For Polyhedron special issue dedicated to Malcolm Chisholm.

Revised version 31st May 2005.

Corresponding author: Dr Mark A. Fox, e-mail m.a.fox@durham.ac.uk

Preparative and structural studies on sulfur-linked carborane icosahedra: ~~1~~2-phenyl-*ortho*-carboranyl-sulfur systems (~~1~~2-Ph-1,2-$C_2B_{10}H_{10})_2X$ (X= S, S_2 or SO), and *ortho*-carborane-di-yl systems (1,2-$C_2B_{10}H_{10}Y)_2$ (Y= S or SO)[*]

Andrei S. Batsanov,[a] William Clegg,[b] Royston C.B. Copley,[a] Mark A. Fox,*,[a] Wendy R. Gill,[a] Rachel S. Grimditch,[a] Thomas G. Hibbert,[a] Judith A.K. Howard,[a] J. A. Hugh MacBride[a] and Kenneth Wade[a]

[a]*Chemistry Department, Durham University Science Laboratories, South Road, Durham, DH1 3LE, U.K.*
[b]*School of Natural Sciences (Chemistry), University of Newcastle, Newcastle upon Tyne, NE1 7RU, U.K.*

Abstract

Details are reported of the preparation and X-ray structural characterisation of the new compounds $(PhCb^o)_2X$, where $PhCb^o$ = ~~1~~2-Ph-1,2-$C_2B_{10}H_{10}$ and X = S(**1**) or SO (**3**), prepared from $PhCb^oLi$ and SCl_2 or $SOCl_2$ respectively, as well as the known compound with X = S_2 (**2**). Hydrogen in the presence of palladium/carbon reduced (**3**) to (**1**). Features of their structures (*exo* C-S and cage C-C distances and substituent orientations) are consistent with significant *exo* S=C dative π-bonding from their sulfur atoms to the cage hypercarbon atoms and weak *exo* π-bonding from the phenyl groups. Attempts to prepare systems $(Cb^oY)_2$, in which two *ortho*-carboran-di-yl residues Cb^o are linked through two bridging units Y (S, SO) are also reported, as are their calculated structures.

Introduction

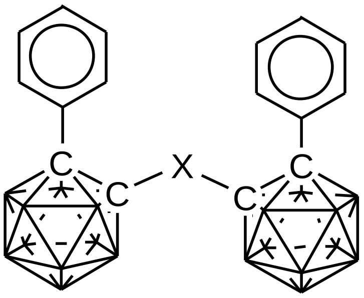
Researches into carboranes with cage C-sulfur substituents were originally developed in the sixties[1,2] and after a quiet period have acquired renewed momentum recently. Reactions between alkali metal (normally lithium) carborane derivatives and elemental sulfur or sulfur halides were used primarily to prepare derivatives of formula types $HCB_{10}H_{10}CSR$, $RCB_{10}H_{10}CSR'$ or $RSCB_{10}H_{10}CSR'$, where R and R' = H, alkyl or aryl.[1,2,3] Derivatives $Cb^o(SR)_2$ of *ortho* carborane have attracted particular interest, in part in connection with their ligand potential, whether as bidentate chelating ligands, or as components of macrocycles when the substituents R are linked through successive ether or thioether units.[4] Where SR is SH they can be used as precursors to form [*closo*-$RC_2B_{10}H_{10}S]^-$ or [*closo*-$C_2B_{10}H_{10}S_2]^{2-}$ anionic residues.[5] They have also been used as precursors from which [*nido*-$C_2B_9H_9(SR)_2]^{2-}$ anionic residues, offering yet further ligand potential, can be prepared.[6]

---

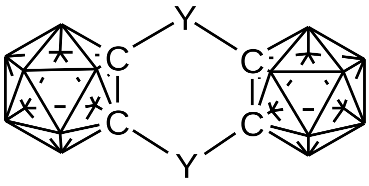
[*] Dedicated to Malcolm Chisholm on the occasion of his 60th birthday

Although many C-sulfur *ortho*-carboranes are now listed in the Cambridge Structural Database,[7] it is perhaps surprising to find that there is only one reported compound, $[Cb^oSCb^oSiMe_2]$,[8] in which two *ortho*-carboran-di-yl residues are linked through their carbon atoms by a single sulfur atom. This compound also contains a dimethylsilyl bridge between the two carboran-di-yl residues.[8] One other compound, $(MeCb^o)_2S$, with a sulfur bridge between *ortho*-carboranyl residues has been reported[2] but it was not structurally characterised.

In previous studies of the derivative chemistry of icosahedral carboranes, we have explored the effect on the 2-phenyl-*ortho*-carborane cage of the attachment of more strongly π-donor substituents to the cage hypercarbon atom C1 and found that the cage opens up from a *closo* to a near *nido* geometry as the *exo* bond order increases.[9,10,11] Our own published work so far has concentrated on one-cage systems and here we extend our investigation to the effect ~~on~~ of one π-donating atom ~~of~~ connect~~ing it~~ed to two *ortho*-carborane cages. We prepared systems $(PhCb^o)_2X$ (X = S(**1**), S_2(**2**) or SO (**3**)) in which the second cage carbon atom bore a phenyl substituent,[10,12] choosing 2-phenyl-*ortho*-carborane derivatives because they generally form suitable crystals for X-ray crystallographic studies (over fifty such compounds have been structurally characterised).[13] We also explored the synthesis of heterocyclic systems $(Cb^oY)_2$ (Y = S(**4**) or SO(**5**)) in which two C-S-C or C-S(O)-C bridges link pairs of *ortho* carborane icosahedra, and report calculated structures of (**4**) and (**5**). (See figure 1 for representative structures of (**1**)-(**5**))



1 X = S
2 X = S_2
3 X = SO



4 Y = S
5 Y = SO

Figure 1. Representative structures of the title compounds (**1**)-(**5**)

A very recent paper[14] by Vinas, Teixidor *et al* on synthesis and structural characterisation of carborane mono- and di-sulfides appeared during submission of this work. While our synthetic route to the monosulfide differed from theirs, their structural findings and interpretations broadly agree with ours.

Results and discussion

Preparative aspects

The new compounds (**1**) and (**3**) prepared in the present work were made from the lithio-carborane $PhCb^{o}Li$ with SCl_2 and $SOCl_2$ respectively, and characterised by NMR spectroscopic, elemental analytical and X-ray crystallographic study. To our knowledge, thionyl chloride has not been used to make carboranyl sulfur compounds previously. Compound **3** represents the first example containing an SO link between two *ortho*-carboranyl residues. It is easily reduced to compound **1** with hydrogen in the presence of palladium-carbon. It is, however, quite susceptible to deboronation. While compound **1** is stable in wet DMSO, compound **3** in wet DMSO gave a mixture of derivatives with *nido*-$C_2B_9H_{12}^-$ residues detected by NMR spectroscopy, and C-S cleavage was also evident. Some carboranyl derivatives are known to be susceptible to deboronation with mild solvents such as DMSO and alcohols.[15] Here, carboranes with C-S(O)R substituents were found to be much more susceptible to C-S bond cleavage and deboronation than those with C-SR substituents, as expected because the S(O)R residue is more electron-withdrawing than SR, facilitating nucleophilic attack on the most positive boron atom at B3 (or B6). The known compound **2** was made from $PhCb^{o}Li$ with sulfur and then oxidised with iodine.[2]

Attempts to prepare and characterise (**4**) and (**5**), from reactions between dilithio-*ortho*-carborane and sulfur dichloride and thionyl chloride respectively, were less successful in that, although the reactions appeared to proceed to formation of lithium chloride and the intended products (**4**) and (**5**)~~,~~ (obtained as colourless microcrystalline materials analysing correctly for the expected products), attempts to grow crystals suitable for X-ray characterisation were unsuccessful. Unlike **4**, compound **5** could not be purified further due to its facile deboronation and C-S bond cleavage with certain solvents.

Structural aspects

Systems $(PhCb^{o})_2S$, $(PhCb^{o}S)_2$, $(PhCb^{o}S)_2S$ and $(PhCb^{o})_2SO$

Compounds **1**, **2** and **3**, like the related trisulfide $(PhCb^{o}S)_2S$ we have~~d~~ described elsewhere,[11] all adopt orientations of their *exo*-SR units, and have cage C-C and *exo* C-S distances, consistent with significant dative S=C π-bonding from their *exo*-sulfur atoms to their cage hypercarbon atoms (see F~~f~~igs. 2-4 and T~~t~~able 1, which lists selected bond distances and angles for compounds **1-3** and the trisulfide $(PhCb^{o}S)_2S$). For compound **1** the *exo* bonds C-S-C lie in a plane roughly perpendicular to the C(2~~1~~)-C(1~~2~~)-S plane whereas for **2**, **3** and the trisulfide these bond orientations depart more from perpendicular (see torsion angle C-S-C/S in T~~t~~able 1). We recently showed, in our discussion of a series of systems $PhCb^{o}Z$ showing *exo* C=Z π-bonding (including $(PhCb^{o}S)_2S$), that such a perpendicular orientation optimised *exo* π-bonding.[11]

The phenyl substituent on C(2~~1~~) in compounds **2** and **3** also lies in a plane roughly perpendicular to the plane C(2~~1~~)-C(1~~2~~)-S whereas in **1** and the trisulfide the orientations depart more from perpendicular. A perpendicular orientation minimises non-bonding repulsions with the other substituent on C(1~~2~~), and maximises the opportunity for dative π-bonding from the π-system of the phenyl group to the carborane cage.[16,17]

The cage carbon-carbon distance, C(1)-C(2), of *ortho* carborane is the cage edge link known to be most sensitive to the presence of π-bonding substituents on the cage hypercarbon atoms.[11,18,19] Its length increases as *exo* π-bonding increases. Steric effects have previously been invoked to explain the lengthening of the cage C-C bond in various disubstituted-*ortho*-carboranes.[13] In *ortho* carborane itself, HCb^{o}H, the C(1)-C(2) distance has been shown to be 1.62 Å by both X-ray studies of crystalline hydrogen-bonded adducts[20] and by gas-phase electron diffraction and calculational studies.[21] Attachment of a phenyl substituent to one carbon atom, oriented (as here) so that its ring plane is roughly perpendicular to the C(1~~2~~)-C(2~~1~~)-C(phenyl) plane, ~~raises~~ increases the cage C(1)-C(2) distance by some 0.04 Å, to 1.66 Å.[22] In compound **2** (Table 1), where the orientations of the sulfur and phenyl substituents offer greater *exo* π-bonding effects compared to the trisulfide, the C(1)-C(2) distance is 1.760(5) Å. The sulfur atom lengthens the C(1)-C(2) bond distance by some 0.1 Å. The trisulfide has a shorter C(1)-C(2) bond distance of 1.735(3), as expected for orientations of the substituents which lead to less effective *exo* π-bonding.

Surprisingly, compounds **1** and **2** have similar C(1)-C(2) and C(1~~2~~)-S distances, suggesting a similar degree of S=C π-bonding in these two compounds. We had expected there to be weaker S=C π-bonding in **1**, where both carborane cages are attached to the same sulfur atom, and so competing for π-electron density from the same source. The C-S-C angle in **1** (112.8(1)^{o}) is significantly greater than the C-S-S angle in **2** (105.5(2)^{o}) which is due to steric repulsion between the two cages. Intramolecular B-H..H-B distances between the two cages are 2.27, 2.40 and 2.49 Å. Interestingly, the C(1)-C(2) bond ~~lengths~~ in **2** is some 0.03 Å longer than in PyCb^{o}SH (X-ray[23]) and PhCb^{o}SH (calc[11]) which suggests that the disulfur bridge (S-S) is a more effective π-bond donor to the *ortho*-carborane cage than is a thiol (S-H) group.

Table 1. Selected bond distances (Å) and angles (°) in X-ray structures of C-sulfur *ortho*-carboranes

Compound	$(PhCb^o)_2S$ (**1**)[a]	$(PhCb^o)_2S_2$ (**2**)[a]	$(PhCb^oS)_2S$ [b]	$(PhCb^o)_2SO$ (**3**) [a]	$PyCb^oSH$ [c]	$PhCb^oSH$ [b,d]
C1-C2	1.751(3)	1.760(5)	1.735(3)	1.729(3)	1.730(3)	1.729
C1-S	1.789(2)	1.796(4)	1.788(3)	1.859(2)	1.775(2)	1.782
C2-C(Ph[e])	1.510(3)	1.497(6)	1.499(3)	1.505(3)	1.507(3)	1.495
C1-B3/6	1.725(10)[g]	1.712(7)	1.716(4)	1.722(10)[g]	1.720(3)	1.705
C1-B4/5	1.714(11)[g]	1.696(7)	1.702(7) [g]	1.700(3)	1.709(3)	1.700
C2-C1-S	116.1(2)	114.4(3)	115.9(2) 117.6(2)	110.7(1) 106.0(1)	117.7(1)	117.5
C1-S-E[f]	112.8(1)	105.5(2)	105.4(1)	106.2(1)	96(1)	95.1
Tors. angle C2-C1-S-E[f]	99.1(2) 97.1(2)	108.1(2) 113.1(2)	123.3(2) -96.1(2)	-124.2(1) 160.4(1)	99(2)	96.8
Tors. angle[h] C1-C2/Ph	74.5(3)	81.9(3) 88.6(3)	73.7(2)	87.6(1) 89.0(1)	84.3(2)	88.7[e]

a) this work; b) ref. 11; c) ref. 23, low-temperature structure; d) MP2/6-31G* calculations; e) Py; f) E = C (**1**, **3**), S (**2**); g) shows statistically significant variations, individual e.s.d.'s 0.003-0.004 Å, which relate to the orientation of the group at sulfur; h) calculated as the angle between the Ph (Py) ring and the C1-C2-C(Ph/Py) moiety

The C(1)-C(2) and C(1~~2~~)-S distances in compound **3**, $(PhCb^o)_2SO$ (Table 1), differ from those in **1** and **2**,though less than expected. The electron-withdrawing oxygen atom on the bridging sulfur atom in **3** was expected to reduce its capacity for S=C *exo* π-bonding relative to the lower oxidation state bridging sulfur atoms in **1** and **2**. Compound **3** appears to be affected (though to a lesser extent than 1) by repulsive interactions between the cages; shortest intramolecular B-H..H-B contacts in **3** are 2.25 and 2.37 Å, and the C-S-C angle is 106.2(1). The *exo*- C-S bond distance in **3** is some 0.07 Å longer (less π-bonding) than that in **1**. Interestingly, **1** and **3** differ in their conformations, **1** is *trans* and **3** is *cis*. Besides our derivatives and those in the very recent report,[14] only two neutral RCb^oSR' systems have been structurally characterised:~~;~~ HCb^oSPy[24] (Py = 2'-pyridyl) and $MeCb^oSPh$[25] with C-S distances of 1.78 Å and cage C(1)-C(2) distances of 1.64 and 1.71 Å respectively.

Figure for **1**

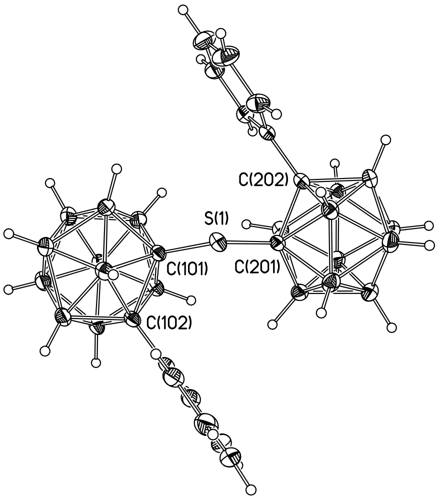


Figure for **2**

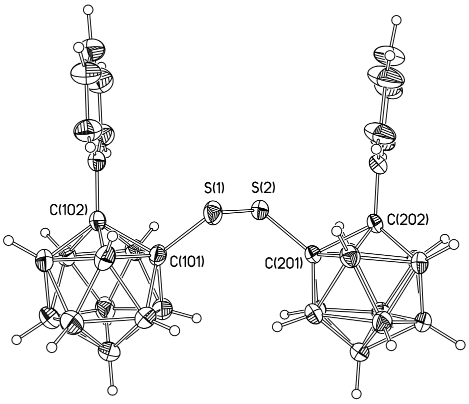
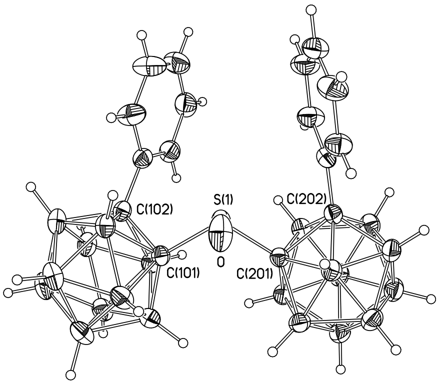


Figure for **3**



Systems $(Cb^{o}S)_2$ and $(Cb^{o}SO)_2$

Although our attempts to prepare crystalline samples of these species suitable for X-ray characterisation were unsuccessful, we carried out calculations to determine their likely structures, encouraged by our previous experience of the reliability of such calculations for calculating the structures of derivatives of *ortho*-carborane containing dative π-bonding substituents for which structures had separately been determined by X-ray studies.[11] Selected bond distances and angles are listed in Table 2, which also gives comparable bond distances and angles determined ~~X-ray~~ crystallographically for the compound $(Cb^{o}SCb^{o}SiMe_2)$.[8]

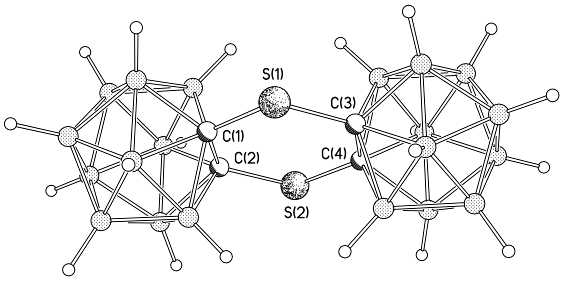
The C-C bond length of 1.62 Å in the calculated structure of **4** is identical to that of parent *ortho*-carborane.[21] This may reflect ~~to~~ both ring strain in the C_4S_2 heterocycle and inappropriate orientations of the bonds at sulfur ~~inappropriate~~ for *exo* dative π-bonding to the cage C-C bond. The reported crystal structure of a related heterocycle, $Cb^{o}S_2C{=}S$, has a cage C-C bond length of 1.632(3) Å.[26] These bond values contrast with long cage C(1)-C(2) distances of 1.80 Å reported for neutral $Cb^{o}(SR)_2$ systems (R = Me or Ph).[19,27] In **5**, the two SO moieties may exist in *trans* or the more stable *cis* configuration. The *cis*-configuration is lower by only 0.1 kcal mol^{-1}. As expected, the C-S distance in the sulfoxy compound is longer than that in the sulphide.

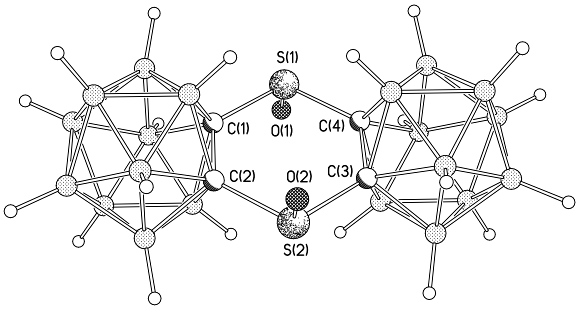
Table 2. Selected bond distances (Å) and angles for the compounds $(Cb^{o}SCb^{o}SiMe_2)$, $(Cb^{o}S)_2$ and $(Cb^{o}SO)_2$

Compound	$(Cb^{o}SCb^{o}SiMe_2)^{a}$	$(Cb^{o}S)_2$ (**4**)^{b}	$(Cb^{o}SO)_2$ (**5**)^{b}	$HCb^{o}H^{c}$
C1-C2	1.652(4)	1.621	1.637	1.62
C1-S	1.794(3)	1.800	1.873	
C1-B3/6	1.721(6)	1.734	1.716	1.71
C-S-C	111.2(2)	106.9	101.5	
C-C-S	126.2(3)	126.6	129.2	

[a] Ref. 8 [b] This work, calculated at MP2/6-31G* [c] Refs. 20,21

Figures of MP2-optimised geometries for **4** and **5**





Conclusions

The monosulfide $(PhCb^o)_2S$ and sulfoxide $(PhCb^o)_2SO$ in which two phenyl-*ortho*-carborane residues were linked at the cage carbon through a sulfur atom were synthesised simply by reactions of the lithio-*ortho*-carborane $PhCb^oLi$ with sulfur dichloride or thionyl chloride respectively. Their structures show significant cage C(1)-C(2) bond lengthening relative to the parent carborane, an effect attributable mainly to π-bonding from the sulfur atom and to a lesser extent to π-bonding from the phenyl substituent.

By contrast, the C(1)-C(2) bond lengths in the heterocyclic system $(Cb^oS)_2$, in which two C-S-C bridges link pairs of *ortho* carborane icosahedra, are calculated to be similar to the parent *ortho* carborane.

Experimental

General

All manipulations were carried out under dry, oxygen-free N_2. Commercial grade acetic acid, 10% palladium on carbon, SCl_2, $SOCl_2$ and *n*-butyllithium in hexanes were used without further purification. Dry Et_2O was obtained by reflux and distillation over Na wire. Demineralised water was used in the aqueous stages of syntheses. Compound **2** was prepared by the literature method.[2]

Elemental analyses were performed using Exeter Analytical CE-440 apparatus. ^{1}H, ^{11}B, ^{13}C NMR spectra were recorded ~~as~~ from room-~~–~~temperature solutions on a Varian Unity 300 MHz spectrometer equipped with the appropriate decoupling accessories. Chemical shift values for ^{11}B-NMR spectra were referenced to external $BF_3{\cdot}OEt_2$, those for ^{1}H- and ^{13}C{^{1}H}- NMR spectra were referenced to $SiMe_4$. ^{1}H-NMR spectra were referenced to residual protio impurity in the solvent ($CDCl_3$, 7.26 ppm). ^{13}C-NMR spectra were referenced to the solvent resonance ($CDCl_3$, 77.0 ppm). Chemical shifts are reported in units of parts per million downfield from reference. Mass spectra (MS) were recorded on a VG Micromass 7070E instrument under E.I conditions (EI) at 70 eV.

Preparation of **1**

Phenyl-*ortho*-carborane (0.71g, 3.2 mmol) was dissolved in diethyl ether (20 ml) and BuLi (2.4ml of 1.6M solution in hexane, 3.8mmol) was added under a nitrogen atmosphere at 0^oC. Sulfur dichloride (0.1ml, 1.6mmol) in diethyl ether (5 ml) was added. The solution was ~~left to~~ stirred at ambient temperature for 2h. The solution was diluted with ether (60ml). A white precipitate (0.22g) was filtered off. The solution was washed with water (3x50ml) and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield white crystals. The crystals were washed with 60-80^o petroleum ether to remove unreacted carborane, then recrystallised from a 50:50 benzene-~~–~~hexane mixture (0.36g, 49%).~~:~~ ~~m~~M.p. 237^{o}C. Found C, 41.0; H, 6.5; $C_{16}H_{30}B_{20}S$ requires C, 40.8; H, 6.4. EI-MS 452-476 (with characteristic carborane isotope pattern). δ_H 7.6-7.2 (phenyl), 3.8-0.8 (BH). δ_B -1.3 (1B), -3.2 (1B), -9.8 (6B), -12.0 (2B).

Preparation of **3**

To a solution of 1-phenyl-*ortho*-carborane (925mg, 4.2 mmol) in dry ether (40ml) at 0^oC was added nBuLi in hexanes (1.6ml, 2.7M, 4.2 mmol), and this was stirred under N_2 for 1h. $SOCl_2$ (0.19ml, 2.1 mmol) was added, forming a white precipitate (LiCl). After warming to room temperature, the solid was removed by filtration, and the ether evaporated, leaving a white solid. Pure **3** was obtained by recrystallisation from a mixture of ethyl acetate and cyclohexane (1:9), affording colourless crystals. (0.35g, 34%). M.p. 262^{o}C. Found C, 39.7; H, 6.3; $C_{16}H_{30}B_{20}SO$ requires C, 39.5; H, 6.2. EI-MS 484-489 (with characteristic carborane isotope pattern). δ_H 7.4-7.2 (phenyl), 3.8-0.8 (BH). δ_B 1.5 (1B), -3.1 (1B), -8.6 (6B), -11.7 (2B). δ_C 131.9, 131.3, 128.8, 128.5, 92.3, 87.3.

Reduction of **3**

Hydrogen gas was slowly bubbled through a stirred suspension of **3** (84mg, 0.17 mmol) and 10% palladium on carbon (15mg) in acetic acid (10ml) for 15h. Removal of the solvent from the filtered solution gave crystalline **1** (54mg, 66%).

Preparation of **4**

Ortho-carborane (1.11g, 7.72 mol) was dissolved at 0°C in dry ether (30ml) under N_2 and nBuLi in hexanes (6.4ml, 2.42 M, 15.4 mmol) was added, precipitating white 1,2-dilithio-*ortho*-carborane. After 15 min stirring, SCl_2 (0.50ml, 811 mg, 7.9 mmol) was added and the reaction was left to warm to room temperature over 1h. Water (30 ml) was added and the ether layer was further washed before being isolated and dried over $MgSO_4$. Filtration and removal of the solvent gave a white solid which was sublimed *in vacuo* at 40°C to remove unreacted *ortho*-carborane, then at 100°C to give a white powder identified as pure **4**. 73.6 mg (5%). M.p. 122°C. Found C, 14.0; H, 5.9; $C_4H_{20}B_{20}S_2$ requires C, 13.8; H, 5.8. EI-MS, 346-352 (typical carborane isotope pattern).

Formatted: Font: Italic

Attempted synthesis of **5**

Ortho-carborane (0.723g, 5.02 mmol), was dissolved at 0°C under N_2 in dry ether (30ml) and nBuLi in hexanes (4.3ml, 2.42M, 10.4 mmol) was added, precipitating white 1,2-dilithio-*ortho*-carborane. After 15 min stirring, $SOCl_2$ (0.37ml, 5.07mmol) was added and the reaction was left to warm to room temperature overnight. Water (30 ml) was added, dissolving the nascent LiCl, and the ether layer was washed with further water (2 x 30ml) before being isolated and dried over $MgSO_4$. Removal of the solvent *in vacuo* gave a white solid. This was sublimed *in vacuo* at 50°C to remove unreacted *ortho*-carborane. The unsublimed material contained **5**, based on mass spectroscopy with a carborane peak pattern observed at 375-381 (EI-MS). Purification attempts of the white powder (458mg) were unsuccessful – several solvents were shown by boron NMR spectroscopy to degrade the carborane cages.

Formatted: Font: Italic

Formatted: Font: Italic

Crystallography

Single-crystal diffraction experiments (Table 3) for **1** and **3** were carried out on a Rigaku AFC6S 4-circle diffractometer, for **2** on a Stoe STADI4 4-circle diffractometer using graphite-monochromated Mo-K_α (**1**) and Cu-K_α (**2**,**3**) radiation. The structures were solved by direct methods and refined by full-matrix least-squares methods with F^2 of all unique data, using SHELXTL software. Hydrogen atoms positions were freely refined (except for the phenyl groups in **3**, in which they were constrained with a riding model). Structure **2** has been reported elsewhere.[14] The non-standard lattice setting used therein can be transformed by the operation (0,0,1 / -1,0,0 / 0,-1,0) to give the reduced cell a=10.511(5), b=11.579(3), c=12.917(4) Å, α=85.09(3), β=69.05(3), γ=77.72(3). The volume of this cell, 1434.5(9) $Å^3$, is *ca* 0.8% larger than found by us, although both experiments were carried out at room temperature. Full crystallographic data, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre, CCDC nos. 269295, 269296 and 269297.

Formatted: Font: Not Bold

Table 3. Crystallographic data

	1	**2**	**3**
Chemical formula	$C_{16}H_{30}B_{20}S$	$C_{16}H_{30}B_{20}S_2$	$C_{16}H_{30}B_{20}OS$
Formula weight	470.7	502.7	486.7
T (K)	150	293	296
λ (Å)	0.71073	1.54184	1.54178
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a (Å)	10.806(2)	10.475(1)	9.783(1)
b (Å)	17.727(4)	11.549(1)	10.360(1)
c (Å)	13.916(3)	12.900(1)	15.167(1)
α (°)	90	85.070(5)	91.94(1)
β (°)	97.81(3)	69.041(6)	95.61(1)
γ (°)	90	77.637(5)	116.10(1)
V, (Å^3)	2641(1)	1423.5(2)	1368.7(2)
Z	4	2	2
D_{calc} (g cm^{-3})	1.184	1.173	1.181
μ (mm^{-1})	0.13	1.72	1.11
Reflections collected	6644	3569	5900
Independent reflections	6325	3569	4999
R_{int}	0.030		0.018
R (F, F^2>2σ)	0.060	0.054	0.049
R_w (F^2, all data)	0.234	0.166	0.131
Goodness-of-fit on F^2	1.05	1.04	1.08
El. density extremes (eÅ^{-3})	0.60, –0.49	0.65, –0.24	0.31, –0.42

~~[Also Crystallography table]~~

Formatted Table

Formatted: Font: Italic

Formatted: Condensed by 6 pt

Formatted: Font: Not Italic

Formatted: Font: Not Italic

Formatted: English (U.K.), Not Raised by / Lowered by

Formatted: Subscript, Not Raised by / Lowered by

Formatted: Font: Not Italic, Superscript

Formatted: Font: Not Italic

Computational Section

The *ab initio* computations were carried out with the Gaussian 03 package.[28] The geometries of **4** and **5** (*cis* and *trans*) were optimised at the HF/6-31G* level with no symmetry constraints. Frequency calculations were computed on these optimised geometries at the HF/6-31G* level and revealed no imaginary frequencies. Optimisation of these geometries were then carried out at the MP2/6-31G* level. Total energies at MP2/6-31G* are -1454.57589 au for **4** and -1604.55461 (*trans*) and -1604.55479 (*cis*) for **5**. The C_4S_2 rings in these geometries are planar.

References

---

1. H. D. Smith, Jr., C. O. Obenland and S. Papetti, *Inorg. Chem.* **1966,** *5*, 1013-15. N. S. Semenuk, S. Papetti and H. Schroeder, *Inorg. Chem.* **1969,** *8*, 2441-4. L. I. Zakharkin and G. G. Zhigareva, *Zh. Obshch. Khim.***1967,** *37*, 2781.
2. L. I. Zakharkin and G. G. Zhigareva, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 1358-60.
3. See for examples, J. Plešek and S. Heřmanek, *Coll. Czech. Chem. Commun.* **1981,** *46*, 687-92. C. Viñas, R. Benakki, F. Teixidor and J. Casabó, *Inorg. Chem.* **1995,** *34*, 3844-5. F. Teixidor, C. Viñas, R. Benakki, R. Kivekäs and R. Sillanpää, *Inorg. Chem.* **1997,** *36*, 1719-1723. F. Teixidor, C. Viñas, J. Casabó, A. M. Romerosa, J. Rius and C. Miravitlles, *Organometallics* **1994,** *13*, 914-19.
4. F. Teixidor, C. Viñas, J. Rius, C. Miravitlles and J. Casabó, *Inorg. Chem.* **1990,** *29*, 149-52. F. Teixidor, A. M. Romerosa, J. Rius, C. Miravitlles, J. Casabó, C. Viñas and E. Sanchez, *J. Chem. Soc., Dalton Trans.* **1990**, 525-9.
5. For examples, see M. Herberhold, H. Yan, W. Milius and B. Wrackmeyer, *Chem. Eur. J.* **2002,** *8*, 388-395. D.-H. Kim, J. Ko, K. Park, S. Cho and S. O. Kang, *Organometallics* **1999,** *18*, 2738-2740. X.-Y. Yu, G.-X. Jin, N.-H. Hu and L.-H. Weng, *Organometallics* **2002,** *21*, 5540-5548. O. Crespo, M. Concepcion Gimeno, P. G. Jones and A. Laguna, *J. Chem. Soc., Chem. Commun.* **1993**, 1696-7. J.-H. Won, H.-G. Lim, B. Y. Kim, J.-D. Lee, C. Lee, Y.-J. Lee, S. Cho, J. Ko and S. O. Kang, *Organometallics* **2002,** *21*, 5703-5712. O. Crespo, M. C. Gimeno, P. G. Jones and A. Laguna, *J. Chem. Soc., Dalton Trans.* **1997**, 1099-1102. J. D. McKinney, H. Chen, T. A. Hamor, K. Paxton and C. J. Jones, *J. Chem. Soc., Dalton Trans.* **1998**, 2163-2168. M. Herberhold, H. Yan, W. Milius and B. Wrackmeyer, *Angew. Chem., Int. Ed. Engl.* **1999,** *38*, 3689-3691.
6. F. Teixidor, J. A. Ayllon, C. Viñas, J. Rius, C. Miravitlles and J. Casabó, *J. Chem. Soc., Chem. Commun.* **1992**, 1279-80. F. Teixidor, J. Casabó, C. Viñas, E. Sanchez, R. Kivekäs and L. Escriche, *Inorg. Chem.* **1991,** *30*, 3053-8. F. Teixidor, J. A. Ayllon, C. Viñas, R. Sillanpää, R. Kivekäs and J. Casabó, *Inorg. Chem.* **1994,** *33*, 4815-18. F. Teixidor, J. A. Ayllon, C. Viñas, R. Kivekäs, R. Sillanpää and J. Casabó, *Inorg. Chem.* **1994,** *33*, 1756-61.
7. Search on the Cambridge Structural Database (CSD Version 5.26) February 2005. See F. H. Allen, *Acta Crystallogr., Sect. B* **2002**, 58, 380-8.
8. L. I. Zakharkin, N. F. Shemyakin, A. V. Polyakov, A. I. Yanovskii and Y. T. Struchkov, *Zh. Obshch. Khim.* **1987,** *57*, 611-16.
9. D. A. Brown, W. Clegg, H. M. Colquhoun, J. A. Daniels, I. R. Stephenson and K. Wade, *J. Chem. Soc., Chem. Commun.* **1987**, 889-91.
10. R. Coult, M. A. Fox, W. R. Gill, K. Wade and W. Clegg, *Polyhedron* **1992,** *11*, 2717-21.
11. L. A. Boyd, W. Clegg, R. C. B. Copley, M. G. Davidson, M. A. Fox, T. G. Hibbert, J. A. K. Howard, A. Mackinnon, R. J. Peace and K. Wade, *Dalton Trans.* **2004**, 2786-2799.
12. W. Clegg, H. M. Colquhoun, R. Coult, M. A. Fox, W. R. Gill, P. L. Herbertson, J. A. H. MacBride and K. Wade, *Spec. Publ. – R. Soc. Chem.* **1994,** *143*, 232-5.
13. For examples see, Z.G. Lewis and A.J. Welch, *Acta Cryst. C*, 1993, **49**, 705; T.D. McGrath and A.J. Welch, *Acta Cryst. C* 1995, **51**, 646; T.D. McGrath and A.J. Welch, *Acta Cryst. C* 1995, **51**, 651. T.D. McGrath and A.J. Welch, *Acta Cryst. C* 1995, **51**, 654; T.D. McGrath and A.J. Welch, *Acta Cryst. C* 1995, **51**, 649. R.L. Thomas and A.J. Welch, *Polyhedron*, 1999, **18**, 1961.

---

14. A. Laromaine, F. Teixidor, R. Kivekäs, R. Sillanpää, R. Benakki, B. Grüner and C. Viñas, *Dalton Trans.*, **2005**, 1785.
15. F. Teixidor, P. Angles and C. Viñas, *Inorg. Chem.* **1999,** *38*, 3605-3608. J. J. Schaeck and S. B. Kahl, *Inorg. Chem.* **1999,** *38*, 204-206. Y.-J. Lee, J.-D. Lee, J. Ko, S.-H. Kim and S. O. Kang, *Chem. Commun.* **2003**, 1364-1365.
16. W. Clegg, R. Coult, M. A. Fox, W. R. Gill, J. A. H. MacBride and K. Wade, *Polyhedron* **1993,** *12*, 2711-17.
17. R. Kivekas, R. Sillanpaa, F. Teixidor, C. Viñas and R. Nuñez, *Acta Cryst. Sect. C* **1994,** *C50*, 2027-30.
18. L.A. Boyd, H. M. Colquhoun, M. G. Davidson, M. A. Fox, W. R. Gill, P. L. Herbertson, T. G. Hibbert, J. A. H. MacBride, R. J. Peace, G. P. Rivers and K. Wade, *Spec. Publ. – R. Soc. Chem.* **1997,** *201*, 289-296. F. Teixidor, C. Viñas, A. Demonceau and R. Nuñez, *Pure Appl. Chem.* **2003,** *75*, 1305-1313.
19. J. Llop, C. Viñas, J. M. Oliva, F. Teixidor, M. A. Flores, R. Kivekäs and R. Sillanpää, *J. Organomet. Chem.* **2002,** *657*, 232-238.
20. M. G. Davidson, T. G. Hibbert, J. A. K. Howard, A. Mackinnon and K. Wade, *Chem. Commun.* **1996**, 2285-2286.R. J. Blanch, M. Williams, G. D. Fallon, M. G. Gardiner, R. Kaddour and C. L. Raston, *Angew. Chem., Int. Ed. Engl.* **1997,** *36*, 504-506. M. J. Hardie and C. L. Raston, *Cryst. Eng. Comm.* **2001**, 3, 162. M. A. Fox and A. K. Hughes, *Coord. Chem. Rev.* **2004,** *248*, 457-476.
21. A. R. Turner, H. E. Robertson, K. B. Borisenko, D. W. H. Rankin and M. A. Fox, *Dalton Trans.* **2005**, 1310-1318.
22. E. S. Alekseyeva, M. A. Fox, J. A. K. Howard, J. A. H. MacBride and K. Wade, *Appl. Organomet. Chem.* **2003,** *17*, 499-508.
23. A. S. Batsanov, M. A. Fox, T. G. Hibbert, J. A. K. Howard, R. Kivekäs, A. Laromaine, R. Sillanpää, C. Viñas and K. Wade, *Dalton Trans.* **2004**, 3822-3828.
24. O. Crespo, M. C. Gimeno and A. Laguna, *Polyhedron* **1999,** *18*, 1279-1283.
25. R. Kivekäs, M. A. Flores, C. Viñas and R. Sillanpää, *Acta Cryst. Sect. C* **2002,** *C58*, o570-o571.
26. J.D. McKinney, T.A. Hamor, C.J. Jones and K. Paxton, *Polyhedron*, 1997, **16**, 1819.
27. A. Laromaine, C. Viñas, R. Sillanpää and R. Kivekäs, *Acta Cryst. Sect. C* **2004,** *C60*, o524-o526.
28. Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.