Inorg. Chem. **1995**, *34*, 1726−1729

Cathodic Cleavage of C−S and C−P in Carboranyl Derivatives

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Received June 3, 1994[⊗]

An electrochemical cathodic study of sulfur− and phosphorus−carbon substituted derivatives of *o*-carborane has shown that C−S and C−P bond fission takes place. The 1,2-dithio-1,2-dicarba-*closo*-dodecaborane(12) derivatives display a marked influence of the S,S′-noncluster linkage in their cathodic behavior. Shorter S,S′ linkages, which produce more strained cycles, give cathodic waves at lower voltages (−1.2 V, Ag/AgCl) than the less strained ones (−1.7 V). These cathodic peaks are attributed to an electrochemical process followed by a chemical one. The compounds with shorter linkages are converted to *o*-carborane, and no C−S retention has been observed. The compounds with longer linkages provide comparable amounts of *o*-carborane, 7,8-$C_2B_9H_{12}^-$ and 7,8-SRS-7,8-$C_2B_9H_{10}^-$. These less strained compounds exhibit some C−S bond retention. The phosphorus derivatives, which are noncyclic, behave like the more strained S mesocycles described above. Only *o*-carborane is found among the products following the electrochemical process, and in no case has C−P retention taken place.

Electron-rich elements C-bonded to a carboranyl cluster greatly influence its activity. The easy partial degradation of 1,2-$(SR)_2$-1,2-$C_2B_{10}H_{10}$, or 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ compounds by means of transitional metal complexes to yield *nido*-7,8-$(SR)_2$-7,8-$C_2B_9H_{10}^-$ or *nido*-7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}^-$ transition metal derivatives proves the former statement.[1,2] The transition metal is stabilized by the two electron-rich donating elements, S or P, and the negative charge of the generated 7,8-$C_2B_9H_{12}^-$ derivative. Figure 1 exemplifies this reaction. It is hypothesized that electron transfer to the carborane cage takes place via overlap of appropriate atomic orbitals (Figure 2). In this process, the sulfur or phosphorus atoms provide a bridge to transmit electron density from the rich transition metal to the electron deficient cluster.

In a recent article, the electrochemical synthesis of *C*-metal *o*-carboranes was described.[3,4] The procedure is based on the cathodic fission of the C−H bond in *o*-carborane or its alkyl derivatives by using transition metal anodes in polar solvents. In the process, complexes $[7\text{-R-}7,8\text{-}C_2B_9H_{11}]_2M\cdot bipy$ (M = Ni, Co) were produced. Thus, the use of transition metal soluble anodes allows the partial degradation of the 12 vertex cluster.

In the first type of reaction electron transfer to the cluster from the transition metal occurs via an electron-rich bridge, and in the second, via electrochemical reduction. These reactions are closely similar; in both cases electron transfer to the carborane cage results in partial degradation of the cluster.

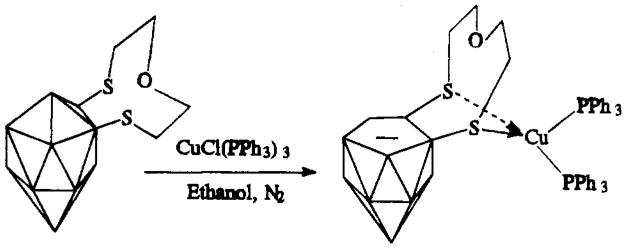

Figure 1. Decapitation of the cluster by means of a transition metal complex.

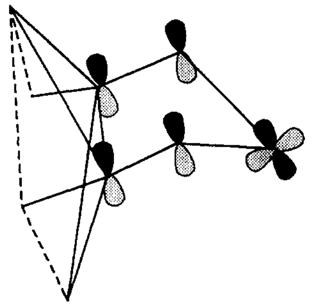

Figure 2. Atomic orbitals overlap facilitating electron transfer from the d metal orbital to the cluster.

Due to this similarity it appeared desirable to investigate the electrochemical behavior of 1,2-$(SR)_2$-1,2-$C_2B_{10}H_{10}$ and 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$. Several objectives were sought: (i) the electrochemical stability of the C−S or C−P bond as compared to C−H, (ii) the dependence of the carborane's partial degradation process in the absence of a transition metal ion (a nondissolving anode is used), (iii) the stability of the C−S vs the C−P bond, and (iv) the ease of reduction of the carborane cage when electron-rich elements are bonded to the cluster carbon atoms.

Results and Discussion

It is known that 1,2-$C_2B_{10}H_{12}$ is a polarographically active compound[5,6] which is reduced in a dropping mercury electrode at potential $E_{1/2}$ = −2.51 V (SCE) through a two-electron mechanism with the formation of the dianion $[1,2\text{-}C_2B_{10}H_{12}]^{2-}$. It appeared possible that the 1,2-$(SR)_2$-1,2-$C_2B_{10}H_{10}$ compounds might tolerate a similar reducing process at a less negative potential.

The electrochemical behavior was studied by cyclic voltammetry utilizing a three electrode configuration. The working

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[⊗] Abstract published in *Advance ACS Abstracts*, February 15, 1995.

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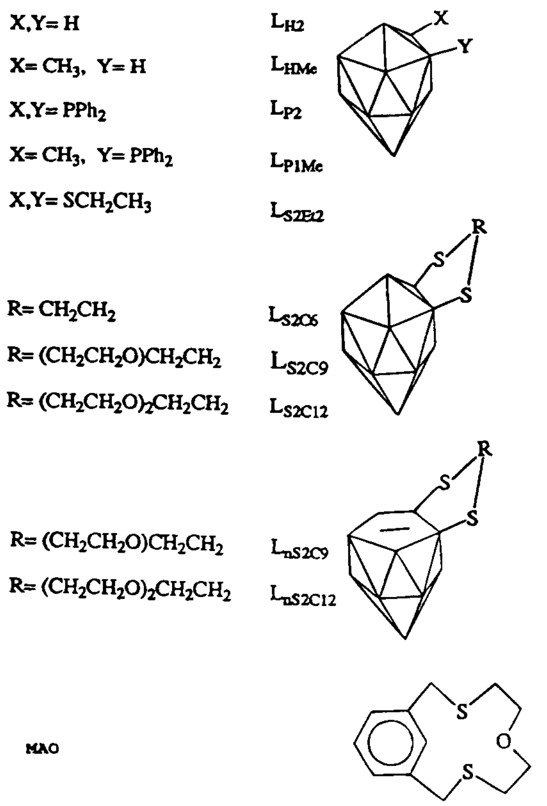

Figure 3. Ligands studied and their representation. The ligands are defined as follows: L represents the moiety $1,2\text{-}C_2B_{10}H_{10}$, Ln represents the moiety $7,8\text{-}C_2B_9H_{10}^-$, and the number of sulfur or phosphorus atoms is indicated next. If the ligand is cyclic there is a c following, with the cycle's size indicated by a number, e.g. L_{S2C12} refers to $1,2\text{-}S_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ moiety externally joined by a chain producing a cycle of total size 12.

Table 1. List of E_{pc} Values (V in Ag/AgCl)[a]

compound	E_{pc}	E_{pc}
L_{H2}		−2.4
L_{HMe}		−2.35
L_{S2C6}	−1.35	−2.4
L_{S2C9}	−1.2	−2.4
L_{S2C12}	−1.3	−2.4
L_{P2}	−1.3	−2.4
L_{P1Me}	−1.4	−2.35
L_{S2Et2}	−1.7[a]	−2.4
L_{nS2C9}^-		
L_{nS2C12}^-		
MAO		
Diphos		

[a] A wide wave starting at −1.7 V and ending at −2.0 V.

and auxiliary electrodes were platinum wire, and a Ag/AgCl electrode was used as a reference. The list of compounds studied is given in Figure 3. Table 1 presents the Epc values found. As a typical example Figure 4 illustrates the cyclic voltammogram of L_{S2C9}. The cyclic voltammograms of *o*-carborane, 1-Me-*o*-carborane, and these of the non-carborane-containing ligands 6-oxo-3,9-dithiobicycle[9,3,1]pentadeca-1(15),11,13-triene (MAO, Figure 3) and 1,2-bis(diphenylphosphino)ethane were also recorded for comparison purposes.

There have been values reported for the half-wave reduction potentials $E_{1/2}$ of *o*-carborane and its methyl derivative, −2.13 and −2.35 V, respectively, relative to Ag/AgCl. They were obtained by voltammetric studies of the tested compounds in 0.1 M solution of Et_4NCl in CH_3CN on Pt.[7] The process was interpreted as the C−H bond cleavage to give the *o*-carboranyl anion $[RC_2B_{10}H_{10}]^-$, eq 1.

$$1\text{-R-}1,2\text{-}C_2B_{10}H_{11} + e^- \rightarrow [1\text{-R-}1,2\text{-}C_2B_{10}H_{10}]^- + H \quad (1)$$

It was also reported[3] that the $[RC_2B_{10}H_{10}]^-$ anions dimerize in polar solvents to afford the dianions $[RC_2B_{10}H_{10}]_2^{2-}$, which by gentle heating are converted into $[7,8\text{-}RC_2B_9H_{11}]^-$.

For comparison purposes, the electrochemical behavior of *o*-carborane and its methyl derivative on the cathode was studied in our laboratory by CV in a 0.1 M solution of Bu_4NPF_6 in THF, CH_3CN, or DMF. The results obtained are very similar with all these solvents, and values of E_{pc} −2.4 and −2.35 V were measured, respectively, which for our system must correspond to eq 1.

The electrochemical behavior of the *o*-carborane sulfur-containing compounds L_{S2Et2}, L_{S2C6}, L_{S2C9}, and L_{S2C12} (see Figure 3) has been studied by CV under similar conditions. All these compounds have the sulfur atoms bonded to the cluster in the same fashion, but differ on the S,S′ noncluster connection; L_{S2Et2} is noncyclic, while L_{S2C6}, L_{S2C9}, and L_{S2C12} are mesocycles. Two irreversible cathodic peaks E_{pc} are found in the CV's of all these compounds, one at a common potential of −2.4 V and the other in the range −1.35 to −2.0 V, depending on the S substituent (Table 1). The absence of anodic peaks corresponding to these cathodic peaks and the constancy of the −2.4 V value in all CV's suggest the existence of coupled chemical reactions following electron transfer. An electrochemical-chemical (EC) reaction scheme leading to a common species is postulated. The constancy of the E_{pc} peak at −2.4 V suggests that the first cathodic reaction leads to a common generated electroactive species in all these thiocarborane derivatives. This common species has been attributed to *o*-carborane because of an exact matching with the electrochemical behavior of plain *o*-carborane. A process such as indicated in Figure 5 is thus proposed, where a cathodic fission of the C−S bond has taken place. A chemical reaction involving the nucleophilic dianion $C_2B_{10}H_{10}^{2-}$ follows, yield the *o*-carborane. The strong dependence of the first cathodic peak with respect to the S,S′-type of substituent is to be noted. When the tested compound is a mesocycle, e.g. for L_{S2C6}, L_{S2C9}, and L_{S2C12}, E_{pc} values close to −1.3 V are found. In contrast when the S,S′ atoms are not externally connected, as in L_{S2Et2}, the −1.7 V value is found.

The *o*-carborane phosphorus-containing compounds L_{P2} and L_{P1Me} display similar electrochemical behavior. Two electrochemical cathodic waves with no corresponding anodic peaks are observed in the CV's. The peaks at E_{pc} = −2.4 V (L_{P2}) and E_{pc} = −2.35 V (L_{P1Me}) suggest a reaction scheme as shown in Figure 6. The C−P fission waves found in these phosphorus derivatives are at −1.3 and −1.4 V, respectively, similar to the C−S fission waves in the mesocyclic sulfur analogues. This result implies a comparable electrochemical stability of the C−S and C−P bonds, which does not correspond to their chemical stability. The C−S bond in *closo*-carborane derivatives is much more stable to partial degradation processes than the C−P bond in similar compounds.

The nature of the species obtained from the cathodic reaction has been studied via preparative electrochemical synthesis. Thus, in the electrolysis of the mesocyclic and open chain compounds, using a 0.1 M solution of Bu_4NPF_6 in CH_3CN with applied E_c = −1.2 V (L_{S2C12}) or −1.7 V (L_{S2Et2}) on a Pt cathode, the ^{11}B-NMR of the crude reaction has shown the presence of *o*-carborane, $7,8\text{-}C_2B_9H_{12}^-$ and $7,8\text{-SRS-}7,8\text{-}C_2B_9H_{10}^-$ in approximate molar ratios 8:5:7 for L_{S2Et2} and 12:3:5 for L_{S2C12}. Their

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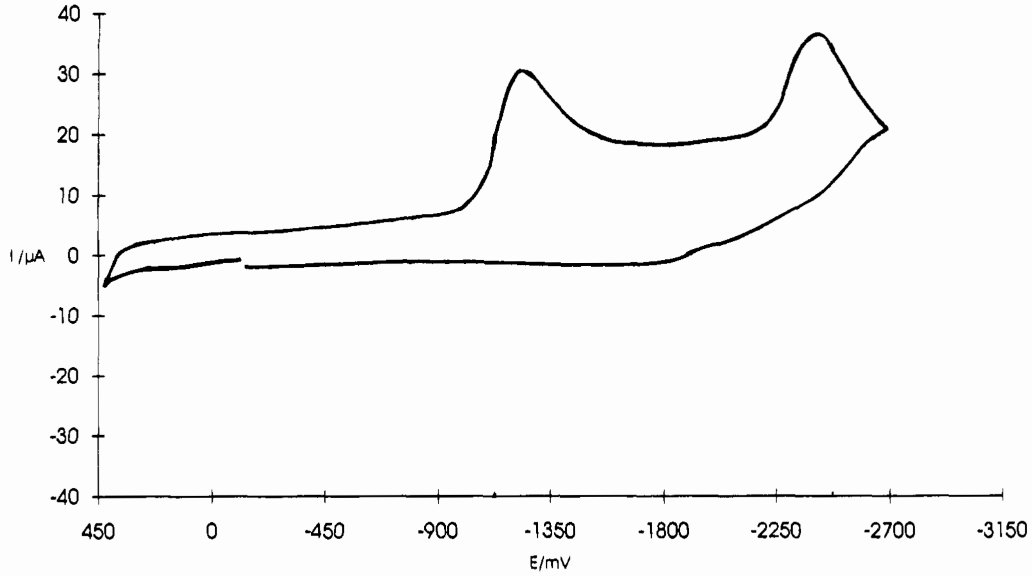

Figure 4. Cyclic voltammogram of L_{S2C9} in the cathodic area. Key: solution, 0.1 M Bu_4NPF_6 in THF; E_r, Ag/AgCl; E_w, Pt; E_{ax}, Pt; $S = 0.043$ V/s.

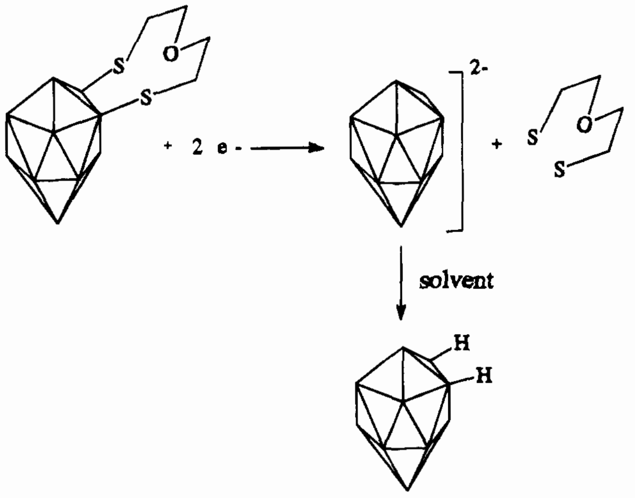

Figure 5. Proposed mechanism for the cathodic reduction of a short chain carborane mesocycle.

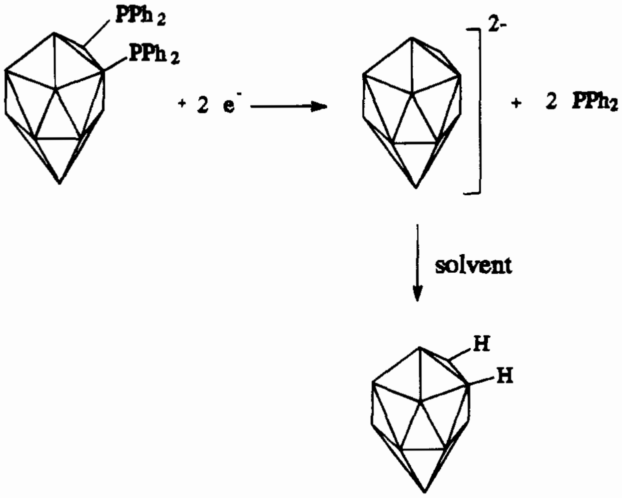

Figure 6. Proposed mechanism for the cathodic reduction of a phosphorus C-substituted carborane.

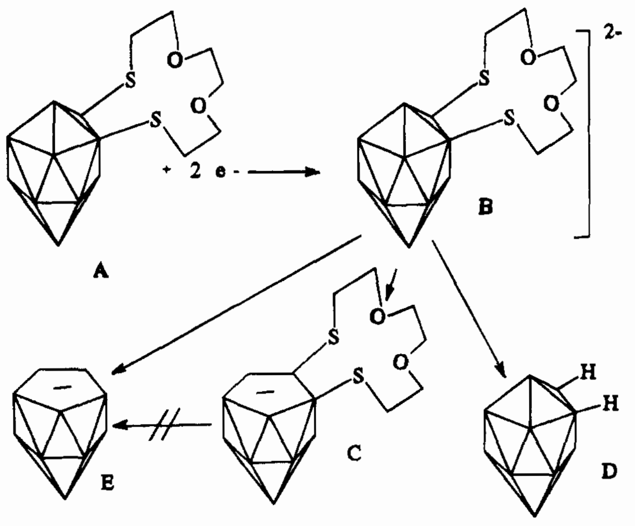

Figure 7. Proposed mechanism for the cathodic reduction of a relaxed mesocyclic carborane.

identity was confirmed by comparison with authenticated samples obtained by chemical procedures. The existence of *o*-carborane as the major product confirms our initial hypothesis but demonstrates that the C−S fission process is more complicated than is indicated in Figure 5. In fact, *o*-carborane is formed in all these electrochemical reactions whether the closo compound studied is a thio or a phosphorus derivative. However, there are noticeable differences in behavior. The short-chain thioether derivatives (e.g. L_{S2C9}) and the phosphorus derivatives produce in the preparative electrochemical synthesis mostly *o*-carborane and much less of the partially degraded anionic species. On the contrary, the more relaxed noncyclic or longer chain thioether compounds (e.g. L_{S2Et2} and L_{S2C12}) had produced, as stated above, comparable amounts of *o*-carborane, *nido*-7,8-$C_2B_9H_{12}^-$ and *nido*-7,8-SRS-7,8-$C_2B_9H_{10}^-$. It is however true that upon a long exposure (5−6 days) to an applied cathodic voltage (e.g. −1.3 V) *o*-carborane gradually degrades to *nido*-7,8-$C_2B_9H_{12}^-$. This was observed in the preparative electrochemical treatment of L_{P2} in CH_3CN where initially all L_{P2} had transformed to *o*-carborane, but growing amounts of the *nido*-7,8-$C_2B_9H_{12}^-$ species were obtained when the electrolysis was protracted.

The proposed general mechanism is indicated in Figure 7 for the specific case of L_{S2C12}. It comprises basically the process indicated in Figure 5, but the ratio of end products (**C**, **D**, **E**) depends on the nature of the species **B**. When **B** is relaxed **C**, **D**, and **E** are formed, but when **B** is strained only **D** is found. Intermediate situations produce variable amounts of **C**, **D**, and

E. Coulometric measurements of the cathodic behavior of L_{S2Et2} in 0.1 M solution of NBu_4PF_6 in CH_3CN with a controlled potential (E_c) = −1.8 V, on a Pt cathode and a Pt anode, have indicated a two-electron character of the electrochemical reaction ($n = 2.11$ e$^-$). Consequently the dithioether carborane molecule acquires two electrons, producing an unstable intermediate **B**, which converts to the compounds indicated. The *nido*-$C_2B_9H_{12}^-$ anion is the direct result of the degradation of the intermediate compound (**B**) and not the result of C−S fission in *nido*-7,8-SRS-7,8-$C_2B_9H_{10}^-$. This has been proven by cyclic voltammetry on an authenticated sample of 7,8-SRS-*nido*-7,8-$C_2B_9H_{10}^-$, which has been shown not to be electroactive in the cathodic region under study. The cathodic peaks described have been attributed to the cluster, and not to the external chain. This is evidenced by the flat response of the compounds 6-oxo-3,9-dithiobicicle[9.3.1]pentadeca-1(15),11,13-triene (MAO) (Figure 3) and 1,2-bis(diphenylphosphino)ethane in the cathodic area studied. These have a S,S′ connection and a P,P′ connection equal to that present in L_{S2C9} and L_{P2}.

It may then be concluded that fission of the C−S and C−P bonds takes place in these sulfur- and phosphorus-containing carborane derivatives at a less negative potential than the C−H fission in *o*-carborane. Moreover, the C−S and C−P fission leads mostly to *o*-carborane. The partially degraded product *nido*-7,8-SRS-7,8-$C_2B_9H_{10}^-$ with C−S retention is produced, but *nido*-$C_2B_9H_{12}^-$ is formed too. No decapitated products with C−P retention have been found. A dependence of the resulting ratio *o*-carborane/*nido*-7,8-$C_2B_9H_{12}^-$/*nido*-7,8-SRS-7,8-$C_2B_9H_{10}^-$ compounds with the S,S′ connection exists. The more strained cycles produce larger amounts of *o*-carborane, but the longer cycles or open chain compounds produce comparable amounts of the three species. It is also evident that in open chain compounds the C−S bond is more stable than C−P to electrochemical reduction. That according to our hypothesis a dianionic unstable species is generated which proceeds to the end products. This would imply that the cage is more easily reduced when incorporating electron-rich elements, but the existence of this species is not proven and consequently the former statement cannot be confirmed.

Experimental Section

Instrumentation. Elemental analysis were performed using a Perkin-Elmer 240-B microanalyzer. IR spectra were obtained with KBr pellets on a Nicolet 710-FT spectrophotometer. The ^{1}H-NMR and ^{11}B-NMR spectra were obtained by using a Bruker AM 400 WB instrument. The cyclic voltammetry measurements at 25 °C were performed using a Dacfamov (CNRS, Toulouse, France) connected to an Apple 2 computer. The electrosynthesis were performed using a potentiostat, Amel 549.

Materials. Before use, *o*-carborane and methyl-*o*-carborane (commercial) were sublimed under high vacuum; MAO,[8] Ln_{S2C9}^-, Ln_{S2C12}^-, L_{S2C6},[9] L_{S2C9},[10] L_{S2C12},[11] L_{P2},[12] and L_{P1Me}[13] were prepared according to the literature. Solvents CH_3CN and DMF were used as purchased, and THF was dried on Na. The supporting electrolyte was PF_6Bu_4N, vacuum dried.

Synthesis of L_{S2Et2} and Ln_{S2Et2}. To a three-necked flask (100 cm^3) equipped with a magnetic stirrer, condenser, and nitrogen inlet was placed 1.99 g (35.4 mmol) of KOH, 80 cm^3 of deoxygenated ethanol, 3.68 g (17.7 mmol) of 1,2-$(SH)_2$-$C_2B_{10}H_{10}$ and 3.86 g (35.4 mmol) of ethyl bromide. The mixture was stirred at room temperature for 0.5 h, and the solution was refluxed for 2 h. Insolubles were separated by filtering the warm mixture, and the solvent was removed under reduced pressure using a rotary evaporator. A water−diethyl ether (1:1) mixture was added. Stirring was continued for 10 min, before the two layers were separated. The diethyl ether extract was dried and evaporated under vacuum. The closo L_{S2Et2} was obtained. Yield 2.8 g (60%). IR (KBr): ν (cm^{-1}) = 2861, 2931, 2973 (C−H), 2594 (B−H), 1454, 1440 (C−H). ^{1}H-NMR (in $CDCl_3$): δ = 1.27 (t, 6, $-CH_3$), 2.89−2.84 (c, 4, $-CH_2-$). ^{11}B-NMR (128 MHz, C_6H_{14}, $BF_3{\cdot}Et_2O$): δ = −3.913 (d, ^1J(B,H) = 150 Hz, 2B), −9.42 (d, ^1J(B,H) = 165 Hz, 4B), −10.6 (d, ^1J(B,H) = 153 Hz, 2B), −11.94 (d, ^1J(B,H) = 174 Hz, 2B). Anal. Calcd for $C_6B_{10}H_{20}S_2$: C, 27.27; H, 7.62; S, 24.25. Found: C, 27.34; H, 7.77; S, 24.03.

Tetramethylammonium chloride was added to the water layer and the tetramethylammonium salt of Ln_{S2Et2} was obtained. Yield 2.32 g (40%). IR (KBr): ν (cm^{-1}) = 2960, 2926 (C−H), 2550, 2517 (B−H), 1481, 948 (C−H). ^{1}H-NMR (in CD_3COCD_3): δ = −2.5 (br, 1, B−**H**−B), 1.11 (m, 6, $-C\mathbf{H}_3$), 2.66 (m, 2, $-CH_2-$), 2.75 (m, 2, $-CH_2-$), 3.45 (s, 12, $N(CH_3)_4$). ^{11}B-NMR (128 MHz, acetone, $BF_3{\cdot}Et_2O$): δ = −7.3 (d, ^1J(B,H) = 138 Hz, 2B), −12.5 (d, ^1J(B,H) = 159 Hz, 1B), −16.4 (d, ^1J(B,H) = 152 Hz, 2B), −17.9 (d, ^1J(B,H) = 183 Hz, 2B), −34.1 (d, ^1J(B,H) = 115 Hz, 1B), −35.5 (d, ^1J(B,H) = 144 Hz, 1B). Anal. Calcd for $C_{10}H_{32}B_9NS_2$: C, 36.64; H, 9.84; N, 4.27; S, 19.56. Found: C, 36.08; H, 10.14; N, 4.62; S, 17.89.

Cyclic Voltammetry. A cell to accommodate three electrodes and a tube for deoxygenating by bubbling with a stream of N_2 has been designed. The working electrode is made of a Teflon-encapsulated Pt wire with an active surface of 0.2 mm^2. The reference electrode is Ag/AgCl in 3 M KCl, and the auxiliary electrode is Pt wire. Solutions are introduced in the cell and are deoxygenated by purging with N_2 for approximately 15 min. The initial potential of the working electrode is set at −0.4 V, and scan rates of 0.043 V/s have been used.

All CV electrochemical measurements were carried out at room temperature under nitrogen atmosphere with 10 cm^3 sample solutions in CH_3CN, THF, and DMF in 0.1 M Bu_4NPF_6 as a supporting electrolyte. The results are collected in Table 1.

Electrochemical Synthesis. Preparative electrolysis were performed potentiostatically in a three compartment cell at room temperature. The anodic, cathodic and reference electrode solutions are separated by glass frits. The cathode is wound Pt wire (0.2 mm^2 section) with a total submerged length of 50 cm. The anode is Pt wire (0.2 mm^2 section). The reference electrode system is Ag/AgCl in 3 M KCl.

All electrochemical syntheses were carried on in a similar manner. The substance to be studied was dissolved in 40 cm^3 of 0.1 M Bu_4NPF_6 in CH_3CN. The chemicals electrolyzed were L_{S2C12}, L_{S2C9}, L_{S2Et2}, and L_{P2}. The reactions were discontinued when the current drops to $^1/_{20}$th of the initial current. The potential applied in volts, the quantity of substances used in milligrams, and the electrolysis time in hours are as follows: L_{S2C12}, −1.3, 50, 48; L_{S2C9}, −1.3, 100, 48; L_{S2Et2}, −1.8, 100, 48; L_{P2}, −1.4, 100, 24.

In all cases the electrolyzed solution was concentrated by partly removing the solvent under reduced pressure, and the ^{11}B-NMR spectrum was run. The spectra of the electrolyzed L_{S2C9} and L_{P2} solutions showed uniquely signals due to *o*-carborane. This was fully confirmed by comparison with the ^{11}B-NMR of authenticated samples of *o*-carborane, L_{S2C9}, and L_{P2} in CH_3CN. The ^{11}B-NMR spectra of the concentrated electrolyzed solutions of L_{S2C12} and L_{S2Et2} was more complicated. The crude product was treated with water−diethyl ether (1:1), and the solid from the organic phase and the solid in the interphase were studied separately by ^{11}B-NMR. Upon comparison with authenticated samples in CH_3CN, it was found that the first corresponded to *o*-carborane, and the second to $C_2B_9H_{12}^-$ and 7,8-$(SR)_2$-7,8-$C_2B_9H_{10}^-$. With these components, it was possible to interpret the ^{11}B-NMR of the crude reaction.

Acknowledgment. The authors are grateful to the agencies CICYT and CIRIT for financial support.

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