

ANNEX-ARTICLES

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“Synthesis, Reactivity and Structural Studies of Carboranyl thioethers and disulfides”.

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Although the oxidation of organic thiols and disulfides has been investigated for long time,¹ it is still a matter of current interest.² Oxidation reactions of organosulfur compounds hold continuing fascination for chemists because of their fundamental roles in biochemical and industrial processes and the variety of mechanistic pathways involved. The oxidation of thiols to disulfides is a characteristic reaction, and further oxidation to thiosulfates (R-S(O)-S-R) and thiosulfonates (R-S(O)₂-S-R) is well known and their biological and chemical behaviour has been reviewed.³ Weak S-S bonds in these compounds impart high reactivity,⁴ and in natural products, these moieties and related cyclic analogues are associated with interesting biological activity and DNA-cleaving properties. On the other hand, in catalytic reactions sulfur-containing compounds have been known to act as catalyst poisons because of their strong coordinating properties.⁵ Therefore, transition-metal complex catalyzed transformation of organic disulfides remains open to study.⁶ Recent progress in this field includes the addition and carbonylative addition reactions of diaryl disulfides to alkynes,⁷ multiple insertion of isocyanides into a sulfur-sulfur bond in diaryl disulfides,⁸ and carbonylation of organic disulfides to thioesters.⁹

Icosahedral *closo* carboranes have been described as three dimensional aromatic systems¹⁰ mostly based in theoretical calculations. The implications of the cluster electronic interaction with substituents is not well understood and experimental data do not fully support the suggested aromatic character of *closo* carboranes.¹¹ From the acidity of the icosahedral carboranes and from the reactions of various derivatives such as *exo*-cluster carboranyl carboxylic acids,¹² thioethers,¹³ phosphines¹⁴ and ketones,¹⁵ it is inferred that the icosahedral carboranes display stronger electron-withdrawing character through the cluster carbon substituents than aromatic phenyl groups.¹⁶

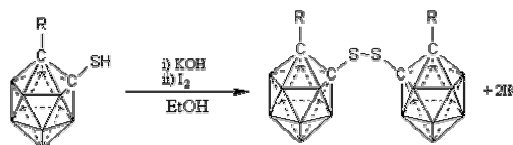
In this paper we describe the synthesis, characterization and some reactivity of dimeric *closo o*-carborane clusters linked through thio and disulfide bridges that bring more information on the differences between icosahedral *closo* carboranes and any other group encountered in organic chemistry.

Results and Discussion

Synthesis and characterization of the dimeric species.

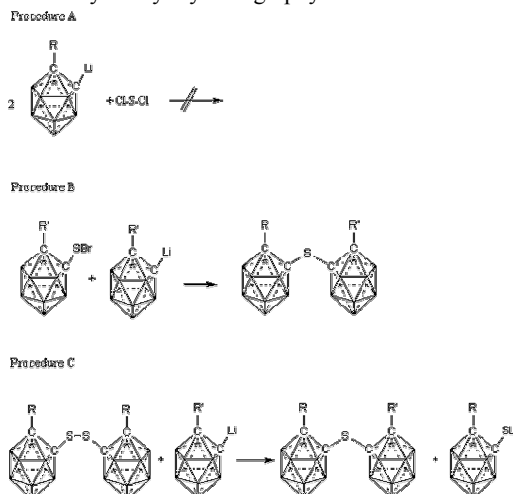
1.a Disulfide bridge (1-S-2-R-1,2-*closo*-C₂B₁₀H₁₀)₂ compounds. Starting compounds to prepare the disulfide bridge ligands were 1-SH-2-R-1,2-*closo*-C₂B₁₀H₁₀ (R= Me, H, Ph).¹⁷ Preparation of 1-SH-1,2-*closo*-C₂B₁₀H₁₁ is complicated by the existing equilibrium, in certain solvents, between the monolithiated *o*-carborane species and the dilithiated and unsubstituted ones.¹⁸ In dimethoxyethane, however, 1-SH-*o*-carborane is obtained in 93% yield.¹⁹ Carboranylmonothioethers, 1-SR-1,2-C₂B₁₀H₁₁ (R = Et, Bz, *i*-

Pr, *n*Bu) are obtained in high-yield in one pot reaction.²⁰ The equimolar reaction of 1-SH-2-R-1,2-*closo*-C₂B₁₀H₁₀ (R= Me, H, Ph) with KOH in ethanol produces the thiolate species that reacts with iodine to give after workup the disulfide, as an analytically pure, white and air-stable solid (Scheme 1).



Scheme 1. Synthesis of disulfide species (1-S-2-R-1,2-*closo*-C₂B₁₀H₁₀)₂ (R= H, Me, Ph).

Disulfides, (1-S-2-R-1,2-*closo*-C₂B₁₀H₁₀)₂ (R=H, Me, Ph), were characterized by elemental analysis, IR, NMR and mass spectroscopies. The IR spectra displays the typical $\nu(\text{B-H})$ absorption at frequencies above 2600 cm⁻¹, characteristic of *closo* carboranes. The peak of highest *m/z* in their mass spectra was at 350.35, 379.35 and 503.40, attributable to ¹²C₄¹H₂₂¹¹B₂₀³²S₂, ¹²C₆¹H₂₆¹¹B₂₀³²S₂, ¹²C₁₆¹H₃₂¹¹B₂₀³²S₂ respectively for R= H, Me, Ph accompanied by the usual carborane isotope distribution pattern, and peaks at 177.10, 188.15 and 251.15 respectively that correspond to the symmetrical molecule fragmentation. The ¹H-, ¹¹B- and ¹³C{¹H}-NMR data of compounds in solution are in complete agreement with their proposed structures which were confirmed by X-ray crystallography.



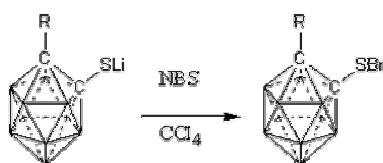
Scheme 2. Procedures envisaged to synthesize (2-R-1,2-*closo*-C₂B₁₀H₁₀)₂S

1.b Thioether bridge (2-R-1,2-*closo*-C₂B₁₀H₁₀)₂S compounds. To obtain this family of compounds three main

strategies were envisaged. These are indicated in Scheme 2 as procedures A, B and C.

In procedure A, the reaction of the monolithiated species with sulfur dichloride (SCl_2) was unsuccessful. For procedure B, the synthesis of the corresponding bromosulphenyl species was necessary (Scheme 3). Reaction of the latter with the monolithiated salt gives the corresponding (2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$) $_2$ S thioether bridged species (see Scheme 2, procedure B).

Bromosulphenyl 1-SBr-2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$ compounds. The synthesis was carried out by the reaction of 1-SH-2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (R= Me, H, Ph) with *N*-bromosuccinimide (NBS) in a non-polar solvent, CCl_4 . Bromosulphenyl compounds are very reactive and their characterization was done by NMR techniques without isolation. Preparation of the NMR sample was done in dry CCl_4 under dinitrogen using a coaxial insert tube. The $^{11}\text{B}\{^1\text{H}\}$ -NMR spectra of 1-SBr-2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (R= H, Me, Ph) derivatives shows slight differences in the peak positions due to the nature of R group. The spectra ranges, between -1.7 and -13.8 ppm., agree with the presence of *closo* species.



Scheme 3. Synthesis of bromosulphenyl compounds 1-SBr-2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (R= H, Me, Ph).

For procedure C the synthesis of the disulfide bridge compounds is required. Disulfide compounds react with the monolithiated salt to afford the corresponding thioether bridged compounds. In procedure C, the secondary product Li [1-S-2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$] can be recovered either as carbonylmonothiol by acidification or as the starting disulfide by oxidation with a solution of iodine in diethyl ether (Scheme 4). Contrarily to their bromosulphenyl-*o*-carborane analogues, disulfide compounds are stable in solid state and may be kept for later use. This is why procedure C was the most convenient one.

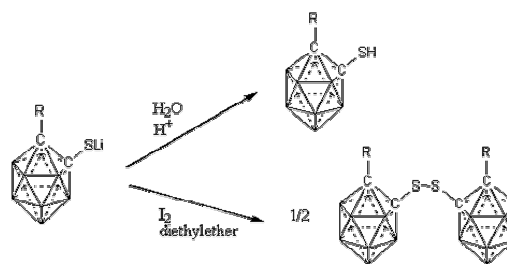
Only (1-Me-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$) $_2$ S was obtained by both procedures. Attempts to produce mixed compounds (1-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$)S(1-R'-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$), R \neq R', either by procedures B or C were unsuccessful.

It has been known for years that the partial degradation reaction on *o*-carborane is driven by a nucleophilic attack which can remove one of their BH units (B(3) or B(6)), formally as BH^+ , leaving *nido* shaped [7,8- $\text{C}_2\text{B}_9\text{H}_{12}$] $^-$ or [7,8- $\text{C}_2\text{B}_9\text{H}_{11}$] $^{2-}$ anions. Several nucleophiles such as alkoxides,²¹ amines,²² fluorides,²³ phosphanes²⁴ have been used. It is also known that the S-S bond in organic disulfides may be cleaved by a nucleophilic process.²⁵

2.a. Deboronation reaction of (1-S-2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$) $_2$ (R= H, Me, Ph), using the well established procedure²¹ with KOH in ethanol, did not lead to the desired [(7-S-8-R-7,8-*nido*- $\text{C}_2\text{B}_9\text{H}_{11}$) $_2$] $^{2-}$ species. The $^{11}\text{B}\{^1\text{H}\}$ spectrum of the reaction crude shows resonances in the range between -2.8 and -13.3 ppm indicative of the *closo*- C_2B_{10} cluster presence, therefore proving that the deboronation process has not taken place. The resulting products were analyzed by MALDI-TOF-MS. The highest m/z peak for the reaction on (1-S-2-Me-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$) $_2$ displays a signal group centered at m/z 188.95 corresponding to the anionic thiolate fragment [1-S-2-Me-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$] $^-$. This was isolated from the reaction mixture as tetraalkylammonium

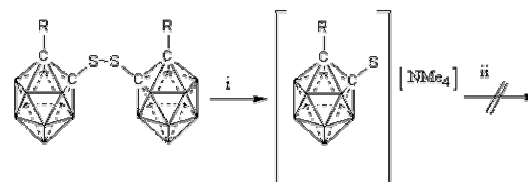
salt in 73-82% yield. The spectroscopic data and elemental analysis were consistent with $[\text{NR}_4][1\text{-S-2-R-1,2-}i\text{closo-C}_2\text{B}_{10}\text{H}_{10}]$ (R= H, Me, Ph).

Scheme 4. Recovery of 1-SH-2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{11}$ and (1-S-2-R-



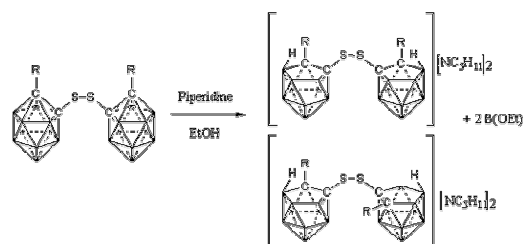
1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$) $_2$ (R= H, Me, Ph) by treatment of the thiolate-*o*-carborane derivatives. Partial Degradation or Deboronation Reaction of Disulfide bridge (1-S-2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$) $_2$ compounds.

Compounds (1-S-2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$) $_2$ possess two susceptible positions to be attacked by a nucleophile: i) the B(3)/B(6) cluster vertexes or ii) the S-S bond. The reaction with EtO^- proves that the most susceptible site is the disulfide bridge and also that the *closo* cluster of the anionic thiolate fragment [1-S-2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$] remains stable in the presence of EtO^- . As a further proof, 1-SH-2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$ (R= H, Me, Ph) could not be deboronated to [7-SH-8-R-7,8-*nido*- $\text{C}_2\text{B}_9\text{H}_{10}$] $^-$ by using EtO^- (Scheme 5).



Scheme 5. Reaction of disulfide (1-S-2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$) $_2$ (R= H, Me, Ph) compounds with $[\text{EtO}]^-$. i) 5 KOH in ethanol heated to reflux for 2 hr. Precipitation with a aqueous solution of $[\text{NMe}_4]\text{Cl}$. ii) Thiolate fragment [1-S-2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$] remains stable in the presence of $[\text{EtO}]^-$ in excess under reflux.

Scheme 6. Partial degradation reaction of [1-S-2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$] $_2$ (R= H, Me, Ph) compounds by using piperidine. A



racemic mixture and a *meso* form are possible.

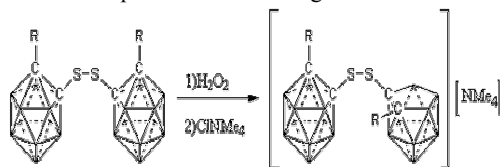
2.b. A second, also well described partial degradation process with piperidine in toluene²² in a 1:4 molar ratio (*closo* disulfide compounds : piperidine) at 20°C did not give the expected *nido* disulfide species while the starting compounds were fully recovered.

2.c. A similar behavior to this indicated above had been found for *closo*-carboranylphosphines. In this case, deboronation with C-P bond retention was successfully obtained using piperidine in ethanol.²⁶

This methodology was applied on (1-S-2-R-1,2-*closo*- $\text{C}_2\text{B}_{10}\text{H}_{10}$) $_2$ (R= H, Me, Ph) with a compound to piperidine

ratio 1:5 in ethanol for 9 hours, producing in high yield the respective $[(7\text{-S-8-R-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{11})_2]^{2-}$ species. The disulfide bridged $[\text{NMe}_4]_2[(7\text{-S-8-R-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{10})_2]$ (R=H, Me, Ph) species were characterized by elemental analysis, MALDI-TOF, IR and NMR spectroscopies. The IR spectra shows the typical $\nu(\text{B-H})$ absorption at frequencies $2525 \leq \nu \leq 2550 \text{ cm}^{-1}$, characteristic of *nido* carborane clusters. The $^{11}\text{B}\{^1\text{H}\}$ -NMR spectrum of $[\text{NMe}_4]_2[(7\text{-S-8-Me-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{10})_2]$ displays a 1:1:1:1:1:1:1:1 pattern (from low to high field) in the range between -6.8 and -35.1 ppm and two broad resonances in the $^1\text{H}\{^{11}\text{B}\}$ -NMR from the hydrogen bridges at -2.23 and -2.44 ppm indicating that partial degradation in both clusters has taken place, and that a mixture of the *meso* ($\approx 50\%$) and *racemic* ($\approx 50\%$) forms has been obtained. (Scheme 6). The MALDI-TOF spectrum shows a peak with isotopic distribution at $m/z = 357.24$ corresponding to the anionic fragment $^{12}\text{C}_6^{14}\text{H}_{26}^{11}\text{B}_{18}^{32}\text{S}_2$ and a peak at 178.99 that corresponds to the symmetrical fragmentation of $[\text{NMe}_4]_2[(7\text{-S-8-Me-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{10})_2]$.

To know the nature of the removed BH units, the deboronation reaction in piperidine/ethanol was carried out at reflux for 2 hours on $(1\text{-S-2-Me-}1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{10})_2$. The $^{11}\text{B}\{^1\text{H}\}$ spectra of the reaction crude displays the pattern 1:1:1:1:1:1:1:1 in the range between -6.8 and -35.1 ppm characteristic of the $[(7,8\text{-nido-C}_2\text{B}_9\text{H}_{10})]^-$ species. An extra resonance at $+17.02$ ppm is always present, that corresponds to a non-hydrogen bonded boron atom that necessary shall correspond to the removed BH vertex. According to the literature,²⁷ chemical shift for ethyl borate had been described at $+17.2$,²⁸ $+17.6$,²⁹ $+18.1$ ppm.³⁰ To isolate this species, the reaction mixture was evaporated at 0.1 mm and volatiles were trapped at -78°C . The ^{11}B spectrum of the remaining mother liquor only shows the pattern for the $[(7\text{-S-8-Me-}7,8\text{-nido-C}_2\text{B}_9\text{H}_{10})_2]^{2-}$ anion. On the contrary the ^{11}B spectrum of the trapped solution only showed the complementary resonance at $+17.02$ ppm, that has been assigned to $\text{B}(\text{OEt})_3$. Once known the fate of the removed BH^{2+} , there remains the question on how this $\text{B}(\text{OEt})_3$ is produced. Our interpretation of this partial degradation process is based on the fact that piperidine, in addition of being a nucleophile, is a base³¹ capable to participate in an acid/base equilibrium with ethanol. Thence piperidinium ethoxide is present in minor concentration in the reaction medium, much less than is required for a quick degradation but sufficient enough to slowly and smoothly remove one boron to produce $\text{B}(\text{OEt})_3$. The low $[\text{EtO}^-]$ concentration creates a mild conditions medium that prevents S-S cleavage.



Scheme 7. Reaction of disulfide $(1\text{-S-}1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{11})_2$ with H_2O_2 .

3. Reaction of disulfide bridge $(1\text{-S-}2\text{-R-}1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{10})_2$ compounds with oxidizing agents.

Organic disulfides R-S-S-R' can lead to thiosulfates $\text{R-S}(\text{O})\text{-S-R'}$ by oxidation.³² Among the electrophilic oxidants, peroxy acids or hydrogen peroxide at room temperature are the more suitable to synthesize thiosulfates. We have used hydrogen peroxide to oxidize $1,2\text{-}(\text{PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$ to the corresponding phosphine oxide.³³ The reaction of $(1\text{-S-}2\text{-R-}1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{10})_2$ (R= H, Me, Ph) in THF with H_2O_2 at room temperature for 24 h leads to deboronation of only one of the two clusters for R= H. The reaction is represented in

Scheme 7. For R= Me and Ph, the $^{11}\text{B}\{^1\text{H}\}$ spectra of the reaction crude indicates that no reaction has taken place. Contrarily, for R= H, the $^{11}\text{B}\{^1\text{H}\}$ spectrum displays the pattern 1:1:6:5:1:1:1:1:1:1 (from low field to high field) in the range between -0.8 and -34.3 ppm. The spectrum pattern and chemical shifts range support the presence of a *closo* and a *nido* cluster in the compound. Subsequent precipitation with $[\text{NMe}_4]\text{Cl}$ led to the formation of $[\text{NMe}_4][(1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{11})\text{S-S}(7,8\text{-nido-C}_2\text{B}_9\text{H}_{11})]$ in 96% yield. Spectroscopic data and elemental analysis were consistent with $[\text{NMe}_4][(1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{11})\text{S-S}(7,8\text{-nido-C}_2\text{B}_9\text{H}_{11})]$. The *nido* and *closo* nature of the clusters were clearly demonstrated in the ^1H -NMR by the presence of the apical proton resonance at $\delta -2.68$ ppm and two broad signals at 4.70 and 2.35 ppm corresponding to $\text{C}_c\text{-H}$ for *closo* and *nido* clusters respectively. MALDI-TOF-MS clearly shows an isotope pattern with a highest m/z peak at 338.18 consistent with the expected species and two peaks at 174.94 and 162.92 that correspond to the S-S cleavage.

We had reported earlier that $1,2\text{-}(\text{PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$, upon oxidation of the phosphorus atoms, progressed to the anionic *nido*- $[\text{C}_2\text{B}_9]$ cluster liberating one boron atom and overall producing a protonated neutral species.³³

To force S oxidation, the carboranyl disulfides $(1\text{-S-}2\text{-R-}1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{10})_2$ (R= H, Me, Ph) compounds were treated with I_2 in a 1:1.5 ratio (disulfide : I_2) at room temperature for 4 days. The $^{11}\text{B}\{^1\text{H}\}$ spectrum of the reaction crude show that the starting compounds were fully recovered in all cases.

We have proven here that carboranyl disulfides $(1\text{-S-}2\text{-R-}1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{10})_2$ (R= H, Me, Ph) do not make way to thiosulfates $\text{R-S}(\text{O})\text{-S-R'}$ by oxidation with H_2O_2 or I_2 as organic disulfides do. On the other hand, we had observed that *closo*-monophosphinocarboranes are less basic than similar organophosphorus compounds, and are less reactive both to oxygen and metal ions. These characteristics were attributed to the *closo* carborane influence on P.^{14b} The π orbital overlap between the aryl or sulfur 'lone-pair' orbital with tangential cluster orbitals has been invoked to explain the cage $\text{C}_c\text{-C}_c$ lengthening in aryl-*ortho*-carborane derivatives.^{34,35} This is so because there is transfer of electronic density from the filled π orbitals on the sulfur atom or the aryl group into the cage LUMO which is σ -antibonding and greatly located on the cage $\text{C}_c\text{-C}_c$ bond. This has been proven by molecular orbital computations on $1,2\text{-}(\text{SPH}_2)_2\text{-}1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{10}$ in which the $\text{C}(1)\text{-C}(2)$ bond length ($1.798(3)$ Å) is very large compared with plain $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$.^{36,11j} This transfer of electron density also supports the different behaviour of organic and carboranyl disulfides in front of H_2O_2 : i) no thiosulfates $\text{R-S}(\text{O})\text{-S-R'}$ formation and, ii) the cluster deboronation.

4. Molecular and crystal structures of $(2\text{-Me-}1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{10})_2\text{S}$, $(1\text{-S-}1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{11})_2$, $(1\text{-S-}2\text{-Me-}1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{10})_2$ and $(1\text{-S-}2\text{-Ph-closo-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10})_2$.

The monthioether $(2\text{-Me-}1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{10})_2\text{S}$ and the disulfides $(1\text{-S-}1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{11})_2$, $(1\text{-S-}2\text{-Me-}1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{10})_2$ and $(1\text{-S-}2\text{-Ph-}1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{10})_2$ (see Figures 1-4) have pseudo two-fold symmetry. The symmetry axis goes through the S atom in the thio bridged compound and through the middle point of the S-S bond in the disulfide compounds. The bonding parameters in both halves of the pseudo symmetric molecules are very similar (consult Tables 2-3). In the discussion and in Table 3, the sulfur atoms of $(1\text{-S-}2\text{-Ph-}1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{10})_2$ refer to S1a and S2a of the major conformation.

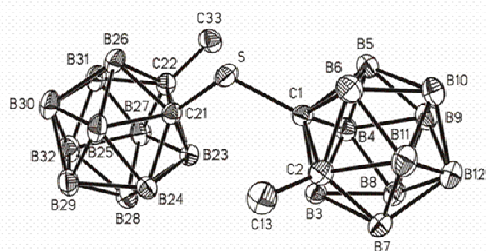


Figure 1. A view of (2-Me-1,2-closo-C₂B₁₀H₁₀)₂S showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Compound	1	2	3	4
Chemical				
Formula	C ₆ H ₂₆ B ₂₀ SC ₄ H ₂₂ B ₂₀ S ₂ C ₆ H ₂₆ B ₂₀ S ₂ C ₁₆ H ₃₀ B ₂₀ S ₂			
Fw	346.53	350.54	378.59	502.72
<i>a</i> , Å	14.107(3)	23.5885(3)	18.538(6)	11.579(3)
<i>b</i> , Å	11.754(2)	7.01160(10)	15.360(7)	12.917(4)
<i>c</i> , Å	14.203(2)	11.5732(2)	15.282(6)	10.511(5)
<i>α</i> , deg	90	90	90	110.95(3)
<i>β</i> , deg	118.95(1)	90	90.22(2)	102.28(3)
<i>γ</i> , deg	90	90	90	85.09(3)
<i>V</i> , Å ³	2060.8(6)	1914.13(5)	4351(3)	1434.5(9)
<i>Z</i>	4	4	8	2
Spacegroup	<i>P</i> 2 ₁ / <i>n</i> (No.14)	<i>P</i> na2 ₁ (No.33)	<i>C</i> 2/ <i>c</i> (No.15)	<i>P</i> -1(No.2)
<i>T</i> _c , °C	23	-100	23	21
<i>λ</i> , Å	0.71069	0.71073	0.71069	0.71069
<i>ρ</i> _{calcd} , g cm ⁻³	1.117	1.216	1.156	1.164
<i>μ</i> , cm ⁻¹	1.45	2.62	2.36	1.95
^a <i>R</i> 1(<i>F</i> _o) [<i>I</i> > 2σ(<i>I</i>)]	0.0612	0.0337	0.0878	0.0690
^b <i>wR</i> 2(<i>F</i> _o ²) [<i>I</i> > 2σ(<i>I</i>)]	0.15030	0.0799	0.1941	0.1558
^a <i>R</i> 1 = Σ <i>F</i> _o - <i>F</i> _c / Σ <i>F</i> _o ; ^b <i>wR</i> 2 = {Σ[w(<i>F</i> _o ² - <i>F</i> _c ²) ²] / Σ[w(<i>F</i> _o ²) ²]} ^{1/2}				

Table 1. Crystallographic Data for (2-Me-1,2-closo-C₂B₁₀H₁₀)₂S (1), (1-S-1,2-closo-C₂B₁₀H₁₁)₂ (2), (1-S-2-Me-1,2-closo-C₂B₁₀H₁₀)₂ (3) and (1-S-2-Ph-1,2-closo-C₂B₁₀H₁₀)₂ (4)

In the four compounds the absolute values of the relevant C_c-C_c-S-C_c, C_c-S-S-C_c and C_c-C_c-S-S torsion angles vary only within *ca.* 16°. However, in the methyl and phenyl substituted compounds orientations of the C(2)-C(13) and C(22)-C(33) bonds, and thus the mutual molecular conformations of the whole molecules, are very different in the thio and disulfide compounds. The C(13)-C(2)⋯C(22)-C(33) dihedral angle is 152.6(3)° for (2-Me-1,2-closo-C₂B₁₀H₁₀)₂S but in the disulfide bridged compounds the corresponding angles for (1-S-2-Me-1,2-closo-C₂B₁₀H₁₀)₂ and (1-S-2-Ph-1,2-closo-C₂B₁₀H₁₀)₂ are 1.5(5) and -1.3(3)°, respectively. The second sulfur atom in the bridge is the reason for the differences.

In (2-Me-1,2-closo-C₂B₁₀H₁₀)₂S the C(1)-S(1)-C(21) angle is 113.1(2)°. This value indicates that the C-S-C thioether bond is opened up from the normal value for this type of bond as the value for such a bond in (1-PPh₂-2-SⁱPr-1,2-closo-C₂B₁₀H₁₀) is 107.1(2)°. The reason for the opening of the C-S-C angle is a mutual steric repulsion of the boron cages.

There are several short intramolecular contacts of H atoms between the cages like H(3)⋯H(23) (2.43 Å), H(3)⋯H(24) (2.46 Å) and H(4)⋯H(23) (2.51 Å). The steric repulsions may be one of the reasons of the nonexistence of the monoethers with more bulky substituents in the clusters because now also the substituent and the cage may repel each other.

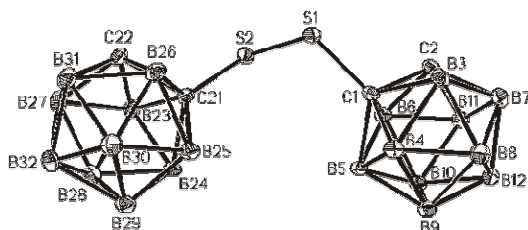


Figure 2. A view of (1-S-1,2-closo-C₂B₁₀H₁₁)₂ showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

S-C(1)		1.783(3)
S-C(21)	1.793(3)	
C(1)-C(2)	1.716(4)	
C(2)-C(13)		1.516(5)
C(21)-C(22)		1.707(4)
C(22)-C(33)		1.522(4)
C(1)-S-C(21)		113.1(2)
C(2)-C(1)-S		117.4(2)
C(13)-C(2)-C(1)	118.3(3)	
C(13)-C(2)-B(3)	117.5(3)	
C(13)-C(2)-B(6)	117.1(3)	
C(13)-C(2)-B(7)	122.2(3)	
C(13)-C(2)-B(11)	121.8(3)	
C(22)-C(21)-S		117.2(2)
C(33)-C(22)-C(21)	118.3(3)	
C(33)-C(22)-B(23)	117.3(3)	
C(33)-C(22)-B(26)	117.3(3)	
C(33)-C(22)-B(27)	121.9(3)	
C(33)-C(22)-B(31)	121.6(3)	
C(2)-C(1)-S-C(21)		-95.9(2)
C(22)-C(21)-S-C(1)		-99.1(2)
S-C(1)-C(2)-C(13)		11.7(4)
S-C(21)-C(22)-C(33)		12.7(4)

Table 2. Selected bond lengths (Å), angles and torsion angles (deg) for (2-Me-1,2-closo-C₂B₁₀H₁₀)₂S

There are also important bond length differences between the four compounds, especially in the C(1)-C(2) distances which has been the object of a discussion in section 3. In the thioether, (2-Me-1,2-closo-C₂B₁₀H₁₀)₂S, the C_c-C_c bond lengths are 1.707 (4) and 1.716(4) Å. In a disulfide, (1-S-1,2-closo-C₂B₁₀H₁₁)₂, with H atoms connected to the cluster carbons C(2) and C(22), the C_c-C_c distances of 1.666(3) and 1.655(3) Å are shorter than in the other disulfides: in (1-S-2-Me-1,2-closo-C₂B₁₀H₁₀)₂ the distances of 1.710(4)-1.711(4) Å are equal within experimental errors and significantly shorter than those of 1.766(5) and 1.763(5) Å in (1-S-2-Ph-1,2-closo-C₂B₁₀H₁₀)₂. These differences fully agree with the observation that hydrogen atom connected to cluster carbon has weakest contribution to the lengthening of the C_c-C_c bond, and contribution of an aryl substituent to the lengthening is greater than that of non-aryl substituent.³⁷ Therefore if the bridge is formed by S or S₂ this does not influence on the C_c-C_c bonds.

Compound	2	3	4
S(1)-S(2)	2.0232(8)	2.030(2)	2.0245(15)
S(1)-C(1)	1.805(2)	1.785(6)	1.803(4)
S(2)-C(21)	1.802(2)	1.791(6)	1.803(4)
C(1)-C(2)	1.666(3)	1.710(8)	1.766(5)
C(2)-C(13)	-	1.521(8)	1.517(5)
C(21)-C(22)	1.665(3)	1.711(8)	1.763(5)
C(22)-C(33)	-	1.532(9)	1.493(6)
C(1)-S(1)-S(2)	105.70(8)	105.6(2)	105.41(15)
C(21)-S(2)-S(1)	105.98(9)	105.8(2)	105.20(15)
C(2)-C(1)-S(1)	114.7(2)	116.0(4)	113.9(2)
C(13)-C(2)-C(1)	-	117.9(5)	119.5(3)
C(13)-C(2)-B(3)	-	116.2(5)	118.6(3)
C(13)-C(2)-B(6)	-	117.0(5)	117.4(3)
C(13)-C(2)-B(7)	-	121.7(5)	122.4(3)
C(13)-C(2)-B(11)	-	122.1(6)	121.7(3)
C(22)-C(21)-S(2)	114.3(2)	116.1(4)	114.6(3)
C(33)-C(22)-C(21)	-	118.9(5)	119.9(3)
C(33)-C(22)-B(23)	-	115.9(6)	118.7(3)
C(33)-C(22)-B(26)	-	118.7(6)	119.0(3)
C(33)-C(22)-B(27)	-	120.8(6)	122.5(4)
C(33)-C(22)-B(31)	-	121.9(6)	122.9(3)

C(1)-S(1)-S(2)-C(21)	100.2(1)	105.1(3)	-101.7(2)
C(2)-C(1)-S(1)-S(2)	108.6(2)	109.0(4)	-113.4(2)
C(22)-C(21)-S(2)-S(1)	111.5(2)	105.6(4)	-107.8(2)
S(1)-C(1)-C(2)-C(13)	-	-4.0(7)	6.5(5)
S(2)-C(21)-C(22)-C(33)	-	-4.2(7)	6.3(5)

Table 3. Selected bond lengths (Å), angles and torsion angles (deg) for (1-S-1,2-*closo*-C₂B₁₀H₁₁)₂ (2), (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ (3) and (1-S-2-Ph-1,2-*closo*-C₂B₁₀H₁₀)₂ (4)

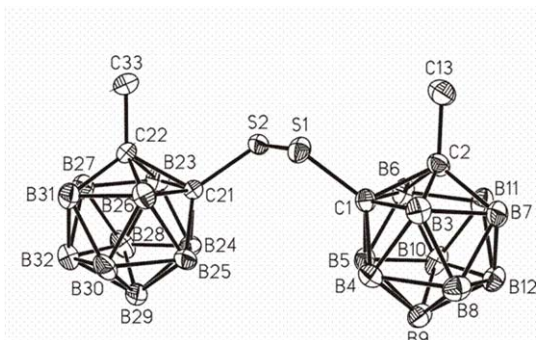


Figure 3. A view of (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

In addition to the above mentioned neutral (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂S thio ether and (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ disulfide compounds, the 1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀ moiety is also found in the [1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀]⁻ thiolate.^{37c} The anionic charge on the sulfur atom lengthens the C_c-C_c bond distance: as can be seen the C_c-C_c bond distance is 1.792(5) Å in the anionic cluster, being *ca.* 0.08 Å longer than the C_c-C_c bonds in (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂S [1.707(4) and 1.716(4)] and (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ [1.710(8) and 1.711(8) Å]. The thiolate on one of the C_c atoms makes the C_c-C_c bond longer and the elongation is an indication of the delocalization of the negative charge on the cluster atoms.

A further interesting difference between (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂S, (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ and (1-S-2-Ph-1,2-*closo*-C₂B₁₀H₁₀)₂ can be noticed in the S-C_c-C_c-C torsion angles. The angles in the thio bridged compound are 11.7(4) and 12.7(4)° while in the disulfide compounds the absolute values of the relevant torsion angles vary from 4.0(7) to 6.3(5)°. These small differences probably arise from the repulsion between the cluster hydrogen atoms as was mentioned early as a reason for the C-S-C angle opening. Thus there is no considerable repulsion between cages in the disulfide compounds.

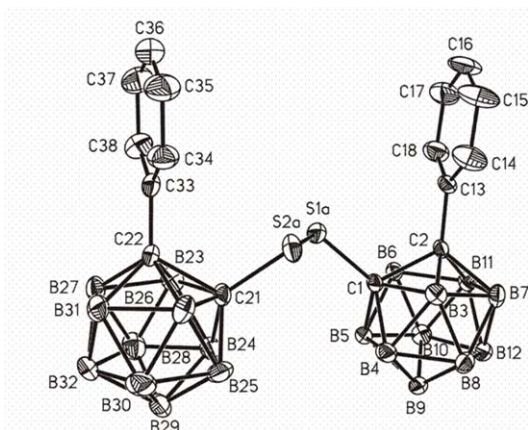


Figure 4. A view of the major conformer of (1-S-2-Ph-1,2-*closo*-C₂B₁₀H₁₀)₂ showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Conclusions

We have described the syntheses, characterisation and some reactivity of dimeric carboranyl thioethers and disulfides and interpreted this as a consequence of the carboranyl-S bond. The carboranyl disulfides (1-S-2-R-1,2-*closo*-C₂B₁₀H₁₀)₂ (R= H, Me, Ph) do not lead to thiosulfates in the reaction conditions organic disulfides do. On the contrary, deboronation of the cluster cage or exploding of the S-S bond leading to thioether has been found. We attribute this behaviour to the presence of the sulfur atom directly bonded to the carbon cluster. This produces electronic transfer from the filled orbitals on the sulfur atom into the cage LUMO that is greatly located on the cage C_c-C_c bond, causing a depletion of electron density on the sulfur, thence impairing sulfur oxidation, and facilitating S-S breaking. Most of the behaviour of these species is supported by the disulfide (1-S-2-R-1,2-*closo*-C₂B₁₀H₁₀)₂ (R= H, Me, Ph) and thioether (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂S crystal structures.

Experimental section

Materials and Methods. Commercial 1,2-*closo*-C₂B₁₀H₁₀ was sublimed under high vacuum at 0.01 mm Hg prior to use. 1-SH-1,2-*closo*-C₂B₁₀H₁₁, 1-SH-2-Me-1,2-*closo*-C₂B₁₀H₁₀ and 1-SH-2-Ph-1,2-*closo*-C₂B₁₀H₁₀, were synthesized according to the literature.³⁸ Solvents were placed under vacuum to eliminate dissolved oxygen. A 1.6 M solution of *n*-butyllithium in *n*-hexane was used as purchased. All organic and inorganic salts were analytical reagent grade and were used as received. All reactions were carried out under a dinitrogen atmosphere employing Schlenk techniques. Microanalyses were performed by using a Perkin-Elmer 240 B microanalyser. IR spectra were obtained as KBr pellets on a Nicolet 710-FT spectrophotometer. The ¹H-NMR (300.13 MHz), ¹³C{¹H}-NMR (75.47 MHz) and ¹¹B-NMR (96.29 MHz) spectra were recorded on a Bruker ARX300 instrument equipped with the appropriate decoupling accessories. Chemical shift values for ¹H-, ¹³C{¹H}- and ¹¹B-NMR spectra were referenced relative to Si(CH₃)₄ and BF₃·OEt₂, respectively. Chemical shifts are reported in units of parts per million downfield from the reference, and all coupling constants are reported in Hertz. Positive ion ESI mass spectra for neutral compounds were obtained with a Hewlett-Packard-MS Engine 5989X equipped with an ion spray source. In EI mode, an ionization potential of 70 eV with an ion source at 200 °C was used. The mass spectra for anionic species were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF-MS [N₂ laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)].

Synthesis of 1-SBr-2-Me-1,2-*closo*-C₂B₁₀H₁₀. To a two necked round bottom flask (100 ml), containing a solution of 1-SH-2-Me-1,2-*closo*-C₂B₁₀H₁₀ (0.45 g, 2.36 mmol) in carbon tetrachloride (15 ml), was added N-bromosuccinimide (0.42 g, 2.36 mmol). The mixture was allowed to stir at room temperature for 4 h. The yellow precipitate was removed by filtration and the filtrate was evaporated in the vacuum line to afford an orange solid, yield: 0.50 g, (78%). ¹H-NMR (CCl₄): δ 2.11 (s, Cc-CH₃). ¹¹B-NMR (CCl₄): δ -2.9 (1B), -4.7 (d, 1J(B,H)= 163, 1B), -8.7 (2B), -9.9 (d, 1J(B,H)= 144, 6B).

Synthesis of 1-SBr-2-Ph-1,2-*closo*-C₂B₁₀H₁₀. This compound was prepared analogously to the method described

for 1-SBr-2-Me-1,2-*closo*-C₂B₁₀H₁₀, using 1-SH-2-Ph-1,2-*closo*-C₂B₁₀H₁₀ (70 mg, 0.277 mmol) as starting material to afford an orange solid. Yield: 70.6 mg (77%). ¹H-NMR (CCl₄): δ 7.3-7.7 (m, Cc-C6H5). ¹¹B-NMR (CCl₄): δ -1.7 (d, 1J(B,H)= 125, 2B), -7.3 (d, 1J(B,H)= 154, 2B), -8.8 (d, 1J(B,H)= 163, 4B), -10.9 (d, 1J(B,H)= 182, 2B).

Synthesis of 1-SBr-1,2-*closo*-C₂B₁₀H₁₁. This compound was prepared analogously to the method described for 1-SBr-2-Me-1,2-*closo*-C₂B₁₀H₁₀, using 1-thiol-o-carborane (36 mg, 0.20 mmol) as starting material to afford an orange oil, yield: 15 mg (30 %). ¹H-NMR (CCl₄): δ 3.71 (bs, 1H, Cc-H). ¹¹B-NMR (CCl₄): δ -2.5 (d, 1J(B,H)= 144, 1B), -5.5 (d, 1J(B,H)= 154, 1B), -9.9 (d, 1J(B,H)= 144, 3B), -11.5 (1B), -13.8 (d, 1J(B,H)= 144, 4B).

Synthesis of (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂. To a two necked round bottom flask (100 ml), containing a solution of KOH (352 mg, 6.28 mmol) in deoxygenated ethanol (15 ml), was added 1-SH-2-Me-1,2-*closo*-C₂B₁₀H₁₀ (1.18 g, 6.28 mmol). After stirring for 10 min a solution of iodine (0.80 g, 3.14 mmol) in ethanol (15 ml) was added drop wise. The mixture was then stirred for 10 min and evaporated. Water (15 ml) was added and the resulting slurry was extracted with diethyl ether (15 ml). After separation, the organic layer was washed with water (2x10 ml), dried over anhydrous magnesium sulfate, and vacuum evaporated. Upon recrystallization from warm petroleum ether, the dimeric (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ compound was obtained. Yield: 1.01g (86%). Anal. Calcd for C₆H₂₆B₂₀S₂: C, 19.03; H, 6.92; S, 16.96. Found: C, 19.83; H, 6.86; S, 16.58. FTIR (KBr): ν (cm⁻¹) 2931(C-H); 2586, 2579(B-H). ¹H-NMR (CDCl₃): δ 2.09 (s, C_c-CH₃). ¹H{¹¹B}-NMR (CD₃COCD₃): δ 2.60, 2.33, 2.23 (br s, B-H), 2.09 (s, C_c-CH₃). ¹¹B-NMR (CDCl₃): δ -0.7 (d, 1J(B,H)= 134, 1B), -3.0 (d, 1J(B,H)= 159, 1B), -7.5 (d, 1J(B,H)= 141, 8B). ¹³C{¹H}-NMR (CDCl₃): δ 81.36 (s, Cc), 80.93 (s, Cc), 23.09 (s, CH₃). EI-MS (m/z): 379.35 (M+1, 91 %), 346.40 (M-SH, 56 %), 188.15 (M/2, 100 %).

Synthesis of (1-S-2-Ph-1,2-C₂B₁₀H₁₀)₂. This compound was prepared using the method described for (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂, using 1-SH-2-Ph-1,2-*closo*-C₂B₁₀H₁₀ (0.35 g, 1.57 mmol), KOH (88 mg, 1.57 mmol) and iodine (0.20 g, 0.78 mmol). A white solid was obtained after recrystallization from petroleum ether. Yield: 0.28 g (70 %). Anal. Calcd for C₁₆H₃₀B₂₀S₂: C, 38.2; H, 6.1; S, 12.7. Found: C, 37.9.1; H, 5.6; S, 13.0. FTIR (KBr): ν (cm⁻¹) 3064(C_{aryl}-H); 2614, 2600, 2586(B-H). ¹H-NMR (CDCl₃): δ 7.3-7.5 (m, Caryl-H). ¹H{¹¹B}-NMR (CDCl₃): δ 7.3-7.5 (m, Caryl-H), 2.50, 2.41, 2.35, 2.23, 2.18 (br s, B-H). ¹¹B-NMR (CDCl₃): δ -1.9 (d, 1J(B, H)= 134, 4B), -9.1 (d, 1J(B, H)= 145, 2B), -11.3 (4B). ¹³C{¹H}-NMR (CDCl₃): δ 133.45, 129.88, 128.83, 127.51 (s, Caryl-H), 60.11 (s, Cc). EI-MS (m/z): 503.40 (M+1, 76 %), 251.15 (M/2, 100 %).

Synthesis of [1-S-1,2-*closo*-C₂B₁₀H₁₁]₂. This compound was prepared using the method described for (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂, using 1-SH-1,2-*closo*-C₂B₁₀H₁₁ (0.88 g, 5.0 mmol), KOH (280 mg, 5.0 mmol) and iodine (0.66 g, 2.62 mmol). A white solid was obtained. Yield: 0.81 g (92 %). Anal. Calcd for C₄H₂₂B₂₀S₂: C, 13.7; H, 6.3; S, 18.3. Found: C, 14.1; H, 6.1; S, 17.5. FTIR (KBr): ν (cm⁻¹) 3057(C-H); 2614, 2600, 2579, 2565(B-H). ¹H-NMR (CDCl₃): δ 4.96 (br s, 2H, C_c-H). ¹H{¹¹B}-NMR (CDCl₃): δ 4.96 (br s, 1H, C_c-H), 2.53(br s, 2H, B-H), 2.42(br s, 2H, B-H), 2.23(br s, 6H, B-H). ¹¹B-NMR (CDCl₃): δ -1.8 (d, 1J(B,H)= 150, 1B), -4.5 (d, 1J(B,H)= 149, 1B), -9.1 (d, 1J(B,H)= 146, 2B), -10.2 (d, 1J(B,H)= 122, 2B); -12.4 (d, 1J(B,H)= 170, 4B). ¹³C{¹H}-NMR (CDCl₃): δ 46.22 (s, Cc), 43.55 (s, Cc). EI-MS (m/z): 350.35 (M+1, 100 %), 174.10(M/2-1, 89 %).

Synthesis of (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂S. Procedure B:

To a solution of 1-Me-1,2-*closo*-C₂B₁₀H₁₀ (265 mg, 1.67 mmol) in dry diethyl ether (15 ml) were added *n*-BuLi (1.04 ml, 1.67 mmol). The mixture was stirred for 30 min at 0°C and another 30 min at room temperature. A solution of [1-SBr-2-Me-1,2-*closo*-C₂B₁₀H₁₀] (0.45 g, 1.67 mmol) in dry diethyl ether (15 ml) was added. The slurry was stirred at room temperature overnight. The mixture was then extracted with water (15 ml) and washed with 0.5 M Na₂CO₃ (2x15 ml). The organic layer was dried over MgSO₄. The diethyl ether filtrate was evaporated to give a yellow oil. Recrystallization from diethyl ether gave microcrystals. Yield: 0.30 g (65 %). The spectroscopic data coincided with this indicated in the next method. **Procedure C:** To a solution of 1-Me-1,2-*closo*-C₂B₁₀H₁₀ (83.6 mg, 0.528 mmol) in dry diethyl ether (15 ml) was added *n*-BuLi (0.34 ml, 0.55 mmol). The mixture was stirred for 30 min at 0°C and for 30 min at room temperature. Then a solution of [1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀]₂ (0.20 g, 0.528 mmol) in dry diethyl ether (15 ml) was added. The slurry was refluxed for 2 h. the mixture was then extracted with water (10 ml) and washed with 0.5M Na₂CO₃ aqueous solution (2x15 ml). The organic layer was dried over MgSO₄. The diethyl ether filtrate was evaporated to give a yellow solid. Recrystallization from petroleum ether provided microcrystals (0.16 g, 88 %). Anal. Calcd for C₆H₂₆B₂₀S: C, 20.8; H, 7.6; S, 9.2. Found: C, 20.8; H, 7.5; S, 9.1. FTIR (KBr): ν (cm-1) 2924(C-H); 2600, 2564(B-H). ¹H-NMR (CDCl₃): δ 2.18 (s, Cc-CH₃). ¹¹B-NMR (CDCl₃): δ (ppm) -2.2 (d, 1J(B,H)= 152, 1B), -5.0 (d, 1J(B,H)= 150, 1B), -8.9 (d, 1J(B,H)= 142, 2B), -9.9 (d, 1J (B,H)= 146.4, 6B). EI-MS (m/z): 346.40 (M, 100 %).

Synthesis of [NBu₄]₂[7-S-7,8-*nido*-C₂B₉H₁₁]₂. An excess of piperidine (0.032 ml, 0.32 mmol) was added to a solution of (1-S-1,2-*closo*-C₂B₁₀H₁₁)₂ (22.3 mg, 0.064 mmol) in degassed absolute ethanol and refluxed for 9 hours. The solvent was removed in the vacuum line and an excess of tetrabutylammonium chloride in water was added to obtain a white solid. This was filtered off, washed with water and diethyl ether and dried under vacuum. Yield: 472mg (92%). Anal. Calcd for C₃₆H₉₄B₁₈S₂N₂: C, 53.13; H, 11.64; N, 3.44; S, 7.88. Found: C, 52.98; H, 11.36; N, 3.54; S, 7.80. FTIR (KBr): ν (cm⁻¹) 2962, 2927, 2875 (C_{alkyl}-H); 2525 (B-H). ¹H-NMR (CD₃COCD₃): δ 3.41 (t, ³J(H,H)= 8.4, NBu₄, 16H), 2.45 (br s, C_c-H, 1H), 2.26 (br s, C_c-H, 1H), 1.83 (q, ³J(H,H)= 7.4, NBu₄, 16H), 1.45 (hex, ³J(H,H)= 7.3, NBu₄, 16H), 0.98 (t, ³J(H,H)= 7.3, NBu₄, 24H). ¹H{¹¹B}-NMR (CD₃COCD₃): δ 3.41 (t, ³J(H,H)= 8.4, NBu₄, 16H), 2.45 (br s, C_c-H, 1H), 2.26 (br s, C_c-H, 1H), 2.33, 2.17, 2.05 (br s, B-H), 1.83 (q, ³J(H,H)= 7.4, NBu₄, 16H), 1.45 (hex, ³J(H,H)= 7.3, NBu₄, 16H), 0.98 (t, ³J(H,H)= 7.3, NBu₄, 24H), 0.63, 0.19 (br s, B-H), -2.46 (br s, B-H-B, 1H), -2.51 (br s, B-H-B, 1H). ¹¹B-NMR (CD₃COCD₃): δ -8.8 (d, ¹J(B,H)= 137, 2B), -14.7 (1B), -15.4(1B), -17.3(1B), -18.4 (1B), -22.2 (d, ¹J(B,H)= 146, 1B), -32.1 (d, ¹J(B,H)= 123, 1B), -35.3 (d, ¹J(B, H)= 139, 1B). ¹³C{¹H}-NMR: 58.54 (s, NBu₄), 53.58 (br s, C_c), 51.65 (br s, C_c), 23.57 (s, NBu₄), 19.48 (s, NBu₄), 13.03 (s, NBu₄). MALDI-TOF (m/z): 134.97 (M/2-S; 81.6%), 166.97 (M/2; 100%), 182.98 (M/2 + O; 35.7%), 198.98 (M/2 + S; 55.1%), 215.01 (M/2 + S + O; 38.8%).

Synthesis of [PNP]₂[7-S-8-Me-7,8-*nido*-C₂B₉H₁₀]₂. This compound was prepared using the method described for [NBu₄]₂[7-S-7,8-*nido*-C₂B₉H₁₁]₂, using (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ (23 mg, 0.06 mmol), piperidine (0.031 ml, 0.31 mmol). A white solid was isolated by precipitation after addition of aqueous [PNP]Cl solution. Yield: 147 mg (85%). Anal. Calcd for C₇₆H₈₆B₁₈S₂N₂P₂+ 2H₂O: C, 63.70; H, 5.99; N, 1.90; S, 4.35. Found: C, 63.46; H, 6.24; N, 1.90; S, 4.16.

FTIR (KBr): ν (cm^{-1}) 3012 (br, H_2O), 2958, 2926 ($\text{C}_{\text{alkyl}}\text{-H}$); 2529 (B-H). $^1\text{H-NMR}$ (CD_3COCD_3): δ 7.73-7.57 (s, PNP, 60H), 2.97 (s, H_2O), 1.81 (br s, CH_3 , 3H), 1.71 (br s, CH_3 , 3H). $^1\text{H}\{^{11}\text{B}\}\text{-NMR}$ (CD_3COCD_3): δ 7.73-7.57 (s, PNP, 60H), 2.97 (s, H_2O), 2.54, 2.43 (br s, B-H), 1.81 (br s, CH_3 , 3H), 1.71 (br s, CH_3 , 3H), 1.61, 1.55, 1.38, 1.19, 1.19, 0.55, 0.07 (br s, B-H), -2.23 (br s, B-H-B, 1H), -2.44 (br s, B-H-B, 1H). $^{11}\text{B-NMR}$ (CD_3COCD_3): δ -6.8 (d, $^1\text{J}(\text{B,H})=128$, 1B), -7.6 (d, $^1\text{J}(\text{B,H})=137$, 1B), -10.9 (d, $^1\text{J}(\text{B,H})=162$, 1B), -14.6 (d, $^1\text{J}(\text{B,H})=128$, 1B), -15.5 (d, $^1\text{J}(\text{B,H})=174$, 1B), -18.9 (d, $^1\text{J}(\text{B,H})=130$, 1B), -19.9 (d, $^1\text{J}(\text{B,H})=134$, 1B), -33.2 (dd, $^1\text{J}(\text{B,H})=126$, $^1\text{J}(\text{H,H})=29$, 1B), -35.1 (d, $^1\text{J}(\text{B,H})=141$, 1B). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (CD_3COCD_3): 133.7, 132.3, 129.4, 128.0 (s, PNP), 24.14 (s, CH_3), 23.68 (s, CH_3). $^{31}\text{P-NMR}$ (CD_3COCD_3): 20.21 (s, PNP). MALDI-TOF (m/z): 357.24 (M; 13.3%), 369.27 (M + O; 82.2 %), 210.90 (M/2 + S; 17.7%), 178.99 (M/2; 100%)

Synthesis of $[\text{NBu}_4]_2[7\text{-S-8-Ph-7,8-C}_2\text{B}_9\text{H}_{10}]_2$. This compound was prepared using the method described for $[\text{NBu}_4]_2[7\text{-S-7,8-nido-C}_2\text{B}_9\text{H}_{11}]_2$, using (1-S-2-Ph-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{11}$)₂ (66 mg, 0.13 mmol), piperidine (0.064 ml, 0.65 mmol) a white solid was isolated. Yield: 94 mg (74 %). Anal. Calcd for $\text{C}_{48}\text{H}_{102}\text{B}_{18}\text{S}_2\text{N}_2 + 4\text{H}_2\text{O}$: C, 55.53; H, 10.68; N, 2.70; S, 6.18. Found: C, 54.98; H, 10.48; N, 2.64; S, 6.24. FTIR (KBr): ν (cm^{-1}) 2994, 2986 ($\text{C}_{\text{aryl}}\text{-H}$), 2534 (B-H). $^1\text{H-NMR}$ (CD_3COCD_3): δ 7.27-6.90 (m, $\text{C}_{\text{aryl}}\text{-H}$, 10H), 3.41 (t, $^3\text{J}(\text{H,H})=8.4$, NBu_4 , 16H), 1.83 (q, $^3\text{J}(\text{H,H})=7.4$, NBu_4 , 16H), 1.45 (hex, $^3\text{J}(\text{H,H})=7.4$, NBu_4 , 16H), 0.98 (t, $^3\text{J}(\text{H,H})=7.4$, NBu_4 , 24H). $^1\text{H}\{^{11}\text{B}\}\text{-NMR}$ (CD_3COCD_3): δ 7.27-6.90 (m, $\text{C}_{\text{aryl}}\text{-H}$, 10H), 3.41 (t, $^3\text{J}(\text{H,H})=8.4$, NBu_4 , 16H), 2.62, 2.28, 2.23 (br s, B-H), 1.83 (q, $^3\text{J}(\text{H,H})=7.4$, NBu_4 , 16H), 1.45 (hex, $^3\text{J}(\text{H,H})=7.4$, NBu_4 , 16H), 0.98 (t, $^3\text{J}(\text{H,H})=7.4$, NBu_4 , 24H), 0.75, 0.55, 0.41 (br s, B-H), -1.84 (br s, B-H-B, 1H), -2.14 (br s, B-H-B, 1H). $^{11}\text{B-NMR}$ (CD_3COCD_3): δ -5.6 (d, $^1\text{J}(\text{B,H})=125$, 1B), -7.4 (d, $^1\text{J}(\text{B,H})=124$, 1B), -12.9 (1B), -15.0 (1B), -17.3 (1B), -18.2 (1B), -19.7 (1B), -32.3 (d, $^1\text{J}(\text{B,H})=121$, 1B), -34.4 (d, $^1\text{J}(\text{B,H})=138$, 1B). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$: 142.70, 133.10, 132.53, 126.15 (s, C_{aryl}), 65.03 (s, C_c), 58.53 (s, NBu_4), 23.55 (s, NBu_4), 19.49 (s, NBu_4), 13.02 (s, NBu_4). MALDI-TOF (m/z): 481.34 (M; 10.5%), 273.07 (M/2 + S; 45.2%), 241.07 (M/2; 100%), 209.07 (M/2 - S; 65.5%).

Synthesis of $[\text{NMe}_4][1\text{-S-2-Ph-1,2-closo-C}_2\text{B}_{10}\text{H}_{10}]$. To a solution of KOH (36 mg, 0.6425 mmol) in degassed absolute ethanol (8 ml) was added (1-S-2-Ph-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$)₂ (64 mg, 0.1285 mmol). The mixture was refluxed for 3 hours and then cooled to room temperature. Then was dried in the vacuum line and added water (4 ml), upon the addition of an aqueous solution of tetramethylammonium chloride. As a result, a orange solid was obtained which was filtered and washed with water and diethyl ether. Yield: 61 mg (73%). Anal. Calcd for $\text{C}_{12}\text{H}_{27}\text{B}_{10}\text{SN}$: C, 44.28; H, 8.36; N, 4.30; S, 9.85. Found: C, 44.58; H, 8.45; N, 4.27; S, 9.76. FTIR (KBr): ν (cm^{-1}) 3008, 2991 ($\text{C}_{\text{aryl}}\text{-H}$), 2591, 2570, 2553 (B-H). $^1\text{H-NMR}$ (CD_3COCD_3): δ 7.60 (d, $\text{C}_{\text{aryl}}\text{-H}$, $^1\text{J}(\text{H,H})=3.1$, 2H), 7.23 (d, $\text{C}_{\text{aryl}}\text{-H}$, $^1\text{J}(\text{H,H})=3.1$, 3H), 3.21 (s, NMe_4 , 12H). $^1\text{H}\{^{11}\text{B}\}\text{-NMR}$ (CD_3COCD_3): δ (ppm) 7.60 (d, $\text{C}_{\text{aryl}}\text{-H}$, $^1\text{J}(\text{H,H})=3.1$ 2H), 7.23 (d, $\text{C}_{\text{aryl}}\text{-H}$, $^1\text{J}(\text{H,H})=3.1$, 3H), 3.21 (s, NMe_4 , 12H). 2.69, 2.60, 2.20, 2.08, 1.81, 1.53, 1.16 (br s, B-H). $^{11}\text{B-NMR}$ (CD_3COCD_3): δ -3.91 (d, $^1\text{J}(\text{B,H})=168$, 1B), -5.53 (d, $^1\text{J}(\text{B,H})=132$, 4B), -9.46 (d, $^1\text{J}(\text{B,H})=188$, 2B), -11.94 (d, $^1\text{J}(\text{B,H})=145$, 3B). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$: 134.90, 131.87, 128.58, 127.42, 119.59 (s, C_{aryl}), 91.72 (s, C_c), 54.96 (s, NMe_4), 46.65 (s, C_c). MALDI-TOF (m/z): 252.07 (M; 91.7%), 241.05 (M-B; 15.3 %), 220.08 (M-S; 24.3%), 209.05 (M-S-B; 100%).

Synthesis of $[\text{NBu}_4][1\text{-S-2-Me-1,2-closo-C}_2\text{B}_{10}\text{H}_{10}]$. To a Schlenck containing a solution of KOH (50 mg, 0.85 mmol)

in deoxygenated ethanol (10 ml), was added (2-Me-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}\text{S}$)₂ (70 mg, 0.17 mmol). We refluxed the mixture for 3 hours and then cooled at room temperature and evaporated. The resulting residue was dissolved with water (5 ml) and we added a solution of tetrabutylammonium bromide. We obtain a white solid, that we filtered and washed with water and diethyl ether. Yield: 120 mg (82%). Anal. Calcd for $\text{C}_{19}\text{H}_{49}\text{B}_{10}\text{NS}$: C, 52.85; H, 11.44; N, 3.24; S, 7.43. Found: C, 52.92; H, 11.74; N, 3.06; S, 6.45. FTIR(KBr): ν (cm^{-1}) 2968 ($\text{C}_c\text{-H}$), 2575 (B-H). $^1\text{H-RMN}$ (CD_3COCD_3): δ = 3.45 (t, $^3\text{J}(\text{H,H})=8.4$, NBu_4 , 8H), 2.12 (br s, CH_3 , 3H), 1.78 (q, $^3\text{J}(\text{H,H})=7.4$, NBu_4 , 8H), 1.45 (hex, $^3\text{J}(\text{H,H})=7.4$, NBu_4 , 8H), 0.98 (t, $^3\text{J}(\text{H,H})=7.4$, NBu_4 , 12H). $^{11}\text{B-RMN}$ (CD_3COCD_3): δ = -5.52 (d, $^1\text{J}(\text{B,H})=172$, 2B), -6.98 (d, $^1\text{J}(\text{B,H})=153$, 3B), -10.55 (d, $^1\text{J}(\text{B,H})=160$, 2B), -12.52 (d, $^1\text{J}(\text{B,H})=122$, 3B). $^{13}\text{C}\{^1\text{H}\}\text{-RMN}$ (CD_3COCD_3): δ =109.82 (s, C_c), 81.71 (s, C_c), 58.50 (s, NBu_4), 23.60 (s, NBu_4), 21.64 (s, CH_3), 19.49 (s, NBu_4), 12.98 (s, NBu_4). MALDI-TOF (m/z): 188.95 (M; 100%), 176.92 (M-Me; 6.1%), 156.96 (M-S; 13.0%), 145.93 (M-S-Me; 10.4%).

Synthesis of $[\text{NBu}_4][1\text{-S-1,2-closo-C}_2\text{B}_{10}\text{H}_{11}]$. To a schlenck containing a solution of KOH (34 mg, 0.61 mmol) in deoxygenated ethanol (10 ml), was added [2-H-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}\text{S}$]₂ (46 mg, 0.12 mmol). We refluxed the mixture for 3 hours and then cooled at room temperature and evaporated. The resulting residue was dissolved with water (5 ml) and we added a solution of tetrabutylammonium bromide. We obtain a white solid, that we filtered and washed with water and diethyl ether. Yield: 60 mg, 81%. Anal. Calcd for $\text{C}_{18}\text{H}_{47}\text{B}_{10}\text{NS}$: C, 51.75; H, 11.34; N, 3.35; S, 7.68 % Found: C, 51.60; H, 11.31; N, 3.45; S, 7.55. FTIR(KBr): ν (cm^{-1}) 3013 (N-H), 2958 ($\text{C}_c\text{-H}$), 2572 (B-H). $^1\text{H-RMN}$ (CD_3COCD_3): δ = 3.90 (br s, $\text{C}_c\text{-H}$, 1H), 3.45 (t, $^3\text{J}(\text{H,H})=8.4$, NBu_4 , 8H), 1.78 (q, $^3\text{J}(\text{H,H})=7.4$, NBu_4 , 8H), 1.45 (hex, $^3\text{J}(\text{H,H})=7.4$, NBu_4 , 8H), 0.98 (t, $^3\text{J}(\text{H,H})=7.4$, NBu_4 , 12H). $^{11}\text{B-RMN}$ (CD_3COCD_3): δ = -2.86 d, $^1\text{J}(\text{B,H})=145$, 1B), -5.95 (d, $^1\text{J}(\text{B,H})=167$, 4B), -9.96 (d, $^1\text{J}(\text{B,H})=178$, 2B), -12.13 (d, $^1\text{J}(\text{B,H})=134$, 2B), -13.27 (d, $^1\text{J}(\text{B,H})=142$, 1B). $^{13}\text{C}\{^1\text{H}\}\text{-RMN}$ (CD_3COCD_3): δ = 74.83 (C_c), 58.50 (s, NBu_4), 23.60 (s, NBu_4), 19.49 (s, NBu_4), 12.98 (s, NBu_4). MALDI-TOF (m/z): 174.93 (M; 100).

Synthesis of $[\text{NMe}_4][(1,2\text{-closo-C}_2\text{B}_{10}\text{H}_{11})\text{S-S}(7,8\text{-nido-C}_2\text{B}_9\text{H}_{11})]$. To a solution of (1-S-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{11}$)₂ (26 mg, 0.069 mmol) in THF (4 ml) was added a solution of H_2O_2 0.2M (1.36 mL, 0.276 mmol). The mixture was stirred for 4 hours and then vacuum evaporated. We added water (4 ml), upon the addition of an aqueous solution of tetramethylammonium chloride. As a result, a white solid was obtained which was filtered and washed with water and diethyl ether (27 mg, 0.065 mmol, 96 %). Anal. Calcd for $\text{C}_8\text{H}_{34}\text{B}_{19}\text{S}_2\text{N}$: C, 23.21; H, 8.28; N, 3.38; S, 15.49. Found: C, 23.77; H, 8.38; N, 3.14; S, 15.22. FTIR(KBr): ν (cm^{-1}) 2571-2520 (B-H). $^1\text{H-NMR}$ (CD_3COCD_3): δ 4.70 (br s, $\text{C}_c\text{-H}$, 1H), 3.44 (s, NMe_4 , 12H), 2.35 (br s, $\text{C}_c\text{-H}$, 1H), 2.61-0.25 (m, B-H), -2.68 (br s, B-H-B, 1H). $^{11}\text{B-NMR}$ (CD_3COCD_3): δ -0.85 (d, $^1\text{J}(\text{B,H})=151$, 1B), -4.41 (d, $^1\text{J}(\text{B,H})=153$, 1B), -8.66 (d, $^1\text{J}(\text{B,H})=130$, 6B), -11.16 (d, $^1\text{J}(\text{B,H})=174$, 5B), -14.00 (d, $^1\text{J}(\text{B,H})=110$, 1B), -15.10 (d, $^1\text{J}(\text{B,H})=115$, 1B), -17.90 (d, $^1\text{J}(\text{B,H})=153$, 1B), -22.02 (d, $^1\text{J}(\text{B,H})=153$, 1B), -32.57 (d, $^1\text{J}(\text{B,H})=132$, 1B), -34.30 (d, $^1\text{J}(\text{B,H})=148$, 1B). MALDI-TOF (m/z): 338.18 (M-1; 29.3%), 174.94 (M- $\text{C}_2\text{H}_{11}\text{B}_9\text{S}$; 100%), 162.92 (M- $\text{C}_2\text{H}_{11}\text{B}_{10}\text{S}$; 21.6%), 141.94 (M- $\text{C}_2\text{H}_{11}\text{B}_9\text{S}_2$; 70.3%), 130.91 (M- $\text{C}_2\text{H}_{11}\text{B}_{10}\text{S}_2$; 18.9%).

X-ray Structure Determinations of (2-Me-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$)₂S, (1-S-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{11}$)₂, (1-S-2-Me-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$)₂ and (1-S-2-Ph-1,2-closo- $\text{C}_2\text{B}_{10}\text{H}_{10}$)₂. Single-crystal data collections for (2-Me-1,2-closo-

C₂B₁₀H₁₀)₂S, (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ and (1-S-2-Ph-1,2-*closo*-C₂B₁₀H₁₀)₂ were performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite monochromatized Mo K α radiation, while a crystal of [1-S-1,2-*closo*-C₂B₁₀H₁₁]₂ was measured on a Nonius KappaCCD diffractometer at -100°C. Totals of 3621, 3192, 3833 and 5059 independent reflections were collected ($2\theta_{\max}=50^\circ$) for (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂S, (1-S-1,2-*closo*-C₂B₁₀H₁₁)₂, (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ and (1-S-2-Ph-1,2-*closo*-C₂B₁₀H₁₀)₂ respectively. Crystallographic data are presented in Table 1.

The structures were solved by direct methods using the SHELXS-97 program and least-squares refinements were performed using the SHELX-97 program.³⁹ For (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂S, (1-S-1,2-*closo*-C₂B₁₀H₁₁)₂ and (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ all non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included in the calculations at fixed distances from their host atoms and treated as riding atoms using the SHELXL-97 default parameters. Carbon and boron atoms of (1-S-1,2-*closo*-C₂B₁₀H₁₁)₂ could be reliably recognized. (1-S-1,2-*closo*-C₂B₁₀H₁₁)₂ crystallizes in a noncentrosymmetric space group, and the structure was refined as a racemic twin.

Refinement of all non-hydrogen atoms of (1-S-2-Ph-1,2-*closo*-C₂B₁₀H₁₀)₂ with anisotropic displacement parameters and including hydrogen atoms at fixed distances from their host atoms revealed two extra electron density maxima (1.32 and 1.19 e \AA^{-3}) between the two carborane cages and near the bridging sulfur atoms. As the distance between the residuals was about 2.0 \AA we supposed the maxima belong to another conformation with minor occupancy. Including the two atom positions in the calculations, the R1 value decreased from 0.0820 to 0.0690 resulting site occupation factors 0.934(2) and 0.066(2) for the two conformers of the structure. Rest of the atoms of the conformer with minor occupancy could not be positioned. The sulfur atoms with occupancy 0.066(2) were refined with isotropic but rest of the non-hydrogen atoms with anisotropic displacement parameters. Hydrogen atoms of the major conformer were included in the calculations at fixed distances from their host atoms and treated as riding atoms using the SHELXL-97 default parameters.

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Supporting Information Available: Tables of X-ray experimental details, hydrogen atom positional parameters and thermal parameters, anisotropic thermal parameters, interatomic distances and angles for (2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂S, (1-S-1,2-*closo*-C₂B₁₀H₁₁)₂, (1-S-2-Me-1,2-*closo*-C₂B₁₀H₁₀)₂ and (1-S-2-Ph-1,2-*closo*-C₂B₁₀H₁₀)₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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