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# The formation, characterisation and structures of *closo*-12-vertex dirhodathiaboranes containing rhodium(II) centres

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Abstract—Reaction of Cs[6-arachno-SB<sub>9</sub>H<sub>12</sub>] with [RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] yields the known complex [8-CO-8,8-(Ph<sub>3</sub>P)<sub>2</sub>-8,7-*nido*-RhSB<sub>9</sub>H<sub>10</sub>], 1. In contrast, treatment of the same thiaborane with [RhCl(CO)(PPh<sub>3</sub>)]<sub>2</sub> affords a number of 12-vertex dirhodathiaboranes of the type  $[2,3-(CO)_2-\mu_{2,3}-CO-2,3-(PPh_3)_2-7-X-2,3,1-closo-Rh_2SB_9H_8]$  in modest yields. For X = H, **3a**, and X = Cl, **4**, single crystal X-ray diffraction studies are reported; crystals of **3a** contain the compound with X = OH, **3b**, in approximately 28% occupancy. © 1997 Elsevier Science Ltd

Keywords: borane; thiaborane; rhodium; phosphine; carbonyl; crystal structure.

Among the heteroatomic derivatives of the binary boranes, by far the most extensively studied are the carbaboranes [1] and their metal complexes [2]. Recently, however, the chemistry of other polyhedral hetero(metalla)boranes has seen greater development [3], in which arguably the most common non-carbon heteroatom has been sulfur. As a result a range of sulfur-containing heteroborane polyhedra is now known which encompasses diverse examples of intermediate- and larger-sized heterothiaboranes [4], metallathiaboranes [5] and metalladithiaboranes [6], and even 'macropolyhedral' dithiaboranes [7].

As part of our continuing synthetic and structural studies [8,9], of these and other larger metallaheteroboranes, we have investigated the reaction of Cs[6-*arachno*-SB<sub>9</sub>H<sub>12</sub>] with the complexes [RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] and [RhCl(CO)(PPh<sub>3</sub>)]<sub>2</sub>, and have obtained from the latter an unexpected series of dimetallic thiaborane-containing products.

# **EXPERIMENTAL**

#### Synthesis and characterization

All reactions were carried out under an atmosphere of dry, oxygen-free dinitrogen using standard Schlenk line techniques, with some subsequent manipulation in air. Solvents were freshly distilled from appropriate drying agents and degassed immediately prior to use. Preparative thin-layer chromatography employed Kieselgel 60  $F_{254}$  plates (Merck), pre-washed in the appropriate solvents. NMR spectra were recorded from CDCl<sub>3</sub> solutions at 298 K. The starting materials Cs[6-*arachno*-SB<sub>9</sub>H<sub>12</sub>] [10], [RhCl(CO)<sub>2</sub>]<sub>2</sub> [11] and [RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] [12] were prepared as described.

Reaction of  $Cs[6-arachno-SB_9H_{12}]$  with [RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>]. Preparation of [8-CO-8,8-(Ph<sub>3</sub>P)<sub>2</sub>-8,7-nido-RhSB<sub>9</sub>H<sub>10</sub>], 1

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To a frozen (77 K) solution of  $[RhCl(CO)(PPh_3)_2]$ (130 mg, 0.19 mmol) in  $CH_2Cl_2$  (15 cm<sup>3</sup>) was added solid Cs[6-*arachno*-SB<sub>9</sub>H<sub>12</sub>] (55 mg, 0.20 mmol). The mixture was allowed to warm to room temperature with stirring, and consumption of the starting Rh

complex was monitored by IR spectroscopy. After ca 18 h, the reaction mixture was evaporated at reduced pressure. The only thiaborane-containing product (identified by <sup>31</sup>P-{<sup>1</sup>H} and <sup>11</sup>B-{<sup>1</sup>H} NMR and infrared spectroscopy) was the known [13] compound [8-CO-8,8-(Ph<sub>3</sub>P)<sub>2</sub>-8,7-*nido*-RhSB<sub>9</sub>H<sub>10</sub>], **1**.

Preparation of compounds 2-4. [RhCl(CO)(PPh<sub>3</sub>)]<sub>2</sub> [14] was formed in situ from [RhCl(CO)<sub>2</sub>]<sub>2</sub> (100 mg, 0.257 mmol) and PPh<sub>3</sub> (134 mg, 0.511 mmol) in benzene (10 cm<sup>3</sup>). This solution of [RhCl(CO)(PPh<sub>3</sub>)]<sub>2</sub> was frozen to 77 K and solid Cs[6-arachno-SB<sub>9</sub>H<sub>12</sub>] (141 mg, 0.514 mmol) added; the mixture was allowed to warm to room temperature and stirred for ca 3 h. During the course of the reaction gas evolution was apparent; the yellow solution became more intensely orange and an apparently yellow solid was deposited. The mixture was filtered and the orange filtrate evaporated at reduced pressure to yield an orange-brown solid. (Infrared spectroscopic analysis of the solid removed by filtration showed a broad absorption in the B-H stretching region, suggesting that this solid is largely residual Cs[SB9H12] or its decomposition products, in addition to CsCl.)

The orange—brown residue was dissolved in a small amount (ca 5 cm<sup>3</sup>) of  $CH_2Cl_2$  and applied to chromatographic plates; repeated preparative thin layer chromatography ( $CH_2Cl_2/i$ -hexane, 3:2) gave bands as follows:

1. Brown:  $R_f$  0.6, (very small amount, <1 mg). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $v_{max}$ (BH) 2528 (m, br);  $v_{max}$ (CO) 2027 (s, br), 1868 (vw, br) cm<sup>-1</sup> (compound **2** was not further pursued).

2. Orange:  $R_f 0.5$ , (37 mg) (compounds **3a**, **3b** and **3c**).

3. Red:  $R_f$  0.4, (33 mg) (compound 4).

Bands 2 and 3 yielded three identifiable metallathiaboranes, namely compounds 3a and 3b, and compound 4 respectively, which were characterised as described in the two following sections.

Characterisation of  $[2,3-(CO)_2-\mu_{2,3}-CO-2,3-(PPh_3)_2-2,3,1-closo-Rh_2SB_9H_9]$  **3a** and partial characterisation of  $[2,3-(CO)_2-\mu_{2,3}-CO-7-OH-2,3-(PPh_3)_2-2,3,1-closo-Rh_2SB_9H_8]$  **3b** 

Band 2, upon repeated crystallisation (slow mutual diffusion of *i*-hexane and a CH<sub>2</sub>Cl<sub>2</sub> solution at  $-30^{\circ}$ C), afforded mainly red-orange *rods* which were very unstable with respect to solvent loss upon removal from the mother liquor; seven red-orange *crystals*, and a larger number of yellow *blocks* were also obtained. A single-crystal X-ray diffraction study (*vide infra*) of one of the second kind of red-orange crystals identified this as primarily [*cis*-2,3-(CO)<sub>2</sub>- $\mu_{2,3}$ -

CO-2,3-(PPh<sub>3</sub>)<sub>2</sub>-2,3,1-*closo*-Rh<sub>2</sub>SB<sub>9</sub>H<sub>9</sub>], **3a**, and a fraction as the 7-OH derivative **3b**. The yellow crystals, **3c**, are as yet unidentified. However, there is very close similarity in the infrared and <sup>31</sup>P NMR spectra of all three crystal types obtained from band 2, and this strongly suggests them simply to be polymorphs of **3a**. (Moreover, microanalytical data are also consistent with compound **3b** being present in only small amounts overall.) Taking the bulk of band 2, therefore, to be of formulation  $[(CO)_3(PPh_3)_2Rh_2SB_9H_9]$ : combined yield (as crystals) of band 2: 27 mg, 0.030 mmol, 5.8% based on {Rh}.

Anal. Found: C, 49.40; H, 4.09 %. Calcd for  $C_{39}H_{39}B_9O_3P_2Rh_2S$ : C, 49.16; H, 4.13%. IR  $(CH_2Cl_2): \nu_{max}(BH) 2529 \text{ (m, br)}; \nu_{max}(CO) 2031 \text{ (s)}, 1863 \text{ (m, br) cm}^{-1}$ . Cluster NMR data for **3a**, in the order  $\delta(^{11}B) [\delta(^{1}H)]$  relative <sup>11</sup>B integral: +10.3 [+3.5] 1B, +6.2(br) [+3.0 (2H), +2.7 (2H), +2.6 (1H)] 5B, -3.2 [+2.4] 2B, -32.9 [+1.0] 1B. In addition:  $\delta(^{1}H) + 7.20 \text{ to } +7.41 \text{ (m, } C_6H_5); \delta(^{31}P) +23.2 \text{ [d, } {}^{1}J(^{31}P^{-103}Rh) \text{ ca } 110 \text{ Hz]}$ . We tentatively assign an additional broad <sup>11</sup>B singlet resonance, at  $\delta(^{11}B)$  ca +19, to the 7-OH substituted position in **3b**; other <sup>11</sup>B resonances due to **3b** appear to coincide with those of **3a**, as do the <sup>31</sup>P resonances of the two species.

*Characterisation of* [2,3-(CO)<sub>2</sub>-µ<sub>2,3</sub>-CO-7-Cl-2,3-(PPh<sub>3</sub>)<sub>2</sub>-2,3,1-*closo*-Rh<sub>2</sub>SB<sub>9</sub>H<sub>8</sub>] **4** 

The compound 4, obtained as band 3 above, was fully characterised spectroscopically (*vide infra*) and was unambiguously identified as  $[cis-2,3-(CO)_2-\mu_{2,3}-CO-7-Cl-2,3-(PPh_3)_2-2,3,1-closo-Rh_2SB_9H_8]$ , by the single crystal X-ray diffraction study reported later. Yield (as crystals): 29 mg, 0.029 mmol, 5.7% based on {Rh}.

Anal. Found: C, 44.30; H, 3.11%. Calcd for  $C_{39}H_{38}B_9ClO_3P_2Rh_2S: C, 47.45; 3.88\%$ . IR  $(CH_2Cl_2):$ 



 $v_{max}(BH) 2535 \text{ (m, br)}; v_{max}(CO) 2064 \text{ (s)}, 1880 \text{ (m, br)} \text{ cm}^{-1}$ . Cluster NMR data for 4, in the order  $\delta(^{11}B)$  [ $\delta(^{1}H)$ ] relative <sup>11</sup>B integral: +23.9 [-] 1B [B(7)], +11.2 [+4.44] 2B, +6.2 [+4.27] 2B, +0.9 [+2.48] 2B, -3.5 [+2.80] 2B, -35.6 [+0.61] 1B. In addition:  $\delta(^{1}H) + 7.26 \text{ to } +7.48 \text{ (m, } C_6H_5); \delta(^{31}P) +22.6 \text{ [d, br, }^{1}J(^{31}P^{-103}Rh) \text{ ca } 88 \text{ Hz]}.$ 

Crystallisation of compound 4 (slow mutual diffusion of *i*-hexane and a concentrated  $CH_2Cl_2$  solution at  $-30^{\circ}C$ ) afforded several well-formed dark red *blocks*, one of which was the subject of analysis by a single crystal X-ray diffraction experiment, as described below.

# Crystallographic studies

Crystal data, and details of data collection and structure refinement, for compounds **3a/b** and **4** are listed in Table 1. Reflection data were measured at 293(2) K on an Enraf-Nonius CAD4 automatic fourcircle diffractometer operating in the  $\omega$ -2 $\theta$  scan mode using graphite-monochromated  $Mo-K_{\pi}$  X-radiation,  $\bar{\lambda} = 0.71073$  Å. Cell parameters and orientation matrices were determined from the setting angles of 25 accurately-measured reflections. Both data sets were corrected [15] for Lorentz and polarisation effects and, following isotropic convergence, benefited from an empirical absorption correction [16]. During data collection, some slight crystal decay (ca 2% for 3a/b; ca 4% for 4) was revealed by monitoring the intensity of two standard reflections measured after every 500 data; the data sets were corrected [15] to allow for this. In the latter stages of refinement, data were weighted according to  $w^{-1} = [\sigma^2(F_0^2) + g_1^2 P^2 + g_2 P]$  where  $P = (F_o^2 + 2F_c^2)/3$ . Fractional atomic co-ordinates, full lists of bond distances and interbond angles and anisotropic thermal parameters have been deposited as supplementary data. Molecular geometry figures were drawn using SHELXTL-PC [17].

 $[2,3-(CO)_2-\mu_{2,3}-CO-2,3-(PPh_3)_2-7-X-2,3,1-closo-Rh_2SB_9H_8]$  (X = H/OH), **3a/b**. An irregular redorange block of approximate dimensions  $0.5 \times 0.3 \times 0.2$  mm was selected for data collection.

Table 1. Crystallographic data and details of data collection and structure refinement for crystals of compounds 3a/b and 4

Compound	3a/b	4
Formula	$C_{39}H_{39}B_9O_3P_2Rh_2S^4$	C <sub>19</sub> H <sub>18</sub> B <sub>9</sub> ClO <sub>3</sub> P <sub>2</sub> Rh <sub>2</sub> S
Mr	952.81 <sup>a</sup>	987.29
System	orthorhombic	triclinic
Space group	$P2_{1}2_{1}2_{1}$	ΡĪ
a/Å	10.802(2)	11.137(6)
b/Å	19.036(7)	13.558(7)
c/Å	20.631(4)	16.688(4)
$\alpha/^{\circ}$	90	108.44(3)
$\dot{\boldsymbol{\beta}}/^{\circ}$	90	97.66(5)
$\nu/^{\circ}$	90	110.96(5)
$U/Å^2$	4242.3(19)	2144.1(17)
Z	4	2
$D_{\rm c}/{\rm M~gm^{-3}}$	1.492 <sup><i>a</i></sup>	1.532
$\mu/\mathrm{mm}^{-1}$	0.939"	0.979
<i>F</i> (000)	1912 <sup>a</sup>	988
$\theta_{\rm orientation}/^{\circ}$	10-11	11-11.5
$ heta_{ m data\ collection}/^{\circ}$	1.46-24.97	1.34-24.97
Period/h	192	228
h, k, l ranges	-12-12, 0-22, 0-24	0-13, -16-15, -19-19
Data measured	8151	7953
Unique data	7451	7526
R <sub>int</sub>	0.0278	0.0096
$T_{\min}, T_{\max}$	0.905, 1.084	0.846, 1.156
Observed data $[F_o > 4\sigma(F_o)]$	5742	6384
R <sub>1</sub> [observed data]	0.0457	0.0270
R <sub>1</sub> [all data]	0.0830	0.0385
$wR_2$ [all data]	0.0959	0.0682
S	1.047	1.048
$g_1, g_2$	0.0444, 0	0.0371, 1.1485
Variables	444	467
Max., min. residue/ $e^{A^{-3}}$	0.427, -0.348	0.432, -0.559

"for 3a only (i.e., ignores partial OH substituent)

The positions of the two rhodia were obtained by direct methods (SHELXS-86 [18]), whilst the B, C, O, P and S atoms were located in subsequent difference Fourier maps (SHELXL-93 [19]). Although most of the cage H atoms could also be located by this method, they would not subsequently satisfactorily refine with independent positions and so were set riding in idealised positions 1.10 Å from the corresponding B atom with isotropic thermal parameters equal to 1.2 times the equivalent isotropic thermal parameter of the parent B atom. The six phenyl rings were constrained to be planar, rigid hexagons (C-C 1.39 Å), with the attached H atoms in calculated positions (C-H 0.93 Å) and having isotropic thermal parameters equal to 1.2 times the equivalent isotropic thermal parameter of the corresponding C atom. This model (with all nine B atoms bearing only terminal H atoms) was refined towards isotropic convergence, at which point it became clear that a substantial residual electron density peak (ca 2  $e^{A^{-3}}$ ) was located ca 1.3 Å from B(7). This was assigned as a (partial) terminal hydroxyl substituent on the basis of a reasonable B-X distance; both the OH group and the terminal H atom attached to B(7) were included with (refining) complementary occupancy. The O-H distance was constrained at 0.82 Å, and the B(7)-O-H angle was constrained to be tetrahedral, with free rotation about the B-O bond allowed such that the H atom was located at the position of maximum electron density (determined via structure factor calculation [19]). The H atom bound to B(7) was not further positionally refined once the partial OH group had been included in the model. At convergence the hydroxyl group had 0.28(2) fractional occupancy; no further attempt to model the disorder was deemed necessary. Refinement throughout was on  $F^2$  using full-matrix least-squares methods (SHELXL-93), converging without difficulty and with no significant residual electron density. The Flack absolute structure parameter  $\times$  was calculated to be 0.01(4), confirming the absolute configuration to be that chosen [20].

[2,3-(CO)<sub>2</sub>-µ<sub>2,3</sub>-CO-7-Cl-2,3-(PPh<sub>3</sub>)<sub>2</sub>-2,3,1-*closo*-Rh<sub>2</sub>SB<sub>9</sub>H<sub>8</sub>], 4. A well-formed dark red block of approximate dimensions  $0.45 \times 0.25 \times 0.15$  mm was chosen for data collection. The positions of the two rhodium atoms were determined by inspection of the Patterson synthesis (SHELX-76 [21]); those of the B, C, O, P, S, Cl and cage H atoms were obtained by difference Fourier syntheses (SHELXL-93 [19]). The Cl atom was identified as such by comparison of its peak height in a difference map to that of a welldefined C atom, and is justified by its successful refinement, the reasonable B-Cl distance, and its chemical sense. The structure was refined by fullmatrix least-squares on F<sup>2</sup> using SHELXL-93. Phenyl rings were treated as in 3a/b above. Cage H atoms were successfully allowed positional refinement, and were assigned a common isotropic thermal parameter,  $U_{\rm H} = 0.062(4)$  Å<sup>2</sup> at convergence. All non-H atoms were permitted anisotropic refinement following the

absorption correction. The model very readily converged and there are no significant residual peaks in the final difference Fourier map.

# DISCUSSION

The reaction of  $[RhCl(CO)(PPh_3)_2]$  with Cs[6-arachno-SB<sub>9</sub>H<sub>12</sub>] in dichloromethane affords the known [13] eleven-vertex *tris*(ligand)-rhodathiaborane [8-CO-8,8-(Ph\_3P)\_2-8,7-*nido*-RhSB<sub>9</sub>H<sub>10</sub>], **1**, whose identity was established by <sup>31</sup>P-{<sup>1</sup>H} and <sup>11</sup>B-{<sup>1</sup>H} NMR and infrared spectroscopy. This complex was previously prepared by the addition of CO to [8,8-(Ph\_3P)\_2-8,7-*nido*-RhSB<sub>9</sub>H<sub>10</sub>] in benzene.

In contrast, the reaction between the dimer  $[RhCl(CO)(PPh_3)]_2$  and the same thiaborane is far less straightforward. The Rh reagent [14] was prepared *in situ* from  $[RhCl(CO)_2]_2$  and one molar equivalent (per Rh) of PPh<sub>3</sub>, and the solid thiaborane salt added directly to this solution. During the reaction, considerable effervescence was noted : the stoichiometry of the products is consistent with evolution of H<sub>2</sub>. Preparative thin layer chromatography of the filtered and concentrated reaction mixture revealed three distinct bands (see Experimental).

The first of these bands, designated compound 2, was recovered in only very small quantity, readily decomposed and ultimately defied detailed characterisation. Nevertheless, given the identities of the other products, and the detection of (probable) terminal- and bridging-CO infrared bands in addition to BH stretching vibrations, we reasonably propose that 2 is related to the more well-defined compounds 3a, 3b and 4 below.

The second 'band' obtained by chromatography in fact consists of *at least* two compounds which proved too similar to be separated by this technique : repeated fractional crystallisation afforded three types of crystal which we believe (on the basis of <sup>31</sup>P-{<sup>1</sup>H} NMR and infrared spectroscopy and microanalytical data) to be polymorphs containing largely a single compound. A single-crystal X-ray diffraction study (see below) showed one of these crystals to consist largely of  $[2,3-(CO)_2-\mu_{2,3}-CO-2,3-(PPh_3)_2-2,3,1-closo-Rh_2SB_9H_9]$ , **3a** : this crystal was found to contain in addition the 7-hydroxyl analogue, **3b** in fractional occupancy (ca 28%). The two other crystal forms were never of adequate quality for a full X-ray diffraction structure determination.\* [Formation of **3b**, pre-

<sup>\*</sup> On a single occasion we succeeded in determining tentative unit cell parameters for a crystal of the form designated 3c during a diffractometer random peak search: the cell volume so obtained was consistent with 3c being at least related to 3a and 3b (primitive monoclinic, Z = 4,  $U \approx 4300$ Å<sup>2</sup>). In this context, we note also the possibility that there may exist an isomer of 3a in which the Rh-bound triphenylphosphine (and terminal carbonyl) ligands are mutually *transoid*.

sumably from 3a, conceivably occurs by reaction with silica (and/or atmospheric H<sub>2</sub>O/O<sub>2</sub>) during work-up.] The third band isolated by chromatography was solely the 7-Cl-substituted relative of compounds 3a and **3b**, that is,  $[2,3-(CO)_2-\mu_{2,3}-CO-2,3-(PPh_3)_2-7-Cl-2,3,1$ closo-Rh<sub>2</sub>SB<sub>9</sub>H<sub>8</sub>], 4, which was also studied by a single-crystal X-ray diffraction analysis, as discussed later. <sup>11</sup>B, <sup>1</sup>H and <sup>31</sup>P NMR spectra for 3a and 4 are consistent with their crystallographically-determined structures. Six resonances occur in their <sup>11</sup>B-{<sup>1</sup>H} NMR spectra in respective ratios (high  $\rightarrow$  low frequency) of 1:2:2:1:2:1. Each of these signals becomes a doublet upon retention of proton coupling, save for the highest frequency resonance in the spectrum of 4 which is, therefore, assigned to the chlorosubstituted vertex B(7). For both 3a and 4, the  ${}^{31}P$ -<sup>1</sup>H} NMR spectra consist of a single <sup>103</sup>Rh-coupled doublet, as expected. Surprisingly, microanalytical results from crystals of 4 always differed significantly from expected values: we are unable fully to account for this (poor combustion may be suggested), given that microanalysis of the closely-related species 3 apparently gives good agreement with calculated figures.

X-ray diffraction studies of single crystals of compounds 3a and 4, to which the above spectroscopic studies are complementary, provided unequivocal identification of these species. Figure 1 shows a perspective view of 4, whilst in Fig. 2 a view of the 'central' cluster and Rh environments in 3a is presented. Selected interatomic distances and interbond angles for 3a/b and 4 are listed in Table 2.

Compounds 3a (and 3b) and 4 are based on a distorted icosahedral 2,3,1-*closo*-Rh<sub>2</sub>SB<sub>9</sub> cluster with approximate  $C_s$  molecular symmetry (ignoring the



Fig. 2. View of the central  $Rh_2SB_9$  cluster and the rhodium co-ordination environments in **3a**, drawn with the same conventions as in Fig. 1. The phenyl rings C(1ni) and C(2ni) (n = 1-3; i = 1-6, numbered cyclically) are bound to P(1) and P(2) respectively. Compound **3b**, which has a terminal hydroxyl substituent [O-H(70)] rather than an H atom bound to B(7), is present in 28(2)% occupancy in the crystal of **3a**.

orientations of the pendant phenyl groups), fully consistent with their <sup>11</sup>B NMR spectra. In both clusters, a sulfur and two rhodium atoms are mutually adjacent at a triangular face. The unique boron atom, B(7), which is bound to both rhodia, has undergone substitution in **3b** and in **4**, whereby the *exo*-terminal H atom present in the unsubstituted parent **3a** has been replaced by -OH and -Cl substituents respectively. The B(7)—X distances determined here [B(7)—O in



Fig. 1. Perspective view of 4 showing 50% probability ellipsoids. H atoms have artificial radii for clarity. H atoms bear the same numerical label as the heavy atom to which they are bound; phenyl rings are numbered cyclically.

Table 2. Selected interatomic distances (Å) and interbond angles (°) for 3a/b and 4

	3a/h	4
<del></del>		
S(1)—Rh(2)	2.447(2)	2.4187(11)
S(1) - Rh(3)	2.433(2)	2.452(3)
S(1) - B(4)	2.066(8)	2.071(4)
S(1) - B(5)	1.981(9)	1.996(4)
S(1) - B(6)	2.096(9)	2.108(4)
Rh(2)— $Rh(3)$	2.7409(10)	2.749(2)
Rh(2) - B(6)	2.323(8)	2.313(4)
Rn(2) - B(7) Ph(2) - B(11)	2.302(9)	2.305(4)
Rn(2) = D(11) Ph(2) = D(1)	2.230(7)	2.203(4)
Rh(2) - C(1)	2.393(2) 2.072(8)	2.377(2)
Rh(2) = C(2)	1 840(8)	1.856(4)
Rh(3) - B(4)	2,330(8)	2.336(4)
Rh(3) - B(7)	2.311(9)	2.308(4)
Rh(3) - B(8)	2.273(8)	2.265(4)
Rh(3) - P(2)	2.373(2)	2.3747(14)
Rh(3) - C(1)	2.066(7)	2.117(3)
Rh(3)—C(3)	1.828(8)	1.850(4)
B(7)—X	1.31(3) <sup>a</sup>	$1.837(4)^{b}$
C(1)—O(1)	1.178(8)	1.145(3)
C(2)—O(2)	1.137(8)	1.136(4)
C(3)—O(3)	1.154(9)	1.136(4)
Rh(2) - S(1) - Rh(3)	68.34(5)	68,72(5)
Rh(2) - S(1) - B(6)	60.9(2)	60.99(11)
Rh(3) - S(1) - B(4)	61.8(2)	61.50(12)
B(4) - S(1) - B(5)	54.7(3)	54.5(2)
B(5) - S(1) - B(6)	55.0(3)	54.5(2)
S(1)-Rh(2)-Rh(3)	55.60(5)	56.21(6)
S(1) - Rh(2) - B(6)	52.1(2)	52.86(10)
S(1) - Rh(2) - P(1)	95.48(6)	95.65(6)
S(1) - Rh(2) - C(1)	95.1(2)	91.51(9)
S(1)— $Rh(2)$ — $C(2)$	168.5(2)	171.17(11)
Rh(3) - Rh(2) - B(7)	53.7(2)	53.48(10)
Rh(3) - Rh(2) - P(1)	127.34(5)	131.85(5)
Rn(3) - Rn(2) - C(1)	48.4(2)	49.53(9)
R(5) = R(12) = C(2) R(5) = R(12) = R(11)	120.1(2)	120.20(12)
B(0) - Ri(2) - B(11) B(6) - Rh(2) - P(1)	43.7(3)	43.7(2) 94 33(12)
B(6) = Rh(2) = C(1)	1430(3)	$142\ 71(12)$
B(6) - Rh(2) - C(2)	117.0(3)	118.9(2)
B(7) - Rh(2) - B(11)	47.5(3)	47.81(14)
B(7) - Rh(2) - P(1)	178.6(2)	173.60(9)
B(7) - Rh(2) - C(1)	79.4(3)	85.73(14)
B(7) - Rh(2) - C(2)	90.4(3)	90.54(14)
B(11) - Rh(2) - P(1)	131.1(2)	125.85(11)
B(11) - Rh(2) - C(1)	126.7(3)	133.53(13)
B(11)-Rh(2)-C(2)	84.0(3)	85.5(2)
P(1) - Rh(2) - C(1)	102.0(2)	100.60(11)
P(1)— $Rh(2)$ — $C(2)$	89.4(2)	87.85(11)
C(1)—Rh(2)—C(2)	94.0(3)	95.82(14)
S(1) - Kh(3) - Kh(2)	51.06(4)	55.07(5)
S(1) - Kn(3) - B(4) S(1) - B(3) - B(3)	51.4(2) 06.50(6)	51.20(10) 06.66(6)
S(1) - KII(3) - F(2) S(1) - Ph(3) - C(1)	90.39(0)	90.00(3) 00.48(0)
S(1) = Rh(3) = C(3)	75.7(2) 167.9(3)	70.40(7) 167 33(11)
Rh(2) - Rh(3) - R(7)	53 4(2)	53 38(9)
Rh(2) - Rh(3) - P(2)	123.87(5)	128.87(4)
Rh(2) - Rh(3) - C(1)	48.6(2)	49.36(9)
Rh(2)— $Rh(3)$ — $C(3)$	129.3(2)	128.93(11)

	3a/b	4
B(4)— $Rh(3)$ — $B(8)$	45.4(3)	45.9(2)
B(4) - Rh(3) - P(2)	103.4(2)	98.26(10)
B(4) - Rh(3) - C(1)	142.9(3)	140.14(13)
B(4) - Rh(3) - C(3)	116.8(3)	116.7(2)
B(7) - Rh(3) - B(8)	48.2(3)	47.86(13)
B(7) - Rh(3) - P(2)	175.5(2)	177.65(9)
B(7) - Rh(3) - C(1)	79.3(3)	85.53(12)
B(7)— $Rh(3)$ — $C(3)$	91.5(3)	90.15(14)
B(8) - Rh(3) - P(2)	136.3(2)	130.00(10)
B(8) - Rh(3) - C(1)	127.3(3)	133.38(13)
B(8) - Rh(3) - C(3)	84.4(3)	83.0(2)
P(2)— $Rh(3)$ — $C(1)$	96.2(2)	96.61(9)
P(2)— $Rh(3)$ — $C(3)$	88.2(2)	88.52(11)
C(1)— $Rh(3)$ — $C(3)$	94.8(3)	100.43(14)
S(1) - B(4) - Rh(3)	66.9(2)	67.30(12)
S(1) - B(6) - Rh(2)	67.0(2)	66.15(11)
Rh(2) - B(7) - Rh(3)	72.9(3)	73.15(11)
Rh(2) - C(1) - Rh(3)	82.9(3)	81.11(11)
Rh(2)-C(1)-O(1)	137.4(6)	139.4(2)
Rh(3) - C(1) - O(1)	136.3(6)	138.8(2)
Rh(2) - C(2) - O(2)	178.4(7)	178.4(3)
Rh(3) - C(3) - O(3)	177.1(7)	177.1(3)
Rh(2) - B(7) - X	119.0(14) <sup>a</sup>	114.6(2) <sup>b</sup>
Rh(3) - B(7) - X	112.7(13) <sup>a</sup>	$113.3(2)^{b}$
B(8)—B(7)—X	113.7(14) <sup>a</sup>	118.4(2) <sup>b</sup>
B(11) - B(7) - X	112.0(13) <sup>a</sup>	118.9(2) <sup>b</sup>
B(12)—B(7)—X	111.3(4)"	114.3(2) <sup>b</sup>

 $^{a}\mathbf{X}=\mathbf{O}.$ 

 ${}^{b}\mathbf{X} = \mathbf{Cl}.$ 

Cluster B—B distance ranges: **3a/b**, 1.735(11) to 1.885(12)Å; **4**, 1.742(5) to 1.883(5)Å

Other cluster acute angles: B—B ranges: 3a/b,  $57.0(5)-65.2(5)^{\circ}$ ; 4,  $57.0(2)-65.0(2)^{\circ}$ .

**Rh—B**—**B** ranges: **3a/b**, 64.9(4)–69.2(4) $^{\circ}$ ; **4**, 64.9(2)–69.1(2) $^{\circ}$ .

S-B-B ranges: 3a/b,  $59.4(4)-65.6(4)^{\circ}$ ; 4,  $59.7(2)-65.8(2)^{\circ}$ .

**3b** is 1.31(3) Å; B(7)—Cl in **4** is 1.837(4) Å] are well within the expected [22] ranges for bonds to such atoms attached to borane polyhedra (ca 1.23–1.63 Å for B—OR; ca 1.73–1.92 Å for B—Cl). Compound **3b** constitutes one of the few examples of an (albeit partially) structurally-characterised borane derivative bearing a terminal hydroxy group, rather than the relatively common alkoxy substituent. Previously reported B—OH distances are in the range 1.35(1)–1.628(19) Å; the relative shortness of the B—OH separation determined here for **3b** is *perhaps* an artefact of the crystallographic disorder.

The remainder of the thiaborane polyhedral fragment is substantially regular, and the ranges of Rh—B [3a/b: 2.256(7)-2.330(8) Å; 4: 2.263(4)-2.336(4) Å],S—B [3a/b: 1.981(9)-2.096(9) Å; 4: 1.996(4)-2.108(4) Å] and B—B [3a/b: 1.735(11)-1.885(12) Å;4: 1.742(5)-1.883(5) Å] distances are typical of such metallaheteroboranes. There are, nevertheless, some significant deviations from ideal mirror symmetry within both clusters. This is evidenced by, for example, the environment of S(1): this atom is somewhat asymmetrically disposed with respect to a notional molecular mirror plane so that in 4 S(1) is 2.4187(11) Å from Rh(2), but 2.452(3) Å from the chemically equivalent Rh(3); a similar situation exists in 3a/b.

Each rhodium vertex has a co-ordination environment resembling a distorted octahedron in which a conical {(CO)( $\mu$ -CO)(PPh<sub>3</sub>)Rh} fragment is  $\eta^{5}$ bonded to the RhSB<sub>3</sub> 'ligating face' of a {*nido*-RhSB<sub>9</sub>} polyhedron. The two terminal CO ligands, and likewise the two triphenylphosphine groups, are mutually cisoid in both 3a/b and 4; the Rh-Rh connectivity is (essentially) symmetrically bridged by one further carbonyl ligand in both cases. The rhodium-to-phosphorus bonding in both structures is unremarkable; and similarly the terminal CO functions are bound to Rh in a typical fashion and are essentially linear at carbon. The Rh(2)-Rh(3) internuclear distance is 2.7409(10) in **3a/b** and 2.749(2) Å in **4**; these are comparable to the length of the same vector in related compounds: For example, in 5 (see Table 3 below), the Rh-Rh separation is 2.6307(9) Å [23], whereas in 6 the unbridged (and perhaps, therefore, less restricted) Rh-Rh connectivity is longer, at 2.778(1) Å [24]. A steric contribution to this distance arising from the

presence (and proximity) of bulky, mutually cis PPh<sub>3</sub> groups, might also be invoked in the present compounds. Both terminal CO ligands lie approximately *trans* to the cluster sulfur vertex in **3a/b** and in **4**. This is most likely a consequence of the greater basicity of the phosphines than of the carbonyl ligands, and we note that in the compound [8-CO-8-(dppm)-8,7-*nido*-RhSB<sub>9</sub>H<sub>10</sub>] [dppm = *bis*-(diphenylphosphino)methane], the CO ligand again is found to lie *trans* to sulfur [9]. (See refs [23-30].)

One possible consequence of this rather large metal vertex separation in 3a/b and 4 is relatively long distances to the bridging carbonyl moiety. This is particularly so in compound 4 where C(1) is distant 2.111(3) Å from Rh(2) and 2.117(3) Å from Rh(3); the equivalent parameters in 3a/b are 2.072(8) Å and 2.066(7) Å, respectively. The longer Rh-C(1) distances in 4 result in relatively poor overlap between Rh d hybrid orbitals and carbonyl  $\sigma$ - and  $\pi$ -type orbitals, so that in 4 C(1)-O(1) [1.145(3) Å] is relatively short for a  $\mu$ -CO function, compared to the same separation, 1.178(8) Å, in 3a/b. To our knowledge, the only other examples of a  $\{\mathbf{M}\cdots\mathbf{M}\}\$ -bridging carbonyl function in comparable clusters are the isomeric pair of dicobalt compounds [(CO)<sub>5</sub>Co<sub>2</sub>B<sub>10</sub>H<sub>8</sub>(SEt<sub>2</sub>)<sub>2</sub>] 15 and 16 [31]. In these, the much shorter intermetal separation (ca 2.49 Å) and the presence of first-row metal centres combine to afford much better orbital

Table 3. Composition of selected related species of formulation {7-X-2,3,1-closo-M<sub>2</sub>EB<sub>9</sub>}<sup>a</sup>



	M	M.	F	v	7	Daf
			L	<u>л</u>	L	Kei.
<b>5</b> <sup><i>b</i></sup>	$(Ph_3P)(Ph_2P-C_6H_4-o-)Rh^c$	(Cl)(Ph <sub>3</sub> P)Rh	S	o-C <sub>6</sub> H <sup>c</sup>	Cl	[23]
<b>6</b> <sup><i>b</i></sup>	$(\eta^{5}-C_{5}Me_{5})Rh$	$(\eta^5 - C_5 Me_5) Rh$	S	Cl		[24]
7	$(\eta^5 - C_5 H_5) Co$	$(\eta^{5}-C_{5}H_{5})Co$	S	н		[25]
<b>8</b> <sup>b</sup>	$(\eta^5 - C_5 H_5) Co$	$(\eta^{5}-C_{5}H_{5})Co$	S	I	_	[25]
9	$(\eta^5 - C_5 Me_5)$ Ir	$(\eta^{5}-C_{5}Me_{5})$ Ir	S	Cl	_	[26]
10	$(\eta^6 - p - \text{cym})$ Ru	$(\eta^{6}-p-\text{cym})\text{Ru}$	S	Н		[27]
11	$(\eta^6$ -p-cym)Ru	$(\eta^{6}-p-\text{cym})$ Ru	S	Cl	_	[27]
12 <sup>b</sup>	$(\eta^{5}-C_{5}H_{5})Co$	$(\eta^{5}-C_{5}H_{5})Co$	С	н		[28]
13	$(\eta^5-C_5H_5)Co$	$(\eta^{5}-C_{5}H_{5})Co$	Se	н	_	[29]
14	$(\eta^{5}-C_{5}Me_{5})Rh$	$(\eta^{5}-C_{5}Me_{5})Rh$	P—Ph	Cl?		[30]

 $^{a}p$ -cym = C<sub>6</sub>H<sub>4</sub>-Me-1-<sup>*i*</sup>Pr-4.

<sup>b</sup>Characterised crystallographically.

<sup>c</sup> One Ph ring of a Rh-bound (formerly) Ph<sub>3</sub>P ligand is ortho-cycloboronated to B(7).

overlap to the bridging carbonyl ligand, with bridging C—O distances (ca 1.18 Å) much closer to that found in 3a/b.

Twelve-vertex complexes of formulation  $\{2,3,1-closo-M_2SB_9\}$  are not without precedent (*cf* Table 3), and the observation of B(7) substitution by a nucleophile is a common feature. The conversion of 7 to 8 has been demonstrated [25] by treatment of the former with I<sub>2</sub> at 250°C, in contrast to our (tentative) observation of the facile conversion of **3a** to **3b** during workup under ambient laboratory conditions. In general, however, both substituted and non-substituted species have previously been isolated from the same reaction mixtures, and the two above observations tend to suggest that the *closo*-12-vertex Rh<sub>2</sub>SB<sub>9</sub> polyhedron may be formed *prior to* B(7) substitution.

The anionic 1-carba- relative (12) [28] of 7 and (tentatively) the 1-selena- analogue (13) [29] of 7 have also been reported, although in the latter compound relative positions of vertices were not established; compound(s) 14, 1-phenyl-1-phospha- relative(s) of compound 6 have also been identified [30]. An isomer of compound 7, in which the cluster was proposed to have a 2,4,1-Co<sub>2</sub>SB<sub>9</sub> architecture, has also been described [32]. We have formed 3 and 4 in a mild reaction at ambient conditions, whereas such compounds have previously been reported largely from reactions at elevated temperature or under 'metal vapour synthesis' conditions. Moreover, we note that the present compounds are, to our knowledge, the first examples of such dirhodathiaboranes where both metal vertices are formally in the +2 oxidation state. {The Rh(2)—C(1)—Rh(3) angles  $[82.9(3)^{\circ} \text{ in } 3a/b]$ and  $81.11(11)^{\circ}$  in 4] and the  $\mu$ -(CO) stretching frequencies (ca 1863 and 1880 cm<sup>-1</sup>, respectively) identify the bridging carbonyl ligands as (CO) rather than  $(CO)^{2-}$  [33]. Clearly the two unpaired electrons from the two isolated, formally Rh(II) fragments must in these compounds be paired in the cluster molecular



orbital scheme : the easy observation of NMR spectra is consistent with diamagnetism.

We had anticipated that the reaction which led to the formation of compounds 2-4 might yield the species [8-CO-8-PPh<sub>3</sub>-8,7-nido-RhSB<sub>9</sub>H<sub>10</sub>], an analogue of the 'non-Wadian' compound [8,8-(PPh<sub>3</sub>)<sub>2</sub>-8,7-nido-RhSB<sub>9</sub>H<sub>10</sub>] [23]. A novel Rh co-ordination environment (involving the phosphine-bound phenyl groups) has been proposed [8] to account for the failure of the latter rhodathiaborane to adopt the predicted [34] closo cluster geometry. However, if one PPh<sub>3</sub> ligand in the latter complex is replaced by CO the possibility of such co-ordination is severely limited, and the above (hypothetical) [nido-(CO)(PPh<sub>3</sub>)RhSB<sub>9</sub>H<sub>10</sub>] complex would be required to 'close up'. It appears that such a scenario may be compromised by the need to accommodate an 'additional' (formerly bridging) H atom within the closed cluster, and the intermediate reacts by 'scavenging' a further metal vertex and appropriate ligands, with the ultimate result that the observed closo-12-vertex products are formed. In related systems where this 'additional' H atom has, in effect, been removed either by deprotonation [35], or by formal replacement of a  $\{BH_2\}$  vertex by  $\{B-PR_3\}$ [13], a closo-11-vertex {1,2-RhSB<sub>9</sub>} cluster is obtained as expected. Perhaps surprisingly, we have thus far been unable significantly to alter the yields of compounds 3 and 4 by adjustment of reactant stoichiometry or reaction conditions.

As has already been noted, and Table 3 further suggests, compounds of this kind appear rather susceptible to nucleophilic substitution at that cluster boron atom [B(7)] which is adjacent to both metal vertices. There is considerable current interest [36] in the formation of *B*-substituted heteroboranes for a number of purposes. The ease of formation of compounds such as 3 and 4 leads us to consider them as candidates for further boron atom functionalisation : this work will be the subject of future contributions.

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