Unusual Cationic Tris(Dimethylsulfide)-Substituted *closo*-Boranes: Preparation and Characterization of [1,7,9-(Me$_2$S)$_3$-B$_{12}$H$_9$] BF$_4$ and [1,2,10-(Me$_2$S)$_3$-B$_{10}$H$_7$] BF$_4$

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S Supporting Information

ABSTRACT: Rational syntheses of trisubstituted sulfur-bearing closo-boranes are presented. In the development of these syntheses unusual cationic *closo*-boranes [1,7,9-(Me$_2$S)$_3$-B$_{12}$H$_9$]$^+$ (**3**) and [1,2,10-(Me$_2$S)$_3$-B$_{10}$H$_7$]$^+$ (**4**) have been identified. These were initially recognized to be intermediates in the formation of the neutral trisubstituted species 1,7-(Me$_2$S)$_2$-9-(MeS)-B$_{12}$H$_9$ (**1**) and 1,10-(Me$_2$S)$_2$-2-(MeS)-B$_{10}$H$_7$ (**2**), respectively. Stable tetrafluoroborate salts were prepared and isolated, and their structures are presented. They are believed to represent the first structural determinations of cationic borane clusters of any type.

[1,7,9-(Me2S)3-B12H9]$^+$ [1,2,10-(Me2S)3-B10H7]$^+$
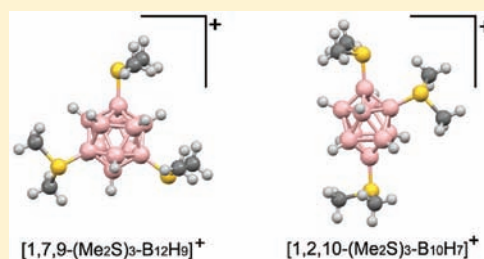
■ INTRODUCTION

Polyhedral boranes bearing sulfur-based substituents have been recognized for their potential utility as precursor agents for use in Boron Neutron Capture Therapy (BNCT).[1−3] While the [B$_{12}$H$_{11}$(SH)]$^{2−}$ anion (or "BSH", in the form of its sodium salt) has been one of the primary therapeutic agents employed in BNCT studies since the early work of Hatanaka et al.,[4,5] introduction of greater numbers of sulfur atoms might offer a simple yet convenient approach to increasing the uptake and retention of the polyborane species by tumor proteins. In this regard, *closo*-B$_{10}$ and B$_{12}$ systems each containing 2 dimethylsulfide ligands are well-known, existing as isomers of the neutral species (Me$_2$S)$_2$B$_{10}$H$_8$ and (Me$_2$S)$_2$B$_{12}$H$_{10}$. These compounds were initially prepared many years ago,[6−9] but have been fully characterized only in more recent times.[10−12] The challenge in the present work is to investigate and improve routes to stable polyborane clusters bearing larger numbers of sulfur-based substituents.

Here we present rational syntheses of trisubstituted sulfur-bearing *closo*-boranes [1,7-(Me$_2$S)$_2$-9-(MeS)-B$_{12}$H$_9$] (**1**) and [1,10-(Me$_2$S)$_2$-2-(MeS)-B$_{10}$H$_7$] (**2**). In the process of developing these syntheses we have identified the unusual cationic *closo*- species [1,7,9-(Me$_2$S)$_3$-B$_{12}$H$_9$]$^+$ and [1,2,10-(Me$_2$S)$_3$-B$_{10}$H$_7$]$^+$. These cluster cations were initially postulated as intermediates in the preparation of neutral compounds **1** and **2**, respectively, but were ultimately isolated and structurally characterized as stable tetrafluoroborate salts, **3** and **4**. The structures of these salts are presented here, and are believed to represent the first examples of cationic *closo*-borane clusters, and indeed the first structural determinations of cationic borane clusters of any type. While a small number of cationic borane species have been reported previously, these have generally been based on smaller (from 1 to 6 boron atoms) and more open cage architectures, and have been characterized only by spectroscopic methods.[13−20] Additionally, a small number of cationic metallacarborane clusters have been reported.[21−25] These generally contain charge-compensated dicarbollide ligands such as [9-(CH$_3$)$_2$S-7,8-*nido*-C$_2$B$_9$H$_{10}$]$^−$ and [10-(CH$_3$)$_2$S-7,8-*nido*-C$_2$B$_9$H$_{10}$]$^−$. While these metal-containing (M = Fe, Ru, Co, Pd) complexes are somewhat different in nature from the all-boron clusters we describe in the present work (since some significant fraction of the positive charge on the cluster can be thought to be borne by the metal center itself) they do represent some of the few examples of cationic boron-based clusters of any type.

First reported in the mid-1960s, the reaction of dimethylsulfoxide (DMSO) with *closo*-borates (B$_n$H$_n^{2−}$) in acidic media was shown to generate monosubstituted inner-sulfonium mono-anions of the type [B$_n$H$_{n−1}$(SMe$_2$)]$^−$, with disubstituted neutral species, B$_n$H$_{n−2}$(SMe$_2$)$_2$, being obtained with extended reaction times. In 1965, Muetterties et al. reported that the reaction between B$_{10}$H$_{10}^{2−}$ and DMSO at temperatures below 60 °C for 1 h produced a mixture of the disubstituted isomers 1,10-(Me$_2$S)$_2$-B$_{10}$H$_8$ and 1,6-(Me$_2$S)$_2$-B$_{10}$H$_8$. The major product, 1,10-(Me$_2$S)$_2$-B$_{10}$H$_8$, underwent thermal rearrangement to 2,7(8)-(Me$_2$S)$_2$-B$_{10}$H$_8$ at 230 °C.[6] Wright and Kaczmarczk later reported that the reaction of B$_{12}$H$_{12}^{2−}$ with DMSO in acetic anhydride over a 2 h period gave [B$_{12}$H$_{11}$(SMe$_2$)]$^−$, with mixtures of isomers of neutral (Me$_2$S)$_2$B$_{12}$H$_{10}$ species detected by ^{11}B NMR after 27 h.[9] Only after stirring for periods as long as 3 weeks at room temperature were the disubstituted

compounds obtained as the major products. This pattern of increasing substitution with time was also reported in 1982 by Wong and co-workers for the *closo*-nonaborate system.[26] Reaction of $B_9H_9^{2-}$ with DMSO for 4 h produced $[B_9H_8(SMe_2)]^-$, while a reaction time of 2 days gave $(Me_2S)_2B_9H_7$.

A more recently developed approach to dimethylsulfide-substituted icosahedral boranes is via pyrolysis of the commercially available monoboron species $BH_3 \cdot SMe_2$ at 125 °C.[10,12] This method possesses potential for preparation of isotopically enriched clusters for therapeutic applications and has been shown to produce all three isomers of $(Me_2S)_2B_{12}H_{10}$, as well as $[Me_3S][B_{12}H_{11}(SMe_2)]$. Furthermore, it avoids the need to handle the large quantities of potentially hazardous diborane required by an earlier similar approach.[8]

Despite the relative facility with which one or two exopolyhedral sulfur-bearing groups can be incorporated into *closo*-dodecaborate structures, the only previously reported icosahedral *closo*-dodecaborane with three sulfur-based substituents, $1,7\text{-}(Me_2S)_2\text{-}9\text{-}(S\text{-}2',4'\text{-}(NO_2)_2C_6H_3)\text{-}B_{12}H_9$, was prepared in this laboratory from the reaction between $1,7\text{-}(Me_2S)_2\text{-}B_{12}H_{10}$ and $2,4\text{-}(NO_2)_2C_6H_3SCl$.[27]

Similarly, the first example of a *closo*-decaborane bearing 3 exopolyhedral sulfur substituents, $1,10\text{-}(Me_2S)_2\text{-}2\text{-}(MeS)\text{-}B_{10}H_7$, was also prepared in this laboratory.[28] Its preparation is particularly interesting for its potential utility as a precursor to $1,2,10\text{-}(SH)_3\text{-}B_{10}H_7^{2-}$, a triply substituted 10-vertex analogue of the ubiquitous $B_{12}H_{11}(SH)^{2-}$ ion.

Here, we present synthetic routes and structural characterization of neutral and cationic *tris*-substituted 10- and 12-vertex *closo*-boranes.

■ RESULTS AND DISCUSSION

Neutral *Closo*-Boranes Bearing 3 Exopolyhedral Sulfur Substituents. As mentioned above, there exists a paucity of examples of *closo*-dodecaboranes bearing more than two exopolyhedral sulfur substituents. The only previously reported species of which we are aware, $1,7\text{-}(Me_2S)_2\text{-}9\text{-}(S\text{-}2',4'\text{-}(NO_2)_2C_6H_3)\text{-}B_{12}H_9$, was prepared in this laboratory from the reaction between $1,7\text{-}(Me_2S)_2\text{-}B_{12}H_{10}$ and $2,4\text{-}(NO_2)_2C_6H_3SCl$.[27] Even using a large excess of 2,4-dinitrobenzenesulfenyl chloride, only a single displacement product was obtained in this reaction, with no evidence of other compounds resulting from further displacement. When this procedure was later attempted with the isomeric $1,12\text{-}(Me_2S)_2\text{-}B_{12}H_{10}$ instead of $1,7\text{-}(Me_2S)_2\text{-}B_{12}H_{10}$ no reaction occurred, even after heating under reflux in acetonitrile for a prolonged period, see Scheme 1, below.

Similarly, no reaction occurred even after several hours upon heating $1,12\text{-}(Me_2S)_2B_{12}H_{10}$ with DMSO in 1.0 M HCl/acetic acid solution. Not only does the overall negative charge on the cluster diminish with each successive (charge-compensating) substitution, but the symmetry of the 1,12- disubstituted cluster means that each B-SMe_2 function is adjacent to 5 of the 10 equivalent unsubstituted (B–H) boron atoms, and that no boron vertex is more than 1 position removed from that of sulfur substitution. Thus the net inductive effect of each substituted vertex is distributed equally over 5 equivalent positions, and does not render any particular vertex susceptible to further electrophilic attack.

In contrast to the low reactivity observed for $1,12\text{-}(Me_2S)_2B_{12}H_{10}$, reaction was evident between $1,7\text{-}(Me_2S)_2B_{12}H_{10}$ and DMSO in acid solution within an hour.

Scheme 1. Reactions of $1,7\text{-}(Me_2S)_2\text{-}B_{12}H_{10}$ and $1,12\text{-}(Me_2S)_2\text{-}B_{12}H_{10}$ with $2,4\text{-}(NO_2)_2C_6H_3SCl$
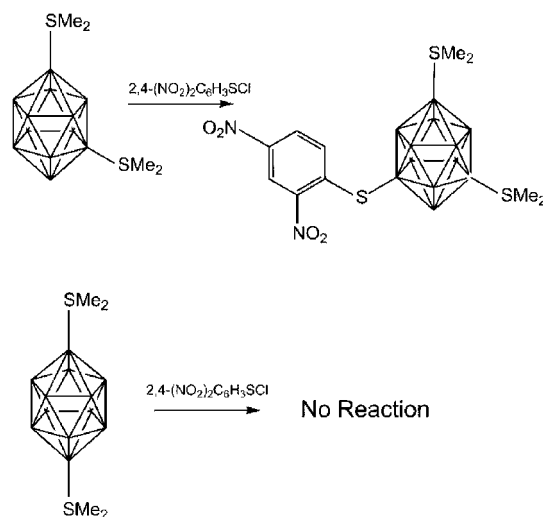

The reaction was monitored by $^{11}B\{^1H\}$ NMR spectroscopy, with the spectrum of the acetic acid reaction solution showing 4 peaks of equivalent intensity, consistent with the effective 3-fold symmetry expected for the $[1,7,9\text{-}(Me_2S)_3\text{-}B_{12}H_9]^+$ cation (see below). Upon addition of water a white solid was isolated, the $^{11}B\{^1H\}$ spectrum of which differed from that of the reaction solution, showing 8 peaks of relative intensities 1:2:1:2:2:2:1:1 indicative of a lower (effective C_s) symmetry environment and very similar to that of the known species $1,7\text{-}(Me_2S)_2\text{-}9\text{-}(S\text{-}2',4'\text{-}(NO_2)_2C_6H_3)\text{-}B_{12}H_9$.[27] The isolated product was consistent with loss of a methyl group from one of the SMe_2 functions. This leads to the neutral $1,7\text{-}(Me_2S)_2\text{-}9\text{-}MeS\text{-}B_{12}H_9$ formulation, as shown by Reaction 1.

$$(1)$$
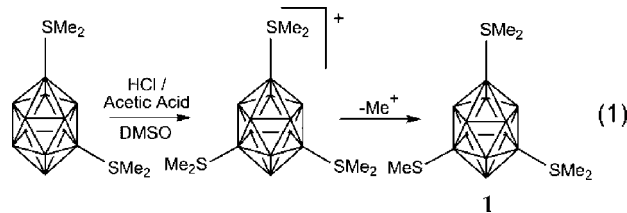
Although the proposed intermediate cationic species appeared to be relatively stable in the reaction mixture, it did not prove possible to directly isolate it, either by precipitation from solution or by removal of volatiles under vacuum. Irrespective of the type of workup employed, the cation invariably lost Me^+ to produce **1**.

The product was recrystallized from methanol. Elemental and mass spectral analysis were consistent with the $1,7\text{-}(Me_2S)_2\text{-}9\text{-}(MeS)B_{12}H_9$ formulation. A single crystal X-ray analysis was performed, and the molecular structure is shown in Figure 1. There are two independent molecules in the asymmetric unit, one of which is shown in Figure 1.

Crystallographic data appear in Table 1. Selected bond lengths and interbond angles for both independent molecules of **1** are given in the Supporting Information, Table S1. The structure suffered from some problems of disorder in the position of one SMe_2 moiety and the SMe function. The major contributions to the dimethylsulfide group connected to B7 (S2, C3, and C4) and to the SMe group on B9 (S3 and C5) possess about 87% occupancy. Only the major contributions S2A, C3A, C4A, S3A, and C5A are shown in Figure 1. Similar
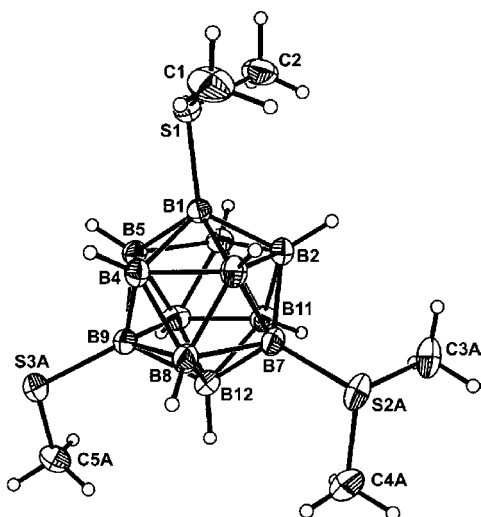
Figure 1. Molecular structure of 1,7-(Me$_2$S)$_2$-9-(MeS)B$_{12}$H$_9$, **1**. Non-hydrogen atoms are represented as 25% probability ellipsoids.

Table 1. Crystallographic Data for Compounds 1, 3, and 4

	1	3	4
empirical formula	C$_5$H$_{24}$B$_{12}$S$_3$	C$_6$H$_{27}$B$_{13}$F$_4$S$_3$	C$_6$H$_{25}$B$_{11}$F$_4$S$_3$
formula weight (amu)	310.14	411.99	388.35
T (K)	299(2)	150(2)	200(2)
crystal system	monoclinic	triclinic	monoclinic
space group	P2(1)/c	P$\bar{1}$	P2(1)/c
a (Å)	13.86920(10)	11.3549(2)	6.8974(1)
b (Å)	14.59720(10)	13.4361(2)	14.8720(2)
c (Å)	18.26530(10)	13.7877(2)	19.7272(2)
α (deg)	90	84.9478(6)	90
β (deg)	110.8446(4)	88.4436(6)	91.0929(6)
γ (deg)	90	88.3986(8)	90
vol (Å^3)	3455.81(4)	2093.89(6)	2023.21(3)
Z	8	4	4
density (calcd, g cm^{-3})	1.192	1.307	1.275
μ (mm^{-1})	0.405	0.377	0.387
crystal size (mm)	0.22 × 0.19 × 0.18	0.12 × 0.08 × 0.04	0.50 × 0.50 × 0.35
θ range (deg)	2.10 − 27.48	2.03 − 25.25	2.48 − 25.02
index ranges	−17 ≤ h ≤ 18	−13 ≤ h ≤ 13	−8 ≤ h ≤ 8
	−18 ≤ k ≤ 18	−15 ≤ k ≤ 15	−17 ≤ k ≤ 17
	−23 ≤ l ≤ 23	−16 ≤ l ≤ 16	−23 ≤ l ≤ 23
reflections collected	15490	14229	13197
independent reflections	7907	7379	3576
R$_{int}$	0.0244	0.0316	0.0213
completeness to θ	99.9%	97.3%	99.9%
data/restraints/parameters	7907/11/533	7379/0/541	3576/3/254
goodness-of-fit on F^2	1.048	1.023	1.018
final R indices [I ≥ 2.0σ(I)]	R1 = 0.0513	R1 = 0.0501	R1 = 0.0542
	wR2 = 0.1314	wR2 = 0. 1164	wR2 = 0.1463
R indices (all data)	R1 = 0.0839	R1 = 0.0788	R1 = 0.0633
	wR2 = 0.1471	wR2 = 0.1304	wR2 = 0.1536

disorder is also present in the second independent molecule, with the corresponding major contributors (S4A, C6A, C7A, S6A, and C10A) possessing around 55% occupancy in this case. No disorder was evident at any other positions. B−B distances involving sulfonium-substituted boron positions within the

boron cages generally appear slightly shorter than others, while those involving the methylthio-substituted boron atom are similar to those involving the remaining unsubstituted (B−H) vertices. The B−S distances are consistently around 1.9 Å, and the shortened distances between B1 or B7 (B21 and B27 in the second molecule) and their neighboring boron atoms appear to be compensated by the lengthening of the connectivity between B2 (B22) and B3 (B23), their common neighbors. Indeed, B2−B3 (B22−B23) is the only B−B connectivity in the molecule whose length exceeds 1.80 Å. These differences would not appear to be statistically significant, however, and the disorder present in the cluster would lead us to exercise extreme caution against overinterpreting these results. Steric repulsion between methyl hydrogens on the substituents and B−H hydrogens on the cage appear to result in some slight asymmetry about the substituted atoms. Specifically, in the case of each sulfur-substituted vertex, the B−S vector is tilted approximately 5 degrees away from a symmetrical position, resulting in two S−B−B angles that are significantly larger than the other three. These features are also observed in the second independent molecule in the crystal structure of **1**, as well as in the structures of all 3 isomers of (SMe$_2$)$_2$-B$_{12}$H$_{10}$.[10,12]

A 10-vertex analogue of compound **1**, 1,10-(Me$_2$S)$_2$-2-(MeS)-B$_{10}$H$_7$, **2**, was prepared previously in this laboratory.[28] The reported synthetic route to **2** (using DMSO as solvent/reactant and passage of HCl gas for 1 h) was based on the earlier work of Knoth, Hertler, and Muetterties who had reported the formation of mixtures of monosubstituted B$_{10}$H$_9$[S(CH$_3$)$_2$]$^-$ and disubstituted B$_{10}$H$_8$[S(CH$_3$)$_2$]$_2$ isomers under these conditions (with no further substitution observed even upon extended reaction times).[6] This reaction is somewhat exothermic, and accurate control of the reaction temperature is challenging. An initial spike in temperature was proposed to be crucial in producing the observed tertiary substitution, with the trisubstituted neutral species 1,10-(Me$_2$S)$_2$-2-(MeS)-B$_{10}$H$_7$, **2**, being isolated in addition to the previously known disubstituted products. Compound **2** was fully characterized,[28] but the previously reported synthetic procedure was ultimately shown to be unreliable. In repeated experiments, isolated yields of compound **2** were typically lower than the 14% reported. Consequently, this synthetic route was studied with a view to improving yields and reliability.

In other reported reactions of *closo*-borates with DMSO, reaction times ranged from a few days to a few weeks.[9,26] The effect of time on the degree of cluster substitution was consistently demonstrated. Muetterties et al. had also reported that under more acidic conditions (using glacial acetic acid as solvent), no monosubstitution was observed, and isomers of B$_{10}$H$_8$[S(CH$_3$)$_2$]$_2$ were produced exclusively, irrespective of reaction time. However, no reaction time exceeding 1 h was described in the report.[6]

With these considerations in mind, the preparative route to **2** was subjected to longer reaction time (2−3 h), and this proved to be successful in producing reliable and reproducible trisubstitution on the cluster in reasonable yields. Two methods were investigated, and each gave similar results. *Method A* involved reaction of Cs$_2$B$_{10}$H$_{10}$ and DMSO with glacial acetic acid as solvent. The mixture was subjected to a slow flow of HCl gas for a period of 2−3 h with stirring at 55−60 °C. It was also possible to obtain reasonable yields of the product with a more prolonged reaction at lower temperature. HCl was allowed to flow for 6 h, then the gas flow was suspended and the mixture was stirred for 18 h at room temperature before the

process was repeated. *Method B* differed only in the use of freshly obtained 1.0 M HCl/acetic acid solution as solvent and thus obviated the need for the use of gaseous HCl. This reaction was similarly held at 55−60 °C for 2−3 h. Both methods shared a common aqueous workup, and each gave yields in the region of 60%.

The reactions were monitored by $^{11}B\{^1H\}$ NMR spectroscopy. Mixtures of disubstituted compounds were evident at early stages of the reaction, along with signals in the vicinity of those for the known compound **2**. As the reaction proceeded the solution turned a clear light yellow and eventually cloudy almond. The distribution of major peaks in its $^{11}B\{^1H\}$ NMR spectrum was very similar to that observed for known compound **2**. The slight differences in chemical shifts between the spectra were initially thought to be due to solvent effects (acetic acid versus CD_2Cl_2, which was commonly used as solvent for NMR spectra of **2**). This assumption was, however, found to be flawed, as discussed below. In an analogous fashion to reaction 1, reaction 2 was ultimately found to proceed via a cationic intermediate, as shown below.
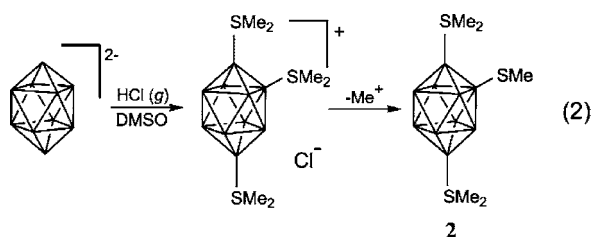
While the reaction mixture displayed peaks in the ^{11}B NMR spectrum that initially appeared similar to those of compound **2**, they were ultimately shown to be attributable instead to the $[1,2,10\text{-}(Me_2S)_3\text{-}B_{10}H_7]^+$ cation (see below). Unlike the case of the dodecaborates $1,7\text{-}(Me_2S)_2\text{-}9\text{-}(SMe)B_{12}H_9$, **1** and $[1,7,9\text{-}(Me_2S)_3\text{-}B_{12}H_9]$ BF_4, **3** (see below) which have markedly different effective cluster symmetries (C_s and C_{3v} respectively), the 10-vertex analogues $1,10\text{-}(Me_2S)_2\text{-}2\text{-}(MeS)\text{-}B_{10}H_7$, **2** and $[1,2,10\text{-}(Me_2S)_3\text{-}B_{10}H_7]^+$, **4** both possess effective C_s symmetry, leading to gross similarity in their $^{11}B\{^1H\}$ spectra.

Preparation, Isolation, and Strucures of Trisubstituted Cationic Boranes. The preparations of the neutral species **1** and **2** raised the question of why only a single methyl group remained on one of the sulfur substituents in $1,7\text{-}(Me_2S)_2\text{-}9\text{-}(MeS)\text{-}B_{12}H_9$ and $1,10\text{-}(Me_2S)_2\text{-}2\text{-}(MeS)\text{-}B_{10}H_7$. This spontaneous loss of a methyl group from a dimethylsulfide function has not been previously reported in the chemistry of inner sulfonium *closo*-borates, although such methyl loss has precedent in metal-containing systems containing charge-compensated dicarbollide ligands such as $[9\text{-}Me_2S\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$ and $[10\text{-}Me_2S\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$.[21,24,25] Upon aerial oxidation, the ferracarborane $[commo\text{-}3,3'\text{-}Fe\text{-}4,4'\text{-}(Me_2S)_2\text{-}1,1',2,2'\text{-}(C_2B_9H_{10})_2]$ produces the $[commo\text{-}3,3'\text{-}Fe\text{-}4,4'\text{-}(Me_2S)_2\text{-}1,1',2,2'\text{-}(C_2B_9H_{10})_2]^+$ cation that can spontaneously lose a methyl group to generate the neutral Fe^{III} species $[commo\text{-}3,3'\text{-}Fe\text{-}4\text{-}(Me_2S)\text{-}4'\text{-}(MeS)\text{-}1,1',2,2'\text{-}(C_2B_9H_{10})_2]$.[21] More recently, a series of related (arene)ruthenacarboranes have been observed to undergo similar demethylations at the dimethylsulfonium function.[24,25] Indeed, apparently stepwise double demethylations have been observed in these cases, resulting first in thioether- and subsequently in mercaptan-substituted ruthenacarboranes

To the best of our knowledge, there are no previous reports of spontaneous loss of a methyl group from DMSO itself under

acidic conditions, lending support to the suggestion that neutral clusters **1** and **2** are formed by loss of Me^+ from an inner sulfonium function attached to boron, rather than by attack on a disubstituted species by a pre-existing MeS^- or $MeSO^-$ nucleophile. This is also consistent with the facile demethylation processes described above for the iron- and ruthenium-containing metallcarboranes. We propose that $1,10\text{-}(Me_2S)_2\text{-}2\text{-}(MeS)\text{-}B_{10}H_7$ is formed via the cationic intermediate species $[1,2,10\text{-}(Me_2S)_3\text{-}B_{10}H_7]^+$, as shown in reaction 2.

In both cases, the predominant borane compound in the acidic reaction solution and the isolated product were clearly quite different. Although the reactions appeared to proceed via the intermediates $[1,7,9\text{-}(Me_2S)_3\text{-}B_{12}H_9]^+$ and $[1,2,10\text{-}(Me_2S)_3\text{-}B_{10}H_7]^+$, more direct evidence for these unusual cationic clusters was necessary. It was initially thought that simple removal of the volatiles from the reaction solutions might directly afford the cationic intermediates. However, this approach did not prove to be successful and the neutral compounds **1** and **2** were again obtained. Thus, addition of water was shown to be unnecessary for the loss of a methyl group from these species. This failure to directly isolate the desired cationic intermediates led to an alternate path. Consequently, methylation of **1** and **2** was carried out using $[Me_3O]$ BF_4 in dichloromethane for 3 h.

Salts **3** and **4**, containing the unusual cluster cations, were easily and cleanly prepared via methylation of $1,7\text{-}(Me_2S)_2\text{-}9\text{-}MeS\text{-}B_{12}H_9$ and $1,10\text{-}(Me_2S)_2\text{-}2\text{-}(MeS)\text{-}B_{10}H_7$ respectively, as shown in reactions 3 and 4, below.
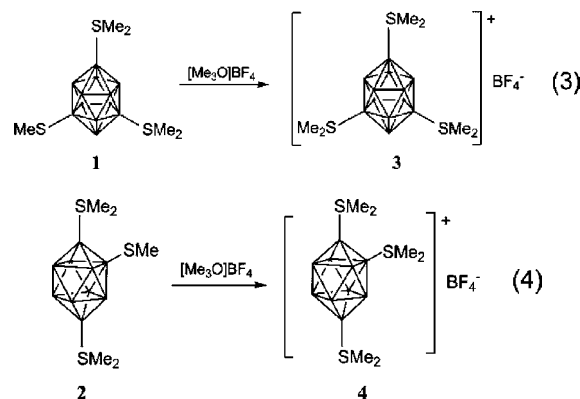

This not only served as support for the cationic intermediates proposed above, but also gave air-stable tetrafluoroborate salts, $[1,7,9\text{-}(Me_2S)_3\text{-}B_{12}H_9]$ BF_4, **3**, and $[1,2,10\text{-}(Me_2S)_3\text{-}B_{10}H_7]$ BF_4, **4**, the structures of which were successfully determined by single crystal X-ray diffraction.

$[1,7,9\text{-}(Me_2S)_3\text{-}B_{12}H_9]$ BF_4, 3. The compound was characterized by ^1H, ^{11}B, and ^{13}C NMR spectroscopy, all of which were consistent with the effective 3-fold symmetry of the cation. Electrospray mass spectrometry revealed a parent ion peak for the $[1,7,9\text{-}(Me_2S)_3\text{-}B_{12}H_9]^+$ ion at 325.2458 amu.

Single crystal X-ray diffraction revealed two independent formulas in the asymmetric unit, which were effectively identical, with only slight differences in torsion angles about the B−S bonds. The $[1,7,9\text{-}(Me_2S)_3\text{-}B_{12}H_9]^+$ cation from one independent formula is shown in Figure 2.

Crystallographic data for $[1,7,9\text{-}(Me_2S)_3\text{-}B_{12}H_9]$ BF_4 are given in Table 1, with selected bond lengths and interbond angles for both independent formulas provided in Supporting Information, Table S2.

The boron−sulfur distances in **3** are consistently around 1.9 Å. The same type of asymmetry about the sulfur-substituted
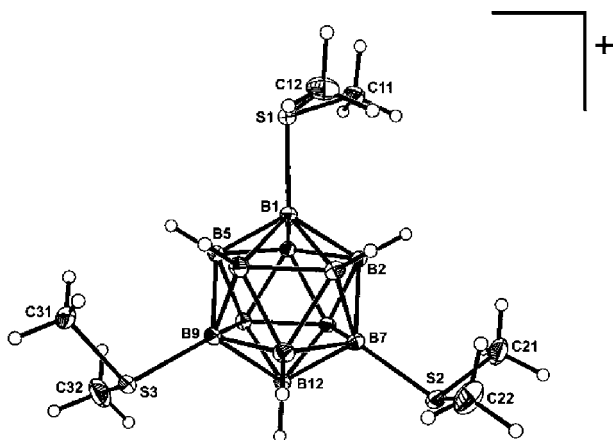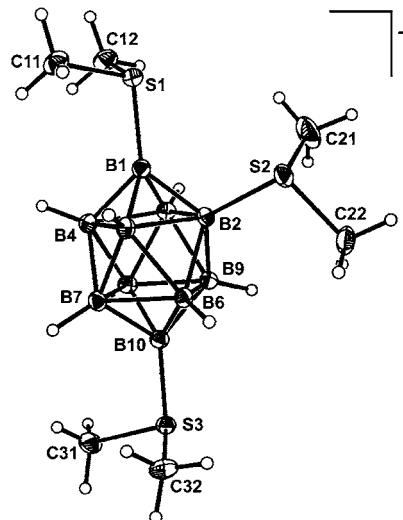
Figure 2. Molecular structure of the $[1,7,9\text{-}(Me_2S)_3\text{-}B_{12}H_9]^+$ cation. Non-hydrogen atoms are represented as 25% probability ellipsoids.

vertices is observed in this structure as in structure **1**, where each B−S vector is slightly tilted with respect to the cage centroid as a result of steric repulsion between methyl- and cage-H atoms. B−B distances involving the sulfonium-substituted boron atoms (B1, B7, B9 and B21, B27, B29) again generally appear slightly shorter than those involving only unsubstituted (B−H) vertices. In an earlier study,[29] Student's t was used to examine the difference between the B-SMe bond distances in $[1\text{-}(MeS)\text{-}7\text{-}(Me_2S)B_{12}H_{10}]^-$ and $[(MeS)\text{-}B_{12}H_{11}]^{2-}$ and the unweighted average of 14 recent determinations of B-SMe$_2$ bond distances. In compound **3**, there appear to exist some unusually long B−B distances, present as part of the bridge between pairs of B-SMe$_2$ moieties. A typical example is the B(2)−B(3) distance, 1.808(5) Å, which forms part of the bridge between B(1) and B(7). The unweighted average value for all 6 such connectivities (3 per independent molecule) is 1.8125(57) Å compared to 1.7720(137) Å for the remaining 54 boron−boron distances in the structure. To investigate the significance of these differences, calculations were performed using the Welch Statistic which is appropriate for use with two samples having different variances.[30] These differences do appear to be statistically significant, and should be considered a genuine structural feature of the cluster.[31] A Bayesian type calculation yielded similar results.[32]

In the simplest analysis, it would appear that the intracage bonding of the sulfonium-substituted boron atoms, B(1), B(7), and B(9) is slightly stronger than that of the other boron atoms. This suggests that these particular boron atoms are more able to devote electron density to cluster bonding, since both electrons in the exopolyhedral pair are being supplied by the (formally positive) −SMe$_2$ substituent. In contrast, the other nine boron atoms must formally dedicate one electron to the exopolyhedral B−H bond.

$[1,2,10\text{-}(Me_2S)_3\text{-}B_{10}H_7]$ BF$_4$, **4**. Compound **4** was recrystallized from methanol, and the $^{11}B\{^1H\}$ NMR spectrum of the pure product was obtained. It is essentially identical to that of the acidic reaction solution from Reaction 2 except for the additional signal from the tetrafluoroborate counterion. The isolated salt $[1,2,10\text{-}(Me_2S)_3\text{-}B_{10}H_7]$ BF$_4$, **4**, was found to be stable and was further characterized by mass spectroscopy and X-ray crystallographic analysis. The structure of the cluster cation is shown in Figure 3.

Crystal data are given in Table 1 and selected bond distances and interbond angles for $[1,2,10\text{-}(Me_2S)_3\text{-}B_{10}H_7]$ BF$_4$ are listed

Figure 3. Molecular structure of the $[1,2,10\text{-}(Me_2S)_3\text{-}B_{10}H_7]^+$ cation. Non-hydrogen atoms are represented as 25% probability ellipsoids.

in Supporting Information, Table S3), which also contains corresponding values for the previously reported neutral compound, **2**.[28,33]

The X-ray structure shows the expected sulfonium substitution at the 1, 2, and 10 positions. While the cluster cation is well behaved, two of the fluorine atoms in the tetrafluoroborate counterion suffer from positional disorder. Apical B−S distances in the cationic cluster are B(1)−S(1) = 1.861(2) Å, and B(10)−S(3) = 1.862(2) Å, and are effectively identical to the two apical B-SMe$_2$ distances in neutral compound **2**, which are both reported as 1.866(2) Å. The equatorial B-SMe distance in compound **2** is 1.854(2) Å, compared to B(2)−S(2) = 1.877(2) Å in cationic cluster **3**. Although this difference is small, B-SMe bonds have previously been reported to be slightly shorter than B-SMe$_2$ bonds, attributed to some small degree of double bond character between boron and sulfur.[29]

Methylation of **2** to produce **4** does not appear to result in any gross structural changes to the cluster. This is unsurprising as the skeletal electron pair count is formally unaffected by methylation. We can, however, point out some features of the structure of **4** that may result from the addition of the extra methyl group at S(2). The most striking features are the distances from B(2) to B(3) and B(5) (within the upper equatorial belt) and to B(6) and B(9) in the lower belt. These distances each appear to suffer from slight contraction, in comparison to other connectivities of their type. The B(2)−B(3) and B(2)−B(5) distances are 1.833(3) Å and 1.834(3) Å respectively, the shortest of all intraequatorial distances in the cluster and approximately 0.030 Å shorter than the average of the six remaining B−B connectivities within the equatorial planes, 1.8638(54) Å. Since only two intraequatorial connectivities appear to undergo this minor contraction, the significance of these differences is questionable. However, out of curiosity calculations were carried out based on the Welch statistical procedure,[30] and resulted in 95% confidence limits of 0.0303 ± 0.0058 Å. The Bayesian method applied in the case of

compound **3** (above) was not applied in this instance as it requires at least 5 samples within each mean.[32]

Interequatorial distances from B(2) to B(6) and B(9) in the lower belt are 1.784(5) Å and 1.788(5) Å respectively, the only connectivities of this type in the structure that are less than 1.8 Å. Calculations were again performed using the Welch statistic[30] to compare the average of these two shorter distances (1.7855(7) Å) with the average of the other 6 interequatorial connectivities (1.8145(87) Å), resulting in 95% confidence limits of 0.0290 ± 0.0093 Å. While any significance of these relatively small distortions should not be overstated, it should be noted that these patterns are not observed in the corresponding distances to the −SMe-bearing B(2) in the structure of neutral compound **2**.

■ EXPERIMENTAL SECTION

General Information. Reactions were generally performed following standard high vacuum and inert atmosphere techniques.[34] Some subsequent workup procedures were conducted in air, where described. CH_2Cl_2, $1,2$-$C_2H_4Cl_2$, and CH_3CN were dried over P_2O_5 and distilled into storage bulbs for use. Toluene was dried by stirring over sodium-benzophenone ketyl, followed by distillation into storage bulbs containing sodium-benzophenone ketyl. DMSO was dried over BaO, distilled under vacuum, and stored in a glovebox over type 4A Linde molecular sieves. HCl-acetic acid solution (1.0 M) was obtained from Aldrich Chemical Co. and used as received.

Column Chromatography. Chromatography was performed using Selecto silica gel, 230−430 mesh (Fisher Scientific). For the separation of boron cages, fractions were obtained after analysis by TLC using a palladium dichloride stain prepared by dissolution of 0.5 g of $PdCl_2$ in 27 mL of concentrated HCl followed by dilution to 1 L with methanol.

Nuclear Magnetic Resonance Spectroscopy. ^1H NMR spectra were obtained on Bruker DRX-500, DPX-400, and AM-250 spectrometers operating at 500.1, 400.1, and 250.1 MHz, respectively, and were referenced to residual proton signals of deuterated solvents. ^{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 peaks. ^{11}B NMR spectra were obtained on Bruker DRX-500, DPX-400, and AM-250 spectrometers operating at 160.5, 128.4, and 80.3 MHz, respectively, and referenced externally to $BF_3 \cdot OEt_2$ complex in C_6D_6 ($\delta = 0.00$ ppm). Coupling constants are reported in hertz (Hz).

Elemental Analysis. Elemental analyses were performed by Galbraith Laboratories, Inc. of Knoxville, Tennessee.

Mass Spectroscopy. Mass spectral data were recorded either on the Micromass QTOF Electrospray (ESI) or VG-70 (EI) mass-spectrometers at the Campus Chemical Instrumentation Center (CCIC) of The Ohio State University.

X-ray Structure Determinations. Single crystal X-ray diffraction data were collected on an Enraf-Nonius Kappa CCD diffraction system, which employed graphite-monochromated Mo−Kα radiation. A single crystal was mounted on the tip of glass fiber coasted 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.[35] The structures were solved by direct methods and refined using SHELXTL (difference electron density calculations, full least-squares refinements).[36]

1,7-(Me$_2$S)$_2$-9-(MeS)-B$_{12}$H$_9$ (1). 1,7-(Me$_2$S)$_2$B$_{12}$H$_{10}$ (0.2641 g, 1.000 mmol) obtained by pyrolysis of BH$_3 \cdot$SMe$_2$[10] was added to fresh 1.0 M HCl-acetic acid solution (15 mL) in a 14/20 25 mL round-bottom flask. DMSO (0.2 mL) was added by syringe, the reaction flask was equipped with a condenser, and placed in a preheated oil bath at 55−60 °C. The solution was heated with moderate stirring for 2 h. The resulting clear solution was allowed to cool to room temperature. Volatiles were then removed under reduced pressure. The white solid residue was partitioned with water and dichloromethane. The

dichloromethane extract was dried over magnesium sulfate, filtered, and the solvent removed under vacuum. A 0.2069 g portion of pure product was obtained (0.667 mmol, 67%). ^{11}B NMR (CD$_3$CN): δ −3.2 (s, B(9)), −9.2 (s, B(1,7)), −13.0 (d, J$_{BH}$ = 157, 1B), −14.1 (d, J$_{BH}$ = 121, 2B), −14.6 (d, J$_{BH}$ = 135, 2B), −15.6 (d, J$_{BH}$ = 152, 2B), −17.0 (d, J$_{BH}$ = 138, 1B), −19.2 (d, J$_{BH}$ = 138, 1B). ^1H NMR (CD$_3$CN): δ 2.49 (s, 6H), 1.88 (q, J$_{BH}$ = 4.1, 1H). ^{1}H{^{11}B} NMR (CD$_3$CN): δ 1.70 (s, 2H, BH), 1.67 (s, 2H, BH), 1.62 (s, 1H, BH), 1.57 (s, 1H, BH), 1.48 (s, 3H, BH). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 25.9 (4C, SMe$_2$), 15.5 (1C, SMe). MS-ESI (1,7-(Me$_2$S)$_2$-9-(MeS)-B$_{12}$H$_9$Na$^+$): 333.2140 (±2.1 ppm) cal. 333.2133. Elemental Analysis: C 19.25%, H 7.76%, cal. 19.36%, H 7.80%.

1,10-(Me$_2$S)$_2$-2-(MeS)-B$_{10}$H$_7$ (2). **Method A.** Cs$_2$B$_{10}$H$_{10}$ (3.8399 g, 10.00 mmol) was added to glacial acetic acid (75 mL) in a 3-necked 14/20 250 mL round-bottom flask equipped with a condenser and a thermometer. DMSO (5.0 mL) was added dropwise via syringe into the stirred reaction vessel. The mixture was stirred moderately for 2−3 h at 55−60 °C with HCl gas slowly bubbling into the solution through a rubber septum via a syringe needle.

Method B. A similar amount of Cs$_2$B$_{10}$H$_{10}$ was charged in a 14/20 250 mL round-bottom flask. DMSO (5.0 mL) was added dropwise via syringe into the stirred reaction vessel. Freshly purchased 1.0 M HCl-acetic acid solution (Aldrich) (125−150 mL) was delivered into the flask, which was equipped with a condenser. The reaction solution was heated to 55−60 °C in an oil bath for 2−3 h.

Workup procedures were common to both methods. The reaction flask was removed from the heat source and allowed to cool to ambient temperature. Acetic acid was then removed under reduced pressure. The residue was partitioned with water and dichloromethane in a separating funnel. The dichloromethane solution was dried over magnesium sulfate, filtered, and the solvent removed under vacuum to give a white solid with a slight yellowish contamination. 1,10-(Me$_2$S)$_2$-2-(MeS)-B$_{10}$H$_7$ was isolated by silica gel column chromatography using 1:1 vol/vol 1,2-dichloroethane/toluene as eluent. The total yield was approximately 60% by either method. The compound was recrystallized using 1:1 vol/vol acetonitrile/water solution.

^{11}B and ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$): 9.0 (s, B(10)), 5.2 (s, B(1)), −11.7 (s, B(2)), −20.9 (d, B(3,5)), −22.6 (d, B(7,8)), −24.1 (d, B(6,9)), −25.9 (d, B(4)).

^1H and ^{1}H{^{11}B} NMR (CD$_2$Cl$_2$): 3.01 (s, 6H), 2.99 (s, 6H), 1.67 (s, 3H), 1.40 (BH, s, 2H), 1.19 (BH, s, 2H), 1.07 (BH, s, 2H), 0.81 (BH, s, 1H)

MS-EI: 286.1895 (±3 ppm) cal. 286.5097

[1,7,9-(Me$_2$S)$_3$-B$_{12}$H$_9$]BF$_4$ (3). In the drybox, trimethyloxonium tetrafluoroborate, [Me$_3$O]BF$_4$, (0.1566 g, 1.059 mmol) was measured into a vial equipped with a screw cap. In a separate flask 1,7-(Me$_2$S)$_2$-9-(MeS)-B$_{12}$H$_9$ (0.2712 g, 0.8744 mmol) was dissolved in dichloromethane (15 mL). The preweighed Me$_3$OBF$_4$ was then added into the solution. The mixture was allowed to stir for about 3 h at room temperature. Volatiles were removed from the resulting clear colorless solution under reduced pressure. The residue was placed in a fritted glass funnel and washed with cold distilled water (25 mL) then transferred into a Solv-Seal flask. The solid was warmed in a water bath for 30 min under vacuum to facilitate the removal of water vapor. A 0.280 g portion of pure solid was obtained (78%). ^{11}B NMR (CD$_3$CN): δ −1.8 (s, BF$_4$$^-$), −8.9 (s, B(1,7,9)), −15.2 (d, J$_{BH}$ = 138, 3B), −15.9 (d, J$_{BH}$ = 132, 3B), −16.6 (d, J$_{BH}$ = 134, 3B). ^1H NMR (CD$_3$CN): δ 2.61 (s, 18H). ^{13}C NMR (CD$_3$CN): δ 25.8. MS-ESI (1,7,9-(Me$_2$S)$_3$-B$_{12}$H$_9$$^+$): 325.2458 (±3.7 ppm) cal. 325.2470.

[1,2,10-(Me$_2$S)$_3$-B$_{10}$H$_7$]BF$_4$ (4). In the drybox, a 14/20 25 mL round-bottom flask was charged with trimethyloxonium tetrafluoroborate, [Me$_3$O]BF$_4$, (0.1894 g, 1.28 mmol). 1,10-(Me$_2$S)$_2$-2-(MeS)-B$_{10}$H$_7$ (0.2852 g, 0.995 mmol) was washed into the flask using dichloromethane (15 mL). The reaction solution was stirred at room temperature for 3 h. The resulting clear colorless solution contained a very small amount of gel-like material. Volatiles were removed under reduced pressure, and the residue was transferred to a fritted glass funnel and washed with cold distilled water. The solid was recrystallized with ethyl alcohol. A 0.3114 g portion of pure compound

was obtained (81%). ^{11}B NMR (CD$_3$CN): δ 12.5 (s, 1B), 5.62 (s, 1B), −1.0 (s, BF$_4^-$), −14.1 (s, 1B), −22.3 (d, J_{BH} = 126, 2B), −23.1 (d, J_{BH} = 123, 3B), −25.7 (d, J_{BH} = 146, 2B)). ^{1}H NMR (CD$_3$CN): δ 3.04 (s, 6H), 3.00 (s, 6H), 2.31 (s, 6H). ^{1}H{^{11}B} NMR (CD$_3$CN): δ 1.42 (br s, 2H, BH), 1.14 (br s, 3H, BH), 1.04 (br s, 2H, BH). MS-ESI (1,2,10-(Me$_2$S)$_3$-B$_{10}$H$_7^+$): 301.2115 (±3.7 ppm) cal. 301.2126.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic files in CIF format and Tables of Selected Distances and Angles for Structures **1**, **3**, and **4**, and a brief statement on statistical methods used in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(31) The statistic t = (xa − xb)/(s1^2/n1 + s2^2/n2)$^{1/2}$ = 13.50 with s1^2/n1 = a = 5.51 × 10^{-6} Å^2, s2^2/n2 = b = 3.50 × 10^{-6} Å^2, and $(a + b)^{1/2}$ = 0.0030 Å. The number of degrees of freedom, V (rounded to the nearest integer) = $(a + b)^2$/[s1^2/(n1−1) + s2^2/(n2−1)] = 12.87 ≈ 13, which is much larger than the 95% significance level for V = 13, $t_{0.05,\,13}$ = 2.182. The 95% confidence interval is 0.0405 ± 0.0065 Å. A Bayesian calculation based on fitting a t-statistic has yielded a similar confidence interval with V = 5.94 ≈ 6: 0.0405 ± 0.0069 Å.[32]

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■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on February 6, 2012, with coauthor Xuenian Chen inadvertently omitted. The corrected version was reposted on February 8, 2012.