

SYNTHESIS OF CYCLIC AND POLYMERIC DERIVATIVES OF 1,2-DITHIOL-*o*-CARBORANE

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Summary

Cyclic compounds containing two symmetrically placed 1,2-dicarboclosododecaboranyl or two 7,8-dicarbauendecaborate(10) moieties have been synthesized. The bridges between the carborane cages are S–S or S–CH₂–CH₂–S for the undegraded species, and S–CH₂–S or S–CH₂CH₂–S for the degraded ones. The sulfur atoms in all cases are bonded to the carborane carbons. Unlike preparations previously reported in the literature, degradation to the partially degraded *o*-carborane cages proceeds without requiring treatment by a conventional base. Ring closure and the presence of sulfur atoms linked to the *o*-carborane carbons are believed to be necessary in order for the degradation to occur. When the number of bonds involved in the bridge between the two cages was seven, no cyclization occurred despite the presence of a square planar nickel template, the reaction instead producing a polymeric material.

Introduction

Searches for new and more efficient methods of obtaining industrially important starting materials has led in recent years to a considerable increase in the numbers of papers on catalysis [1]. In a recent review, Muetterties [2] has pointed out that there are some catalytic reactions (for example, hydrogenation of N₂ to yield ammonia) that occur with catalysts in the solid state but that do not occur with homogeneous catalysts, the conclusion being that for the reaction to occur, more than one catalytic metallic center must be in close proximity. As a consequence of this argument, it would appear that a homogeneous catalyst with two or more catalytic centers held in a fixed spatial arrangement might show increased selectivity compared to heteroge-

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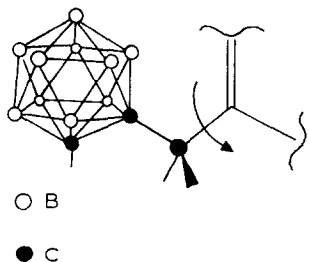


Fig. 1. An *o*-carboranyl moiety linked to a porphyrin ring through a CH₂ bridge showing the possibility of rotation of the cage.

neous catalysts and expand the area of usefulness of this type of catalyst. An obvious class of compounds to investigate are metal clusters: they are soluble, they have metal atoms in close proximity and they have delocalized electron systems similar to metals. However, not only metal clusters exhibit the preceding characteristics: boron hydrides as well have a delocalized system of electrons and derivatives of these compounds incorporating appropriate metals have been shown to have catalytic activity, e.g., 3,3-(PPh₃)₂-3-H-3,1,2-RhC₂B₉H₁₁ [3]. Although this molecule has only one metal atom per molecule, comparable catalytic activity has been observed in [(PPh₃)RhC₂B₉H₁₁]₂ [4].

The properties of metallocarboranes containing more than one metal atom per molecule have been reviewed by Dunks and Hawthorne [5]. One characteristic of all of the metallocarboranes surveyed is that the metal atom plays an important role in holding the molecule together, and therefore processes characteristic of catalysts, such as addition of the substrate, either split the molecule or do not occur because the metal is coordinatively saturated. In this laboratory, we are approaching the problem by seeking compounds in which the metal atoms can be kept sufficiently close together for the catalytic center to have the necessary catalytic activity but for which the catalyzed reaction does not endanger the existence of the catalyst molecule. Progress towards this objective has been made with the synthesis of ligands such as H₂(CH₂-C₂B₁₀H₁₁)₄ [6] which can be incorporated into a metal complex after partial degradation of the carborane cage [7]. However, since the metallo-carborane moiety in the compound reported was linked to a porphyrin ring by only one bond (Fig. 1), the relative distance of the metal atoms could not remain fixed.

In this paper we present the synthesis of ligands that can coordinate to two metal atoms in such a way that their spatial arrangement is fixed, allowing the two metals to be separated by a short distance while retaining their association with a delocalized system of electrons.

Experimental

General

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Melting points were done in sealed tubes and are uncorrected. Infrared spectra were obtained using a Perkin-Elmer Model 457. The ¹H and ¹¹B NMR spectra were obtained using either a JEOL FX-90Q, or a Bruker WM-360. Mass

spectra were recorded with a Finnigan 4023 GC/MS.

o-Carborane (Dexil Chemical Corporation) was sublimed before use; 1,2-dithiol-*o*-carborane (I) was prepared from *o*-carborane according to the literature [8]. The *n*-butyllithium 1.6 *M* solution in hexane (Aldrich) was used as received. Absolute ethyl ether (Mallinckrodt) and benzene was stored on a vacuum line with Na/benzophenone and distilled in vacuo prior to use. All other reagents and solvents were reagent grade and used as received. Reactions were conducted under a N₂ atmosphere.

1,1',2,2'-tetrathio-bis-o-carborane (II)

To a nitrogen-blanketed solution containing 0.20 g (0.96 mmol) of 1,2-dithiol-*o*-carborane (I), in 40 ml of dry benzene, were added all at once 0.27 g (1 mmol) of I₂ followed immediately by 0.5 g of sodium bicarbonate. The reaction vessel was a 3-necked flask fitted with reflux condenser and filled with glass beads. Nitrogen was allowed to bubble through the solution by means of an inlet inserted through one neck. The N₂ flow was regulated to agitate the solution but without forming a liquid obstruction in the lower part of the cooling system. The solution was heated under reflux for 24 h after which it was still iodine colored. At that point, a drying tube was connected to the third neck of the flask and the N₂ rate was increased sufficiently to evaporate most of the benzene. Before attaining dryness the apparatus was dismantled (under N₂) and the residual benzene was pumped off. The solid was collected in a glove bag and then sublimed at 90°C (0.01 Torr) until the residue lost most of the brownish color. The residue was then collected, put in a Soxhlet thimble and extracted with dry benzene overnight. Evaporation and drying in vacuo gave 110 mg (55% yield) of a pale tan solid. (The color was probably due to a small residual I₂ impurity.) The product sublimed at 180°C (0.01 Torr) very slowly; m.p. 235°C with decomposition. It reacted with moisture and had to be stored under vacuum or very dry N₂.

Analysis: Found B, 52.0; S, 30.8. C₄H₂₀B₂₀S₄ calcd: B, 52.4, S, 31.0%. Mass spectrum, base peak envelope centered at 206.1 (100%), molecular peak envelope centered at 412.3 (50%), cut off peak at 418. Intensity ratio of 412/418 = 66.

Reaction of 1,2-dithiol-o-carborane with liquid ammonia.

Ammonium 1,2-dithiolate-o-carborane (III). In a 50 ml three-necked flask with the middle neck connected to a dry ice cold-finger condenser, 0.2 g (0.96 mmol) of 1,2-dithiol-*o*-carborane (I) were placed under N₂. The flask was flushed with N₂ for 15 min before NH₃(g) was introduced via the one neck and NH₃(l) allowed to condense on the cold finger. About 15 ml of liquid ammonia were condensed (−77°C). The solution was stirred for 30 min with a magnetic stirrer and the NH₃ then allowed to evaporate (about 1 h) by removing the dry ice from the condenser. Last traces of NH₃ were swept out using a N₂ stream to give a product ranging in color from light yellow to white.

Analysis: Found: B, 44.37; N, 11.15; S, 26.42. C₂H₁₈B₁₀N₂S₂ calcd.: B, 44.63; N, 11.57; S, 26.44%.

Tetramethylammonium 7,7'; 8,8'-di-(1,2-dithioethane)-bis(7,8-dicarbaundecaborate-(10)) (IV). The total amount of III obtained from 0.2 g I (0.96 mmol) was dissolved in 40 ml of absolute ethanol in a 100 ml 3-neck flask equipped with a condenser, and 0.1 ml (1.16 mmol) of 1,2-dibromoethane were added. The solution was stirred

overnight, during which time the yellowish color of the solution was observed to fade substantially. (In some runs a small amount of solid is obtained.) The solution then was transferred to a beaker and 150 ml of distilled water added. (If a turbidity appeared the solution was filtered.) [9] While N_2 was bubbled through the solution an excess of Me_4NCl in 20 ml of water was added and a solid precipitated. After the solution stood for 15 min the solid was collected by filtration and dried in vacuum ($100^\circ C$, 0.01 Torr for 5 h). The solid was recrystallized from acetic acid affording 94 mg (44% yield). M.p.(dec) $255^\circ C$. Analysis: Found: C, 28.18; H, 7.88; B, 28.87; N, 4.02; S, 19.20. $C_{16}H_{52}B_{18}N_2S_4 \cdot 4.5 H_2O$ calcd.: C, 28.42; H, 9.03; B, 28.78; N, 4.14; S, 18.95%.

Tetramethylammonium 7,7'; 8,8'-di-(dithiomethane)-bis(7,8-dicarbaundecaborate-(10)) (V). The procedure was similar to that for the preparation of IV. The amount of III obtained from 0.35 g of I (1.68 mmol) was dissolved in 40 ml of absolute ethanol and 3 ml (46.8 mmol, 28 times excess) of dichloromethane and 1.9 g of NaI were added to the stirred solution which was maintained at reflux until the yellow color disappeared (3.5 h).

The subsequent workup was similar to that of compound IV. The product was recrystallized using methanol/ethanol 2/1 with heating followed by evaporation and cooling (sometimes repeatedly). Heating at $150^\circ C$ for 15 h gave 227 mg (49% yield) of a dry, white solid which melted at $260\text{--}261^\circ C$ with decomposition.

Analysis: Found: C, 29.40; H, 8.50; B, 34.56; N, 4.90; S, 22.34. $C_{14}H_{48}B_{18}N_2S_4$ calcd.: C, 29.66; H, 8.47; B, 34.32; N, 4.94; S, 22.60%.

TABLE I
MASS SPECTRA VALUES

Compound ^{a,e}	EI ^f m/e	Assignment ^g	CI ^f m/e	Assignment
VI ^b	223.1(100%)	M/2 - 1	223(27.4%)	M/2 - 1
	239.1(75%)	M/2 + CH ₂ + 1	239.1(100%)	M/2 + CH ₂ - 1
	253.2(27%)	M/2 + S - 3	252(84%)	M/2 + S - 4
	442.3(2%)	M - 6	268(5%)	M/2 + CH ₂ S - 2
VII ^c	206.3(80%)	M/2 - 4		
	224.2(100%)	M/2 + CH ₂		
	252 (32%)	M/2 + CH ₂ S - 4		
	414 (7%)	M - 6		
IX ^d	234.2(100%)	M/2	235.2(100%)	M/2 + 1
	467.2(0.3%)	M - 1	265.2(36.9%)	M/2 + S - 1
			280.2(31.6%)	M/2 + CH ₂ S
			292.2(22.8%)	M/2 + C ₂ H ₄ S - 2

^a The numbers in parentheses represent the intensities referred to the base peak in the spectrum.

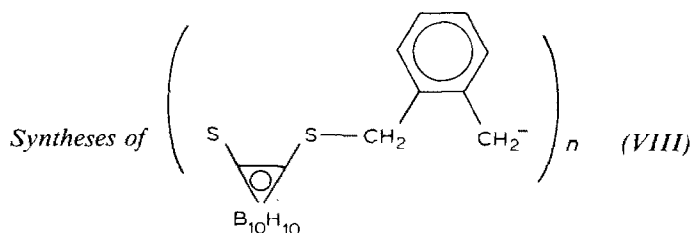
^b $M = {}^{12}C_8{}^1H_{30}{}^{10}B_4{}^{11}B_{14}{}^{32}S_4$ $M = 448$. ^c $M = {}^{12}C_6{}^1H_{26}{}^{10}B_4{}^{11}B_{14}{}^{32}S_4$ $M = 420$. ^d $M = {}^{12}C_8{}^1H_{28}{}^{10}B_4{}^{11}B_{16}{}^{32}S_4$ $M = 468$. ^e The atoms in the fragments are considered ${}^{12}C$, 1H and ${}^{32}S$. ^f EI = electron impact; CI = chemical ionization. ^g Numbers subtracted represent unit atomic weights (protons) missing.

Reaction of 7,7'; 8,8'-di- μ -(1,2-dithioethane)-bis-(7,8-dicarbaundecaborate(10)) with hydrochloric acid

A solution of 30 ml of water saturated with NaCl was added to a suspension of 20 mg of compound IV in 20 ml of ethyl ether. After stirring for 10 min a few drops of concentrated HCl (aq) were added and both layers became clear. The flask was shaken vigorously and then the ethereal layer was separated and dried over anhydrous magnesium sulfate. Filtration and evaporation of the ether solution gave an oil. Toluene was added to the oil and evaporated repeatedly (6 times) until a white solid was obtained, (VI). see Table 1 for characterization.

Reaction of 7,7'; 8,8'-di- μ -(1,2-dithiomethane)-bis-(7,8-dicarbaundecaborate(10)) with hydrochloric acid

The same procedure as in the previous case was used. The solid obtained was highly hygroscopic, (VII). See Table 1 for characterization.



Under N_2 , 0.12 g (2.14 mmol) of KOH were added to a solution of 0.15 g (0.72 mmol) of I in 15 ml of methanol. The solution was stirred for 25 min and then CO_2 was passed through the solution to eliminate excess KOH after which 0.21 g (0.77 mmol) of α, α' -dibromo-*o*-xylene in methanol (30 ml) were added to the solution (total volume of reaction 40–45 ml). After a few minutes a white precipitate was formed and the stirring was continued for 2 h. The precipitate was collected by filtration and washed three times with 5 ml portions of methanol. Drying at 0.01 Torr yielded 142 mg of a white solid (63% yield), M.p. $> 260^\circ C$. Compound VIII is insoluble in most organic solvents but slightly soluble in THF.

Analysis: Found: C, 38.09; H, 5.85; B, 33.94; S, 19.97. $C_{10}H_{18}B_{10}S_2$ calcd.: C, 38.71; H, 5.81; B, 34.83; S, 20.64%.

Upon evaporating the supernatant solution a white solid was obtained. The ^{11}B NMR and IR of the soluble fraction proved to be a mixture of partially degraded and undegraded species (1/2 respectively) [10]. The 1H NMR also indicated that at least two more species besides unreacted α, α' -dibromo-*o*-xylene were contained.

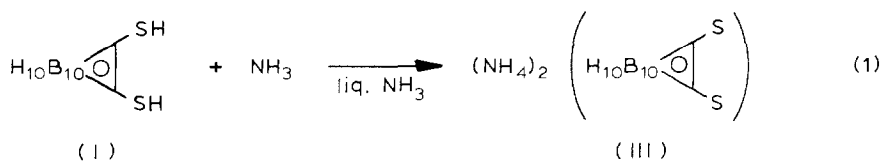
*Syntheses of 1,1'; 2,2'-di- μ -(1,2-dithioethane)-bis-*o*-carborane (IX)*

To a solution of 0.205 g (0.986 mmol) of 1,2-dithiol-*o*-carborane in absolute ethanol (40 ml) were added 0.166 g (2.9 mmol) of KOH. After a few minutes the solution appeared pale yellow; after 30 min, CO_2 was bubbled through the solution to eliminate the excess KOH by filtration as the carbonate. Ethanol was added to restore the initial volume and also 0.1 ml (1.16 mmol) of 1,2-dibromoethane. The reaction mixture was stirred overnight and the product was recovered by evaporation. By ^{11}B NMR the product composition was 42% IV and 52% the potassium salt of III [11]. The flask was refilled with absolute ethanol (40 ml) and was heated at

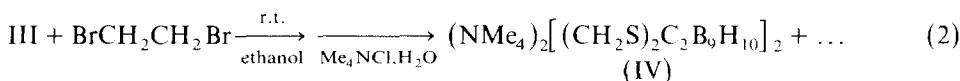
reflux for 3 h. After cooling, a white solid (soluble in water and giving no precipitate adding Me_4N) was separated by filtration. The ethanolic filtrate was evaporated and dried in vacuum. The ^{11}B NMR of the product showed it to be composed of IV (50%) and IX (50%). The solid mixture was extracted with benzene to leave IV as a solid which was collected by filtration and a solution which after being evaporated gave IX. See Table 1 for characterization of IX.

Results

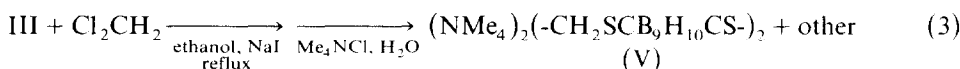
The reaction of 1,2-dithiol-*o*-carborane (I) with liquid ammonia quantitatively gave ammonium 1,2-dithiolate-*o*-carborane (III) (eq. 1). Further reaction of III with



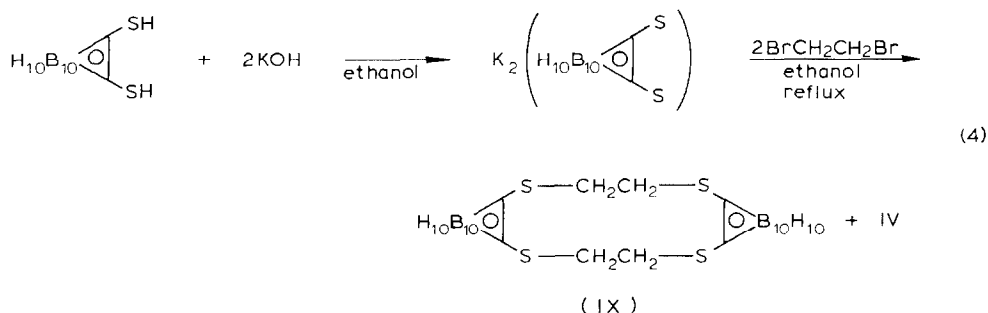
1,2-dibromoethane in ethanol afforded ammonium 7,7'-8,8'-di- μ -(1,2-dithioethane)-bis-(7,8-dicarbaundecaborate(10)) (IV) which was precipitated in water in the form of the tetramethylammonium salt.



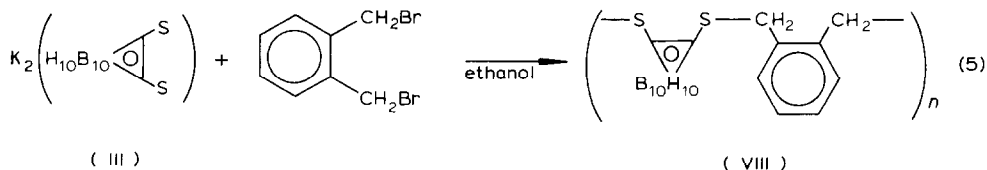
Reaction of III with excess of dichloromethane in ethanol in the presence of NaI afforded ammonium 7,7'-8,8'-di- μ -(dithiomethane)-bis-(7,8-dicarbaundecaborate(10)) (V) which was also precipitated in water in the form of the tetramethylammonium salt (eq. 3).



Reaction of 1,2-dithiol-*o*-carborane (I) with 1.5 times the amount of KOH necessary to remove both protons in the dithiol molecule afforded a salt (presumably the dipotassium salt) which by reaction with 1,2-dibromoethane afforded IV and 1,1'-



2,2'-di- μ -(1,2-dithioethane)-bis-*o*-carborane (IX) (eq. 4) or by reaction with 1,2-di-



bromo-*o*-xylene afforded a compound insoluble in most of the usual solvents. Analysis of VIII indicated the composition shown in eq. 5.

Compounds IV and V were proven not to be monomeric by treatment with hydrochloric acid in an ether/water solution and by studying the mass spectra of the solid obtained after evaporation of the ether. In both cases, peaks assignable to fragments of the molecule bigger than the monomer and with higher intensity than the monomer have been observed (See Table 1), but no direct proof of the n value has been obtained. Nevertheless, the authentic molecular dimers II and IX lead us to believe that IV and V are dimeric. Structural considerations of the *o*-xylyl moiety suggest that a polymeric structure for VIII may be more favorable than a dimer.

Reaction of 1,2-dithiol-*o*-carborane with I_2 in benzene afforded 1,1'-2,2'-tetrathio-bis-*o*-carborane (eq. 6)

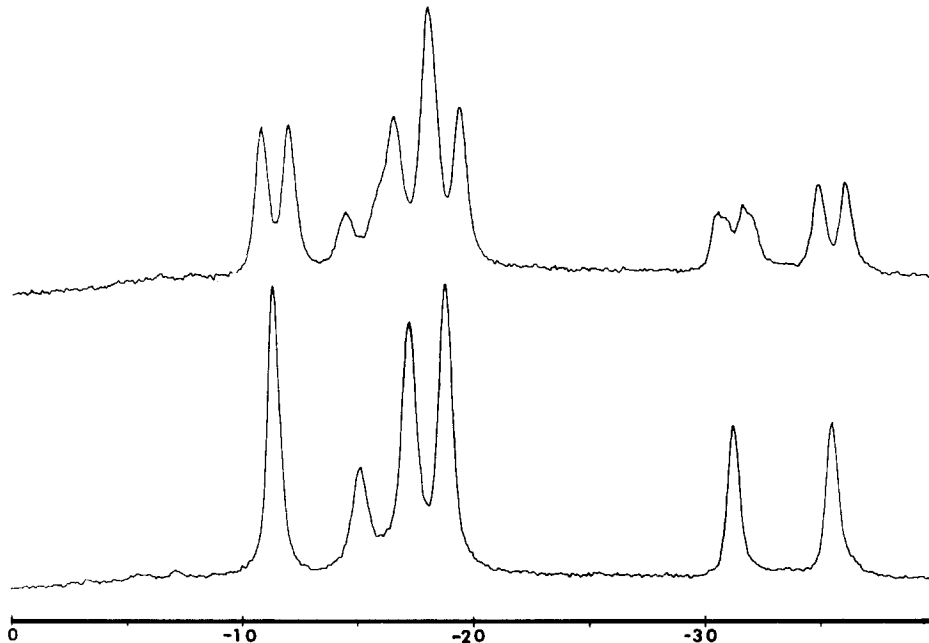
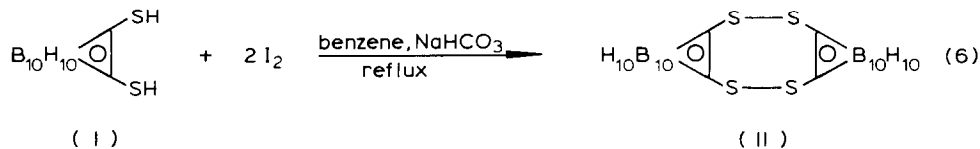


Fig. 2. The ^{11}B NMR spectra (coupled and decoupled) of tetramethylammonium 7,7':8,8'-di(dithiomethane)-bis-(7,8-dicarbaundecaborate(10)) in $\text{DMSO-}d_6$. Chemical shifts are relative to an external sample of F_3B , OEt_2 . See Table 2 for coupling constants and chemical shifts.

TABLE 2

¹¹B NMR SPECTRAL DATA

Compound	Absorption ^{h,i} δ(ppm)					
I ^{h,f}	-4.04(2);		-8.08(6);		-10.04(2)	
	152		171		171	
I ^{e,f}	-4.07(2);		-7.16-7.66(6)		-10.12(2)	
	146		165		162	
II ^{h,g}	-3.57(2)		-7.27(8)			
	141		161			
III ^{d,g}	-2.37(2)		-9.00(6)		-11.38(2)	
	171		156		137	
IV ^{e,f}	-7.87(2)	-10.59(1)	-17.88(2)	-18.84(2)	-33.05(1)	-36.64(1)
	140	168	130	143	122	140
V ^{e,f}	-11.36(2)	-15.16(1)	-17.28(2)	-18.81(2)	-31.22	-35.55(1)
	134	159	159	146	130	134
IX ^{d,g}	-3.56(2)		-7.32(8)			
	~170		149			

^a Values referred to external BF₃·Et₂O. ^b Solvent chloroform-*d*. ^c Solvent ethanol. ^d Solvent acetone-*d*. ^e Solvent dms_o-*d*. ^f Observed frequency 115 MHz. ^g Observed frequency 28.7 MHz. ^h *J*(B-H) are below the chemical shifts. ⁱ The number in parenthesis indicates the relative integrations.

The ¹¹B NMR spectra (Table 2) clearly indicate that partial degradation of the *o*-carborane cage occurred in the synthesis of IV and V, and the spectra show a 2/1/2/2/1/1 pattern indicating a mirror plane going through three unique atoms and dividing the other six into 3 groups of two atoms each (See Fig. 2). The chemical shifts of these groups of atoms are close to those of the 7,8-C₂B₉H₁₂⁻ ion [12] and at the same time the ¹¹B NMR spectra indicate that no degradation of the cage occurred in II, III and IX. The position of the B-H absorption band in the IR spectrum in compound VIII (2570 cm⁻¹) agrees with what is expected for an undegraded carborane cage (2560-2640 cm⁻¹ for substituted carborane and 2470-2550 cm⁻¹ for the 7,8-dicarbaundecaborate(10)) [13]. We have found 2515-2510 cm⁻¹ for partially degraded 1,2-dithioderivatives (compounds IV and V) and 2570 cm⁻¹ for nondegraded derivatives (Table 3).

TABLE 3

INFRARED SPECTRAL DATA

II	2600vs, 2570vs, 1075m, 975w, 875w, 790w, 720m.
IV	3450m, b, 3020w, 2920w, 2775sh, 2515vs, 2475sh, 1480s, 1065w, 1015w, 945s, 880w, 720w, 460w.
V	3020w, 2985w, 2920w, 2575sh, 2510vs, 2475sh, 1480s, 1065w, 945s, 880w.
VIII	3055w, 3020w, 2935w, 2845w, 2570vs, 2300w, 1660b, m, 1490m, 1450m, 1425m, 1300m, 1230m, 1215w, 1125s, 1000m, 970m, 880m, 800w, 775s, 770s, 705s, 600w, 550w, 460w.

vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, b = broad.

TABLE 4

¹H NMR SPECTRAL DATA

Compound	Absorption ^a				
I ^{b,e}		3.73			
IV ^{c,f}	3.35(3)	3.08(24)		2.87(8) ^h	-2.5
V	3.94	3.77	3.52	3.34(2)	3.10(12)
IX ^{d,g}		2.89			

^a Values are given in δ (ppm) referred to TMS. The number in parenthesis indicate the relative interpretations. ^b Solvent chloroform-*d*. ^c Solvent dms_o-*d*₆. ^d Solvent acetone-*d*. ^e Observed frequency 60 MHz. ^f Observed frequency 360 MHz. ^g Observed frequency 90 MHz. ^h First 4 frequencies belonging to an AB system. Total integration 2.

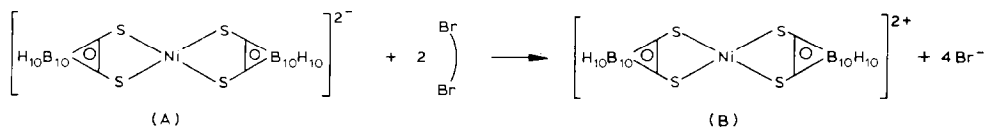
The ¹H NMR (Table 4) is in accordance with the structures indicated, showing an AB pattern (J 10.5 Hz) in compound V and a more complicated pattern for compound IV with 21 observed absorptions, clearly indicative of an AA'BB' [14] system as would be expected for the indicated geometry [15].

Discussion

As indicated earlier, the ultimate goal in the current research was to synthesize a molecule in which four metal centers are held in relatively close proximity in a fixed configuration. One approach to this goal is to use rigid *o*-carborane cages as building blocks and attach them to a macrocycle. Linkage of the cages to the macrocycle by both carbon atoms would prevent rotation of the cages, and partial degradation would allow insertion of metal atoms in the cages to give the desired product.

One complication when four *o*-carborane cages are attached to a single framework is that upon degradation isomers will be produced which differ in the orientation of the cages with respect to the plane of the macrocycle. If α is used to designate a cage above the plane of the macrocycle and β to designate one below the plane, the isomers can be described as $\alpha\alpha\alpha\alpha$, $\alpha\alpha\alpha\beta$, $\alpha\beta\alpha\beta$ and $\alpha\alpha\beta\beta$. Physical properties of these isomers may be expected to be quite similar and therefore separation of the various species following the degradation reaction would be difficult. A simpler approach, which is described here as an initial step in the program, is to focus on a two cage system in which, after degradation, only two isomers would exist in the degradation mixture, the $\alpha\alpha$ and the $\alpha\beta$ species, and the severity of the separation problem would be significantly lessened.

For a number of reasons, 1,2-dithiol-*o*-carborane is attractive as the choice of a carborane cage: (a) there are two reactive groups present, (b) the presence of lone pairs and accessible *d*-orbitals on the sulfur could facilitate interaction between cages, and (c) the compound $[(C_2H_5)_4N]_2Ni(B_{10}H_{10}C_2S_2)_2$ [17] could possibly be utilized as a template, if necessary, in order to obtain the desired geometry. The template reaction was based on the work by Thompson and Busch [18], from which the following reaction was projected.



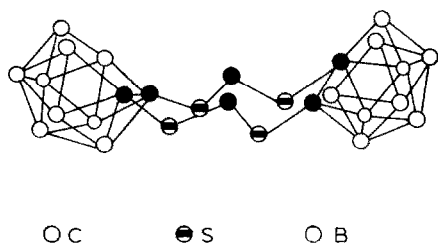


Fig. 3. Proposed structure of the α,α isomer of 7,7'; 8,8'-di-(dithiomethane)-bis-(7,8-dicarbaundecaborate(10))ion. The hydrogen atoms have been omitted for clarity.

In order to explore the reaction conditions needed to produce a two cage ligand, α,α' -dibromo-*o*-xylene was employed instead of the 1,2-bis-bromomethyl-*o*-carborane since the similarities in their geometries suggested that the two would undergo analogous reactions and the expensive carborane material could be conserved. The reaction of A with α,α' -dibromo-*o*-xylene produced a white solid that was very insoluble (VIII) and subsequent reaction with 1,2-dibromoethane led to IV in a 60% yield.

As it turned out, the same compounds could be obtained more simply by means of the reaction of III with the indicated reagents, which implies that the presence of a template was unnecessary, or that upon the formation of the thioether, the S–Ni bond was broken with the loss of the template effect. Either would explain the formation of VIII. However, in this case the steric effects operating would favor a more relaxed structure leading to a polymer with the carboranyl moiety undegraded [19]. On the other hand, with a shorter bridge such as $-\text{CH}_2-$ or CH_2CH_2- (IV, V), the ring closure is favored, making borons 3 or 6 very susceptible to nucleophilic attack and resulting in a partially degraded molecule. The fact that IX exists and is stable in ethanol implies that the partial degradation is a consequence of the mechanism employed in the ring formation, and that one or more other mechanisms exist in which the partial degradation does not take place. In Fig. 3 one of the isomers of V is represented.

The degradation that occurred resulting in IV and V was unexpected. The methods described in the literature to partially degrade *o*-carborane all require nucleophilic agents such as methoxide, trialkylamines, hydrazine, ammonia or similar compounds [16] whereas the reactions indicated in equations 2 and 3 proceeded to the degraded carborane without the introduction of a base. The only step in which a conventional base (ammonia) was employed was in the formation of III, and in this case the analyses and the ^{11}B NMR spectra clearly indicated that the product contained a non-degraded *o*-carborane cage.

Up to now few papers have appeared concerning the chemistry of the thiol (mono and di) derivatives of *o*-carborane [20]. As can be seen from the present work, the chemistry of the 1,2-dithiol-*o*-carborane (I) exhibits previously unknown reactions compared to other known derivatives of *o*-carborane. Even the chemistry of I seems to differ from that of 1-thio-*o*-carborane. For example, Zakharkin and coworkers do not indicate any problem in the oxidation of $^R\text{C}_2\text{B}_{10}\text{H}_{11}\text{S}^-\text{Na}^+$ with I_2 in order to obtain the disulfide [21]. However, reaction of III with iodine in ethanol gives a salt, the ^{11}B NMR of which no longer corresponds to undegraded carborane [22]. It is our

opinion that it is the possibility of ring formation together with the presence of lone pairs and available *d*-orbitals of the sulfur that causes these differences. A plausible explanation may be that the increased stability of the molecule is to be expected as a result of the delocalization of the sulfur lone pair. This could occur through overlap of the *s*-orbitals with those of the open face of the degraded cage. This delocalization is less feasible when the thiols are not adjacent to the boron atom which is removed upon degradation. Recently, Hermanek and coworkers [23] have synthesized 9,12-(CH₂S₂)-1,2-C₂B₁₀H₁₀ which supports our explanation.

Our results further suggest to us that an interaction between the two cages exists in compounds II, IV and V. We believe that this interaction will be increased if the linking atoms, instead of being saturated carbons, are atoms with available *d*-orbitals and lone pair electrons. Current efforts are being directed towards obtaining compounds with these characteristics, and to solve the stereochemistry of the $\alpha\alpha$ and $\alpha\beta$ isomers.

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