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# Preparative and structural studies on sulfur-linked carborane icosahedra: 2-Phenyl-*ortho*-carboranyl-sulfur systems $(2-Ph-1,2-C_2B_{10}H_{10})_2X$ (X = S, S<sub>2</sub> or SO), and *ortho*-carboran-di-yl systems $(1,2-C_2B_{10}H_{10}Y)_2$ (Y = S or SO)

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Dedicated to Malcolm Chisholm on the occasion of his 60th birthday.

#### Abstract

Details are reported of the preparation and X-ray structural characterisation of the new compounds  $(PhCb^{\circ})_2X$ , where  $PhCb^{\circ} = 2$ -Ph-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> and X = S (1) or SO (3), prepared from PhCb<sup>o</sup>Li and SCl<sub>2</sub> or SOCl<sub>2</sub> respectively, as well as the known compound with X = S<sub>2</sub> (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  $\pi$ -bonding from their sulfur atoms to the cage hypercarbon atoms and weak *exo*  $\pi$ -bonding from the phenyl groups. Attempts to prepare systems (Cb<sup>o</sup>Y)<sub>2</sub>, in which two *ortho*-carboran-di-yl residues Cb<sup>o</sup> are linked through two bridging units Y (S, SO) are also reported, as are their calculated structures.

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Keywords: Carborane; Sulfur; Thionyl chloride; Cycles; Crystal structure

# 1. Introduction

Researches into carboranes with cage C–sulfur substituents were originally developed in the 1960s [1–4] 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 [1–8]. Derivatives  $Cb^{\circ}(SR)_2$  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 [9,10]. Where SR is SH they can be used as precursors to form [*closo*-RC<sub>2</sub>B<sub>10</sub>H<sub>10</sub>S]<sup>-</sup> or [*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>S<sub>2</sub>]<sup>2-</sup> anionic residues [11–18]. They have also

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been used as precursors from which  $[nido-C_2B_9H_9(SR)_2]^{2-}$  anionic residues, offering yet further ligand potential, can be prepared [19–22].

Although many C-sulfur *ortho*-carboranes are now listed in the Cambridge Structural Database [23], it is perhaps surprising to find that there is only one reported compound, [Cb<sup>o</sup>SCb<sup>o</sup>SiMe<sub>2</sub>] [24], 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 carborandi-yl residues [24]. One other compound, (MeCb<sup>o</sup>)<sub>2</sub>S, with a sulfur bridge between *ortho*-carboranyl residues has been reported [4] 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  $\pi$ -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 [25-27]. Our own published work so far has concentrated on one-cage systems and here we extend our investigation to the effect of one  $\pi$ -donating atom connected to two ortho-carborane cages. We prepared systems  $(PhCb^{\circ})_{2}X (X = S(1), S_{2}(2) \text{ or } SO(3))$  in which the second cage carbon atom bore a phenyl substituent [26,28], 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) [29-34]. We also explored the synthesis of heterocyclic systems (Cb<sup>o</sup>Y)<sub>2</sub> (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 Fig. 1 for representative structures of (1)–(5).)

A very recent paper [35] by Viñas, 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.



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

#### 2. Results and discussion

#### 2.1. Preparative aspects

The new compounds (1) and (3) prepared in the present work were made from the lithio-carborane PhCbºLi with SCl<sub>2</sub> and SOCl<sub>2</sub>, 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 [36–38]. 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<sup>o</sup>Li with sulfur and then oxidised with iodine [4].

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.

#### 2.2. Structural aspects

# 2.2.1. Systems $(PhCb^{o})_{2}S$ , $(PhCb^{o}S_{2}, (PhCb^{o}S)_{2}S$ and $(PhCb^{o})_{2}SO$

Compounds 1–3, like the related trisulfide  $(PhCb^{\circ}S)_{2}S$  we have described elsewhere [27], all adopt orientations of their *exo*-SR units, and have cage C–C and *exo* C–S distances, consistent with significant dative S=C  $\pi$ -bonding from their *exo*-sulfur atoms to their cage hypercarbon atoms (see Figs. 2–4 and Table 1, which lists selected bond distances and angles for compounds 1–3 and the trisulfide (PhCb^{\circ}S)\_{2}S). For compound 1 the *exo* bonds C–S–C lie in a plane roughly perpendicular to the C(2)–C(1)–S plane whereas for 2,



Fig. 2. Molecular structure of 1, showing thermal ellipsoids at 50% probability level.



Fig. 3. Molecular structure of 2.

**3** and the trisulfide these bond orientations depart more from perpendicular (see torsion angle C–S–C/S in Table 1). We recently showed, in our discussion of a series of systems PhCb<sup>o</sup>Z showing *exo* C=Z  $\pi$ -bonding (including the trisulfide (PhCb<sup>o</sup>S)<sub>2</sub>S), that such a perpendicular orientation optimised *exo*  $\pi$ -bonding [27].

The phenyl substituent on C(2) in compounds 2 and 3 also lies in a plane roughly perpendicular to the plane C(2)-C(1)-S, whereas in 1 and the trisulfide the orientations depart more from perpendicular. A perpendicular orientation minimises non-bonding repulsions with the



Fig. 4. Molecular structure of 3.

other substituent on C(1), and maximises the opportunity for dative  $\pi$ -bonding from the  $\pi$ -system of the phenyl group to the carborane cage [39,40].

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  $\pi$ -bonding substituents on the cage hypercarbon atoms [27,41-43]. Its length increases as *exo*  $\pi$ -bonding increases. Steric effects have previously been invoked to explain the lengthening of the cage C-C bond in various disubstituted-ortho-carboranes [29-34]. 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 [44-47] and by gas-phase electron diffraction and calculational studies [48]. Attachment of a phenyl substituent to one carbon atom, oriented (as here) so that its ring plane is roughly perpendicular to the C(1)-C(2)-C(phenyl) plane, increases the cage C(1)-C(2) distance by some 0.04 Å to 1.66 Å [49]. In compound 2 (Table 1), where the orientations of the sulfur and phenyl substituents offer greater exo  $\pi$ -bonding effects compared to the trisulfide, the C(1)-C(2) distance is 1.755(4) 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) A, as expected for orientations of the substituents which lead to less effective *exo*  $\pi$ -bonding.

Surprisingly, compounds 1 and 2 have similar C(1)– C(2) and C(1)–S distances, suggesting a similar degree of S=C  $\pi$ -bonding in these two compounds. We had expected there to be weaker S=C  $\pi$ -bonding in 1, where both carborane cages are attached to the same sulfur atom, and so competing for  $\pi$ -electron density from the same source. The C–S–C angle in 1 (112.8(1)°) is significantly greater than the C–S–S angle in 2 (105.5(2)°) which is due to steric repulsion between the two cages. Intramolecular B–H····H–B distances between the two A.S. Batsanov et al. | Polyhedron 25 (2006) 300-306

Table 1

Selected bond distances (Å) and angles (°) (averaged where variations are statistically insignificant) in X-ray structures of C-sulfur ortho-carboranes

Compound	$(PhCb^{o})_{2}S(1)^{a}$	$(PhCb^{o})_{2}S_{2} (2)^{a}$	$(PhCb^{o}S)_{2}S^{b}$	(PhCb <sup>o</sup> ) <sub>2</sub> SO (3) <sup>a</sup>	PyCb <sup>o</sup> SH <sup>c</sup>	PhCb <sup>o</sup> SH <sup>b,d</sup>
C(1)–C(2)	1.751(3)	1.755(4)	1.735(3)	1.729(3)	1.730(3)	1.729
C(1)–S	1.789(2)	1.796(3)	1.788(3)	1.859(2)	1.775(2)	1.782
C(2)–C(Ph)	1.510(3)	1.499(5)	1.499(3)	1.505(3)	$1.507(3)^{e}$	1.495
C(1)-B(3)/(6)	1.725(10) <sup>g</sup>	1.709(5)	1.716(4)	1.722(10) <sup>g</sup>	1.720(3)	1.705
C(1)-B(4)/(5)	1.714(11) <sup>g</sup>	1.698(5)	$1.702(7)^{g}$	1.700(3)	1.709(3)	1.700
C(2)-C(1)-S	116.1(2)	114.6(2)	115.9(2)	110.7(1)	117.7(1)	117.5
			117.6(2)	106.0(1)		
$C(1)-S-E^{f}$	112.8(1)	105.5(1)	105.4(1)	106.2(1)	96(1)	95.1
$C(2)-C(1)-S-E^{f}$	99.1(2)	108.0(2)	123.3(2)	-124.2(1)	99(2)	96.8
	97.1(2)	113.1(2)	-96.1(2)	160.4(1)		
$C(1)-C(2)/Ph^h$	74.5(3)	81.7(3)	73.7(2)	87.6(1)	$84.3(2)^{e}$	88.7
		88.9(3)		89.0(1)		

<sup>a</sup> This work. <sup>b</sup> Ref [27]

<sup>b</sup> Ref. [27].

<sup>c</sup> Ref. [50], low-temperature structure.

<sup>d</sup> MP2/6-31G\* calculation.

<sup>e</sup> Py for Ph.

<sup>f</sup> E = C (1, 3), S (2).

<sup>g</sup> Shows statistically significant variations, individual e.s.d.'s 0.003–0.004 Å, which relate to the orientation of the group at sulfur.

<sup>h</sup> Calculated as the angle between the Ph (Py) ring and the C1–C2–C(Ph/Py) moiety.

cages are 2.27, 2.40 and 2.49 Å. Interestingly, the C(1)–C(2) bond in **2** is some 0.03 Å longer than in PyCb<sup>o</sup>SH (X-ray [50]) and PhCb<sup>o</sup>SH (calc [27]) which suggests that the disulfur bridge (S–S) is a more effective  $\pi$ -bond donor to the *ortho*-carborane cage than is a thiol (S–H) group.

The C(1)–C(2) and C(1)–S distances in compound 3, (PhCb<sup>o</sup>)<sub>2</sub>SO (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 $\rightarrow$ C exo  $\pi$ -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  $\pi$ -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 [35], only two neutral RCb<sup>o</sup>SR' systems have been structurally characterised: HCb<sup>o</sup>Spy [51] (Py = 2'-pyridyl) and MeCb<sup>o</sup>SPh [52] with C–S distances of 1.78 A and cage C(1)-C(2) distances of 1.64 and 1.71 Å, respectively.

# 2.2.2. 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  $\pi$ -bonding substituents for which structures had separately been determined by X-ray studies [27]. Selected bond distances and angles are listed in Table 2, which also gives comparable bond distances and angles determined crystallographically for the compound (Cb<sup>o</sup>SCb<sup>o</sup>SiMe<sub>2</sub>) [24].

The C–C bond length of 1.62 Å in the calculated structure of **4** (see Fig. 5) is identical to that of parent *ortho*-carborane [48]. This may reflect both ring strain in the C<sub>4</sub>S<sub>2</sub> heterocycle and inappropriate orientations of the bonds at sulfur for *exo* dative  $\pi$ -bonding to the cage C–C bond. The reported crystal structure of a related heterocycle, Cb<sup>o</sup>S<sub>2</sub>C=S, has a cage C–C bond length of 1.632(3) Å [53]. These lengths contrast with long cage C(1)–C(2) distances of 1.80 Å reported for neutral Cb<sup>o</sup>(SR)<sub>2</sub> systems (R = Me or Ph) [43,54]. 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<sup>-1</sup>. As expected, the C–S distance in the sulfoxy compound is longer than that in the sulfide.

Table 2

Selected bond distances (Å) and angles for the compounds (Cb<sup>o</sup>SCb<sup>o</sup>-SiMe<sub>2</sub>), (Cb<sup>o</sup>S)<sub>2</sub> and (Cb<sup>o</sup>SO)<sub>2</sub>

Compound	(Cb°SCb°SiMe <sub>2</sub> ) <sup>a</sup>	$\begin{array}{c} (Cb^oS)_2 \\ (4)^b \end{array}$	$(Cb^{o}SO)_{2}$ $(5)^{b}$	HCb <sup>o</sup> H <sup>c</sup>
C(1)–C(2)	1.652(4)	1.621	1.637	1.62
C(1)–S	1.794(3)	1.800	1.873	
C(1)-B(3)/(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	

<sup>a</sup> Ref. [24].

<sup>b</sup> This work, calculated at MP2/6-31G\*.

<sup>c</sup> Refs. [44–48].



Fig. 5. MP2-optimised geometries for 4 and 5.

#### 3. Conclusions

The monosulfide (PhCb<sup>o</sup>)<sub>2</sub>S and sulfoxide (PhCb<sup>o</sup>)<sub>2</sub>SO in which two phenyl-*ortho*-carborane residues are linked at the cage carbon through a sulfur atom were synthesised simply by reactions of the lithio-*ortho*-carborane PhCb<sup>o</sup>Li 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  $\pi$ -bonding from the sulfur atom and to a lesser extent to  $\pi$ -bonding from the phenyl substituent. By contrast, the C(1)-C(2) bond lengths in the heterocyclic system (Cb<sup>o</sup>S)<sub>2</sub>, in which two C–S–C bridges link pairs of *ortho* carborane icosahedra, are calculated to be similar to the parent *ortho* carborane.

# 4. Experimental

#### 4.1. General

All manipulations were carried out under dry, oxygen-free N<sub>2</sub>. Commercial grade acetic acid, 10% palladium on carbon, SCl<sub>2</sub>, SOCl<sub>2</sub> and *n*-butyllithium in hexanes were used without further purification. Dry Et<sub>2</sub>O 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 [4].

Elemental analyses were performed using Exeter Analytical CE-440 apparatus. <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C NMR spectra were recorded from room-temperature solutions on a Varian Unity 300 MHz spectrometer equipped with the appropriate decoupling accessories. Chemical shift values for <sup>11</sup>B NMR spectra were referenced to external BF<sub>3</sub> · OEt<sub>2</sub>, those for <sup>1</sup>H- and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced to SiMe<sub>4</sub>. <sup>1</sup>H NMR spectra were referenced to residual protio impurity in the solvent (CDCl<sub>3</sub>, 7.26 ppm). <sup>13</sup>C NMR spectra were referenced to the solvent resonance (CDCl<sub>3</sub>, 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.

# 4.2. Preparation of 1

Phenyl-ortho-carborane (0.71 g, 3.2 mmol) was dissolved in diethyl ether (20 ml) and BuLi (2.4 ml of 1.6 M solution in hexane, 3.8 mmol) was added under a nitrogen atmosphere at 0 °C. Sulfur dichloride (0.1 ml, 1.6 mmol) in diethyl ether (5 ml) was added. The solution was stirred at ambient temperature for 2 h. The solution was diluted with ether (60 ml). A white precipitate (0.22 g) was filtered off. The solution was washed with water  $(3 \times 50 \text{ ml})$  and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure to yield white crystals. The crystals were washed with 60-80° petroleum ether to remove unreacted carborane, then recrystallised from a 50:50 benzene-hexane mixture (0.36 g, 49%). M.p. 237 °C. Anal. Calc. for C<sub>16</sub>H<sub>30</sub>B<sub>20</sub>S: C, 40.8; H, 6.4. Found: C, 41.0; H, 6.5%. EI-MS 452-476 (with characteristic carborane isotope pattern).  $\delta_{\rm H}$ 7.6–7.2 (phenyl), 3.8–0.8 (BH).  $\delta_{\rm B}$  –1.3 (1B), –3.2 (1B), -9.8 (6B), -12.0 (2B).

# 4.3. Preparation of 3

To a solution of 1-phenyl-*ortho*-carborane (925 mg, 4.2 mmol) in dry ether (40 ml) at 0 °C was added *n*BuLi in hexanes (1.6 ml, 2.7 M, 4.2 mmol), and this was stirred under N<sub>2</sub> for 1 h. SOCl<sub>2</sub> (0.19 ml, 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. (0.35 g, 34%). M.p. 262 °C. *Anal.* Calc. for C<sub>16</sub>H<sub>30</sub>B<sub>20</sub>SO: C, 39.5; H, 6.2. Found: C, 39.7; H, 6.3%. EI-MS 484-489 (with characteristic carborane isotope pattern).  $\delta_{\rm H}$  7.4–7.2 (phenyl), 3.8–0.8 (BH).  $\delta_{\rm B}$  1.5 (1B), -3.1 (1B), -8.6 (6B), -11.7 (2B).  $\delta_{\rm C}$  131.9, 131.3, 128.8, 128.5, 92.3, 87.3.

#### 4.4. Reduction of 3

Hydrogen gas was slowly bubbled through a stirred suspension of 3 (84 mg, 0.17 mmol) and 10% palladium

#### 4.5. Preparation of 4

ortho-Carborane (1.11 g, 7.72 mol) was dissolved at 0 °C in dry ether (30 ml) under N<sub>2</sub> and *n*BuLi in hexanes (6.4 ml, 2.42 M, 15.4 mmol) was added, precipitating white 1,2-dilithio-ortho-carborane. After 15 min stirring, SCl<sub>2</sub> (0.50 ml, 811 mg, 7.9 mmol) was added and the reaction was left to warm to room temperature over 1 h. Water (30 ml) was added and the ether layer was further washed before being isolated and dried over MgSO<sub>4</sub>. 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. Anal. Calc. for C<sub>4</sub>H<sub>20</sub>B<sub>20</sub>S<sub>2</sub>: C, 13.8; H, 5.8. Found: C, 14.0; H, 5.9%. EI-MS, 346–352 (typical carborane isotope pattern).

### 4.6. Attempted synthesis of 5

Ortho-carborane (0.723 g, 5.02 mmol), was dissolved at 0 °C under N<sub>2</sub> in dry ether (30 ml) and *n*BuLi in hexanes (4.3 ml, 2.42 M, 10.4 mmol) was added, precipitating white 1,2-dilithio-ortho-carborane. After 15 min stirring, SOCl<sub>2</sub> (0.37 ml, 5.07 mmol) 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  $(2 \times 30 \text{ ml})$  before being isolated and dried over MgSO<sub>4</sub>. 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 (458 mg) were unsuccessful - several solvents were shown by boron NMR spectroscopy to degrade the carborane cages.

#### 4.7. 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 $\alpha$  (1) and Cu K $\alpha$  (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 [35]. The non-standard unit cell setting used in that report can be transformed by the

	1	2	3
Chemical formula	C16H30B20S	$C_{16}H_{30}B_{20}S_2$	C <sub>16</sub> H <sub>30</sub> B <sub>20</sub> OS
Formula weight	470.7	502.7	486.7
<i>T</i> (K)	150	293	296
$\lambda$ (Å)	0.71073	1.54184	1.54178
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P\overline{1}$	$P\bar{1}$
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)
$V, (\text{Å}^3)$	2641(1)	1423.5(2)	1368.7(2)
Ζ	4	2	2
$D_{\text{calc}} (\text{g cm}^{-3})$	1.184	1.173	1.181
$\mu (\text{mm}^{-1})$	0.13	1.72	1.11
Reflections collected	6644	3569	5900
Independent reflections	6325	3569	4999
R <sub>int</sub>	0.030		0.018
$R(F, F^2 > 2\sigma)$	0.060	0.046	0.049
$R_w$ ( $F^2$ , all data)	0.234	0.132	0.131
Goodness-of-fit on $F^2$	1.05	1.06	1.08
El. density extremes (e $Å^{-3}$ )	0.60, -0.49	0.18, -0.27	0.31, -0.42

operation  $(001, \overline{1}00, 0\overline{1}0)$  to give the reduced cell a = 10.511(5) Å, b = 11.579(3) Å, c = 12.917(4) Å,  $\alpha = 85.09(3)^{\circ}$ ,  $\beta = 69.05(3)^{\circ}$ ,  $\gamma = 77.72(3)^{\circ}$ . The volume of this cell (1434.5(9) Å<sup>3</sup>) is ca. 0.8% larger than found by us, although both experiments were carried out at room temperature. Our data gave rather lower residual electron density peaks near the sulfur atoms, but these can be successfully refined also as part of a very minor disorder component, with an occupancy of 0.059(3), similar to that recently reported. This disorder has no significant effect on the geometry of the molecule. Overall our results are of greater precision. Full crystallographic data, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 269295, 269296 and 269297.

#### 4.8. Computational section

The ab initio computations were carried out with the GAUSSIAN 03 package [55]. 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 a.u. for 4 and -1604.55461 (*trans*) and -1604.55479 (*cis*) for 5. The C<sub>4</sub>S<sub>2</sub> rings in these geometries are planar.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.poly. 2005.06.046.

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