; H, 6.79.

Preparation of [NMe$_4$]$_2$[MeSB$_{12}$H$_{11}$] ([NMe$_4$]$_2$[2]). In a typical experiment a 50 mL three-necked round-bottom flask equipped with a condenser and a stirbar was charged with 0.4924 g (19.5 mmol) of 95% NaH in a glovebox. About 8 mL of absolute ethanol was added, and the resulting pressure was released through a bubbler. After the gas evolution had ceased, 1.60 mL of 97% EtSH (21.0 mmol) was added to the flask by syringe via a rubber septum. While the apparatus was being purged with N$_2$, 1.1603 g (4.142 mmol) of [Me$_3$S][Me$_2$SB$_{12}$H$_{11}$] was added through one of the necks along with 30 mL of acetonitrile. The mixture was refluxed for 12 h. The resulting solution was filtered into a 250 mL round-bottom flask, and volatiles were removed on a flash evaporator. EtOH (95%, 40 mL) was added to the residue followed by 1.58 g of NMe$_4$OH•5H$_2$O (8.72 mmol). The precipitate was dissolved in hot acetonitrile, the resulting solution was filtered, and the solvent was removed. The product was washed with ethanol and pentane and dried overnight at 70 °C (1.2576 g, 90%). The ^{11}B NMR spectra were identical to those of the [MePPh$_3$]$^+$ salt; ^{1}H and ^{13}C spectra were different only in the cationic part.

Preparation of Isomers of [NMe$_4$][(MeS)(Me$_2$S)B$_{12}$H$_{10}$]. Potassium Phthalimide Method. [NMe$_4$][1-(MeS)-2-(Me$_2$S)B$_{12}$H$_{10}$] ([NMe$_4$][O^{1-}]). A 25 mL three-necked round-bottom flask equipped with a stirbar was charged with 0.1392 g (0.527 mmol) of **O** after chromatography, 0.1066 g (0.564 mmol) of 98% potassium phthalimide, and 10 mL of DMF. The mixture was refluxed overnight under nitrogen followed by solvent removal. Distilled water (15 mL) was added to the residue, and a white precipitate was filtered off and washed with more water. The filtrate and washings (total volume 20 mL) were combined in a beaker, and solid [NMe$_4$]Cl was added until completeness of precipitation was achieved. The precipitate was recrystallized from water to afford 0.1044 g of pure [NMe$_4$][**O^{1-}**] (61%). ^{1}H NMR (CD$_3$CN): δ 3.08 (s, 12H, N(CH_3)$_4$), 2.51 (s, 6H, S(CH_3)$_2$), 1.91 (bq, 3H, $J_{H-B} = 3.9$ Hz, SCH_3). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 56.3 (t, $J_{C-N} = 4$ Hz), 25.4 (s), 15.4 (s). ^{11}B NMR (CD$_3$CN): δ −6.3 (s, B(1)), −8.8 (s, B(2)), −13.1 (d, B(4,5)), −14.1 (d, B(9)), −15.6 (d, B(3,6) and B(8,10)), −16.5 (d, B(7,11) and B(12)). IR (KBr): 3035 (m), 2928 (m), 2487 (vs), 1486 (s), 1426 (s), 1334 (m), 1289 (w), 1054 (w), 1040 (m), 1005 (m), 971 (s), 948 (s), 855 (s), 840 (s), 723 (m).

[NMe$_4$][1-(MeS)-7-(Me$_2$S)B$_{12}$H$_{10}$] ([NMe$_4$][M^{1-}]). The procedure was analogous to that described above for [NMe$_4$][**O^{1-}**] except that in a typical preparation a 50 mL three-necked round-bottom flask was charged with 1.2835 g (4.860 mmol) of **M**, 0.9518 g (5.036 mmol) of 98% potassium phthalimide, and 30 mL of dry DMF. After 3.5 h of reflux, standard workup, and recrystallization, pure [NMe$_4$][**M^{1-}**] was obtained (1.3063 g, 83%).

^{1}H NMR (CD$_3$CN): δ 3.08 (s, 12H, N(CH_3)$_4$), 2.45 (s, 6H, S(CH_3)$_2$), 1.85 (bq, 3H, $J_{H-B} = 4.2$ Hz, SCH_3). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 56.2 (t, $J_{C-N} = 4$ Hz), 26.0 (s), 15.6 (s). ^{11}B NMR (CD$_3$CN): δ −4.5 (s, B(1)), −9.9 (s, B(7)), −13.1 (d, B(5)), −13.7 (d, B(4,6)), −14.8 (d, Hz, B(9,10)), −15.2 (d, B(2,3)), −16.3 (d, B(8,11)), −18.4 (d, B(12)). IR (KBr): 3018 (m), 2917 (m), 2485 (vs), 1479 (s), 1419 (s), 1405 (s), 1332 (w), 1313 (w), 1277 (w), 1066 (w), 1049 (m), 1035 (m), 998 (m), 958 (s), 943 (s), 858 (m), 814 (s), 731 (m). Anal. Calcd: B, 40.14; S, 19.84; C, 26.01; H, 9.67. Found: B, 41.40; S, 19.92; C, 26.01; H, 10.22.

[NMe$_4$][1-(MeS)-12-(Me$_2$S)B$_{12}$H$_{10}$] ([NMe$_4$][P^{1-}]). In a typical experiment a 25 mL three-necked round-bottom flask was charged with 0.6932 g (2.625 mmol) of P, 0.5177 g (2.739 mmol) of 98% potassium phthalimide, and 13 mL of dry DMF. Then the procedure was the same as for the synthesis of the 1,7-isomer. After recrystallization of crude product from water, 0.5861 g of pure [NMe$_4$][**P^{1-}**] was isolated (69%). ^{1}H NMR (CD$_3$CN): δ 3.08 (s, 12H, N(CH_3)$_4$), 2.44 (s, 6H, S(CH_3)$_2$), 1.83 (bq, 3H, $J_{H-B} = 4.2$ Hz, SCH_3). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 56.3 (t, $J_{C-N} = 4$ Hz), 26.3 (s), 15.6 (s). ^{11}B NMR (CD$_3$CN): δ −3.4 (s, B(1)), −10.4 (s, B(12)), −13.6 (d, $J_{B-H} = 133$ Hz, B(2−6)), −16.2 (d, $J_{B-H} = 133$ Hz, B(7−11)). IR (KBr): 3029 (m), 3018 (m), 2963 (m), 2911 (m), 2494 (vs), 2363 (s), 1482 (s), 1448 (w), 1438 (w), 1425 (m), 1412 (w), 1333 (w), 1312 (w), 1288 (w), 1069 (w), 1047 (m), 1035 (s), 1005 (s), 943 (s), 875 (s), 863 (s), 721 (m). Anal. Calcd: S, 19.84; C, 26.01; H, 9.67. Found: S, 20.67; C, 25.94; H, 9.70.

***n*-BuLi Method ([NMe$_4$][M^{1-}] and [NMe$_4$][P^{1-}]).** A 25 mL three-necked round-bottom flask equipped with a stirbar was charged with 0.3660 g (1.386 mmol) of **M**. The flask was evacuated, and 10 mL of dry THF was condensed onto the borane. The flask was warmed up to room temperature and purged with nitrogen, and 0.82 mL of 1.87 M *n*-BuLi in pentane was added to the suspension by syringe via a rubber septum. Within a minute after addition, the solid dissolved completely. After stirring for 3.5 h the reaction was quenched by addition of 2 mL of methanol, solvents were removed, and 20 mL of distilled water was added to the residue. **M** was filtered off, and enough solid [NMe$_4$]Cl was added to ensure the complete precipitation of **M^{1-}**. The precipitate was filtered, washed with 1 mL of water followed by 5 mL of cold ethanol and 10 mL of pentane, and dried overnight at 70 °C (0.3657 g, 82% yield). In a similar experiment 0.2976 g (1.127 mmol) of **P** was stirred in 10 mL of THF with 0.68 mL of 1.84 M *n*-BuLi in pentane for 3 h 10 min. After workup 0.2402 g of [NMe$_4$][**P^{1-}**] was isolated (66%). The products obtained by the *n*-BuLi method were identical by ^{11}B and ^{1}H NMR to those obtained by the potassium phthalimide method.

Sodium Ethanethiolate Method ([NMe$_4$][M^{1-}] and [NMe$_4$][P^{1-}]). In a typical experiment a 25 mL three-necked round-bottom flask equipped with a condenser and a stirbar was charged with 0.1120 g (4.43 mmol) of 95% NaH in a glovebox. About 3 mL of ethanol was added, and the resulting pressure was released through a bubbler. After

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(20) Hamilton, W. C. *Statistics in Physical Science*; Ronald Press Company: New York, 1964; pp 104−107.

(21) Otwinowsky, Z.; Minor, W. Processing of X-ray Diffraction Data Collected in Oscillation Mode. In *Methods in Enzymology, Vol. 276: Macromolecular Crystallography, part A*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; pp 307−326.

(22) *SHELXTL*, version 5.10; Bruker Analytical X-ray Systems; 1997.

the gas evolution had ceased, 0.16 mL of 97% EtSH (2.10 mmol) was added to the flask by syringe via a rubber septum. While the apparatus was purged with N_2, 0.5506 g (2.085 mmol) of **M** was added through one of the necks along with 10−12 mL of acetonitrile. The mixture was refluxed for 2 h. The resulting solution was transferred into a 100 mL round-bottom flask, and volatiles were removed on a flash evaporator. Distilled water (30 mL) was added to the residue and the resulting cloudy solution filtered through a pad of Celite. Solid $[NMe_4]$-Cl was added until the precipitation of $\mathbf{M}^{1-}$ as a white solid was complete. The solid was filtered off, washed with 2−3 mL of distilled water, 4 mL of cold ethanol, and 15 mL of pentane, and dried overnight at 70 °C. The mass of the crude product was 0.5863 g (87% yield). After recrystallization from water 0.5104 g of pure $[NMe_4][\mathbf{M}^{1-}]$ was isolated (76% yield). Using the same procedure 0.3405 g (86%) of crude tetramethylammonium salt of $\mathbf{P}^{1-}$ was obtained from 0.3245 g (1.23 mmol) of **P**, 0.0749 g (2.97 mmol) of NaH, and 0.095 mL (1.25 mmol) of EtSH. The products obtained by the sodium ethanethiolate method were identical by ^{11}B and ^{1}H NMR to those obtained by the potassium phthalimide and *n*-BuLi methods.

Preparation of Isomers of $[NMe_4]_2[(MeS)_2B_{12}H_{10}]$. $[NMe_4]_2[1,2\text{-}(MeS)_2B_{12}H_{10}]$ ($[NMe_4]_2[\mathbf{O}^{2-}]$). A 50 mL round-bottom flask equipped with a stirbar was charged with 0.1967 g (0.745 mmol) of **O** after chromatography and 0.1416 g of sodium (6.16 mmol). The flask was evacuated, and 4−5 mL of dry ammonia was condensed into it with liquid nitrogen. The flask was warmed to −40 °C by being placed into an ethanol−dry ice bath. The solution was stirred for 15 min at −40 ± 5 °C, and ammonia was evaporated. EtOH (20 mL) was added to the residue, the resulting solution was filtered, and solid $NMe_4OH\cdot 5H_2O$ was added until completeness of precipitation. The crude product was recrystallized from methanol−1-propanol, yielding 0.1669 g (59%) of pure $[NMe_4]_2[\mathbf{O}^{2-}]$ (59%). ^{1}H NMR (CD_3CN): δ 3.10 (s, 24 H, $N(CH_3)_4$), 1.87 (bq, 6H, SCH_3). $^{13}C\{^{1}H\}$ NMR (CD_3CN): δ 56.4 (t, $J_{C-N} = 4$ Hz), 15.4 (s). ^{11}B NMR (CD_3CN): δ −5.4 (s, B(1,2)), −14.3 (d, B(3,6)), −14.7 (d, B(4,5,7,11)), −16.7 (d, B(8,10)), −17.5 (d, B(9,12)). IR (KBr): 3032 (m), 3014 (m), 2966 (w), 2955 (w), 2912 (m), 2831 (w), 2485 (s), 1483 (m), 1449 (w), 1442 (w), 1420 (w), 1284 (w), 1036 (w), 963 (m), 950 (m), 849 (m), 723 (w).

$[NMe_4]_2[1,7\text{-}(MeS)_2B_{12}H_{10}]$ ($[NMe_4]_2[\mathbf{M}^{2-}]$). Alkali Metal Reduction Method. In a typical reaction 0.6205 g (2.350 mmol) of **M** was placed in a 100 mL round-bottom flask equipped with a stirbar, followed by 0.3839 g (16.70 mmol) of sodium. Then a procedure similar to that of the preparation of $[NMe_4]_2[\mathbf{O}^{2-}]$ was employed. The anion was precipitated with an ethanol solution of $NMe_4OH\cdot 5H_2O$. After recrystallization from methanol−1-propanol, 0.7009 g of $[NMe_4]_2[\mathbf{M}^{2-}]$ was obtained (78%). ^{1}H NMR (CD_3CN): δ 3.11 (s, 24 H, $N(CH_3)_4$), 1.83 (bq, 6H, $J_{H-B} = 3.7$ Hz, SCH_3). $^{13}C\{^{1}H\}$ NMR (CD_3CN): δ 56.3 (t, $J_{C-N} = 4$ Hz), 15.7 (s). ^{11}B NMR (CD_3CN): δ −5.8 (s, B(1,7)), −13.6 (d, B(2,3)), −14.6 (d, B(4,6,8,11)), −15.8 (d, B(9,10)), −16.8 (d, B(5,-12)). IR (KBr): 3025 (m), 2977 (w) 2916 (m), 2833 (w), 2485 (vs), 1485 (s), 1448 (w), 1437 (w), 1420 (w), 1286 (m), 1038 (m), 962 (s), 949 (s), 859 (m), 814 (s), 731 (m). Anal. Calcd: C, 31.42; H, 10.55; N, 7.33. Found: C, 31.00; H, 11.12; N, 7.28.

Sodium Ethanethiolate Method. A synthesis was carried out similar to that of $[NMe_4]_2[\mathbf{2}]$, except that 0.1983 g of 95% NaH (7.85 mmol), 5 mL of absolute EtOH, 0.60 mL of 97% EtSH (7.85 mmol), and 25 mL of CH_3CN were used with 0.4801 g of **M** (1.818 mmol). After 10.5 h reflux and the usual workup, 0.6216 g of $[NMe_4]_2[\mathbf{M}^{2-}]$ was isolated (89% yield). The product was identical to that obtained by the alkali metal reduction method.

$[NMe_4]_2[1,12\text{-}(MeS)_2B_{12}H_{10}]$ ($[NMe_4]_2[\mathbf{P}^{2-}]$). This preparation was similar to that of $[NMe_4]_2[\mathbf{O}^{2-}]$ and $[NMe_4]_2[\mathbf{M}^{2-}]$. In a typical reaction 0.2745 g (1.04 mmol) of **P** was used with 0.1632 g (7.10 mmol) of sodium. A saturated solution of tetramethylammonium hydroxide pentahydrate in ethanol was used to precipitate the dianion from the ethanol solution obtained after destroying excess sodium. The solid was recrystallized from methanol−1-propanol, yielding 0.2994 g of $[NMe_4]_2[\mathbf{P}^{2-}]$ (75%). ^{1}H NMR (CD_3CN): δ 3.10 (s, 24 H, $N(CH_3)_4$), 1.81 (bq, 6H, $J_{H-B} = 3.4$ Hz, SCH_3). $^{13}C\{^{1}H\}$ NMR ($(CD_3)_2SO$): δ 56.4 (t, $J_{C-N} = 4$ Hz), 15.4 (s). ^{11}B NMR (CD_3CN): δ −6.9 (s, B(1,12)), −14.5 (d, $J_{B-H} = 127$ Hz, B(2−11)). IR (KBr): 3025 (s), 2993 (m), 2971 (m), 2911 (s), 2853 (w), 2823 (w), 2480 (vs), 1482 (s), 1434 (m), 1424 (m), 1412 (m), 1312 (w), 1292 (m), 1282 (m), 1170 (w), 1035 (s), 962 (m), 948 (s), 878 (s), 868 (s), 719 (m). Anal. Calcd: S, 16.77; C, 31.42; H, 10.55. Found: S, 17.36; C, 31.60; H, 11.04.

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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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