Appendix

Assuming that the overall signal intensity is the result of two coordination symmetries, the total signal intensity (I) will be the sum of the relative intensities of the individual signals (I_1, I_2).

$$I = I_1 + I_2 \qquad (9)$$

With $I_1 = k_1[\text{Fe(III)–Zeol}_1]$ and $I_2 = k_2[\text{Fe(III)–Zeol}_2]$

$$I = k_1[\text{Fe(III)–Zeol}_1] + k_2[\text{Fe(III)–Zeol}_2] \quad k_1 \neq k_2 \qquad (10)$$

If $[\text{Fe(III)–Zeol}_F]$ is the concentration of Fe(III) ion in the fully ion-exchanged zeolite, then

$$[\text{Fe(III)–Zeol}_i] = \lambda_i[\text{Fe(III)–Zeol}_F] \qquad (11)$$

where λ_i is the percentage of exchange from Fe(III) ions in site i, and from eq 9–11

$$I = (\lambda_1 k_1 + \lambda_2 k_2)[\text{Fe(III)–Zeol}_F] \qquad (12)$$

Since $\lambda_1 + \lambda_2 = X$ = total Fe(III) percentage of exchange, it is clear that linearity of I with X is only obtained when $k_1 = k_2$ or when all Fe(III) ions belong to the same coordination symmetry. An alternative explanation, less likely, is that the relative site occupancy remains the same as Fe(III) concentration increases.

Registry No. CO, 630-08-0; ethylene, 74-85-1.

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Synthesis and Crystal and Molecular Structure of Trimethylammonium 7,8-Dimercapto-7,8-dicarbaundecaborate(10) and Trimethylammonium *anti*-7,7′:8,8′-Bis(dithio)bis(7,8-dicarbaundecaborate(10))

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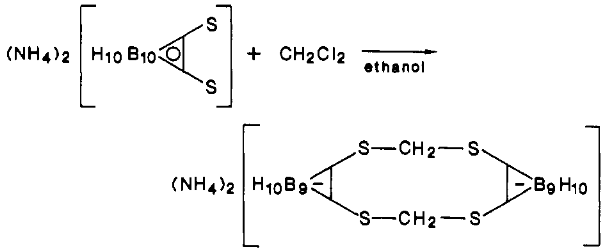
Received April 30, 1986

Removal of B3 in 1,2-dimercapto-*o*-carborane is achieved when its ammonium salt is refluxed in ethanol in the presence of NaI. Upon addition of NMe_3HCl in water, trimethylammonium 7,8-dimercapto-7,8-dicarbaundecaborate(10) is precipitated. The NH_4^+ ion seems to act both as the source of the proton and as the base that removes B3. This compound, $7,8\text{-}(SH)_2\text{-}7,8\text{-}C_2B_9H_{10}^-$, has been characterized by microanalysis, ^{11}B NMR spectroscopy, and an X-ray crystal structure determination. Crystals of $NMe_3H[7,8\text{-}(SH)_2\text{-}7,8\text{-}C_2B_9H_{10}]$ are monoclinic, space group $P2_1/a$, with a = 14.711 (2) Å, b = 9.609 (2) Å, c = 10.604 (1) Å, β = 90.64 (1)°, and Z = 4. The anion 7,8-dimercapto-7,8-dicarbaundecaborate(10) has the form of an 11-apex fragment of an icosahedron with an ortho disposition of the C atoms in the open face with two exocluster sulfurs, one bonded to C7 and the other one to C8. Open-face distances of $7,8\text{-}(SH)_2\text{-}7,8\text{-}C_2B_9H_{10}^-$ are compared to those of $9,10,11\text{-}Me_3\text{-}7,8\text{-}C_2B_9H_9^-$ and discussed. A good correlation has been found between these distances and the bond orders in the cyclopentadienide anion and butadiene. The reaction of $[7,8\text{-}(SH)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ with I_3^- yields 7,7′:8,8′-bis(dithio)bis(7,8-dicarbaundecaborate(10)). The structure of this anion, as the trimethylammonium salt, has been characterized by single-crystal X-ray diffraction methods. Crystals of $(NMe_3H)_2[(7,8\text{-}(S)_2\text{-}7,8\text{-}C_2B_9H_{10})_2]$ are monoclinic, space group $P2_1/a$, with a = 13.318 (4) Å, b = 15.432 (5) Å, c = 7.084 (2) Å, β = 100.45 (2)°, and Z = 2. The anion consists of two 7,8-dicarbaundecaborate(10) moieties bridged by two –S–S– units in such a way that there is an inversion center in the middle of the molecule. Reaction of $[(7,8\text{-}(S)_2\text{-}7,8\text{-}C_2B_9H_{10})_2]^{2-}$ with $CoCl_2$ and cyclopentadiene yields *trans*-$[(\eta^5\text{-}C_5H_5)(3,1,2\text{-}CoB_9C_2S_2H_9)]_2$.

Introduction

Many *o*-carborane derivatives are known as a consequence of the high resistance of the *o*-carborane cage to chemical attack.[1] However, Hawthorne and co-workers discovered that B3 can be selectively removed from the cage by using a strong base, such as CH_3O^- in methanol.[2] Other nucleophiles are known to act in the same fashion, among them piperidine and trialkylamines.[1] The nucleophilic attack takes place at B3 (or B6) because these atoms are adjacent to the more electronegative atoms C1 and C2. It is hypothesized that an increase in the electron-withdrawing ability of C1 and C2 will facilitate B3 (or B6) removal). This may be observed in 1,2-dihalo derivatives degraded by both methanol and ethanol.[3] Though the electron-withdrawing ability of the substituted carbons may well explain these cases, it does not explain the observed partial degradations[4] in 1,2-dimercapto-*o*-carborane salts. We have recently reported that partial degradation of the *o*-carborane moiety happens when either ammonium or potassium salts of *o*-carborane-1,2-dithiolate react with dihaloalkanes[5] (see eq 1).

It was proposed that some stabilization may be acquired through the delocalization of the sulfur lone pair into the open-face orbitals of the partially degraded cage. Because partial degradation had been observed only when rings were formed, it was inferred that ring formation was a necessary, but not sufficient, condition for the partial degradation to occur.



(1)

Herein we describe the synthesis and characterization of 7,8-dimercapto-7,8-dicarbaundecarborate(10) salts from the ammonium salt of 1,2-dimercapto-*o*-carborane. Contrary to what we initially thought, the partial degradation of *o*-carborane-1,2-dithiolate (ammonium salt) takes place without ring formation. In addition, the syntheses and characterization of *anti*-7,7′:8,8′-bis(dithio)bis(7,8-dicarbaundecaborate(10)) and *trans*-$[(\eta^5\text{-}C_5H_5)(3,1,2\text{-}CoB_9C_2S_2H_9)]_2$ are reported.[6]

Experimental Section

General Procedures. Before use, *o*-carborane (Dexsil Chemical Corp.) was sublimed; 1,2-dimercapto-*o*-carborane (I) was prepared from *o*-

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(1) Grimes, R. N. *Carboranes*; Academic: New York, 1970.

(2) Wiesboeck, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642–1643.

(3) Zakharkin, L. I.; Podvisotskaya, L. S. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1966**, 771.

(4) By partial degradation we mean removal of B3, yielding 7,8-dicarbaundecaborate derivatives.

(5) Teixidor, F. T.; Rudolph, R. W. *J. Organomet. Chem.* **1983**, *241*, 301–312.

(6) A preliminary report has been published. See: Viñas, C.; Butler, W. M.; Teixidor, F.; Rudolph, R. W. *Organometallics* 1984, *3*, 503.

0020-1669/86/1325-4369$01.50/0

carborane according to the literature.[7] A 1.7 M solution of *n*-butyllithium in hexane (Aldrich) and *o*-dichlorobenzene were used as given.

Elemental analyses were perfomred by Galbraith Laboratories, Inc., Knoxville, TN. The ^1H and ^{11}B NMR spectra were obtained by using either a JEOL FX-90Q or a Brucker WM-360. Chemical shift data relative to $Et_2O\cdot BF_3$ (minus values upfield) are given in ppm, followed by a description of the multiplet (e.g. d = doublet), its relative intensity (in parentheses), and observed coupling constants given in Hz.

Synthesis. Tetramethylammonium 7,8-Dimercapto-7,8-dicarbaundecaborate(10) (II). The title compound can be prepared by either of the following two methods.

Method A. To a nitrogen-blanketed solution of 1.17 g (4.8 mmols) of ammonium *o*-carborane-1,2-dithiolate[5] in 40 mL of ethanol contained in a three-necked flask equipped with a reflux condenser and a magnetic stirrer were added 3.3 mL of *o*-dichlorobenzene and 1.9 g of NaI. The resulting solution was refluxed for 4 h. After being cooled to room temperature, the liquid was rotoevaporated and the residue dried on a vacuum line to remove the last amounts of *o*-dichlorobenzene. The air-stable solid was transferred to a 40-mL beaker and dissolved in 200 mL of distilled water. Insoluble material, when present, was eliminated by filtration through Celite. While the mixture was stirring, tetramethylammonium chloride was added to the solution and a white solid precipitated. The solid was collected by filtration, rinsed three times with distilled water and dried on a vacuum line. Yield: 1.2 g (93%) based on *o*-carborane-1,2-dithiolate.

The crude solid was recrystallized twice by using ethanol/water, filtering the hot solution, and cooling it to room temperature.

Anal. Calcd for $C_6H_{24}B_9NS_2$: C, 26.54; H, 8.85; B, 35.84; N, 5.16; S, 23.59. Found: C, 26.48; H, 8.39; B, 35.93; N, 5.07; S, 23.98.

The ^{11}B NMR spectrum in acetone-d_6 displayed the following absorptions: −5.9, d (2), J_{BH} = 140; −7.48, d (1), J_{BH} = 165; −16.2, d (4), J_{BH} = 142; −33.02, d (1), J_{BH} = 124.41; −34.20, d (1), J_{BH} = 127. The ^1H NMR spectrum in acetone-d_6 displayed the following absorptions: 3.41, s (6); 2.74, s (1).

Method B. The experimental conditions and concentration of reagents are as in method A, but *o*-dichlorobenzene is not added. The refluxing time has to be increased to 48 h.

Trimethylammonium 7,8-Dimercapto-7,8-dicarbaundecaborate(10) (III). The same procedure was followed as in the previous synthesis. Trimethylammonium chloride was used as the precipitating salt. Yield: 86%.

Reaction of the Potassium Salt of I with *o*-Dichlorobenzene. The same equipment and conditions as in the previous reactions were used. To a solution of 0.509 g of I (2.44 mmol) in 50 mL of ethanol, were added 0.41 g (7.34 mmol) of solid KOH. After complete solution, 1.9 g of NaI and 3.5 mL of *o*-dichlorobenzene were introduced and the resulting solution was stirred at room temperature for 1 h, followed by 15 h at reflux. Upon heating, the solution becomes yellow. The liquid was rotoevaporated and the resulting solid dried under vacuum.

The ^{11}B NMR of the solid in d_6-acetone displayed absorptions at −1.22*, −2.2, −6.06*, −10.0*, −12.0*, −15.5, −16.5, −21.0, −31.8, −36.2.[8]

Reaction of I with *o*-Dichlorobenzene. The reaction was conducted as in the previous case, yet no addition of KOH was effected. After refluxing, the solution color had turned from colorless to pinkish. The ^{11}B NMR spectrum in acetone-d_6 of the solid obtained after removal of the solvent, displayed absorptions between −1.0 and −12 ppm, the more intensive existing at −4.3 (2), −7.05 (6) and −9.45 (2) ppm, attributed to 1,2-dimercapto-*o*-carborane.

Trimethylammonium *anti*-7,7′:8,8′-Bis(dithio)bis(7,8-dicarbaundecaborate(10)) (IV). To a nitrogen-blanketed solution of 0.6 g (2.33 mmol) of III in water (50 mL) was added a small amount of sodium hydrogen carbonate. The mixture was heated to reflux, and 0.6 g of iodine (2.364 mmol) in aqueous potassium iodide (25 mL) was slowly added.

The resulting green solution was kept under reflux for 15 min more. The still warm mixture was cleared from any insoluble material by filtration through Celite and was allowed to cool to room temperature. A good yield of IV was obtained upon the addition of trimethylammonium chloride. The collected solid was washed twice with distilled water and once with ether and dried on the vacuum line. Yield: 0.549 g (92%).

Anal. Calcd for $C_{10}H_{40}B_{18}N_2S_4$: C, 23.51; H, 7.83; B, 38.08; N, 5.48; S, 25.05. Found: C, 23.71; H, 7.54; B, 38.26; N, 5.20; S, 25.00.

The ^{11}B NMR spectrum in acetone-d_6 displayed the following absorptions: −4.23, d (2), J_{BH} = 142; −9.35, d (1), J_{BH} = 168; −15.01, d (2), J_{BH} = 139; −17.14, d (2), J_{BH} = 146; −32.49, d (1), J_{BH} = 122.49; −34.55, d (1), J_{BH} = 125.

Table I. Summary of Crystal Data, Intensity Collections, and Structure Refinement Parameters for $[NMe_3H][B_9C_2H_{12}S_2]$ and $[NMe_3H]_2[B_9C_2H_{10}S_2]_2$

	$[NMe_3H]$-$[B_9C_2H_{12}S_2]$	$[NMe_3H]_2$-$[B_9C_2H_{10}S_2]_2$
M_r	257.6	511.3
space group	$P2_1/a$	$P2_1/a$
cell const		
a, Å	14.711 (2)	13.318 (4)
b, Å	9.609 (2)	15.432 (5)
c, Å	10.604 (1)	7.084 (2)
β, deg	90.64 (1)	100.45 (2)
V, Å^3	1498.9 (4)	1431.8 (8)
d(calcd), g cm^{-3}	1.13	1.186
Z	4	2
cryst dimens, mm	0.47 × 0.45 × 0.91	0.21 × 0.19 × 0.18
radiation	Mo Kα (0.71069 Å)	Mo Kα (0.71069 Å)
abs coeff (μ), cm^{-1}	3.11	3.26
scan speed, deg/min	2.5–12	2.5–12
max 2θ, deg	55	55
total no. of reflcns	4060	3790
no. of unique data ($I > 3\sigma(I)$)	1973	1935
$R_1 = \sum\|\|F_o\| - \|F_c\|\|^2/\sum\|F_o\|^2$	5.6	4.7
$R_2 = [\sum w_o(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	6	5.3

***trans*-$[(\eta^5\text{-}C_5H_5)(3,1,2\text{-}CoB_9C_2S_2H_9)]_2$.** To a nitrogen-blanketed solution of 0.4 g (0.783 mmol) of IV in absolute ethanol was added 0.13 g (2.321 mmol) of KOH. The solution was taken to reflux until the evolved gas did not show a basic reaction in contact with pH-indicator paper.

A solution of 2 g (30.4 mmol) of KOH in absolute ethanol (20 mL) contained in a three-necked round-bottom flask equipped with a magnetic stirrer, a condenser, and an addition funnel was prepared. After the solution was cooled to 15 °C, 0.66 mmol (7.97 mmol) of cyclopentadiene recently cracked was added and the mixture was stirred for 5 min. Anhydrous $CoCl_2$ (0.44 g, 3.38 mmol) in ethanol was added, and the stirring was maintained for 1 h. The solution containing the potassium salt of IV was added, and the reaction mixture was stirred for 17 h. Solid KOH (1 g) was added, and the mixture was stirred for 3 h at room temperature and 1 h at reflux. The resulting suspension was poured into degassed water, collecting the precipitate by filtration. This was washed with water and suspended in acetone (25 mL). Dichlorobenzene (12 mL) was added, and the resulting solution was dried with magnesium sulfate. After filtration the liquid was stripped off and a very small amount of a semisolid mass was obtained. Its mass spectrum shows the appropriate boron envelope centered at 318.1 *m/e*, which exactly corresponds to M/2. No molecular peak was observed.

Reaction of IV with $ClRh(PPh_3)_3$. To a nitrogen-blanketed solution of 0.1 g (0.196 mmol) of IV in warm absolute ethanol (40 mL) was added 0.363 g (0.392 mmol) of $ClRh(PPh_3)_3$. The mixture was refluxed for 35 min. After the mixture was cooled to room temperature a green-brown solid separated. The ^{11}B NMR spectrum of this solid in CD_2Cl_2 clearly showed that it was at least composed of two compounds, but neither had rhodium in the cluster.

X-ray Data Collection and Reduction. White crystals of $[NMe_3H][B_9C_2H_{12}S_2]$ (III) and $[NMe_3H]_2[B_9C_2H_{10}S_2]_2$ (IV) were obtained by slow evaporation of the respective compounds in acetonitrile. Diffraction experiments were performed with a Syntex $P2_1$ automatic diffractometer with a Mo X-ray tube equipped with a graphite monochromator. Data collection parameters for both compounds are summarized in Table I. The data were reduced by methods previously described.[9]

Both structures were solved by direct methods using the MULTAN crystallographic program.[10]

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(7) Smith, H. D., Jr; Obenland, C. O.; Papetti, S. *Inorg. Chem.* **1966**, *5*, 1013–1015.

(8) The peaks with larger intensity, representing 85% of the number of boron atoms, are denoted with an asterisk.

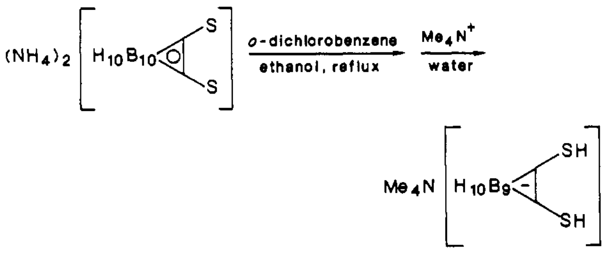
(9) Computations were carried out on an Amdahl 470-V8 computer. Computer programs used during the structural analysis were SYNCOR (data reduction by William Schmonsees), FORDAP (Fourier refinement by A. Zalkin), ORFLS (full-matrix least-squares refinement, by Busing, Martin, and Levy), RFFE (distances and angles and their esd's, by Busy, Martin, and Levy), ORTEP (thermal ellipsoid drawings, by S. L. Johnson), HATOMS (hydrogen atom positions, by A. Zalkin), and PLANES (least-squares planes, by D. M. Blow).

(10) MULTAN-78 by Peter Main.

Hydrogen positions were found in a difference Fourier map and these (but not the temperature factors) were adjusted in subsequent least-squares refinements, assuming an isotropic temperature parameter of 5.0 Å^2 for all hydrogen atoms. Least-squares convergence gave R_1 = 0.056 and R_2 = 0.060 for III, and R_1 = 0.047 and R_2 = 0.053 for IV.

Results and Discussion

Synthesis and Characterization. Tri- and Tetramethylammonium 7,8-Dimercapto-7,8-dicarbaundecaborate(10). Removal of B3 in ammonium *o*-carborane-1,2-dithiolate and protonation of the sulfido groups readily takes place by refluxing this salt in ethanol, in the presence of *o*-dichlorobenzene (eq 2). In a preliminary report,[6] we indicated that this compound could be made simply by refluxing for 48 h the ammonium salt in ethanol. With the inclusion of *o*-dichlorobenzene in the reaction flask the reaction time was shortened to only 4 h.



(2)

In order to gain insight into this uncommon partial degradation process, this reaction was studied by using other cations (K$^+$ or H$^+$) in place of NH$_4$$^+$, but in these cases removal of B3 did not take place. These results led us to believe that the ammonium ion is the source of a base and a proton, both necessary to cause boron removal and sulfido protonation:

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

Precipitation of the 7,8-dimercapto-7,8-dicarbaundecaborate(10) anion was achieved by adding tetramethylammonium or trimethylammonium salt to an aqueous solution of the dithiol.

The ^{11}B NMR spectrum in acetone-d_6 displays five absorptions at −5.9, −7.48, −16.2, −33.02, and −34.20 ppm, with intensities 2:1:4:1:1, in accordance with a degraded *o*-carborane cage including a mirror plane containing three unique boron atoms. The absorptions of intensity 4 may be due to the coincidental occurrence of two signals of intensity 2 at the same chemical shift. Upon comparison of these chemical shifts with data available in the literature, these signals have been attributed to B9,11, B3, B2,4,5,6, B10, and B1, respectively.

The ^{1}H NMR of the tetramethylammonium salt in acetone-d_6 shows resonances attributable to N(CH_3) (3.41 ppm) and SH (2.74 ppm) with relative intensities 6:1, respectively.

Trimethylammonium *anti*-7,7′:8,8′-Bis(dithio)bis(7,8-dicarbaundecaborate(10)). Compound III reacts with 1 equiv of I$_3$$^-$ in boiling water to give after workup the dimer compound, as an analytically pure, white, air-stable solid.

The ^{11}B NMR spectrum in acetone-d_6 displays six regions of resonance at −4.23, −9.35, −15.01, −17.14, −32.49, and −34.55 ppm with relative intensities 2:1:2:2:1:1 in agreement with the proposed structure. The signals are assigned to B9,11, B3, B2,4,5,6, B10, and B1. The signal at −32.49 ppm is in fact a doublet of doublets due to a terminal hydrogen (J_{BH} = 122 H), and a bridge hydrogen J_{BH_b} = 49 Hz).

The ^{1}H NMR spectrum in acetone-d_6 only displays signals attributable to the trimethylammonium cation.

***trans*-[(η^5-C$_5$H$_5$)(3,1,2-CoB$_9$C$_2$S$_2$H$_9$)]$_2$.** Reaction of IV with anhydrous CoCl$_2$ and potassium cyclopentadienide in absolute ethanol yielded a semisolid mass after workup. Due to the low yield, a good characterization was not possible. The mass spectrum showed a peak with the highest m/e ratio at 318, which corresponds to M/2. This peak displayed a typical boron envelope.

Table II. Bond Distances (Å) and Angles (deg) with Esd's for [HNMe$_3$][C$_2$B$_9$S$_2$H$_{12}$]

	Bond Lengths		
S1–C7	1.801 (4)	B3–B4	1.737 (9)
S2–C8	1.786 (4)	B3–B1	1.764 (9)
C7–C8	1.581 (5)	B9–B5	1.769 (7)
C7–B11	1.651 (6)	B9–B10	1.799 (7)
C7–B2	1.676 (6)	B9–B4	1.800 (7)
C7–B3	1.732 (9)	B10–B6	1.774 (7)
C8–B9	1.658 (6)	B10–B5	1.781 (7)
C8–B4	1.675 (6)	B6–B1	1.797 (7)
C8–B3	1.719 (8)	B6–B5	1.816 (7)
B11–B6	1.755 (8)	B1–B4	1.782 (7)
B11–B2	1.788 (8)	B1–B5	1.790 (7)
B11–B10	1.808 (7)	B4–B5	1.768 (7)
B2–B3	1.759 (9)	N1–C3	1.472 (7)
B2–B6	1.759 (7)	N1–C5	1.482 (8)
B2–B1	1.802 (8)	N1–C4	1.488 (7)
	Bond Angles		
C8–C7–B11	113.89 (32)	B3–B2–B6	107.77 (40)
C8–C7–B2	112.73 (34)	B3–B2–B11	108.86 (39)
C8–C7–B3	62.33 (32)	B3–B2–B1	59.36 (35)
C8–C7–S1	116.86 (27)	B6–B2–B11	59.32 (29)
B11–C7–B2	65.01 (31)	B6–B2–B1	60.59 (29)
B11–C7–B3	117.06 (40)	B11–B2–B1	108.44 (35)
B11–C7–S1	119.87 (31)	C8–B3–C7	54.52 (30)
B2–C7–B3	62.12 (35)	C8–B3–B4	57.97 (32)
B2–C7–S1	118.14 (28)	C8–B3–B2	102.48 (44)
B3–C7–S1	113.76 (33)	C8–B3–B1	104.17 (43)
C7–C8–B9	111.43 (30)	C7–B3–B4	102.16 (44)
C7–C8–B4	111.95 (33)	C7–B3–B2	57.39 (32)
C7–C8–B3	63.15 (33)	C7–B3–B1	103.57 (43)
C7–C8–S2	119.16 (28)	B4–B3–B2	109.49 (45)
B9–C8–B4	65.37 (29)	B4–B3–B1	61.22 (35)
B9–C8–B3	116.53 (38)	B2–B3–B1	61.52 (35)
B9–C8–S2	116.81 (28)	C8–B9–B5	103.40 (34)
B4–C8–B3	61.54 (34)	C8–B9–B10	105.55 (33)
B4–C8–S2	120.41 (29)	C8–B9–B4	57.77 (26)
B3–C8–S2	118.67 (33)	B5–B9–B10	59.88 (29)
C7–B11–B6	102.96 (37)	B5–B9–B4	59.39 (29)
C7–B11–B2	58.18 (27)	B10–B9–4	107.99 (35)
C7–B11–B10	104.24 (34)	B6–B10–B5	61.44 (30)
B6–B11–B2	59.52 (30)	B6–B10–B9	106.98 (35)
B6–B11–B10	59.68 (29)	B6–B10–B11	58.68 (30)
B2–B11–B10	107.96 (38)	B5–B10–B9	59.23 (28)
C7–B2–B3	60.49 (33)	B5–B10–B11	107.08 (36)
C7–B2–B6	101.76 (34)	B9–B10–B11	104.65 (33)
C7–B2–B11	56.80 (27)	B11–B6–B2	61.16 (30)
C7–B2–B1	104.25 (34)	B11–B6–B10	61.65 (30)
B11–B6–B1	110.13 (34)	C8–B4–B9	56.86 (26)
B11–B6–B5	107.85 (35)	B3–B4–B5	108.47 (41)
B2–B6–B10	110.83 (35)	B3–B4–B1	60.13 (35)
B2–B6–B1	60.87 (30)	B3–B4–B9	108.59 (41)
B2–B6–B5	107.55 (34)	B5–B4–B1	60.54 (29)
B10–B6–B1	109.47 (35)	B5–B4–B9	59.45 (29)
B10–B6–B5	59.47 (29)	B1–B4–B9	108.30 (35)
B1–B6–B5	59.39 (29)	B4–B5–B9	61.17 (28)
B3–B1–B4	58.65 (34)	B4–B5–B10	110.23 (37)
B3–B1–B5	106.33 (41)	B4–B5–B1	60.13 (29)
B3–B1–B6	105.93 (41)	B4–B5–B6	106.70 (34)
B3–B1–B2	59.12 (34)	B9–B5–B10	60.90 (30)
B4–B1–B5	59.33 (29)	B9–B5–B1	109.35 (34)
B4–B1–B6	106.93 (35)	B9–B5–B6	106.45 (36)
B4–B1–B2	105.59 (36)	B10–B5–B1	109.46 (37)
B5–B1–B6	60.85 (29)	B10–B5–B6	59.08 (29)
B5–B1–B2	106.86 (37)	B10–B5–B6	59.76 (29)
B6–B1–B2	58.54 (29)	C3–N1–C5	112.29 (53)
C8–B4–B3	60.48 (34)	C3–N1–C4	111.04 (56)
C8–B4–B5	102.75 (35)	C5–N1–C4	110.97 (52)
C8–B4–B1	105.23 (36)		

Description of the Structures. The compounds [NMe$_3$H][B$_9$C$_2$H$_{12}$S$_2$] (III) and [NMe$_3$H]$_2$[B$_9$C$_2$H$_{10}$S$_2$]$_2$ (IV) belong to the monoclinic system with space group $P2_1/a$ (Table I). The structures of [B$_9$C$_2$H$_{12}$S$_2$]$^-$ (III$^-$) and [B$_9$C$_2$H$_{10}$S$_2$]$_2$$^{2-}$ (IV$^-$) are illustrated in Figures 1 and 2, respectively. Selected intera-

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(11) $R_1 = \sum[F_o - F_c]^2/\sum F_o^2$; $R_2 = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$.
(12) Supplementary material.

Table III. Bond Distances (Å) and Angles (deg) with Esd's for $[HNMe_3]_2[C_2B_9S_2H_{10}]_2$

Bond Lengths

S1–S2′	2.061 (1)	B2–B6	1.756 (6)
S1–C7	1.774 (3)	B2–B3	1.763 (5)
S2–C8	1.794 (3)	B2–B11	1.806 (6)
C7–C8	1.594 (4)	B3–B4	1.766 (5)
C7–B11	1.634 (5)	B4–B5	1.749 (6)
C7–B2	1.718 (5)	B4–B9	1.786 (5)
C7–B3	1.723 (5)	B5–B9	1.761 (6)
C8–B9	1.611 (5)	B5–B10	1.776 (6)
C8–B4	1.726 (5)	B5–B6	1.824 (7)
C8–B3	1.733 (5)	B6–B11	1.777 (6)
B1–B2	1.721 (6)	B6–B10	1.781 (6)
B1–B4	1.763 (6)	B9–B10	1.811 (6)
B1–B3	1.768 (6)	B10–B11	1.838 (7)
B1–B5	1.793 (6)	N1–C1	1.485 (6)
B1–B6	1.806 (6)	N1–C2	1.486 (6)
		N1–C3	1.488 (6)

Bond Angles

C7–B3–B1	103.85 (27)	B3–C7–S1	114.64 (22)
C8–B3–B2	102.67 (25)	C7–C8–B9	114.22 (26)
C8–B3–B4	59.10 (20)	C7–C8–B4	111.83 (25)
C8–B3–B1	103.17 (26)	C7–C8–B3	62.21 (20)
B2–B3–B4	107.79 (29)	C7–C8–S2	119.92 (21)
B2–B3–B1	59.44 (24)	B9–C8–B4	64.62 (22)
B4–B3–B1	59.85 (24)	B9–C8–B3	116.50 (27)
C8–B4–B5	101.00 (27)	B9–C8–S2	118.99 (23)
C8–B4–B1	103.67 (27)	B4–C8–B3	61.40 (21)
C8–B4–S33	59.50 (21)	B4–C8–S2	114.55 (21)
C8–B4–B9	54.57 (20)	B3–C8–S2	112.17 (12)
B5–B4–B1	61.41 (25)	B2–B1–B4	108.48 (28)
B5–B4–B3	108.74 (31)	B2–B1–B3	60.14 (22)
B5–B4–B9	59.74 (24)	B2–B1–B5	108.02 (30)
B1–B4–B3	60.12 (22)	B2–B1–B6	59.16 (25)
B1–B4–B9	108.18 (30)	B4–B1–B3	60.03 (23)
B3–B4–B9	106.39 (28)	B4–B1–B5	58.91 (24)
B4–B5–B9	61.18 (24)	B4–B1–B6	107.82 (29)
B4–B5–B10	111.87 (3)	B3–B1–B5	101.70 (28)
B4–B5–B1	59.69 (24)	B3–B1–B6	106.86 (28)
B4–B5–B6	107.66 (31)	B5–B1–B6	60.88 (26)
B9–B5–B10	61.59 (25)	C7–B2–B1	104.81 (28)
B9–B5–B1	107.96 (30)	C7–B2–B6	102.32 (27)
B9–B5–B6	106.54 (31)	C7–B2–3	59.33 (20)
B10–B5–B1	109.55 (54)	C7–B2–B11	55.21 (20)
B10–B5–B6	59.28 (26)	B1–B2–B6	62.00 (25)
B1–B5–Bo	59.91 (25)	B1–B2–B3	60.42 (23)
B2–B6–B11	61.45 (24)	B1–B2–B11	108.84 (30)
B2–B6–B10	111.91 (29)	B6–B2–B3	109.30 (31)
B2–B6–B1	58.85 (23)	B6–B2–B11	59.85 (24)
B2–B6–B5	106.44 (29)	B3–B2–B11	106.38 (27)
B11–B6–B10	62.19 (25)	C7–B3–C8	54.94 (18)
B11–B6–B1	107.63 (28)	C7–B3–B2	59.03 (21)
B11–B6–B5	106.65 (29)	C7–B3–B4	104.06 (26)
B10–B6–B1	108.78 (31)	B5–B9–B10	59.62 (25)
B10–B6–B5	59.04 (25)	B4–B9–B10	108.55 (29)
B1–B6–B5	59.21 (24)	B5–B10–B6	61.67 (27)
C8–B9–B5	105.25 (29)	B5–B10–B9	58.79 (25)
C8–B9–B4	60.80 (22)	B5–B10–B11	106.08 (30)
C8–B9–B10	106.28 (29)	B6–B10–B9	106.24 (29)
B5–B9–B4	59.07 (24)	B6–B10–B11	58.81 (24)
S1–S2–C3	202.44 (12)	B9–B10–B11	101.94 (28)
S1–Si–C8	102.95 (11)	C7–B11–B6	104.88 (28)
C8–C7–B11	110.72 (26)	C7–B11–B2	59.67 (21)
C8–C7–B2	110.96 (25)	C7–B11–B10	106.66 (29)
C8–C7–B3	62.85 (21)	B6–11–B2	58.70 (23)
C8–C7–S1	121.29 (21)	B6–B11–B10	59.00 (25)
B11–C7–B2	65.12 (22)	B2–B11–B10	107.11 (30)
B11–C7–B3	116.62 (27)	C1–N1–C2	111.04 (45)
B11–C7–S1	118.70 (24)	C1–N1–C3	112.93 (37)
B2–C7–S1	117.12 (22)		

tomic distances and angles for both compounds are compiled in Tables II and III. Positional and Thermal parameters are indicated in Tables IV–VII.

The anion 7,8-dimercapto-7,8-dicarbaundecaborate(10) has the form of an 11-apex fragment of an icosahedron with an ortho disposition of the C atoms in the open C7C8B9B10B11 face with two exocluster sulfurs, one bonded to C7 and the other one to C8. The mean values of the interatomic distances are as follows: for B–B, 1.78 (4) Å; for C–B, 1.68 (4) Å; and for C–C 1.581 (5) Å. These values are in agreement with those reported for cesium 9,10,11-trimethyl-*nido*-dicarbaundecaborate(1–), 1.81 (4), 1.68 (3), and 1.58 (3) Å, respectively.[13] However, the distance B9–B10 in this latter compound is considerably larger than the corre-

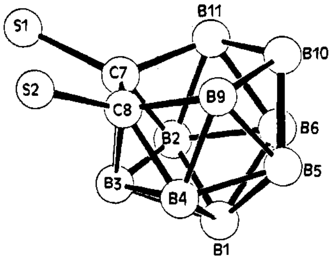

Figure 1. Perspective drawing of the anion 7,8-dimercapto-7,8-dicarbaundecaborate(10).

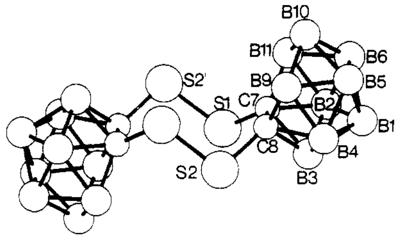

Figure 2. Perspective drawing of the anion 7,7′:8,8′-bis(dithio)bis(7,8-dicarbaundecaborate(10)).

Table IV. Positional Parameters and Their Estimated Standard Deviations for $[HNMe_3][C_2B_9S_2H_{12}]$

atom	*x/a*	*y/b*	*z/c*
S1	0.3891 (1)	0.4794 (1)	0.9156 (1)
S2	0.4404 (1)	0.4223 (1)	0.6210 (1)
C7	0.3130 (3)	0.3723 (4)	0.8234 (4)
C8	0.3416 (2)	0.3401 (4)	0.6832 (4)
B11	0.2021 (3)	0.3855 (6)	0.8426 (5)
B2	0.2643 (3)	0.2356 (6)	0.8940 (5)
B3	0.3556 (5)	0.2083 (8)	0.7912 (7)
B9	0.2517 (3)	0.3290 (6)	0.5881 (5)
B10	0.1546 (3)	0.3484 (6)	0.6883 (5)
B6	0.1630 (3)	0.2176 (6)	0.8059 (5)
B1	0.2572 (3)	0.1053 (6)	0.7721 (5)
B4	0.3140 (3)	0.1778 (6)	0.6398 (5)
B5	0.1939 (3)	0.1802 (6)	0.6441 (5)
H11	0.1742 (40)	0.4636 (67)	0.9123 (55)
H2	0.2775 (40)	0.2263 (66)	0.9900 (60)
H9	0.2605 (44)	0.3575 (66)	0.4887 (64)
H10	0.0877 (41)	0.3885 (65)	0.6541 (57)
H6	0.1015 (41)	0.1773 (65)	0.8434 (57)
H1	0.2399 (40)	0.4968 (68)	0.2138 (57)
H4	0.3492 (41)	0.1282 (68)	0.5746 (58)
H5	0.1571 (41)	0.1131 (65)	0.5860 (57)
N1	0.5100 (3)	0.2513 (4)	0.2386 (4)
C3	0.4137 (4)	0.2809 (9)	0.2636 (8)
C4	0.5546 (6)	0.1839 (8)	0.3495 (7)
C5	0.5221 (6)	0.1667 (8)	0.1232 (7)
HN	0.5419 (44)	0.3263 (71)	0.2263 (62)
HC3	0.3760 (48)	0.1953 (74)	0.2898 (63)
HC3	0.4106 (43)	0.3334 (69)	0.3537 (63)
HC3	0.3812 (50)	0.2843 (88)	0.2072 (68)
HC4	0.5414 (44)	0.2367 (73)	0.4247 (63)
HC4	0.5272 (44)	0.0830 (74)	0.3592 (60)
HC4	0.6158 (46)	0.1962 (77)	0.3186 (64)
HC5	0.4871 (46)	0.2197 (75)	0.0643 (63)
HC5	0.5670 (47)	0.2016 (78)	0.0853 (69)
HC5	0.4995 (44)	0.0680 (73)	0.1423 (60)

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Table V. Thermal Parameters and Their Estimated Standard Deviations for $[HNMe_3][C_2B_9S_2H_{12}]$

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	0.0042 (1)	0.0105 (2)	0.0072 (1)	−0.0021 (1)	−0.0003 (1)	−0.0017 (1)
S2	0.0028 (0)	0.0104 (2)	0.0075 (1)	−0.0012 (1)	+0.0010 (1)	−0.0000 (1)
C7	0.0028 (2)	0.0076 (5)	0.0054 (4)	−0.0006 (2)	−0.0000 (2)	−0.0005 (3)
C8	0.0023 (2)	0.0070 (5)	0.0059 (4)	−0.0002 (2)	−0.0004 (2)	0.0004 (3)
B11	0.0029 (2)	0.0104 (7)	0.0067 (5)	0.0000 (3)	0.0006 (3)	−0.0006 (4)
B2	0.0036 (2)	0.0091 (7)	0.0058 (4)	−0.0009 (3)	−0.0002 (3)	0.0009 (4)
B3	0.0034 (4)	0.0088 (10)	0.0078 (7)	0.0005 (5)	−0.0003 (4)	0.0003 (7)
B9	0.0028 (2)	0.0094 (6)	0.0054 (4)	−0.0001 (3)	−0.0002 (2)	+0.0001 (4)
B10	0.0028 (2)	0.0088 (7)	0.0075 (5)	0.0007 (3)	−0.0001 (3)	−0.0001 (4)
B6	0.0029 (2)	0.0092 (7)	0.0068 (5)	−0.0012 (3)	0.0004 (3)	0.0007 (4)
B1	0.0034 (2)	0.0067 (6)	0.0096 (6)	−0.0003 (3)	−0.0005 (3)	0.0008 (5)
B4	0.0032 (2)	0.0073 (6)	0.0070 (5)	0.0003 (3)	0.0001 (3)	−0.0004 (4)
B5	0.0029 (2)	0.0091 (6)	0.0067 (5)	−0.0011 (3)	0.0001 (3)	−0.0008 (4)
N1	0.0042 (2)	0.0083 (5)	0.0091 (4)	−0.0007 (3)	−0.0002 (2)	−0.0010 (4)
C1	0.0040 (3)	0.0190 (12)	0.0152 (9)	−0.0001 (5)	−0.0001 (4)	−0.0016 (8)
C2	0.0093 (5)	0.0150 (10)	0.0115 (7)	0.0024 (6)	−0.0035 (5)	−0.0002 (7)
C3	0.0104 (6)	0.0152 (10)	0.0101 (7)	−0.0008 (6)	0.0019 (5)	−0.0019 (7)

Table VI. Positional Parameters and Their Estimated Standard Deviations for $[HNMe_3]_2[C_2B_9S_2H_{10}]_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*
S1	0.0909 (1)	0.6045 (1)	0.5617 (1)
S2	−0.0107 (1)	0.4482 (1)	0.2433 (1)
C7	0.1663 (2)	0.5159 (2)	0.5103 (4)
C8	0.1193 (2)	0.4411 (2)	0.3657 (4)
B1	0.3167 (3)	0.4652 (3)	0.3144 (6)
B2	0.2903 (3)	0.5377 (3)	0.4893 (6)
B3	0.1967 (3)	0.5175 (3)	0.2840 (5)
B4	0.2044 (3)	0.4069 (3)	0.2241 (6)
B5	0.2979 (3)	0.3573 (3)	0.3953 (7)
B6	0.3528 (3)	0.4403 (3)	0.5667 (7)
B9	0.1689 (3)	0.3469 (3)	0.4174 (6)
B10	0.2667 (3)	0.3613 (3)	0.6286 (7)
B11	0.2528 (3)	0.4767 (3)	0.6827 (6)
N1	0.0703 (2)	0.2236 (2)	0.0089 (4)
C1	0.0047 (5)	0.1590 (5)	0.0835 (8)
C2	0.1684 (5)	0.1841 (4)	−0.0186 (11)
C3	0.0172 (4)	0.2686 (4)	−0.1670 (8)
H1	0.3671 (37)	0.4767 (31)	0.2198 (71)
H2	0.3179 (36)	0.6035 (31)	0.5199 (69)
H3	0.1629 (36)	0.5654 (30)	0.1796 (71)
H4	0.1789 (36)	0.3867 (30)	0.0683 (70)
H5	0.3429 (37)	0.3007 (31)	0.3611 (68)
H6	0.4278 (37)	0.4389 (33)	0.6350 (69)
H7	0.1174 (36)	0.2855 (32)	0.3812 (68)
H8	0.2984 (36)	0.3095 (32)	0.7327 (68)
H9	0.2661 (36)	0.5030 (31)	0.8238 (72)
H10	0.1962 (38)	0.3953 (32)	0.6735 (70)
H11	−0.0219 (43)	0.1286 (36)	−0.0171 (78)
H12	−0.0629 (41)	0.1989 (34)	0.0868 (75)
H13	0.0324 (39)	0.1335 (36)	0.1982 (79)
H14	0.2105 (39)	0.2336 (35)	−0.0745 (74)
H15	0.1934 (41)	0.1544 (35)	0.1021 (77)
H16	0.1271 (41)	0.1516 (36)	−0.1303 (76)
H17	0.0051 (40)	0.2191 (36)	−0.2471 (76)
H18	0.0721 (38)	0.3082 (34)	−0.2103 (71)
H19	−0.0394 (42)	0.2917 (38)	−0.1295 (79)
H20	0.0852 (36)	0.2744 (34)	0.1092 (71)

sponding one in III: they are 1.93 (4) and 1.80 (1) Å, respectively. This point will be referred to later.

The anion *anti*-7,7′:8,8′-bis(dithio)bis-(7,8-dicarbaundecaborate(10)) consists of two 7,8-dicarbaundecaborate(10) clusters bridged by two –S–S– units in such a way that there is an inversion center in the middle of the molecule. Each of the 7,8-dicarbaundecaborate(10) moieties is correctly described as the corresponding one in 7,8-dimercapto-7,8-dicarbaundecaborate(10). As a consequence of the inversion center the two cluster components are relatively placed in an anti fashion. The cations NMe_3H^+ are placed sideways to the anionic moiety and not above the pentagonal face with the missing borons. The bond distances in the clusters are similar to these observed in III. It is worth commenting on the C–S bond lengths in III and IV. C–S distances of 1.775 (3) or 1.786 (4) Å are found in III or IV, respectively, which is slightly shorter than the C–S bond length of 1.826 (7) reported for (2,6-bis(ethylthiomethyl)pyridine)zinc dibromide[14] while being slightly longer than the C–S distance of 1.737 (5) Å in the copper thiolato complex Cu(cyclam)$(SC_6F_5)_2$. Accordingly, there appears to be an apparent relationship between the carbon hybridization and the C—S distances, with C(sp^2) < C(III) < C(sp^3), which could imply a certain C═S double bond character in III or IV through delocalization of the sulfur lone pair into the cluster open-face orbitals.

Discussion. Unlike many boron hydrides, the *o*-carborane cage system is generally stable toward alcohols. However, 1,2-dihalo derivatives are degraded by both methanol and ethanol, yielding 7,8-dihalo derivatives of 7,8-dicarbaundecaborate(10).[1] This may be understood if we consider the fact that the halogen substituents accentuate the carbon's electronegativity, thus making B3 more positive and, consequently, more susceptible to nucleophilic attack.

Nevertheless, such an explanation does not account for the degradation of 1,2-dithio derivatives of *o*-carborane by ethanol. We recently reported[5] that when either the ammonium or potassium salt of 1,2-dimercapto-*o*-carborane was reacted with 1,2-dibromomethane or dichloromethane, dimer derivatives of 7,8-dicarbaundecaborate(10) in ethanol were formed (eq 1), yet no degradation happened when α,α'-dibromo-*o*-xylene was used as a bridge precursor. With this compound, a polymer resulted. On the basis of these experimental results, we proposed that the removal of B3 by a weak base is facilitated by the stabilization caused through the presence of lone pairs on the S, which can delocalize through the orbitals of the 7,8-dicarbaundecaborate(10) anion's open face. We also believe that the ring formation, which permits an interaction between the two cluster moieties, is a contributing factor.

With the synthesis of the 7,8-dimercapto-7,8-dicarbaundecaborates(10) II and III, we present another example of a facile partial degradation of the carborane cage, which, as before, may be accounted for by the presence of the sulfurs. But, in contrast to what was argued before, no ring was formed in II or III. It is interesting to note, however, that no difference was observed in the synthesis of tetramethylammonium 7,7′,8,8′-bis(1,2-dithioethyl)bis(7,8-dicarbaundecaborate(10)), irrespective of the use of the ammonium or potassium salt of 1,2-dimercapto-*o*-carborane, whereas II and III were not obtained when the potassium salt of I was used. The ^{11}B NMR of the evaporated reaction mixture indicated mostly undegraded carborane derivatives (not isolated) and a small amount of degraded *o*-carborane derivatives (not II or III).

A further corroboration of our assumption that the ammonium ion is both a source of the proton and the base that removes the

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Table VII. Thermal Parameters and Their Estimated Standard Deviations for $[HNMe_3]_2[C_2B_9S_2H_{10}]_2$

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	0.0048 (1)	0.0025 (0)	0.0187 (2)	−0.0003 (0)	0.0023 (1)	−0.0005 (1)
S2	0.0042 (1)	0.0043 (0)	0.0119 (2)	−0.0004 (0)	0.0002 (1)	−0.0004 (1)
C7	0.0037 (2)	0.0025 (1)	0.0142 (7)	−0.0001 (1)	0.0009 (3)	−0.0003 (3)
C8	0.0039 (2)	0.0029 (1)	0.0128 (6)	−0.0002 (1)	0.0008 (3)	−0.0002 (3)
B1	0.0046 (3)	0.0036 (2)	0.0221 (10)	0.0006 (2)	0.0036 (4)	0.0021 (4)
B2	0.0038 (2)	0.0040 (2)	0.0167 (9)	−0.0007 (2)	0.0008 (4)	0.0008 (4)
B3	0.0047 (2)	0.0032 (2)	0.0147 (8)	−0.0001 (2)	0.0017 (4)	0.0009 (3)
B4	0.0058 (3)	0.0031 (2)	0.0174 (9)	0.0000 (2)	0.0037 (4)	−0.0002 (3)
B5	0.0056 (3)	0.0037 (2)	0.0285 (12)	0.0010 (2)	0.0053 (5)	0.0023 (4)
B6	0.0041 (2)	0.0050 (2)	0.0231 (11)	0.0004 (2)	0.0015 (4)	0.0034 (4)
B9	0.0055 (3)	0.0028 (2)	0.0200 (10)	0.0004 (2)	0.0035 (4)	0.0006 (3
B10	0.0050 (3)	0.0038 (2)	0.0231 (11)	0.0006 (2)	0.0016 (4)	0.0037 (4)
B11	0.0044 (2)	0.0042 (2)	0.0161 (9)	−0.0005 (2)	0.0003 (4)	0.0011 (3)
N1	0.0064 (2)	0.0044 (2)	0.0200 (7)	−0.0008 (2)	0.0015 (3)	0.0007 (3)
C1	0.0101 (4)	0.0109 (5)	0.0280 (14)	−0.0051 (4)	0.0008 (7)	0.0058 (6)
C2	0.0104 (5)	0.0057 (3)	0.0529 (22)	0.0017 (3)	0.0087 (9)	0.0028 (6)
C3	0.0093 (4)	0.0068 (3)	0.0276 (13)	−0.0018 (3)	−0.0025 (6)	0.0035 (5)

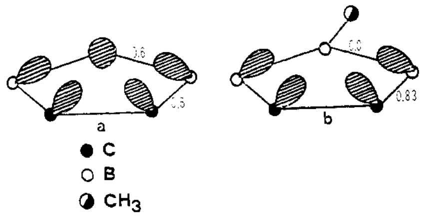

Figure 3. Schematic drawing of the open face of (a) 7,8-$(SH)_2$-$C_2B_9H_{10}^-$ and (b) 9,10,11-Me_3-7,8-$C_2B_9H_9^-$. The thiol groups in part a and the 9 and 11 methyl groups in part b have been omitted for clarity. The shaded lobes represent sp^3 orbitals pointing to the boron unoccupied vertex. The numbers represent the fraction of a second bond between pairs of atoms (see text for derivation of these fractional bonds).

labilized B3[14] comes from the nonpartial degradation under the same reaction conditions as for 1,2-dimercapto-*o*-carborane. Until our preliminary report,[6] the geometry, syn or anti, of partially degraded bis(*o*-/*m*-dicarbadodecaborane) clusters, where there is restricted rotation of the cages, had not been established. The 7,8-dimercapto-7,8-dicarbaundecaborate(10) unit appeared as a good precursor of these type of systems since by oxidation of the –SH units a dimer containing two 7,8-dicarbaundecaborate moieties was expected. In addition, both cages would be joined by two disulfido bridges, and as has been indicated before, some kind of orbital interaction was presupposed between the sulfur and the cluster open face. In this situation, some electronic delocalization between the two open faces was envisaged through the disulfido bridges, and it was expected that the geometry adopted would be imposed not only by steric requirements but also electronic requirements. As can be seen in Figure 2 the crystal structure of this iodine-oxidized compound revealed clearly an anti arrangement of the two clusters. This was, a priori, the expected result in order to minimize the electrical repulsions. The anti geometry adopted by this ligand forces any pair of suitable metals to occupy the anti positions. This is the most probable structure for $[(\eta\text{-}C_5H_5)Co(\eta^3\text{-}1,2\text{-}B_{C_2}S_2H_9)]_2$. When Wilkinson's catalyst was used as the metal source no insertion was obtained in the open face of the cluster. On the contrary, results seem to indicate an oxidative addition of the Rh^I in the disulfide bridge, $-S-Rh^{III}-S-$.

Regarding the structure of III, it is interesting to compare the B9–B10 distance in 9,10,11-Me_3-7,8-$C_2B_9H_9^-$[13] against its equivalent in III. The observed values are 1.93 (4) and 1.799 (7) Å, respectively. This shortening can be explained by a larger bonding order betwen B9–B10 in III compared to its equivalent in 9,10,11-Me_3-7,8-$C_2B_9H_9^-$ due to partial overlap of the five orbitals pointing to the apical proton centered over the pentagonal face (Figure 3).

In accordance with the shorter distance B10–B11, there is in III also, a larger distance, C8–B9, compared to that in 9,10,11-Me_3-7,8-$C_2B_8H_9^-$. Distances of 1.654 (9) Å, (III) and 1.59 (4) Å (9,10,11-Me_3-7,8-$C_2B_9H_{10}^-$) for C8–B9 have been found.[17] The observed differences in distances in the open faces of III and 9,10,11-Me_3-7,8-$C_2B_9H_9^-$ may be explained by treating the open faces in the same way as Cp^- and butadiene. In Cp^-, all bonds are equivalent and have a bond order of 1.6, while in butadiene there are two bonds with a bond order of 1.83 and another with a bond order of 1.33. The fraction of a second bond between atoms is represented in Figure 3.

In II and III the ^{11}B NMR resonances of the apical boron B1 and the borons adjacent to carbons appear at a lower field[16] than in 7,8-$B_9C_2H_{12}^-$. We have noticed a similar effect in *closo*-boranes when a particular boron is replaced by a main-group element richer in electrons (e.g. a boron in $B_{10}H_{10}^{2-}$ is substituted by a carbon to give $CB_9H_{10}^-$).[18]

In the II and III case, the NMR shift may be interpreted as due to a larger electron density around the carbons, compared to that in 7,8-$B_9C_2H_{12}^-$, due to an inductive sulfur effect. The largest downfield shift is experienced by B3 ($\Delta\delta = +9.42$ ppm) as is expected by a symmetrically placed boron, adjacent to two substituted atoms (SNE: symmetrical neighbor effect). The effect on the neighbor atoms is a common observation in substituted *closo*-boranes.

Acknowledgment. F.T. thanks the Spanish Ministerio de Universidades e Investigación for a grant. We are indebted to Prof. R. C. Taylor (University of Michigan) for consultation. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Supplementary Material Available: A table of calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

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(17) When the standard deviations are considered, these numbers resemble each other considerably. This is probably due to the low resolution of the 9,10,11-Me_3-7,8-$C_2B_9H_{10}^-$. However we fell that the comparison is consistent enough to be included.

(18) Teixidor, F.; Viñas, C.; Rudolph, R. W. *Inorg. Chem.* **1986**, *25*, 3339–3345.