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Recent studies on $RR'S{\cdot}C_2B_9H_{11}$ charge-compensated ligands Crystal structures of 10-($S(CH_3)_2$)-7,8-$C_2B_9H_{11}$ and 10-($S(CH_2)_4$)-7,8-$C_2B_9H_{11}$

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Abstract

In this paper we report the synthesis of three new carborane derivatives of the series 7,8-R,R′-10-L-7,8-$C_2B_9H_9$ (R = R′ = H, L = SEtPh; R = CH_3, R′ = H, L = SMe_2 and L = SEt_2) along with the enhanced characterization of formerly described compounds 7,8-R,R′-10-L-7,8-$C_2B_9H_9$ (R = R′ = H, L = SMe_2 (**1**), L = SEt_2 (**2**) and L = $S(CH_2)_4$ (**3**)). They have been fully characterised using ^{1}H-, ^{11}B- and ^{13}C-NMR spectroscopy. Their bridging proton resonances have been located for the first time. Individual sulfonium substituent contributions have been calculated that have permitted to establish a rule to predict its position in the ^{1}H-NMR spectrum. The crystal structures of **1** and **3** have been resolved for the first time. Thermolysis of **1**, **2** and **3** in aromatic solvents at reflux temperature yielded a mixture of the corresponding 9-substituted derivative via isomerisation and 2,3-*closo*-$C_2B_9H_{11}$ via elimination of SR_2. This reaction has been demonstrated to be tuneable upon convenient choice of the aromatic solvent, the ligand and the reaction time, leading to a new and more straightforward preparation of the series 9-L-7,8-*nido*-$C_2B_9H_{11}$ and the cluster 2,3-*closo*-$C_2B_9H_{11}$.

Keywords: Zwitterionic clusters; Cluster's isomerization; Nido-carboranylmonosulfonium; Cluster's thermolisis

1. Introduction

The dicarbollide dianions, $[7,8\text{-}C_2B_9H_{11}]^{2-}$ and $[7,9\text{-}C_2B_9H_{11}]^{2-}$, have been extensively used as ligands in organometallic chemistry because of their similarities with the cyclopentadienide ion, $[C_5H_5]^-$, to which are formally isolobal [1]. To certain extent, this analogy is enough to establish comparisons however, discrepancies have been observed as a result of the higher negative charge of the dicarbollide anion. A proper comparison would be with isomeric monoanionic charge-compensated ligands of the type $[LC_2B_9H_{10}]^-$ (L = pyridine, THF, SR_2, PPh_3, OEt_2, etc.) derived from both dicarbollide dianions [2]. Known charge-compensated carborane ligands derived from the *o*-carborane are those of general formula 7-L-8-R-7,8-$C_2B_9H_{10}$, 7-R^1-8-R^2-9-L-7,8-$C_2B_9H_9$, and 7,8-R_2-10-L-7,8-$C_2B_9H_9$ in which the charge-compensating substituent (L) is located on the 7, 9 or 10-position of the open face, respectively (Fig. 1a). On the other hand, isomers derived from the *m*-carborane are also known (Fig. 1b).

The procedure to prepare 10-substituted charge-compensated ligands containing a sulfonium group 10-L-7,8-$C_2B_9H_{11}$ (L = SR_2) has been described by Plesek et al. by treating the *nido*-carborane with the corresponding sulfide in the presence of CH_3CHO and acid [2d]. To prepare the 9-substituted isomer, 9-L-7,8-$C_2B_9H_{11}$, two different methods have been reported: the first one is restricted to L = SMe_2, and consists in the

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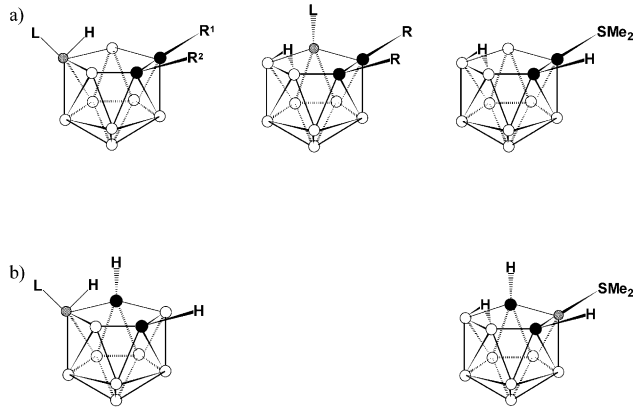
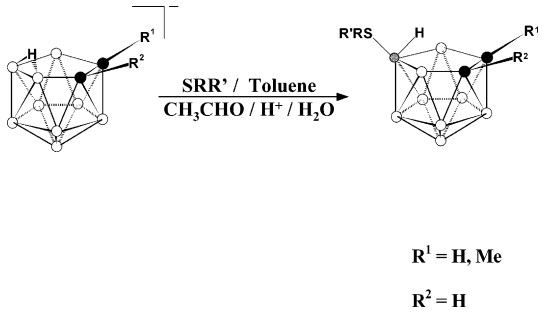


Fig. 1. Schematic representation of the charge-compensated carborane compounds derived from the *o*- and *m*-carborane.



Scheme 1. General reaction for preparing charge-compensated sulfide carborane ligands.

reaction of the *nido*-carborane with DMSO in water in strong acidic media [2b,3] and the second one which is adequate for different L groups, involves the ferric chloride-driven oxidative coupling reaction of [*nido*-7,8-$C_2B_9H_{12}$]$^-$ with an electron pair donor (L) [4]. The last one, however, leads to a mixture of both isomers 9-L-7,8-$C_2B_9H_{11}$ and 10-L-7,8-$C_2B_9H_{11}$ in different ratios depending on L. On the other hand, the 10-L-7,9-$C_2B_9H_{11}$ isomer has been prepared directly by the reaction of *closo*-2,3-$C_2B_9H_{11}$ with L in benzene [2a,5].

In this paper we report the synthesis of three new 10-substituted charge-compensated carborane derivatives and the bridging proton resonances of the previously synthesized [10-L-7,8-$C_2B_9H_{11}$] (L = SRR′) which had not been located in other examples of the series reported. Besides, individual sulfonium substituent contributions have been calculated and a rule has been established to predict its position in the ^{1}H-NMR. Also, a new way to get asymmetric 9-substituted isomers and the 2,3-*closo*-$C_2B_9H_{11}$ by thermolysis of 10-substituted ligands, in aromatic solvents at reflux temperature, is reported. It is also demonstrated that the reaction is fully tuneable upon convenient choice of the temperature and the reaction time.

2. Results and discussion

2.1. Synthesis and characterization of charge-compensated carborane ligands 7-R-10-L-7,8-$C_2B_9H_{10}$

The reaction of K[7-R-7,8-$C_2B_9H_{11}$] (R = H, Me) with SRR′ in the presence of acid and CH_3CHO leads to the formation of charge-compensated carborane ligands.

Following the known Plesek's et al. [2d] procedure (see Scheme 1) 10-SMe_2-7,8-$C_2B_9H_{11}$ (**1**), 10-SEt_2-7,8-$C_2B_9H_{11}$ (**2**), 10-$S(CH_2)_4$-7,8-$C_2B_9H_{11}$ (**3**), and the new ligands 10-SEtPh-7,8-$C_2B_9H_{11}$ (**4**), 7-Me-10-SMe_2-7,8-$C_2B_9H_{10}$ (**5**) and 7-Me-10-SEt_2-7,8-$C_2B_9H_{10}$ (**6**) have been synthesized. All compounds were obtained in good yield as white solids and were fully characterized by elemental analysis and NMR spectroscopies corroborating their formation.

The ^{1}H-NMR spectra of all these charge-compensated ligands show a broad resonance in the negative region, between −0.97 and −1.26 ppm, which collapses to a singlet in the ^{1}H{^{11}B}-NMR spectra. This signal is, in fact, a broad quadruplet due to the ^{1}H–^{11}B coupling (ca. 75 Hz), probably with the B10. This was unexpected since Plesek et al. [2d] previously reported that no sign of B–H–B bridge signal had been found for compounds **1**, **2** and **3**. This resonance is observed at lower field than in non-charge-compensated *nido*-carboranes (ca. −2.50 ppm), perhaps providing some hints about the acidity of the proton. For compounds **1**, **2**, **3** and **4**, broad singlets of intensity 2 were observed between 2.23 and 2.19 ppm, which were assigned to the cage C–H protons. For **5** and **6**, which have a methyl on one carbon cluster, the corresponding C–H signal is found at higher field, 2.11 and 2.10 ppm, respectively. The ^{1}H-NMR spectra of **1** and **5** showed one singlet assigned to the S–CH_3 group. For compounds **2**, **3**, **4** and **6** the S–CH_2 protons are chemically non-equivalent, which is reflected in the ^{1}H-NMR spectra. Two J(H, H) coupling constants, one for the geminal protons (^2J(H, H) ca. 13.5 Hz) and a second one for the neighbor CH_3 or CH_2 protons (^3J(H, H) ca. 7 Hz) were observed. Something similar was already observed by Welch and co-workers in compounds 7,8-Ph_2-10-(SMeEt)-7,8-*nido*-$C_2B_9H_9$ and 7,8-Ph_2-10-SEt_2-7,8-*nido*-$C_2B_9H_9$ [2f]. The ^{13}C{^{1}H}-NMR spectra in addition to the resonances due to the substituents on the molecule, displayed broad resonances in the region between 42.6 and 59.8 ppm, which were attributed to the cluster carbon atoms. The ^{11}B{^{1}H}-NMR spectra of all compounds appear in the region −10.0– −37.0 ppm. Compounds **1**, **2** and **3** display very similar ^{11}B{^{1}H}-NMR spectra showing a six signal 2:2:1:2:1:1 pattern and suggesting a C_s molecular symmetry. Nevertheless, the presence of two different groups bonded to the

sulfur atom, in compound **4**, destroys the C_s symmetry, causing the splitting of one resonance of intensity 2 into two 1:1 [2f]. The $^{11}B\{^1H\}$-NMR spectra of compounds **5** and **6** reflect the molecule asymmetry producing a 1:1:1:2:1:1:1:1 pattern. All these compounds display a resonance near −26 ppm, which has been attributed to the L-substituted B10 atom based on the ^{11}B- and $^{11}B\{^1H\}$-NMR looks. The ^{11}B spectrum of **1**, **2** and **3** was already assigned in the literature by $^{11}B\{^1H\}$–$^{11}B\{^1H\}$ correlated spectroscopy. To assign the ^{11}B resonances of the new compounds **4**, **5** and **6** to specific boron atoms 2D-COSY NMR espectra were performed. This has permitted to draw the diagrams shown in Fig. 2. The asymmetry introduced substituting the 7-position, has modified considerably the look of the spectrum, as shown in Fig. 3.

2.2. Molecular structures of 10-SMe_2-7,8-nido-$C_2B_9H_{11}$ and 10-$S(CH_2)_4$-7,8-nido-$C_2B_9H_{11}$

Although 10-SMe_2-7,8-$C_2B_9H_{11}$ (**1**) and 10-$S(CH_2)_4$-7,8-$C_2B_9H_{11}$ (**3**) had been long ago synthesized by Plesek et al. [2d] their molecular geometry had been assigned only by spectroscopic methods. Considering the relevance these compounds may have as alternatives to Cp, efforts were made to get good crystals suitable of X-ray analysis. In this regard crystals of **1** and **3** were obtained from a solution of chloroform/hexane in a 1/1 ratio.

X-ray analyses of **1** and **3** confirmed that the SMe_2 and $S(CH_2)_4$ substituents are connected to B10 of the *nido* carborane cage. Some selected bond parameters for **1** and **3** and perspective drawings of the ligands are shown in Figs. 4 and 5.

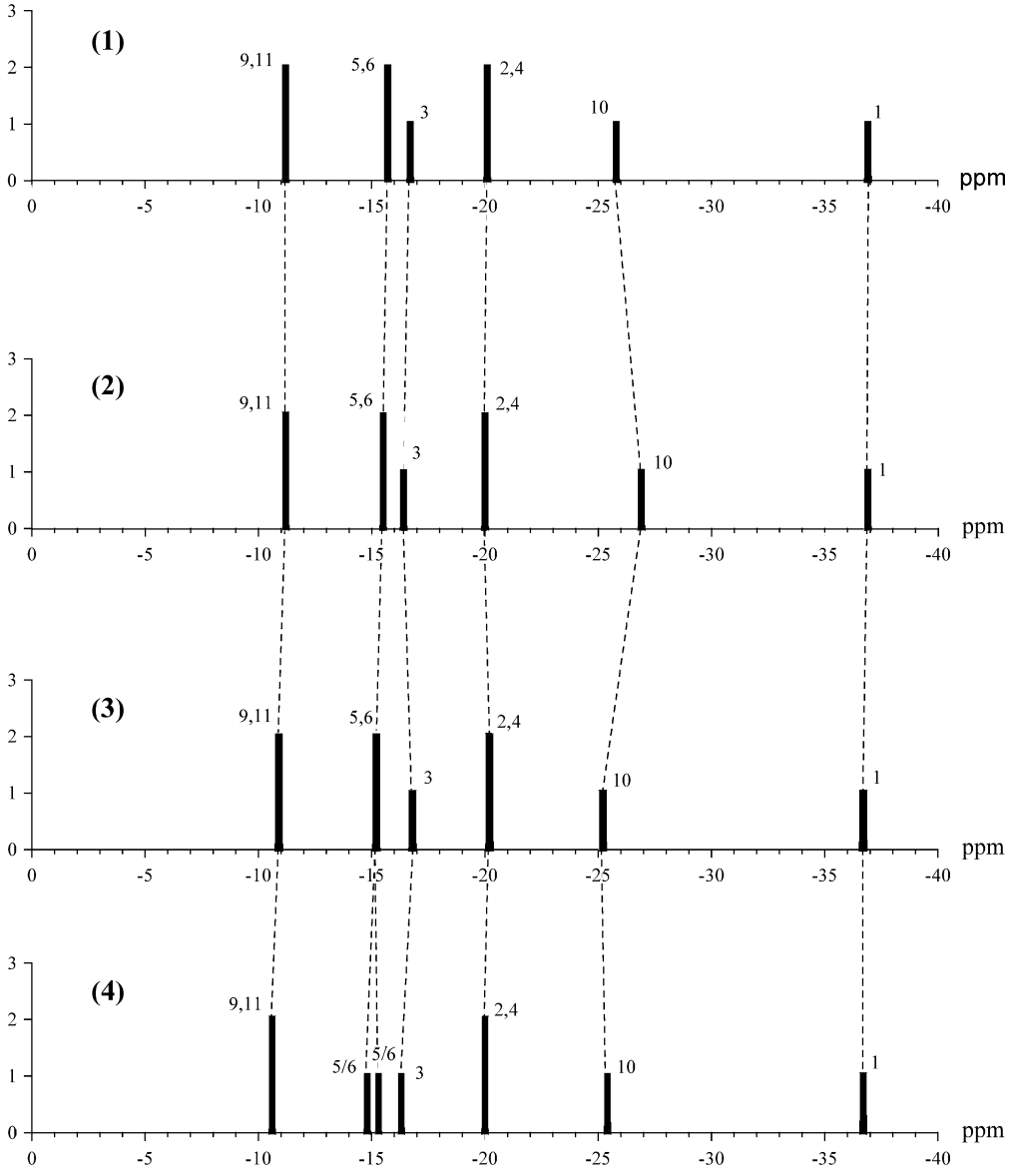


Fig. 2. Representation of the $^{11}B\{^1H\}$ resonances for compounds **1**, **2**, **3** and **4**.

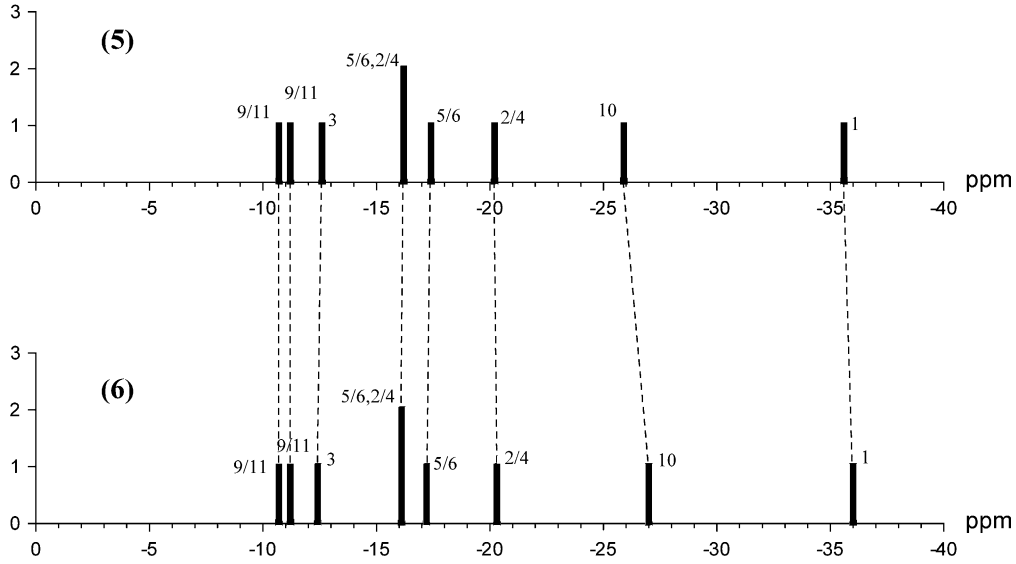


Fig. 3. Representation of the $^{11}B\{^1H\}$ resonances for compounds **5** and **6**.

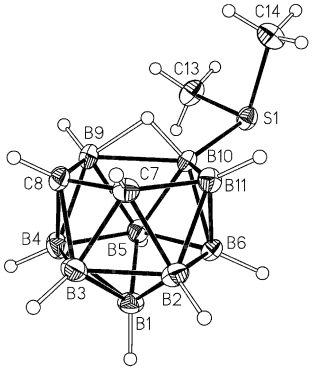


Fig. 4. Perspective drawing of compound **1**. Selected bond lengths (Å) and angles and torsion angles (°): S1–B10 1.895(3), S1–C13 1.804(3), S1–C14 1.798(3), C8–B9 1.612(4), B9–B10 1.853(4), B10–B11 1.792(4), B10–S1–C13 104.01(13), B10–S1–C14 102.92(13), S1–B10–B9 126.05(18), B11–B10–S1 124.35(19), B9–B10–S1–C13 −11.1(3), B11–B10–S1–C14 −55.3(2), C7–C8 1.547(4) distance.

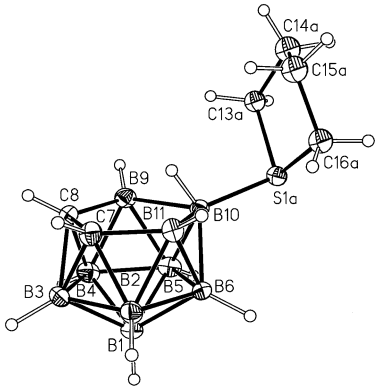


Fig. 5. Simplified drawing of compound **3**. Conformation **B** of the disordered $S(CH_2)_4$ group, having minor occupancy, is omitted. Selected bond lengths (Å) and angles and torsion angles (°): S1a–B10 1.888(4), S1a–C13a 1.833(5), S1a–C16a 1.806(5), C8–B9 1.594(5), B9–B10 1.819(6), B10–B11 1.835(5), C13a–S1a–C16a 94.8(2), B10–S1a–C13a 104.4(2), S1a–B10–B9 122.8(3), S1a–B10–B11 130.4(3), B9–B10–S1a–C13a 39.0(4), B11–B10–S1a–C16a −17.7(4), C7–C8 1.546(5) distance.

In **1**, mutual orientation of the methyl groups with respect to the C_2B_3 open face are different as indicated by the B9–B10–S1–C13 and B11–B10–S1–C14 torsion angle values of −11.1(3) and −55.3(2)°, respectively. Lengthening of the B9–B10 bond (1.853(4) Å) compared with the B10–B11 bond (1.792(4) Å) can be attributed to the orientation of the methyl group C13. The B9–B10 edge carries an asymmetric H-bridge with bond distances B10–H10 = 1.18(2) and B9–H10 = 1.42(2) Å.

In **3**, the $S(CH_2)_4$ ring is disordered assuming two conformations (**A** and **B**) with site occupation parameters 0.773(7) and 0.227(7). The two conformations are partly superimposed and oriented so that the sulphur lone pair of electrons is *anti* to the C_2B_3 open face. Bond lengths to S1 in **1** and **3** agree well with the comparable distances in 9-SMe_2-7,8-$C_2B_9H_{11}$ [6], 7-Ph-11-SMe_2-7,8-$C_2B_9H_{10}$ [2e] and 7,8-Ph_2-10-SMe_2-7,8-$C_2B_9H_9$ [2f] and the C7–C8 distances of 1.547(4) and 1.546(5) Å in **1** and **3** fall in the range normally found for the *nido*-cages bearing H atoms at the cluster carbons.

Nature of the hydrogen atoms at B10 in compounds **1** and **3** is clearly different. In **1** H10 is bridging between B10 and B9 but in **3** H10 is terminal with the B10–H10, B9···H10 and B11···H10 distances of 1.10(3), 1.83(3) and 1.67(3) Å, respectively.

2.3. Prediction of the B–H–B chemical shift for charge-compensated ligands in the ^{1}H-NMR

The B–H–B chemical shift in charge-compensated ligands 10-SRR′-7-R1-8-R2-7,8-$C_2B_9H_{11}$ has been shifted to lower field with regard to their *nido*-*o*-carborane derivative precursors (Table 1). This could be expected considering that in 10-SRR′-7,8-$C_2B_9H_{11}$ the open face proton is mainly located on the B10 atom which has an electron-withdrawing substituent (SRR'^+). Therefore the B–H–B chemical shift in the ^{1}H-NMR will be affected by changes on B10 and, given the case, its position in the ^{1}H-NMR spectrum could be calculated by considering additive individual contributions. Indeed this seems to work this way and the chemical shifts can be reasonably well calculated. Table 2 contains the calculated contribution of each group, which appears to be independent of the different starting *nido*-*o*-carborane derivative whether it is *o*-carborane or methyl-*o*-carborane. The computed individual values permit us to predict the B–H–B chemical shift for other charge-compensated carborane ligands, that otherwise could be difficult to be distinguished in the ^{1}H-NMR spectrum due to the overlap with other cluster B–H protons. In this regard, Welch and co-workers [2f] have prepared charge-compensated ligands derivatives of the 7,8-Ph_2-7,8-$C_2B_9H_{10}$ for which the open face B–H–B position in the ^{1}H-NMR has not been discussed. The B–H–B chemical shifts of these compounds in the ^{1}H-NMR spectra therefore could be calculated by using the additive method suggested here (see Table 1).

2.4. Isomerization by the temperature

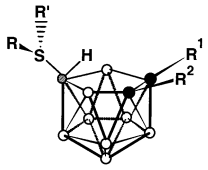
Thermolysis of **1**, **2** and **3** in mesitylene (b.p. = 163 °C) and xylene (b.p. = 140 °C) at refluxing temperature has been carried out and monitored (see Tables 3 and 4). Scheme 2 shows the results of the thermolysis of **2** in mesitylene for 1 h, which leads to the formation of two compounds. No attempt was made to isolate the new generated species however, they were identified in solution by ^{11}B{^{1}H}-NMR. The two species were 9-SEt_2-7,8-$C_2B_9H_{11}$ (**7**) and the cluster *closo*-2,3-$C_2B_9H_{11}$ (**8**). We can extend this procedure to other members of the series finding that the rate and ratio of products obtained depend on the starting compound, the solvent used, and the reaction time.

Thermolysis of **1**, **2** and **3** in mesitylene was followed by ^{11}B{^{1}H}-NMR spectroscopy (see Section 3). Again, the rate and percentage of isomerization in these compounds depends clearly on the substituent (SR_2) bonded to the B10 atom in the cluster. For (**1**) (L = SMe_2) the reaction is very fast (see Fig. 6) and after 40 min, the starting compound has been completely converted into the isomer 9-SMe_2-7,8-$C_2B_9H_{11}$ (**9**) and the *closo*-species (**8**) in a ratio 32:68, respectively. We can also observe that after 5 h of reaction only the *closo*-species (**8**) is in solution (Fig. 7). This implies that the *closo*-species is generated from **9**, however, we do not have any conclusive evidence whether **8** can also be generated directly from the 10-substituted isomer **1**. For (**2**) (L = SEt_2) the reaction is slower as after 2 h there is a 1:1 formation of **7** and **8**. When the reaction is left to go for several hours, the 9-substituted isomer **7** is trans-

Table 1
Experimental and predicted B–H–B chemical shift in the ^{1}H-NMR spectrum for charge-compensated carborane compound [10-L-7-R^1-8-R^2-7,8-$C_2B_9H_9$]

L	R^1	R^2	δ_{B-H-B} (ppm)	Predicted δ (ppm)
–H	H	H	−2.90	–
–Sme_2	H	H	−1.17	−1.17
–SEt_2	H	H	−1.26	−1.26
–$S(CH_2)_4$	H	H	−1.19	−1.19
–SEtPh	H	H	−0.98	−0.98
–H	CH_3	H	−2.71	–
–Sme_2	CH_3	H	−0.97	−0.98
–SEt_2	CH_3	H	−1.07	−1.07
–H	Ph	Ph	−1.71	–
–Sme_2	Ph	Ph	–	0.02
–SMeEt	Ph	Ph	–	−0.02
–SEt_2	Ph	Ph	–	−0.07

Table 2
Individual contribution of the sulfonium substituent ($\Delta\delta$) B–H–B chemical shift in the ^{1}H-NMR spectrum



Substituents R/R′	$\Delta\delta$ (ppm)
–Me	0.86
–Et	0.82
–$(CH_2)_2$–	0.85
–Ph	1.10

Table 3
Thermolysis of ligands **1**–**3** in xylene

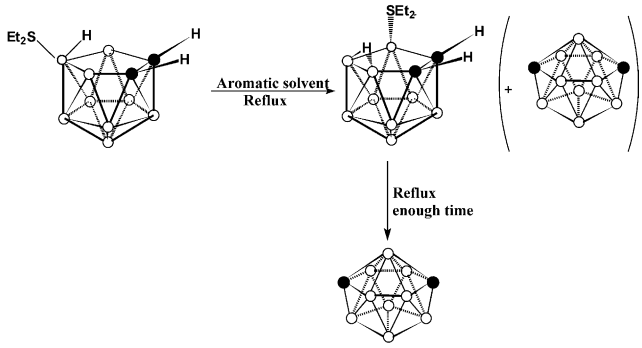
Time (min)	Ligand **1**		Ligand **2**		Ligand **3**	
	% **9**	% **8**	% **7**	% **8**	% **10**	% **8**
10	5	1	3	0	3	0
40	12	9	8	0.5	12	0
120	22	46	23	3	32	0
300	28	66	47	6	58	0

Percentage of 9-isomers and 2,3-*closo*-$C_2B_9H_{11}$ at different times.

Table 4
Thermolysis of ligands **1**–**3** in mesitylene

Time (min)	Ligand **1**		Ligand **2**		Ligand **3**	
	% **9**	% **8**	% **7**	% **8**	% **10**	% **8**
10	31	25	15	15	33	2
40	35	65	48	40	74	6
120	19	81	49	49	83	11
300	7	93	–	–	79	16

Percentage of 9-isomers and 2,3-*closo*-$C_2B_9H_{11}$ at different times.



Scheme 2. Isomerization of 10-SEt_2-7,8-$C_2B_9H_{11}$ in aromatic solvents.

formed to **8**. Compound (**3**) (L = $S(CH_2)_4$) behaves a little bit different mainly producing the 9-isomer [9-$S(CH_2)_4$-7,8-$C_2B_9H_{11}$] (**10**) (83%) after 2 h of thermolysis, however, as for the other members (given enough time), it is transformed into the *closo*-species.

No difference is observed when **1** is refluxed in xylene, since it leads to the same results as those obtained in mesitylene although, in this case, the reaction occurs more slowly. Different results have been obtained for **2** and **3**. In both cases, the reaction leads mainly to 9-substituted isomers, a 90% for ligand **2** and 100% for ligand **3**. For the latter, no formation of *closo*-species (**8**) is observed at any time as can be observed from the graphic in Fig. 8.

Zakharkin et al. had described positional isomerization by protonation/deprotonation reaction [7]. The procedure reported in this paper is based on sulfonium derivatives while Zakharkin's was applied only to alkyl derivatives. Similar conditions leaded to the *closo*-2,3-$C_2B_9H_{11}$ from $[7,9\text{-}C_2B_9H_{12}]^-$ in a 36% yield [2a]. Nevertheless, the best synthetic method till now was by thermolysis of $[Ni(7,8\text{-}C_2B_9H_{12})_2]$ at 300 °C in a nitrogen atmosphere with a 41% yield [2b].

As a conclusion, it appears that open face positional isomers of X-SRR′-7-R^1-8-R^2-7,8-$C_2B_9H_9$ (X = 9, 10) can be synthesized according to the needs. Probably the 10-SRR′-isomer is the kinetically more stable while the 9-SRR′-isomer is the thermodynamically preferred. Therefore controlled thermolysis of 10-SRR′-isomer leads to the respective 9-SRR′-isomer. However, when

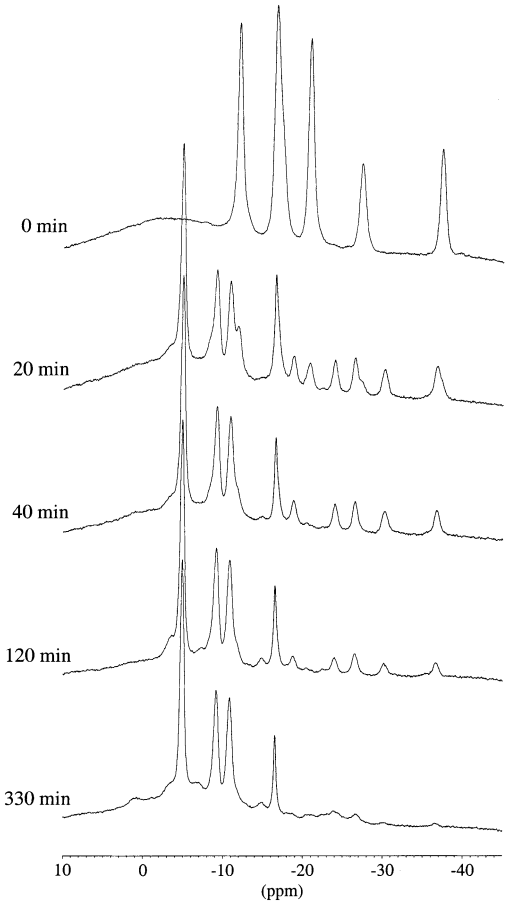


Fig. 6. $^{11}B\{^1H\}$-NMR spectra corresponding to the thermolysis reaction of **1** in mesitylene at different times.

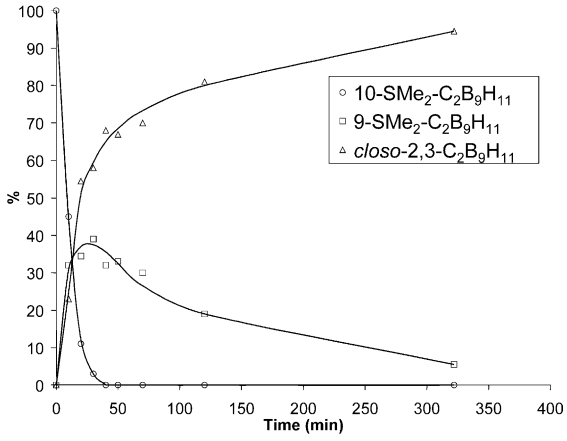


Fig. 7. Thermolysis of compound **1** in mesitylene.

$R^1 = R^2 = H$, the latter is susceptible to undergo SRR′ cleavage followed by a rearrangement to *closo*-2,3-$C_2B_9H_{11}$. It is thus clear that *closo*-2,3-$C_2B_9H_{11}$ originates from 9-SRR′-isomer, but we cannot rule out that, additionally, it may also be originated from the 10-SRR′-isomer. By tuning up the reaction conditions, mainly the temperature, the 9-SRR′-isomers free of *closo*-2,3-$C_2B_9H_{11}$ can be synthesized. These studies

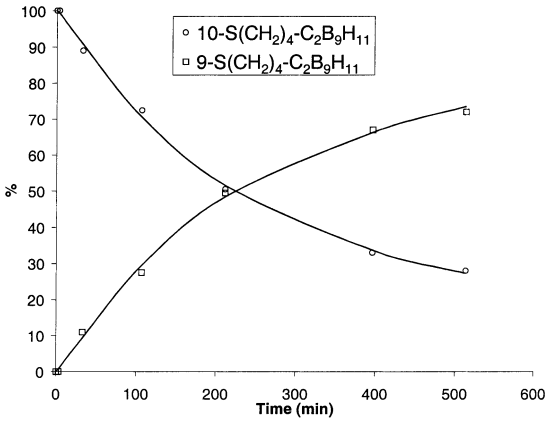


Fig. 8. Thermolysis of compound **3** in xylene.

bring about the possibility to generate different positional isomers with different substituents, and we expect that the method can be of general use. These compounds have the same charge as the Cp or Cp* and can find a good application in catalysis.

We believe that the thermolysis procedure reported here can be precisely controlled and should permit easy reproducibility.

3. Experimental

3.1. Instrumentation

Microanalyses were performed in our analytical laboratory using a Carlo Erba EA1108 microanalyser. IR spectra (ν, cm^{-1}; KBr pellets) were obtained on a Nicolet 710-FT spectrophotometer. The ^{1}H- (300.13 MHz), ^{11}B- (96.29 MHz), and $^{13}C\{^{1}H\}$-NMR (75.47 MHz) spectra were obtained on a Bruker ARX 300 instruments. All NMR measurements were performed in $CDCl_3$ at 22 °C. The ^{11}B-NMR shifts are referenced to external $BF_3 \cdot O(Et)_2$, while the δ ^{1}H and ^{13}C data are referenced to $Si(Me)_4$. Chemical shifts are reported in units of parts per million (ppm). According to the IUPAC convention, positive values of the chemical shifts are to high frequency. All coupling constant values are reported in Hertz.

3.2. Materials

Before use, 1-methyl-*o*-carborane and *o*-carborane (Katchem Ltd. Prague) were sublimed under high vacuum. The 1 M aqueous solution of potassium 7,8-dicarba-*nido*-undecaborate and potassium 7-methyl-7,8-dicarba-*nido*-undecaborate were prepared from *o*-carborane and methyl-*o*-carborane, respectively, according to the method reported previously [8]. The thioethers SMe_2, SEt_2, $S(CH_2)_4$ from Fluka and SEtPh, $^{t}BuOK$ and CH_3CHO from Aldrich were used as purchased. 10-SMe_2-7,8-*nido*-$C_2B_9H_{11}$ (**1**), 10-SEt_2-7,8-*nido*-$C_2B_9H_{11}$ (**2**) and 10-$S(CH_2)_4$-7,8-*nido*-$C_2B_9H_{11}$ (**3**) were synthesized by standard literature methods [2d]. Although compounds **1**–**3** have been already synthesized and characterized, no complete details on their spectroscopic characterization had been reported. These data are reported here. Diethyl ether and $C_6H_5CH_3$ were dried with Na/benzophenone and distilled. EtOH, C_6H_{14} and $CHCl_3$ were dried with molecular sieves. Unless mentioned elsewhere, all reactions were carried out under N_2 atmosphere and used solvents were oxygen free and dry.

3.3. Characterization of 10-SMe_2-7,8-*nido*-$C_2B_9H_{11}$ (**1**)

Following the method described by Plesek et al. [2d], compound **1** was obtained. IR: ν 3014 (C_c–H); 2924 (C–H); 2542 (B–H). ^{1}H-NMR: δ −1.17 (br quadruplet, 1H, $^{1}J(B, H) = 74$, B–H–B); 2.23 (br s, 2H, C_c–H); 2.56 (s, 6H, CH_3). ^{11}B-NMR: δ −11.2 (d, 2B, $^{1}J(B, H) = 144$, B(9,11)); −15.7 (d, 2B, $^{1}J(B, H) = 131$, B(5,6)); −16.7 (d, 1B, $^{1}J(B, H) = 166$, B(3)); −20.1 (d, 2B, $^{1}J(B, H) = 156$, B(2,4)); −25.8 (d, 1B, $^{1}J(B, H) = 74$, B(10)); −36.9 (d, 1B, $^{1}J(B, H) = 144$, B(1)). $^{13}C\{^{1}H\}$-NMR: δ 26.5 (s, CH_3); 46.9 (br s, C_c–H).

3.4. Characterization of 10-SEt_2-7,8-*nido*-$C_2B_9H_{11}$ (**2**)

Following the method described by Plesek et al. [2d], compound **2** was obtained. IR: ν 3028 (C_c–H); 2970, 2936, 2875 (C–H); 2539 (B–H). ^{1}H-NMR: δ −1.26 (br quadruplet, 1H, $^{1}J(B, H) = 79$, B–H–B); 1.56 (dd, 6H, $^{3}J(H_a, H) = 7.0$, $^{3}J(H_b, H) = 7.6$, CH_3); 2.23 (br s, 2H, C_c–H); 2.90 (dq, 2H, $^{2}J(H_a, H_b) = 13.5$, $^{3}J(H_a, H) = 7.0$, S–CH_a (S–CH_2)); 3.02 (dq, 2H, $^{2}J(H_b, H_a) = 13.5$, $^{3}J(H_b, H) = 7.6$, S–CH_b (S–CH_2)). ^{11}B-NMR: δ −11.2 (d, 2B, $^{1}J(B, H) = 142$, B(9,11)); −15.5 (d, 2B, $^{1}J(B, H) = 131$, B(5,6)); −16.4 (d, 1B, $^{1}J(B, H) = 173$, B(3)); −20.0 (d, 2B, $^{1}J(B, H) = 156$, B(2,4)); −26.9 (d, 1B, $^{1}J(B, H) = 79$, B(10)); −36.9 (d, 1B, $^{1}J(B, H) = 146$, B(1)). $^{13}C\{^{1}H\}$-NMR: δ 11.8 (s, CH_3); 34.9 (s, S–CH_2); 46.7 (br s, C_c–H).

3.5. Characterization of 10-$S(CH_2)_4$-7,8-*nido*-$C_2B_9H_{11}$ (**3**)

Following the method described by Plesek et al. [2d], compound **3** was obtained. IR: ν 3029 (C_c–H); 2940, 2865 (C–H); 2521 (B–H). ^{1}H-NMR: δ −1.19 (br quadruplet, 1H, $^{1}J(B, H) = 79$, B–H–B); 2.10 (m, 2H, CH_2); 2.21 (br s, 2H, C_c–H); 2.35 (m, 2H, CH_2); 3.30 (m, 4H, S–CH_2). ^{11}B-NMR: δ −10.9 (d, 2B, $^{1}J(B, H) = 143$, B(9,11)); −15.2 (d, 2B, $^{1}J(B, H) = 138$, B(5,6)); −16.8 (d, 1B, $^{1}J(B, H) = 167$, B(3)); −20.2 (d, 2B, $^{1}J(B, H) = 156$, B(2,4)); −25.2 (d, 1B, $^{1}J(B, H) = 79$, B(10)); −36.7 (d, 1B, $^{1}J(B,H) = 144$, B(1)). $^{13}C\{^{1}H\}$-

NMR: δ 30.4 (s, CH_2); 43.7 (s, S–CH_2); 46.7 (br s, C_c–H).

3.6. Synthesis of 10-SEtPh-7,8-nido-$C_2B_9H_{11}$ (4)

Following the method of Plesek et al. [2d], to a two-necked round bottom flask (25 ml) containing a cooled and stirring 1 M aqueous solution of [K][7,8-$C_2B_9H_{12}$] (5 ml), were added dropwise SEtPh (2.8 ml, 20 mmol) in $C_6H_5CH_3$ (5 ml) and concd. HCl (2.5 ml). The mixture was vigorously stirred for 5 min to turn slightly orange. After this time, 16% aq. CH_3CHO (3.75 ml) was added. After stirring for 4 h, the organic phase was separated and water (7.5 ml) was added. The solution was evaporated at room temperature, and the solid formed was extracted with $CHCl_3$ (5 ml). Compound **4** was purified on flash chromatopraphy on silica using $CHCl_3$ as eluent. Removal of solvent afforded **1** as a white solid. Yield: (478 mg, 35%). Anal. Calc. for $C_{10}H_{21}B_9S$ (%): C, 44.41; H, 7.77; S, 11.84. Found: C, 44.12; H, 7.56; S, 11.02. IR: ν 3051 (C_{aryl}–H); 2979, 2936, 2869 (C–H); 2545 (B–H). ^{1}H-NMR: δ −0.98 (br quadruplet, 1H, B–H–B); 1.26 (t, 32 H, ^3J(H, H) = 7.4, CH_3); 2.19 (br s, 2H, C_c–H); 3.30 (m, 4H, S–CH_2); 7.72 (m, 5H, S–C_6H_5). ^{11}B-NMR: δ −12.2 (d, 2B, ^1J(B, H) = 140, B(9,11)); −16.2 (d, 1B, ^1J(B, H) = 135); −16.9 (d, 1B), −17.8 (d, 1B, ^1J(B, H) = 119); −21.5 (d, 2B, ^1J(B, H) = 147); −26.9 (d, 1B, B(10)); −38.2 (d, 1B, ^1J(B, H) = 143). ^{13}C{^{1}H}-NMR: δ 12.0 (s, CH_3); 39.4 (s, S–CH_2); 46.6 (br s, C_c–H); 126.1 (s, C_{aryl}); 131.2 (s, C_{aryl}); 132.1 (s, C_{aryl}); 133.3 (s, C_{aryl}).

3.7. Synthesis of 7-Me-10-SMe_2-7,8-nido-$C_2B_9H_{10}$ (5)

The same procedure was used as before, using SMe_2 (1.2 ml, 16 mmol) in $C_6H_5CH_3$ (4 ml), concd. HCl (2 ml), 1 M aqueous solution of [K][7,8-$C_2B_9H_{12}$] (4 ml) and 16% aq. CH_3CHO (3 ml). After stirring for 4 h, the organic phase was evaporated and extracted with $CHCl_3$. The solid formed was dissolved in $CHCl_3$ and purified by flash chromatography on silica, using $CHCl_3$ as eluent. Compound **5** was obtained as a white solid. Yield: (592 mg, 63%). Anal. Calc. for $C_5H_{19}B_9S$ (%): C, 28.82; H, 9.13; S, 15.37. Found: C, 29.05; H, 8.89; S, 14.99. IR ν: 3016 (C_c–H); 2953, 2926, 2868 (C–H); 2544 (B–H). ^{1}H-NMR: δ −0.97 (br quadruplet, 1H, ^1J(B, H) = 77, B–H–B); 1.49 (s, 3H, CH_3); 2.11 (br s, 1H, C_c–H); 2.55 (s, 6H, CH_3). ^{11}B-NMR: δ −10.7 (d, 1B, ^1J(B, H) = 141); −11.2 (d, 1B, ^1J(B, H) = 143); −12.6 (d, 1B, ^1J(B, H) = 162); −16.2 (d, 2B, ^1J(B, H) = 148); −17.4 (d, 1B, ^1J(B, H) = 138); −20.2 (d, 1B, ^1J(B, H) = 156); −25.9 (d, 1B, ^1J(B, H) = 77); −35.9 (d, 1B, ^1J(B, H) = 143). ^{13}C{^{1}H}-NMR: δ 24.7 (s, CH_3); 25.8 (s, CH_3); 52.6 (br s, C_c–H).

3.8. Synthesis of 7-Me-10-SEt_2-7,8-nido-$C_2B_9H_{10}$ (6)

The same procedure was used as before, using SEt_2 (2.2 ml, 20 mmol) in $C_6H_5CH_3$ (5 ml), concd. HCl (2.5 ml), 1 M aqueous solution of [K][7,8-$C_2B_9H_{12}$] (5 ml) and 16% aq. CH_3CHO (3.75 ml). After stirring for 4 h, the organic phase was evaporated and extracted with $CHCl_3$. The solid formed was dissolved in $CHCl_3$ and purified by flash chromatography on silica, using $CHCl_3$ as eluent. Compound **6** was obtained as a white solid. Yield: (620 mg, 52%). Anal. Calc. for $C_7H_{23}B_9S$ (%): C, 35.56; H, 9.73; S, 13.54. Found: C, 35.05; H, 9.56; S, 13.06. IR ν: 2974, 2925, 2868 (C–H); 2546. ^{1}H-NMR: δ −1.07 (br quadruplet, 1H, ^1J(B, H) = 80, B–H–B); 1.48 (dd, 6H, ^3J(H_a, H) = 7.4, ^3J(H_b, H) = 7.7, CH_3); 1.49 (s, 3H, CH_3); 2.10 (br s, 1H, Cc–H); 2.89 (dq, 2H, ^2J(H_a, H_b) = 13.2, ^3J(H_a, H) = 7.4, S–CH_a, S–$CH_{a'}$ (SCH_2)); 3.02 (dq, 2H, ^2J(H_b, H_a) = 12.9, ^3J(H_b, H) = 7.7, S–CH_b, S–$CH_{b'}$ (SCH_2)). ^{11}B-NMR: δ −10.7 (d, 1B, ^1J(B, H) = 141); −11.2 (d, 1B, ^1J(B, H) = 142); −12.4 (d, 1B, ^1J(B, H) = 161); −16.1 (d, 2B, ^1J(B, H) = 149), −17.2 (d, 1B, ^1J(B, H) = 138); −20.3 (d, 1B, ^1J(B, H) = 155); −27.0 (d, 1B, ^1J(B, H) = 80); −36.0 (d, 1B, ^1J(B, H) = 143). ^{13}C{^{1}H}-NMR: δ 11.9 (s, CH_3); 25.4 (s, CH_3); 35.0 (s, S–CH_2); 53.3 (br s, C_c); 59.8 (br s, C_c).

3.8.1. Thermolysis

The charge-compensated ligands **1**–**3** (50 mg) were dissolved in 10 ml of aromatic solvent (mesitylene or xylene). The solutions were refluxed under dinitrogen for several hours depending on the ligand. Samples were taken at various time intervals and the thermolysis was followed by ^{11}B-NMR spectroscopy. Estimations of the relative concentrations of species were made from all peak areas (see Tables 3 and 4).

3.9. X-Ray Studies of 1 and 3

Single-crystal data collections for **1** and **3** were performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite monochromatized Mo–Kα radiation. The unit cell parameters were determined by least-squares refinement of 25 carefully centred reflections. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 techniques using the SHELX-97 program package. [9] For **1**, all non-hydrogen atoms were refined with anisotropic displacement parameters. For **3**, $S(CH_2)_4$ group is disordered assuming two orientations with site occupation parameters 0.773(7) (conformation **A**) and 0.227(7) (conformation **B**). Non-hydrogen atoms of the carborane cage and S1a and S1b were refined with anisotropic displacement parameters and the disordered carbon atoms with isotropic displacement parameters. Constraint U(S1a) = U(S1b) and DFIX restraints were used for the disordered part of the molecule in the refinement.

Table 5
Crystallographic data for compounds **1** and **3**

	1	**3**
Empirical formula	$C_4H_{17}B_9S$	$C_6H_{19}B_9S$
Formula weight	194.53	220.56
Wavelength (Å)	0.71069	0.71069
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbcn* (no. 60)	*Pbca* (no. 61)
Unit cell dimensions		
a (Å)	10.9985(15)	14.186(3)
b (Å)	14.1274(16)	14.843(2)
c (Å)	14.8928(15)	12.2443(16)
V (Å^3)	2314.0(4)	2578.2(7)
Z	8	8
D_{calc} (g cm^{-3})	1.117	1.136
μ (cm^{-1})	2.24	2.09
Number of unique reflections	2042	2269
Number of parameters	145	160
$R_1(F_o)$ [a] $[I > 2\sigma(I)]$	0.0439	0.0599
$wR_2(F_o^2)$ [b] $[I > 2\sigma(I)]$	0.1072	0.1440
Goodness-of-fit on F^2	1.017	1.034
Largest differential peak and hole (e/Å^{-3})	0.228 and −0.194	0.335 and −0.262

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma\, w(|F_o^2|-|F_c^2|)^2/\Sigma\, w|F_o^2|^2]^{1/2}$.

For both compounds, hydrogen atoms were included in the calculations at fixed distances from their host atoms and treated as riding atoms using the SHELX-97 default parameters or refined isotropically (hydrogen atoms at C7, C8, B9, B10 and B11). Crystallographic data are listed in Table 5.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 168130 and 168131 for compounds **1** and **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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