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Synthesis and Chemistry of 9-Cyclohexyl-5(7)-(dimethyl sulfide)-*nido*-decaborane(11), $B_{10}H_{11}C_6H_{11}S(CH_3)_2$

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Cyclohexene adds to $B_{10}H_{12}[S(CH_3)_2]_2$ to give 9-cyclohexyl-5(7)-(dimethyl sulfide)-*nido*-decaborane(11), $B_{10}H_{11}C_6H_{11}S(CH_3)_2$. The asymmetric environment at B5 causes two methyl resonances to appear at 26.3 and 24.6 ppm. Through ^{11}B and ^{13}C NMR, the structure of $B_{10}H_{12}S(CH_3)_2$ has been shown to be similar, with a hydrogen replacing the cyclohexyl ring. When $B_{10}H_{11}C_6H_{11}S(CH_3)_2$ is reacted with diethyl sulfide at 90 °C, there appear several products including $B_{10}H_{11}C_6H_{11}S(CH_2CH_3)_2$; when pyridine is used instead of diethyl sulfide, only one product is seen at room temperature, specifically $B_{10}H_{11}C_6H_{11}[NC_5H_5]_2$. Sodium hydride in reaction with $B_{10}H_{11}C_6H_{11}S(CH_3)_2$ produces $2-C_6H_{11}-B_{10}H_9^{2-}$. According to reactivity indices derived from extended Hückel calculations, the most likely positions of nucleophilic attack on $B_{10}H_{11}C_6H_{11}S(CH_3)_2$ and $B_{10}H_{12}S(CH_3)_2$ are B8 and B9.

Introduction

The production of *o*-carborane, 1,2-dicarba-*closo*-do-decaborane(12), and a number of C-substituted derivatives was shown in 1963 to readily take place when bis(dimethyl sulfide)-*arachno*-decaborane(12) is reacted with an appropriate alkyne, such as acetylene (Scheme I).³⁻⁵ Hill, Johnson, and Novak, 1975, studied the kinetics of this reaction and of ligand exchanges involving $B_{10}H_{12}[S(CH_3)_2]_2$.⁶ From this work, the simplistic and abbreviated mechanistic scheme in Scheme I is suggested. First one ligand reversibly dissociates from $B_{10}H_{12}[S(CH_3)_2]_2$ to give a reactive isomer of $B_{10}H_{12}S(CH_3)_2$. This is followed by a slow step involving addition of acetylene in some manner, to the boron framework, and subsequent steps involving loss of H_2 and dimethyl sulfide from the borane moiety.

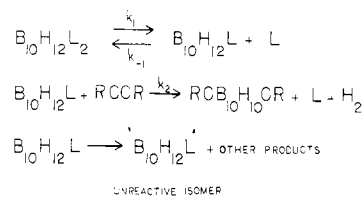
No intermediate in this reaction has been characterized; however, another isomer of $B_{10}H_{12}S(CH_3)_2$ was isolated following the heating of $B_{10}H_{12}[S(CH_3)_2]_2$ in mesitylene at 110 °C.⁷ This isomer has also been prepared directly from decaborane.⁸ That the two isomers are indeed different is clear from the lack of reactivity of the second isomer with acetylenes.

One may hypothesize that addition of the alkyne proceeds by sequential involvement of the two π bonds. Addition of an alkene rather than of an alkyne to bis(dimethyl sulfide)-decaborane(12) should then proceed, yielding a product that can be related to an intermediate involved in carborane formation. We have performed such reactions and in this paper, report the nature of the products formed and related chemistry.

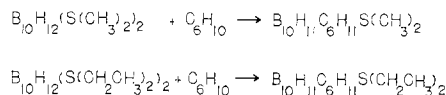
Results and Discussion

Reaction of $B_{10}H_{12}(SR_2)_2$ with Cyclohexene. When reacting bis(dimethyl sulfide)-*arachno*-decaborane(12) with excess cyclohexene, essentially one product is formed of chemical composition $B_{10}H_{11}C_6H_{11}S(CH_3)_2$. The reaction takes an

Scheme I



Scheme II



analogous course when bis(diethyl sulfide)-*arachno*-decaborane(12) is used, the product being of composition $B_{10}H_{11}C_6H_{11}S(CH_2CH_3)_2$ (see Scheme II). Both of these products when chromatographed on silica gel sheets by using benzene as a solvent have similar R_f values, being respectively 0.70 and 0.73.

The hydrogen-decoupled ^{11}B NMR spectrum of $B_{10}H_{11}C_6H_{11}S(CH_3)_2$ at 28.875 MHz is shown in Figure 1. A total of eight resonances can be seen, indicating the lack of nontrivial symmetry elements. A similar ^{11}B NMR spectrum is seen for $B_{10}H_{11}C_6H_{11}S(CH_2CH_3)_2$, except here the resonances are all noticeably broader (30%).^{11,12} The positions of the peaks and the shape of these spectra are like those reported for $(C-H_3)_4NB_{10}H_{13}$ and $B_{10}H_{12}S(CH_3)_2$, suggesting that the borane structures in these four compounds have analogous features.^{7,8,10}

Structural aspects of the exo hydrocarbon groups in both $B_{10}H_{11}C_6H_{11}S(CH_3)_2$ and $B_{10}H_{11}C_6H_{11}S(CH_2CH_3)_2$ can be deduced from the 1H and ^{13}C NMR spectra (Tables II and III). In the 1H spectrum of the dimethyl sulfide derivative, the singlet at 2.64 ppm (area 6) is attributable to the methyl

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- (2) Boston University.
- (3) M. M. Fein, J. Bobinski, N. Mayes, M. Schwartz, and M. Cohen, *Inorg. Chem.*, **2**, 1111 (1963).
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- (11) Broadening due to faster relaxation rates is here attributed to longer quadrupolar relaxation times (τ_c) associated with slower molecular tumbling. Such is expected as the bulkiness of the molecule increases when diethyl sulfide is substituted for dimethyl sulfide. Note the Stoke-Einstein relationship: $\tau_c = 4a^3\eta/3kT$, for isotropic tumbling (a = molecular radius, η = viscosity).
- (12) (a) B. Lindman and S. Forson "NMR. Basic Principles and Progress", Vol. 12, P. Diehl, E. Fluck, and R. Kosfeld, Eds., Springer-Verlag, Berlin, 1976, Chapter 1. (b) W. T. Huntress, Jr., *Adv. Magn. Reson.*, **4**, 1 (1970).

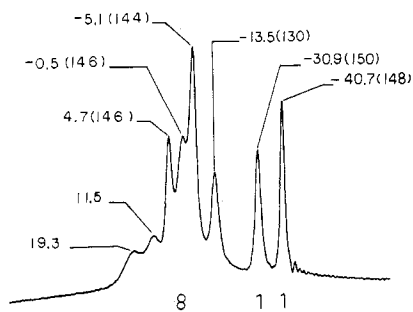


Figure 1. The hydrogen-decoupled ^{11}B spectrum of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ in perdeuteriotoluene. Chemical shifts in ppm relative to an external sample of boron trifluoride-ethyl etherate are shown above peaks with coupling constants ($J_{\text{B-H}}$) in Hz given in parentheses. Listed below the spectrum are the relative areas of the associated resonances.

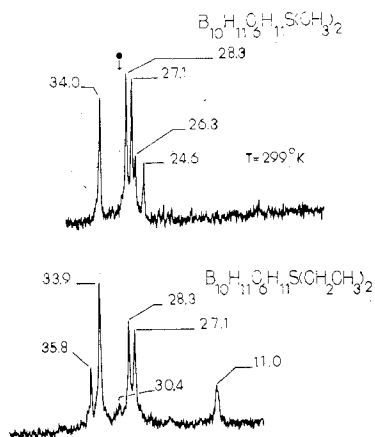


Figure 2. The hydrogen-decoupled ^{13}C NMR spectra of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ and $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_2\text{CH}_3)_2$ recorded at 299 K. The solvent used was perdeuteriotoluene. Chemical shifts are relative to internal Me_4Si . The black dot in the spectrum of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ indicates the position of the methyl resonance in $\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_3)_2]_2$.

groups, while the complex pattern at 1.53 ppm is indicative that the cyclohexyl ring is fully saturated. The spectrum of the latter is more difficult to interpret. A similar pattern for the cyclohexyl ring is seen centered on 1.5 ppm; however, another complex pattern is centered at 2.33 ppm of area 4 in addition to two triplets at 0.81 and 0.77 ppm ($J_{\text{H-H}}$, 7.4 Hz) in the area ratio of 5:1.

The ^{13}C spectra of both derivatives are useful in understanding the just described ^1H spectrum. In particular, ^{13}C NMR of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ shows five resonances, one of which, at 24.6 ppm (relative to tetramethylsilane), has an outstanding temperature dependence (Figure 2). Between 210 and 341 K, this shift can be expressed in the form $y = 0.0177T \pm 19.32$, where T is the temperature in Kelvin and y is the chemical shift. Such temperature dependence is often associated with an intramolecular dynamic process.¹³ The assignment of this resonance and the others can be made through comparison with the spectrum of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{C}-\text{H}_2\text{CH}_3)_2$ (Figure 2).

Of the six ^{13}C resonances found in $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_2\text{C}-\text{H}_3)_2$, the two at 35.8 and 11.0 ppm are positioned similarly to the two at 35.4 and 11.0 ppm found in the parent compound, $\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_2\text{CH}_3)_2]_2$; in both compounds the resonance downfield is assigned to the methylene group of the diethyl sulfide ligand⁴ while the one upfield is assigned to the methyl groups. The four resonances at 33.9, 30.4, 28.3, and 27.1 ppm

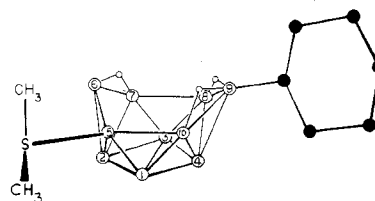


Figure 3. The molecular structure of one enantiomorph of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$. Each open large circle represents a boron atom with one terminal hydrogen attached. The closed circles are carbons, while the small open circles are bridge hydrogens.

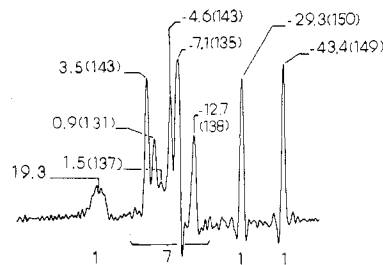


Figure 4. The hydrogen-decoupled ^{11}B spectrum of $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$ in perdeuteriotoluene. The spectrum has undergone line narrowing to enhance resolution; the areas, given below the resonances, have been taken from integrals on an unenhanced spectrum. Chemical shifts relative to an external sample of $\text{F}_3\text{B}\cdot\text{OEt}_2$ are given in ppm, and coupling constants ($J_{\text{B-H}}$) in parentheses, are expressed in Hz.

in $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}[\text{S}(\text{CH}_2\text{CH}_3)]_2$ are attributed to a cyclohexyl ring. The weak, broadened resonance at 30.4 ppm suggests that the associated carbon nucleus is bonded to a cage boron atom, which is causing rapid scalar relaxation. The shape of the resonance is that expected for JT_1 of the order 0.16, where J is the carbon-boron coupling constant and T_1 is the spin-lattice relaxation time of the boron nucleus.^{14,15} This interpretation and the observation of four ring resonances are most compatible with a molecular structure having a σ bonded cyclohexyl ring. Looking back at the spectrum of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$, we can attribute cyclohexyl resonances to peaks at 34.0, 28.3, and 27.1 ppm. The fourth peak of the ring, presumably near 30.4 ppm, is not clearly discernible. The two peaks at 26.3 and 24.6 ppm must then be associated with chemical shift inequivalent methyl resonances. Both these peaks are shifted upfield relative to the methyl resonance in $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$ located at 29.3 ppm (quartet, $J_{\text{C-H}}$, 143 Hz). This interpretation requires that the ligand is attached to a boron atom in an asymmetric environment with the temperature dependence of the 24.6 ppm resonance corresponding to a change in populations of rotational isomers.^{13b,17} The presence of more than one triplet in the ^1H spectrum of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_2\text{CH}_3)_2$ is also consistent with an analogous interpretation.

The NMR data above are compatible with a number of different structures, all having the boron atoms arranged in a *nido*-decaborane type structure. For an unambiguous assignment of the structure here, the compound was also subjected to an X-ray diffraction study by E. Mizusawa, S. Rudnick, and K. Eriks (see following paper in this issue). One enantiomorph of the subsequently resolved structure is shown in Figure 3.¹⁸ The dimethyl sulfide ligand is found terminally

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(15) After resolving the structure of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$, we experimentally obtained T_1 times for both substituted borons of 0.002 s. Using the ballpark figure of 70 Hz for $J_{\text{B-C}}$ from ref 16, we obtain JT_1 of 0.01, corresponding closely to that predicted from the ^{13}C resonance shape.

(16) P. D. Ellis, J. D. Odom, D. W. Lowman, and A. D. Cardin, *J. Am. Chem. Soc.*, **93**, 6704 (1971).

(17) R. M. Silverstein and R. G. Silberman, *J. Chem. Educ.*, **50**, 484 (1973).

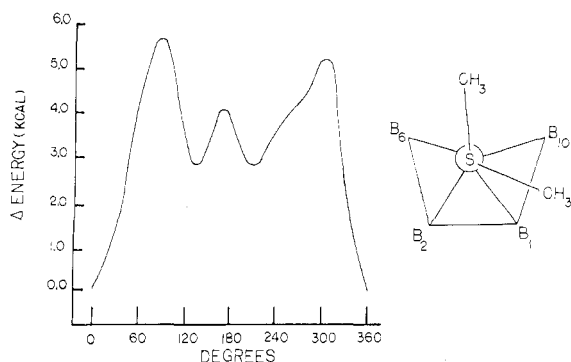


Figure 5. Right: solid-state conformation of the dimethyl sulfide group in $B_{10}H_{11}C_6H_{11}S(CH_3)_2$. Left: increase in energy due to clockwise rotation of this group in $B_{10}H_{12}S(CH_3)_2$.

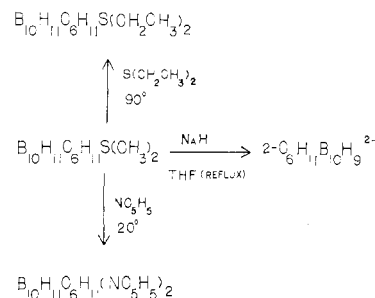
bonded to B5 whereas the cyclohexyl ring is attached to B9. The arrangement of hydrogen atoms on the borane cage and the short, unbridged B5–B6 distance (1.64 Å) are remarkably, though not unsurprisingly (see ^{11}B NMR above), similar to those found for $B_{10}H_{13}^{-10}$. The mental transformation of $B_{10}H_{11}C_6H_{11}S(CH_3)_2$ into this borane anion can be made by simply replacing the dimethyl sulfide ligand by a hydride ion and the cyclohexyl ring by a hydrogen atom.

It is clear that $B_{10}H_{11}C_6H_{11}S(CH_3)_2$ is a simple derivative of 5-(dimethyl sulfide)-*nido*-decaborane(12), and the question arises whether this is related to the unreactive isomer reported by Knoth and Muetterties.⁷ A line-narrowed ^{11}B spectrum of the latter material is shown in Figure 4, displaying considerable improvement in resolution over the originally reported spectrum. Nine resonances are apparent, consistent with a lack of nontrivial symmetry. The ^{13}C NMR spectrum (Table III) shows two methyl resonances at 26.3 and 24.5 ppm with the latter having a strong temperature dependence. These two spectra unambiguously identify “unreactive” $B_{10}H_{12}S(CH_3)_2$ as the parent compound of $B_{10}H_{11}C_6H_{11}S(CH_3)_2$, having a terminal hydrogen in place of a cyclohexyl ring. Like its parent compound, $B_{10}H_{11}C_6H_{11}S(CH_3)_2$ shows little reactivity toward alkynes, with no apparent reaction after heating in refluxing benzene for 24 h. A similar lack of reactivity is shown toward cyclohexene.

As expected by ^{13}C NMR data, the boron atom bonded to dimethyl sulfide, that is B5, is in a locally asymmetric position on the borane skeleton. In the solid state, one methyl group containing a carbon designated C1 is positioned above the open face while the other containing carbon designated C2 is directed toward the basal boron atom B4 (see Figure 5). The significant differences in the spatial positions of the methyl groups in this conformer could well account for the observed chemical shift differences if this conformer predominates in solution.

If we assume that intramolecular forces primarily dictate ligand orientation in solution, then information on the stability of various rotamers can be obtained through ground state energy calculations on the molecule of interest. In this regard, while rotating the dimethyl sulfide group,^{19–21} we performed extended Hückel calculations on $B_{10}H_{12}S(CH_3)_2$; a somewhat similar calculation was performed by Hoffmann on ethane.²²

Scheme III



The coordinates here were taken from structural data for $B_{10}H_{11}C_6H_{11}S(CH_3)_2$. The cyclohexyl ring in the latter was replaced by a hydrogen having an interatomic distance of 1.20 Å. In addition, the C–H bond distances in the methyl groups were all adjusted to 1.09 Å. Parameters for the extended Hückel calculation were taken from the literature.^{19–24}

The results of these calculations are plotted in Figure 5, the ligand being rotated clockwise relative to its orientation in the solid state. The lowest energy conformation is just that found in the solid state, indicating that intramolecular forces rather than crystal-packing forces are primarily responsible for the dimethyl sulfide orientation in the solid state. The barrier to rotation is approximately 5.5 kcal/mol which is the order expected by ^{13}C behavior. The maxima on the energy plot are at approximately 90, 180, and 300° and correspond to nearest approaches of the methyl groups to B2 and B6. According to the calculated, reduced Mulliken population matrix, the most significant antibonding interactions occur between the carbons C1 and C2 and the borons B2 and B6. No simple argument involving Coulombic attractive and repulsive interactions between formally charged atoms can in itself account for the maxima seen. The distinct minima seen allow us to expect the population of associated rotamers and the consequential temperature dependence of the ^{13}C resonances, as was observed.

Chemical Reactions of $B_{10}H_{11}C_6H_{11}S(CH_3)_2$. Although chemical bonding in the borane skeletons of $B_{10}H_{13}^{-}$, $B_{10}H_{12}S(CH_3)_2$, and $B_{10}H_{11}C_6H_{11}S(CH_3)_2$ may be considered to be akin to that found in $B_{10}H_{14}$, the lack of the fourth bridge hydrogen on the face and the nature of the exosubstituent on B5 should make the chemical reactivity of the former compounds distinct from that of the latter. In the first report concerning the reaction of $B_{10}H_{12}S(CH_3)_2$, Knoth and Muetterties described its ready conversion into 6,9-bis(pyridine)-*arachno*-decaborane(12), $B_{10}H_{12}(NC_5H_5)_2$, in the presence of excess pyridine;⁷ the course of the reaction was identical with that found when $B_{10}H_{14}$ was used.^{25,26} Bis-(ligand)decaborane(12) structures such as $B_{10}H_{12}(NC_5H_5)_2$ can be described as having skeletal bonding similar to that of $B_{10}H_{14}^{2-27}$. A related product is formed when $B_{10}H_{13}^{-}$ is reacted with various ligands, L, to yield the $B_{10}H_{13}L^{-}$ anion, which can also be considered to be similar to $B_{10}H_{14}^{2-}$.^{7,27–30} Although $B_{10}H_{11}C_6H_{11}S(CH_3)_2$ is closely related to $B_{10}H_{12}S(CH_3)_2$ and $B_{10}H_{13}^{-}$, the nature of products formed by nucleophilic reagents might be different due to possible steric blocking of the B9 position by the cyclohexyl ring. In order to determine if this was so, we reacted with $B_{10}H_{11}C_6H_{11}S(CH_3)_2$ a number of nucleophilic reagents, in particular diethyl

(18) Private communication from E. Mizusawa and K. Eriks, Department of Chemistry, Boston University, Boston, MA. The figure shown is one enantiomorph of the determined structure.

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Table I. ^{11}B NMR Spectra

compd	chem shifts, ^a ppm	rel intens
$\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2^b$	19.3, 11.5, 4.7 (146), -0.5 (146), -5.1 (144), -13.5 (130), -30.9 (150), -40.7 (148)	$(6 \times \frac{4}{3})$, 1, 1
$\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_2\text{CH}_3)_2^b$	20.6, 12.1, 5.9 (146), -0.3 (110), ^c -3.7 (127), ^c -11.4 (120), ^c -29.5 (150), -39.2 (141)	$(6 \times \frac{4}{3})$, 1, 1
$\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2^b$	19.3, 3.5 (143), 0.9 (131), ^d -1.5 (137), -4.6 (143), -7.1 (135), -12.7 (138), -29.3 (150), -43.4 (149)	1, $(6 \times \frac{7}{6})$, 1, 1
$\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}(\text{NC}_5\text{H}_5)_2$	20.2, 4.9 (136), -1.0 (140), -16.0 (110), ^c -18.5 (110), ^c -38.5 (144)	$(5 \times \frac{8}{3})$, 2
$[(\text{CH}_3)_4\text{N}]_2\text{B}_{10}\text{H}_9\text{C}_6\text{H}_5^{2-}$	-1.0 (136), -2.3 (130), -16.2, -28.0 (126) ^c	1, 1, 1, 7
$\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_9\text{S}(\text{CH}_3)_2$	19.7, -10.3, 5.6 (144), -0.3 (130), -3.01 (142), -12.1 (133), -30.0 (156), -39.8 (148)	$(6 \times \frac{4}{3})$, 1, 1

^a Chemical shifts, relative to external $\text{BF}_3 \cdot \text{OEt}_2$, are positive downfield. Coupling constants ($J_{\text{B-H}}$, Hz) are in parentheses. ^b Solvent used was toluene- d_6 . ^c Incomplete resolution of peaks in coupled spectra. Coupling constants probably in error by up to 20 Hz. ^d Only half of doublet was resolved (coupled spectra).

sulfide, pyridine, and the hydride anion.

Reacting $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ with neat diethyl sulfide at 90 °C for 24 h produced at least four products, detected by thin-layer chromatography on silica gel. Not one of these products overwhelmingly predominated the mixture. One of the products having the same R_f value as $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{C}_2\text{H}_5)_2$ was subsequently isolated by preparative chromatography on silica gel. Both ^{11}B and ^{13}C NMR identified this compound as 9-cyclohexyl-5-(diethyl sulfide)-*nido*-decaborane(12) which we had earlier prepared directly from $\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_2\text{CH}_3)_2]$. Efforts are continuing in our laboratory to isolate and identify the other products.

Although the above reaction did not proceed readily at room temperature, reaction of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ with pyridine did, giving exclusively one product formed as yellow crystals having the composition $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}(\text{NC}_5\text{H}_5)_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$. This product is analogous to the one reported for the reaction of $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$ with pyridine.⁷ A comparison of the ^{11}B NMR of $\text{B}_{10}\text{H}_{12}(\text{NC}_5\text{H}_5)_2$ with that of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}(\text{NC}_5\text{H}_5)_2$ (Table I) indicates that the pyridines are substituted at the B6 and B9 positions. The ^{13}C and ^1H spectra are consistent with the microanalysis, both showing an extra resonance downfield attributable to the benzene present as solvate in the crystal structure.

Finally, when $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ was reacted with excess NaH in refluxing THF, a single ionic product was formed which was isolated as the tetramethylammonium salt. By microanalysis, the chemical formula was found to be consistent with $[(\text{CH}_3)_4\text{N}]_2\text{B}_{10}\text{H}_9\text{C}_6\text{H}_{11} \cdot \frac{3}{2}\text{H}_2\text{O}$. ^{11}B NMR shows that closure of the cage has taken place and the presence of a single substituent at an equatorial position. The singlet attributed to the substituted boron is at -16.2 ppm, shifted downfield from the overlapping doublets of the other equatorial boron atoms, centered at -28.0 ppm. Two apex doublets were seen at -1.0 and -2.3 ppm. Such equatorial substitution of $\text{B}_{10}\text{H}_{10}^{2-}$ upon closure of a 6-substituted *nido*-decaborane is consistent with the proposed closure mechanism.³¹

It is clear from the above results that the reaction course between $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ and a nucleophile is quite dependent on the nature of the nucleophile. Regarding the reaction with diethyl sulfide, we cannot deduce from the one product isolated whether the reaction proceeded via an initial $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ mechanistic step. On the other hand, the ease with which pyridine reacted with $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ suggests strongly that an initial $\text{S}_{\text{N}}1$ step did not occur here. Instead the reaction course likely followed an initial $\text{S}_{\text{N}}2$ step, involving either addition of a pyridine to the borane or abstraction of a bridge hydrogen by pyridine acting as a Brønsted-Lowry base. Abstraction of a proton as an initial step is almost certain in the reaction of NaH with $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$. This is based on the known reactions of NaH with *nido* boranes.³²

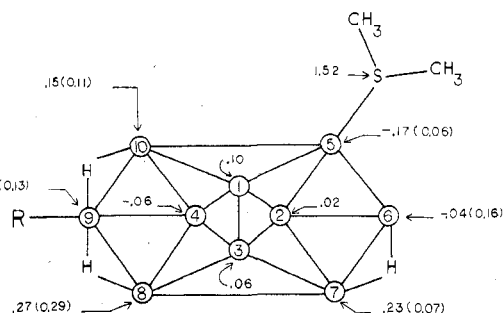


Figure 6. A topological drawing of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$, with R being the cyclohexyl group. Next to each atom is the calculated atomic charge and in parentheses the atomic population of the LUMO.

The above differences in behavior exhibited by $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ toward diethyl sulfide and pyridine are not seen with $\text{B}_{10}\text{H}_{14}$. The products isolated in the latter case are of the same type, being bis(ligand)-*arachno*-decaborane(12) structures. Kinetic evidence indicates that the *nido*-decaborane(14) reactions proceed by an $\text{S}_{\text{N}}2$ mechanism with nucleophile attack clearly preferring the 6,9 positions.³³⁻³⁵ Such preferential attack correlates well with various reactivity indices determined by Lipscomb and co-workers, who performed both extended Hückel and SCF calculations.^{23,36}

Analogous sets of reactivity indices calculated for $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$ and $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ can be of value in identifying nucleophilic substitution/addition reactions that proceed via $\text{S}_{\text{N}}2$ mechanisms, especially if different reactivity indices give common results. For such reactions, these indices can also allow the synthetic chemist some insight into the possible types of compounds producible under various reaction conditions. Such reactivity indices can be expected to be useful in predicting sites of nucleophilic attack on both $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ and $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$. A strong correlation between the predicted sites of substitution and the observed sites would support an $\text{S}_{\text{N}}2$ mechanism in the experiments concerned.

Two reactivity indices based on our extended Hückel calculations were used by us to examine $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ and $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$. The first index involved ground-state charges as determined by a Mulliken population analysis.³⁷ For a number of boranes, there appears to be a good correlation between an ordering of atoms based on positive charge and the order of nucleophilic substitution. For $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$, the charges calculated are shown in Figure 6. (It should be noted that the charges calculated by this method are well-known to be exaggerated relative to those obtained by the SCF method; however, the ordering of atoms by charge is often the same.)¹⁵ The following order for nucleophilic

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Table II. ^1H Chemical Shifts Relative to Me_4Si^c

compd	chem shifts, ^{a,b} ppm	rel intens
$\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$	2.64 (s), 1.5 (c)	6:11
$\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_2\text{CH}_3)_2$	2.33 (c), 1.51 (c), 0.81 (t, 7.4), 0.77 (t, 7.4)	4:11:5:1
$\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$	2.68	1
$\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}(\text{NC}_5\text{H}_5)_2$	8.88 (t, 4.4), 8.00 (t, 7.8), 7.55 (t, 6.7), 7.36 (s), 1.59 (c)	4:2:4:3:11
$[\text{C}_6\text{H}_5]_2\text{B}_{10}\text{H}_9\text{C}_6\text{H}_{11}$	4.76 (s), 3.17 (s), 1.49 (c)	3:24:11
$\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_9\text{S}(\text{CH}_3)_2$	5.81 (q), 1.70 (c), 1.60 (s)	2:7:6

^a Solvent used was toluene- d_6 . ^b Solvent used was D_2O . Reference here was DSS (3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt hydrate). ^c Coupling constants ($J_{\text{H-H}}$), given in Hz, are enclosed in parentheses as are the types of splitting patterns using the following notation: s, singlet; d, doublet; t, triplet; q, quartet; c, complex pattern.

substitution is suggested: $\text{B9} > \text{B8} \geq \text{B7} > \text{B10} \geq \text{B1} > \text{B3} \approx \text{B2} > \text{B6} \approx \text{B4} > \text{B5}$. Replacing the cyclohexyl ring by a hydrogen to give $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$ changes the order somewhat to the following [charges (eV) in parentheses]: $\text{B8} (0.31) \geq \text{B9} (0.26) \approx \text{B7} (0.23) > \text{B10} (0.17) > \text{B1} (0.10) \geq \text{B3} (0.06) \approx \text{B2} (0.03) > \text{B6} (-0.03) \approx \text{B4} (-0.04)$. In $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$, the preference for B9 may be attenuated somewhat by steric hindrance from the cyclohexyl ring. However, as evidenced by formation of 9-cyclohexyl-6,9-bis(pyridine)-*arachno*-decaborane(12), $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}(\text{NC}_5\text{H}_5)_2$, through its reaction with pyridine, such steric factors cannot be *unduly* obstructive. In both $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ and $\text{B}_{10}\text{H}_{12}\text{S}(\text{C}_6\text{H}_5)_2$, the differences in charge between the more positive borons are relatively small, suggesting that the above ordering and consequential selectivity based on ground-state charges may not be rigidly observed.

Another useful reactivity index is based on the lowest unoccupied molecular orbitals (LUMO). For $\text{B}_{10}\text{H}_{14}$, this index has also predicted well the observed order of nucleophilic substitution.³⁶ For both $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ and $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$, the atomic populations contributed by the LUMO for boron atoms on the face follow the same order, which is as follows (atomic populations of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ in parentheses): $\text{B8} (0.29) > \text{B6} (0.19) \geq \text{B9} (0.13) \approx \text{B10} (0.11) > \text{B7} (0.05) \approx \text{B5} (0.06)$. A significant gap of 2.5 eV between LUMO and the next higher unoccupied molecular orbital suggests that even more sophisticated calculations will not change the designation of the LUMO. If we sum the populations of the five lowest unoccupied MO's and normalize them, we find only one boron atom on the face with a population greater than 0.1, and that is B8 (0.22), the others varying between 0.03 and 0.09. For this index, B8 is clearly preferred over other facial boron atoms as the initial site of nucleophilic substitution. Such a clear-cut preference is not found by using criteria based on ground-state charges. Weighting similarly both bonding indices suggests that B8 and B9 will be the preferred positions for ligand attachment in substitution/addition reactions which proceed by an $\text{S}_{\text{N}}2$ type mechanism.

Reaction of $\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_3)_2]_2$ with an Alkadiene. Reaction of $\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_3)_2]_2$ with an alkyne results in insertion of the alkenic carbons into the boron framework, while as we have just discussed an analogous reaction with an alkene, specifically, cyclohexene, results instead in hydroboration of the alkenic bond. The question then arises whether insertion or hydroboration will take place with an alkadiene, an unsaturated molecule that can be compared in some ways to alkenes and also to alkynes. In particular, we investigated cyclohexadiene, which is structurally similar to cyclohexene. The principal product isolated from the reaction between this diene and $\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_3)_2]_2$ was assigned the hydroboration structure 9-cyclohexenyl-5-(dimethyl sulfide)-*nido*-deca-

Table III. ^{13}C Chemical Shifts Relative to Me_4Si^a

compd	chem shifts, ppm
$\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$	34.0, 28.3, 27.1, 26.3, 24.6 ^b
$\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_2\text{CH}_3)_2$	35.8, 33.9, 30.4, 28.3, 27.1, 11.0
$\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$	26.3, 24.5
$\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_3)_2]_2$	29.3 (q, 143 Hz)
$\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_2\text{CH}_3)_2]_2$	35.4, 11.0
$\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}[\text{NC}_5\text{H}_5]_2$	147.6, 146.4, 139.9, 139.6, 128.3, 125.1, 124.5, 36.6, 28.9, 26.8
$\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_9\text{S}(\text{CH}_3)_2$	132.42, 125.04, 29.77, 26.28, 25.55, 24.82, 23.02

^a Solvent used was toluene- d_6 . Spectra were taken at 298 K while decoupling hydrogen with broad-band irradiation. ^b Each peak on the quartet is split more finely into a triplet: the apparent coupling constant here is 3.5 Hz.

borane(11), $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_9\text{S}(\text{CH}_3)_2$, on the basis of the NMR spectra (Tables I–III). In particular, the ^{11}B NMR spectrum was very similar to that of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$. In the ^{13}C spectrum, the alkenic resonances were observed at 132.4 and 125.0 ppm; the remaining saturated carbons were all observed between 23 and 30 ppm except for the one attached to the borane cage. The ^1H spectrum was likewise consistent with a hydroboration structure, showing alkenic hydrogen absorptions at 5.81 ppm.

Mechanistic Considerations. The mechanisms of the above hydroborations are likely the same. Both reactions are inhibited by dimethyl sulfide, and therefore, as in acetylenic addition,⁶ the first step appears to involve dissociation of one dimethyl sulfide from $\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_3)_2]_2$ at B9.³⁸ The structure of the resulting borane “reactive $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$ ” has not been resolved; however, it is likely that the topology of the boron framework remains unchanged from the present compound with dimethyl sulfide bound to B6 [i.e., 6- $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$]. Support for the proposed reactive $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$ structures comes from the isoelectronic compound, 6- SB_9H_{11} , which, remarkably, readily hydroborates both alkenes and alkynes at the B9 position, in parallel with the hydroboration products of $\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_3)_2]_2$. [In terms of electron counting, the sulfur atom can be considered equivalent to a BHL group (i.e., $\text{BHS}(\text{CH}_3)_2$).⁴⁰]

Our experimental results show that the two carbons in an alkenic bond do not readily add to the framework of “reactive $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$ ” derived from $\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_3)_2]_2$; instead hydroboration takes place. Dimethyl sulfide migration from B6 to B5 (B7) must take place after alkenic attack at B9 inasmuch as 5(7)- $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$ is unreactive under similar conditions.

In commencing this work, we expected that the product formed by reaction of an alkene with $\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_3)_2]_2$ might bear relationship to an intermediate involved in *o*-carborane formation. The hydroboration products observed, however, cannot be directly related to any reasonable, postulated intermediate; however, their exclusive production here suggests that irreversible addition of the acetylenic carbons to the decarborane framework during *o*-carborane formation takes place only after involvement of both π bonds.

Experimental Section

Spectra and Analyses. ^{11}B , ^{13}C , and ^1H NMR were obtained at 28.9, 22.6, and 90.0 MHz, respectively, by using a Bruker WH-90-DX spectrometer with Fourier transform and a deuterium lock. ^{11}B chemical shifts were referenced to an external sample of $\text{BF}_3\cdot\text{OEt}_2$ while ^{13}C and ^1H resonances were referenced relative to internal

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tetramethylsilane (Me_4Si). In addition, ^{13}C spectra were taken at fixed temperatures by using the variable-temperature accessory.

Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Samples were run as KBr pellets. The following symbolic descriptions are used: s, strong; m, medium; w, weak; sh, shoulder; br, broad. Visible and ultraviolet spectra were taken on a Cary Model 14 spectrophotometer.

Chemical analyses were performed by Schwarzkopf Microanalytical Laboratory of Woodside, NY. Mass spectra were performed on a Finnigan instrument by using either electron impact or chemical ionization techniques.

Chromatography. Thin-layer chromatography (TLC) was carried out as described elsewhere by using Baker-Flex silica gel IB-F thin-layer chromatography sheets.⁴¹ Visualization was achieved by using silver nitrate solution. Preparative plates, coated with silica gel, were manufactured by Analtech, Inc.

Materials and Product Storage. Chemicals and solvents were of reagent quality, being further purified only when indicated. After reaction under nitrogen and isolation, all products were sealed in glass tubes under vacuum and stored at -10°C . Under such conditions, the products did not show deterioration after several months.

9-Cyclohexyl-5-(dimethyl sulfide)-nido-decarborane(11), $\text{B}_{10}\text{H}_{11}\text{-C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$. A solution containing 100 mL of cyclohexene and 80 mL of benzene under nitrogen was added to 5.0 g of $\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_3)_2]_2$. With stirring, the solution was warmed in an oil bath at 80°C for 6 h. After the solution was cooled, the solvents were removed on a rotary evaporator. The residue was dissolved in a mixture of benzene-hexane (1:5) and chromatographed on silica gel by using this solvent combination. The product ($R_f = 0.80$ when run on silica gel sheets using ethyl acetate) was collected, and the solvents were removed. The residue was recrystallized by dissolving in benzene-hexane (1:4) at 50°C , filtering, and cooling. The resulting white crystals (1.5 g) melt at $75\text{--}76^\circ\text{C}$. Infrared bands: 3250 (w), 2930 (m), 2850 (m), 2500 (s), 2845 (m), 1910 (w), 1560 (m), 1430 (m), 1360 (m), 1330 (w), 1160 (w), 900 (w) cm^{-1} . Anal. Calcd for $\text{B}_{10}\text{C}_6\text{H}_{28}\text{S}$: B, 40.88; C, 36.34; H, 10.67; S, 12.10. Found: B, 41.01; C, 35.83; H, 10.63; S, 12.02.

9-Cyclohexyl-5-(diethyl sulfide)-nido-decarborane(11), $\text{B}_{10}\text{H}_{11}\text{-C}_6\text{H}_{11}\text{S}(\text{CH}_2\text{CH}_3)_2$. The reaction was run as above except that 1.1 g of $\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_2\text{CH}_3)_2]_2$ was used instead of $\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_3)_2]_2$. The product was isolated off preparative silica gel plates after elution with benzene-hexane (1:1). The resulting yellow oil solidified into a white solid (0.63 g) upon pumping in vacuo (0.1 mm) for 3 days. Infrared bands: 2920 (m), 2855 (m), 2510 (s), 1540 (m), 1445 (m), 1420 (w), 1353 (w), 1250 (m), 970 (w), 857 (m), 690 (w) cm^{-1} . Anal. Calcd for $\text{B}_{10}\text{C}_{10}\text{H}_{32}\text{S}$: B, 36.96; C, 41.97; H, 11.03; S, 10.94. Found: B, 37.28; C, 41.22; H, 11.17; S, 9.98.⁴² A mass spectrum by electron impact shows a cutoff at 294 corresponding to $^{11}\text{B}_{10}^{12}\text{C}_{10}^{32}\text{S}^1\text{H}_{32}$.

Reaction of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ with $\text{S}(\text{CH}_2\text{CH}_3)_2$. A solution containing 1.0 g of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$ in 20 mL of diethyl sulfide

was heated on an oil bath at 90°C for 24 h. Following careful removal of the solvents, 0.19 g of the product, 9-cyclohexyl-5(7)-(diethyl sulfide)-nido-decarborane(11), was isolated off silica gel plates after multiple solvent advancements with benzene-hexane (1:4). The material was characterized by ^{11}B and ^{13}C NMR and IR.

6-Cyclohexyl-6,9-bis(pyridine)-arachno-decarborane(11)-Hemi-benzene, $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}[\text{NC}_5\text{H}_5]_2 \cdot \frac{1}{2}\text{C}_6\text{H}_6$. To 6 mL of benzene and 3 mL of pyridine was added 0.360 g of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$. After 24 h at room temperature, yellow crystals appeared. The solvent was removed by filtration, and the crystals were washed with benzene-hexane (1:2). After being dried in vacuo, the product weighed 0.435 g (94% yield) and had a melting point of 113°C . With use of silica gel and benzene, the compound had an $R_f = 0.30$. Infrared bands: 2815 (m), 2820 (w), 2500 (s), 1620 (m), 1485 (s), 1453 (m), 1210 (w), 1110 (w), 1090 (w), 765 (w), 690 (w) cm^{-1} . Anal. Calcd for $\text{B}_{10}\text{C}_{19}\text{H}_{35}\text{N}_2$: B, 27.05; C, 57.11; H, 8.83; N, 7.01. Found: B, 27.12; C, 56.94; H, 8.71; N, 7.00.

Tetramethylammonium Nonahydro-2-cyclohexyl-closo-decarborate(2-) Sesquihydrate, $[(\text{CH}_3)_4\text{N}]_2\text{B}_{10}\text{H}_9\text{C}_6\text{H}_{11} \cdot \frac{3}{2}\text{H}_2\text{O}$. Into 100 mL of dry tetrahydrofuran were added 0.760 g of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{C}-\text{H}_3)_2$ and 1.9 g of NaH. After being heated with an oil bath at 90°C for 24 h, the solution was cooled and 25 mL of H_2O added slowly over 1 h. After the solvent was removed on a rotary evaporator, AG-50W-X8 resin (200-400 mesh) in the H^+ form was added until the pH was 7. The solution was filtered and reduced in volume to 10 mL. Upon the addition of excess aqueous tetramethylammonium chloride, the product precipitated. After the product was dried, it weighed 1.01 g (96% yield). Two recrystallizations from ethanol-water (6:1) gave crystals shaped like thin white plates. Infrared bands: 3380 (w), 3020 (m), 2918 (m), 2840 (m), 2440 (s), 1485 (s), 1445 (w), 1420 (w), 1405 (w), 1130 (w), 1000 (m), 950 (s), 820 (w), 460 (w) cm^{-1} . Anal. Calcd for $\text{B}_{10}\text{C}_{14}\text{H}_{47}\text{N}_2\text{O}_{3/2}$: B, 29.41; C, 45.74; H, 12.89; N, 7.62. Found: B, 27.14; C, 45.91; H, 12.75; N, 7.44.

9-Cyclohexenyl-5-(dimethyl sulfide)-nido-decarborane(11), $\text{B}_{10}\text{-H}_1\text{C}_6\text{H}_9\text{S}(\text{CH}_3)_2$. To a solution containing 10 mL of 1,3-cyclohexadiene and 30 mL of benzene was added 1.81 g of $\text{B}_{10}\text{H}_{12}[\text{S}(\text{C}-\text{H}_3)_2]_2$. After 24 h at 20°C , the solvents were removed. A viscous oil was isolated following chromatography on preparative silica gel plates with benzene as an eluant. The product (1.14 g) had an $R_f = 0.70$ on analytical silica gel sheets using benzene. Infrared bands: 3005 (w), 2928 (m), 2855 (w), 2838 (w), 2520 (s), 1545 (w), 1425 (m), 1374 (w), 1330 (w), 1287 (w), 993 (w), 915 (w), 850 (w) cm^{-1} . A mass spectrum shows a cutoff at 264 corresponding to $^{11}\text{B}_{10}^{12}\text{C}_8^{32}\text{S}^1\text{H}_{26}$.

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Registry No. $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_3)_2$, 72765-44-7; $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_2\text{CH}_3)_2$, 72765-43-6; $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}[\text{NC}_5\text{H}_5]_2$, 72765-41-4; $[(\text{C}-\text{H}_3)_4\text{N}]_2\text{B}_{10}\text{H}_9\text{C}_6\text{H}_{11}$, 72868-00-9; $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_9\text{S}(\text{CH}_3)_2$, 72765-39-0; $\text{B}_{10}\text{H}_{12}\text{S}(\text{CH}_3)_2$, 72765-37-8; $\text{B}_{10}\text{H}_{12}[\text{S}(\text{CH}_3)_2]_2$, 28377-92-6; $\text{B}_{10}\text{-H}_{12}[\text{S}(\text{CH}_2\text{CH}_3)_2]_2$, 32124-79-1; cyclohexene, 110-83-8; $\text{S}(\text{CH}_2\text{CH}_3)_2$, 352-93-2; pyridine, 110-86-1; 1,3-cyclohexadiene, 592-57-4.

(41) G. R. Wellum, E. I. Tolpin, L. P. Anderson, and R. Sneath, *J. Chromatogr.*, **103**, 153 (1975).

(42) On multiple analyses of the same sample of $\text{B}_{10}\text{H}_{11}\text{C}_6\text{H}_{11}\text{S}(\text{CH}_2\text{CH}_3)_2$, the sulfur content decreased, indicating decomposition.