

## Ten-vertex rhodadithiaborane chemistry: [8-{I(CH<sub>2</sub>)<sub>5</sub>}-3-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-*arachno*-3,7,8-RhS<sub>2</sub>B<sub>8</sub>H<sub>9</sub>]

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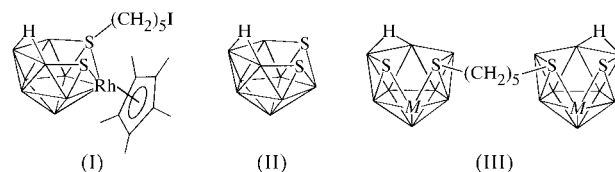
Neutral 8-(5-iodo-*n*-pentyl)-3-( $\eta^5$ -pentamethylcyclopentadienyl)-*arachno*-3-rhoda-7,8-dithiaundecaborane, [Rh(C<sub>5</sub>H<sub>9</sub>B<sub>8</sub>IS<sub>2</sub>)(C<sub>10</sub>H<sub>15</sub>)], obtained from the [*arachno*-7,8-S<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>−</sup> anion by treatment with I(CH<sub>2</sub>)<sub>5</sub>I followed by [Rh(C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>]<sub>2</sub> and *N,N,N',N'*-tetramethyl-1,8-diaminonaphthalene, has the 11-vertex cluster geometry of [*arachno*-7,8-S<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>−</sup>, but with an {Rh(C<sub>5</sub>Me<sub>5</sub>)} unit in the 3-position instead of a {BH} unit, and with a -(CH<sub>2</sub>)<sub>5</sub>I chain attached *exo* to an S atom.

### Comment

A contemporary survey of boron chemistry (Davidson *et al.*, 2000) shows that there is much current interest in the linking together of boron-containing clusters with varying degrees of intimacy to give a remarkable variety of larger macromolecular assemblies (Lamrani *et al.*, 2000; Hawthorne, 2000; Grimes, 2000; Colquhoun *et al.*, 2000; Bould *et al.*, 1999; Barton *et al.*, 2000; Sivaev *et al.*, 2000). Within this variety, there is a classification that may be described as consisting of 'bola' boranes, in which two clusters are linked together by a long flexible chain, for example, the {-P-C-C-P-}-linked rhodathiaborane clusters in [(dppe)RhSB<sub>9</sub>H<sub>8</sub>(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-PPh<sub>2</sub>)B<sub>9</sub>H<sub>8</sub>SRh(dppe)] (Barton, 2000) and the {-O-C-C-C-}-linked borane and carborane units in the [B<sub>12</sub>H<sub>11</sub>O(CH<sub>2</sub>)<sub>4</sub>C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>]<sup>2-</sup> dianion (Sivaev *et al.*, 2000). In this context, we report the formation and structural characterization of a potential precursor, *viz.* [8-{I(CH<sub>2</sub>)<sub>5</sub>}-5-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-*arachno*-5,7,8-RhS<sub>2</sub>B<sub>8</sub>H<sub>9</sub>], (I), to another type of labolaborane species.

The heteroborane cluster architecture (Fig. 1) is seen to be based on the *arachno*-type 11-vertex cluster structure of the starting [S<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>−</sup> anion, (II), but with the {BH(*exo*)} vertex at the 3-position replaced by the 'isolobal' cluster contributor

{Rh( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)}. It is of interest that, during the course of the reaction, there has been an effective replacement of {BH(*exo*)} by {Rh( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)}. However, since this is a very intimately bound cluster position (cluster connectivity five), it implies that the replacement mechanism will be complex. Interestingly, in the closely related reaction of neutral [MeS<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] with [[Rh( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Cl<sub>2</sub>]<sub>2</sub>], the product [( $\eta^4$ -C<sub>5</sub>Me<sub>5</sub>H)RhSB<sub>9</sub>H<sub>9</sub>SMe] is quite different (Macías *et al.*, 1997) in that (a) it retains all B atoms, (b) there is an H atom transfer



to the hydrocarbon ligand and an associated reduction in intimacy of the rhodium-to-hydrocarbon bonding, and (c) the alkylated S atom is partially extruded from the cluster into a boron-boron bridging position. In [8-{I(CH<sub>2</sub>)<sub>5</sub>}-3-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-*arachno*-3,7,8-RhS<sub>2</sub>B<sub>8</sub>H<sub>9</sub>], the other feature different from the [S<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>−</sup> anion is of course the alkylation of one of the S atoms, S8, by the long-chain -(CH<sub>2</sub>)<sub>5</sub>I moiety. There is some precedent for *S*-alkylation in the structurally characterized neutral [MeS<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] species obtainable from [S<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>−</sup> by iodide displacement from MeI (Holub *et al.*, 1994), but here the alkylated sulfur is again extruded to a boron-boron bridging position, in contrast to the present compound. As expected, the bridging H atom on the open face is at the B10-B11 site distal from the alkylated, formally positive, S8 sulfur site, rather than at the adjacent B9-B10 position. The distance from the Rh atom to the alkylated S8 atom of

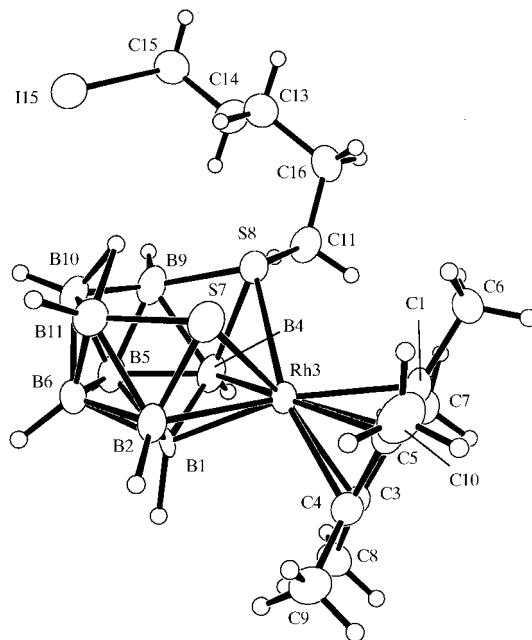


Figure 1

The crystallographically determined molecular structure of (I) drawn with 40% probability ellipsoids and with H atoms shown as small circles of artificial radii.

2.6185 (16) Å is significantly longer than that to non-alkylated S7 of 2.3922 (16) Å, and the boron–sulfur distance B4–S8 of 2.064 (8) Å is similarly longer than the otherwise corresponding B2–S7 distance of 1.938 (9) Å. Comparison of the dimensions given in Table 1 shows that there are related differential effects throughout the cluster associated with the *S*-alkylation and the concomitant siting of the bridging H atom at B10–B11. The establishment of compound (I) leads to the interesting idea of a potential bolaborane (Barton, 2000) by use of an excess of the starting thiaborane, followed by excess of the organometallic substrate, to give [8,8'-{ $\alpha,\omega$ -(CH<sub>2</sub>)<sub>5</sub>}-{3-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-*arachno*-3,7,8-RhS<sub>2</sub>B<sub>8</sub>H<sub>9</sub>}<sub>2</sub>], (III), and analogous structures when the concept is extended to other related systems. We are currently examining these and related possibilities.

## Experimental

A solution of [tmndH]<sup>+</sup>[S<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>-</sup> (500 mg, 1.3 mmol; tmnd is *N,N,N',N'*-tetramethyl-1,8-diaminonaphthalene) and I(CH<sub>2</sub>)<sub>5</sub>I (200 mg, 0.1 ml, 0.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) was heated at reflux under N<sub>2</sub> for 24 h. The resulting pale-yellow solution was filtered and the solvent removed from the filtrate (rotary evaporator). The resulting yellow solid was extracted with hexane. Evaporation of the hexane extract gave a colourless oily residue, for which integrated <sup>1</sup>H NMR spectroscopy indicated a *ca* 50% conversion of I(CH<sub>2</sub>)<sub>5</sub>I. The <sup>11</sup>B NMR spectrum showed nine different resonances, at  $\delta(^{11}\text{B})$  +32.9, +13.0, +9.8, +0.8, -1.8, -9.2, -18.6, -21.7 and -34.2 p.p.m. These are very similar to those reported for [MeS<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (Holub *et al.*, 1994), supporting mono-*S*-alkylation and the generation of [I(CH<sub>2</sub>)<sub>5</sub>-S<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (185 mg, 0.6 mmol, 50%). This crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 ml) and stirred with tmnd (128 mg, 0.6 mmol), and then [(C<sub>5</sub>Me<sub>5</sub>)RhCl<sub>2</sub>]<sub>2</sub> (185 mg, 0.3 mmol) was added. The brown–black solution was stirred for 1 h, filtered through silica and reduced in volume. Preparative thin-layer chromatography (Silica GF254; 60% CH<sub>2</sub>Cl<sub>2</sub>/40% hexane) yielded a number of coloured components. The principal species was dark amber [8-[I(CH<sub>2</sub>)<sub>5</sub>]-3-( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-*arachno*-3,7,8-RhS<sub>2</sub>B<sub>8</sub>H<sub>9</sub>] [compound (I), *R<sub>F</sub>* *ca* 0.5; 12 mg, 0.02 mmol, 3%]. Crystallization was from dichloromethane–hexane. Selected NMR data for the CD<sub>2</sub>Cl<sub>2</sub> solution of [I(CH<sub>2</sub>)<sub>5</sub>](C<sub>5</sub>Me<sub>5</sub>)RhS<sub>2</sub>B<sub>8</sub>H<sub>9</sub>, (I), at 294–300 K is as follows: cluster assignments by [<sup>11</sup>B–<sup>11</sup>B], [<sup>1</sup>H–<sup>1</sup>H] and (<sup>1</sup>H)–(<sup>11</sup>B) correlation experiments (Heřmánek, 1999; Reed, 1993); ordered as assignment  $\delta(^{11}\text{B})$ /p.p.m. [ $\delta(^1\text{H})$ ]/p.p.m. for directly attached *exo*-hydrogen]: BH1 -4.9 [+1.84], BH2 +4.6 [+2.42], BH4 -14.1 [+1.06], BH5 +8.9 [+3.81], BH6 -16.9 [+1.72], BH9 -8.4 [+2.11], BH10 -33.9 [+0.59] and BH11 -1.6 [+3.11], with  $\delta(^1\text{H})(\mu-10,11)$  -1.75 (stronger coupling to B10 than to B11), and  $\delta(^1\text{H})(\text{C}_5\text{Me}_5)$  at +1.89, {S(CH<sub>2</sub>)<sub>5</sub>I} {CH<sub>2</sub>} groups along the chain successively at  $\delta(^1\text{H})$  +2.40 ( $\alpha$  to S), +1.76, +1.51, +1.85 and +3.24 ( $\alpha$  to I).

### Crystal data

[Rh(C<sub>5</sub>H<sub>19</sub>B<sub>8</sub>IS<sub>2</sub>)(C<sub>10</sub>H<sub>15</sub>)]  
*M<sub>r</sub>* = 594.83  
 Monoclinic, *C*2/*c*  
*a* = 28.6498 (4) Å  
*b* = 10.6700 (2) Å  
*c* = 18.2997 (4) Å  
 $\beta$  = 121.5240 (10)<sup>o</sup>  
*V* = 4768.53 (15) Å<sup>3</sup>  
*Z* = 8

*D<sub>x</sub>* = 1.657 Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation  
 Cell parameters from 31844 reflections  
 $\theta$  = 1.67–26.00<sup>o</sup>  
 $\mu$  = 2.186 mm<sup>-1</sup>  
*T* = 180 (2) K  
 Prism, dark red  
 0.33 × 0.20 × 0.13 mm

### Data collection

Nonius KappaCCD area-detector diffractometer	4616 independent reflections
1 <sup>o</sup> $\varphi$ exposure scans	<i>R</i> <sub>int</sub> = 0.100
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	$\theta_{\text{max}}$ = 26.0 <sup>o</sup>
<i>T</i> <sub>min</sub> = 0.532, <i>T</i> <sub>max</sub> = 0.764	<i>h</i> = -35 → 35
31844 measured reflections	<i>k</i> = -13 → 12
	<i>l</i> = -22 → 22
	Intensity decay: none

### Refinement

Refinement on <i>F</i> <sup>2</sup>	$w = 1/[\sigma^2(F_o^2) + (0.0723P)^2 + 27.1436P]$
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )] = 0.058	where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.162	( $\Delta$ / $\sigma$ ) <sub>max</sub> = 0.001
<i>S</i> = 1.094	$\Delta\rho_{\text{max}}$ = 1.84 e Å <sup>-3</sup>
4616 reflections	$\Delta\rho_{\text{min}}$ = -1.16 e Å <sup>-3</sup>
250 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997)
H atoms: see below	Extinction coefficient: 0.0022 (2)

**Table 1**

Selected geometric parameters (Å, °).

Rh3–B1	2.249 (6)	B2–S7	1.938 (9)
Rh3–B2	2.326 (7)	B4–B5	1.715 (10)
Rh3–B4	2.354 (6)	B4–B9	1.852 (10)
Rh3–S7	2.3922 (16)	B4–S8	2.064 (8)
Rh3–S8	2.6185 (16)	B5–B9	1.713 (12)
C11–S8	1.839 (7)	B5–B6	1.745 (13)
C15–I15	2.163 (8)	B5–B10	1.796 (12)
B1–B5	1.753 (11)	B6–B11	1.755 (12)
B1–B4	1.776 (11)	B6–B10	1.803 (12)
B1–B6	1.831 (10)	S7–B11	1.943 (8)
B1–B2	1.854 (12)	S8–B9	1.925 (7)
B2–B6	1.754 (11)	B9–B10	1.799 (11)
B2–B11	1.929 (11)	B10–B11	1.840 (12)
S7–Rh3–S8	79.83 (6)		

Cage H atoms were located from the Fourier difference syntheses, and although their positional parameters were included in the structure-factor calculations; they were not refined. Non-cage H atoms were constrained in calculated positions with isotropic displacement parameters of 1.2*U*<sub>eq</sub> of the parent C atom.

Data collection: COLLECT (Nonius, 1999); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP (McArdle, 1995); software used to prepare material for publication: WC (Thornton-Pett, 2000).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1313). Services for accessing these data are described at the back of the journal.

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