

# Chemistry of 11-vertex rhodathiaboranes: reactions with monodentate phosphines

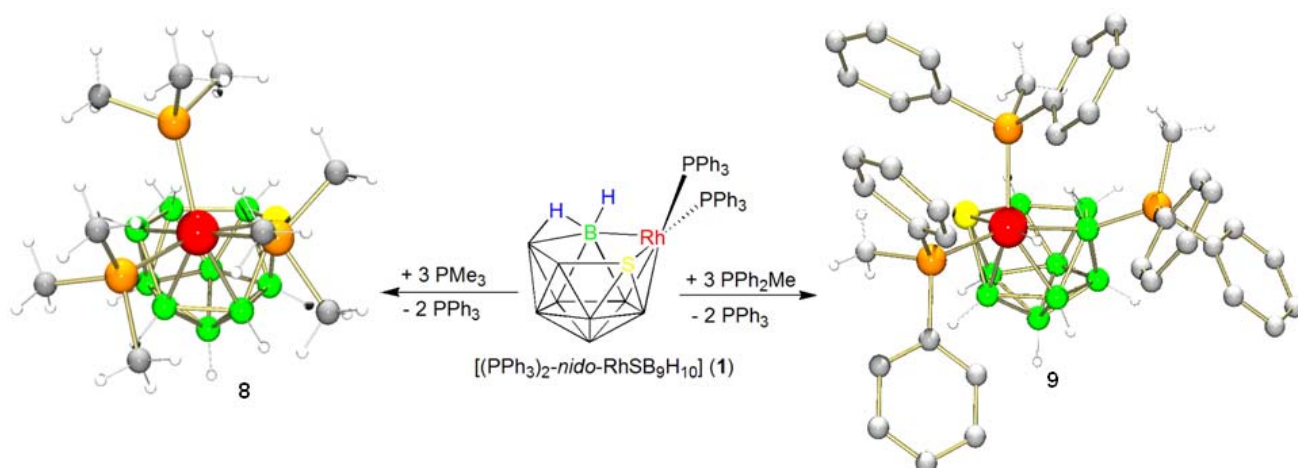
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## Graphical entry and synopsis



Reactions of  $[8,8-(PPh_3)_2-nido-8,7-RhSB_9H_{10}]$  (1) with  $PR_3$  afford 11-vertex rhodathiaboranes in which the resulting ligand configuration is driven by the nature of the monodentate phosphine. The lability of some of the species is demonstrated by variable NMR studies, which give mechanistic insights on the substitutional chemistry of 11-vertex *nido*-rhodathiaboranes.

## Abstract

The reaction of [8,8-(PPh<sub>3</sub>)<sub>2</sub>-*nido*-8,7-RhSB<sub>9</sub>H<sub>10</sub>] (**1**) with PR<sub>3</sub> in a 1:2 ratio affords mixtures that contain the mono-substituted *bis*-PR<sub>3</sub>-ligated rhodathiaboranes [8,8-(PPh<sub>3</sub>)(L)-*nido*-8,7-RhSB<sub>9</sub>H<sub>10</sub>] [L = PMe<sub>2</sub>Ph (**5**), PMe<sub>3</sub> (**6**)] and the corresponding *tris*-PR<sub>3</sub>-ligated compounds [8,8,8-(L)<sub>3</sub>-*nido*-8,7-RhSB<sub>9</sub>H<sub>10</sub>] [L = PMe<sub>2</sub>Ph (**7**), PMe<sub>3</sub> (**8**)]. These latter species are more conveniently prepared from the reaction of **1** with three equivalents of the monodentate phosphines, PMe<sub>2</sub>Ph and PMe<sub>3</sub>. Reaction between **1** and PMePh<sub>2</sub> in a 1:2 ratio yields the disubstituted rhodathiaborane [8,8-(PMePh<sub>2</sub>)<sub>2</sub>-*nido*-8,7-RhSB<sub>9</sub>H<sub>10</sub>] (**4**), whereas the use of three equivalents of phosphine leads to the formation of B-ligated eleven-vertex [8,8,8-(PMePh<sub>2</sub>)<sub>2</sub>(H)-*nido*-8,7-RhSB<sub>9</sub>H<sub>9</sub>-9-(PMePh<sub>2</sub>)] (**9**). Compounds **4-9** have been characterized by NMR spectroscopy, and the structures of **8** and **9** confirmed by X-ray diffraction analyses. The characterization of the cluster compounds has been aided by the use of DFT calculations on some of the species. Variable-temperature NMR studies have demonstrated a lability of the ligands of the PMePh<sub>2</sub>-ligated clusters **4** and **9**, providing mechanistic insights about the ligand substitutional chemistry in these eleven-vertex rhodathiaboranes.

## Introduction

Recent research has led to the discovery that the eleven-vertex rhodathiaborane [8,8-(PPh<sub>3</sub>)<sub>2</sub>-*nido*-8,7-RhSB<sub>9</sub>H<sub>10</sub>] (**1**)<sup>1</sup> reacts with pyridine to form the the B-pyridine-substituted hydridorhodathiaborane [8,8,8-(PPh<sub>3</sub>)<sub>2</sub>(H)-*nido*-8,7-RhSB<sub>9</sub>H<sub>9</sub>-9-(NC<sub>5</sub>H<sub>5</sub>)] (**2**), which undergoes thermal dehydrogenation to afford [1,1-(PPh<sub>3</sub>)<sub>2</sub>-*closo*-1,2-RhSB<sub>9</sub>H<sub>8</sub>-3-(NC<sub>5</sub>H<sub>5</sub>)] (**3**).<sup>2</sup> Compounds **2** and **3** have been shown to be active catalyst precursors for the homogeneous hydrogenation and isomerization of alkenes.<sup>3</sup> In addition, reactivity studies of the reaction of alkynes with the hydrido-rhodathiaborane **2** have demonstrated that the de-hydrogenation of **2** can promote the oxidative addition of *sp* C–H bonds,<sup>4</sup> suggesting that other E–H bonds in, for example, alkanes, silanes, or boranes, could also be activated

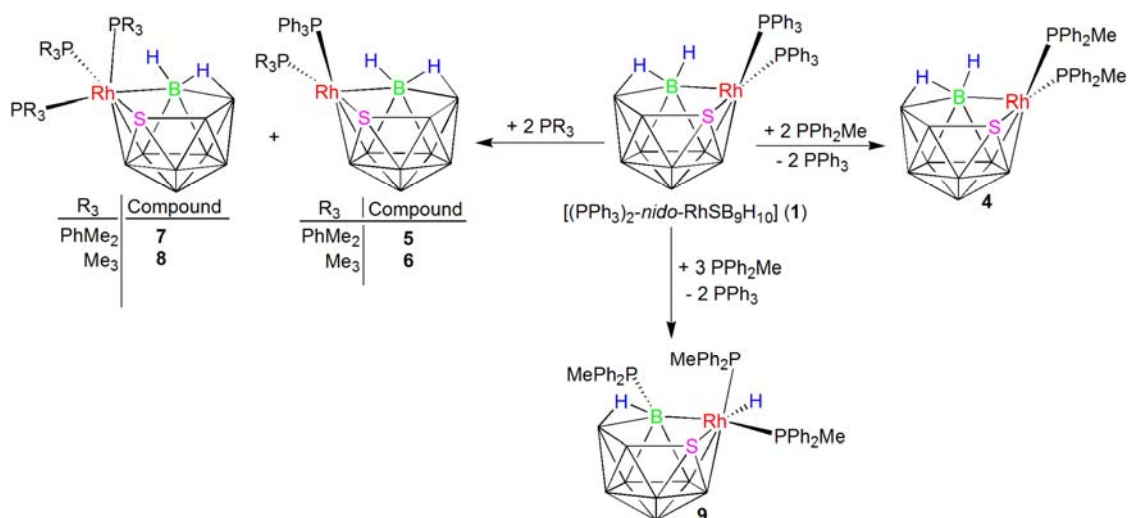
by modifying the reaction conditions and / or by an appropriate tailoring of the clusters.

The ease of preparation, the versatility, and the stability of these eleven-vertex cluster compounds make them attractive candidates for homogeneous catalyst precursors.<sup>3,4</sup> This consideration prompted us to examine how we might modify the *exo*-polyhedral phosphine-ligand sphere in order to explore the reactivity of new phosphine-ligated derivatives of **2**, the overall target being the optimization of the catalytic activity of these cluster species. In this regard, it has previously been demonstrated that the rhodathiaborane **1** undergoes facile substitution of PPh<sub>3</sub> by other monodentate, and also bidentate, phosphines,<sup>5, 6</sup> and we have examined reactions of **1** and **2** with the monodentate phosphines PPhMe<sub>2</sub>, PPhMePh and PPhMe<sub>3</sub>.

## Results and Discussion

### Reactions of [8,8-(PPh<sub>3</sub>)<sub>2</sub>-*nido*-8,7-RhSB<sub>9</sub>H<sub>10</sub>] (**1**) with PPhMe<sub>2</sub> and PPhMe<sub>3</sub>

Treatment of the *bis*-(PPh<sub>3</sub>) compound **1** with two equivalents of PPhMe<sub>2</sub> affords the disubstituted rhodathiaborane, [8,8-(PPhMe<sub>2</sub>)<sub>2</sub>-*nido*-8,7-RhSB<sub>9</sub>H<sub>10</sub>] (**4**). In contrast, the use of two equivalents of PPhMePh or PPhMe<sub>3</sub> gives mixtures that contain both the monosubstituted *bis*-(phosphine) species, [8,8-(PPh<sub>3</sub>)(L)-*nido*-8,7-RhSB<sub>9</sub>H<sub>10</sub>], where L = PPhMe<sub>2</sub> (**5**) or PPhMe<sub>3</sub> (**6**), together with the products of addition of a third phosphine at the metal, *viz.* the *tris*-(phosphine) species [8,8,8-(L)<sub>3</sub>-*nido*-8,7-RhSB<sub>9</sub>H<sub>10</sub>], where L = PPhMe<sub>2</sub> (**7**) or PPhMe<sub>3</sub> (**8**). These last two *tris*-(phosphine) {Rh(PR<sub>3</sub>)<sub>3</sub>}-containing cluster compounds are more conveniently prepared from the reactions of **1** with three equivalents of phosphine. In interesting contrast, the same reaction, but now with PPhMe<sub>2</sub> in a 1:3 rhodathiaborane:phosphine molar ratio, yields the boron-substituted hydridorhodathiaborane [8,8,8-(PPhMe<sub>2</sub>)<sub>2</sub>(H)-*nido*-8,7-RhSB<sub>9</sub>H<sub>9</sub>-9-(PPhMe<sub>2</sub>)] (**9**). Scheme 1 illustrates these results, and it can be used as a guide throughout the paper.



**Scheme 1**

The 160 MHz  $^{11}\text{B}$ - $\{^1\text{H}\}$  NMR spectra of the  $\text{PMe}_3$  and  $\text{PMe}_2\text{Ph}$  mixed *bis*-(phosphine) species **5** and **6** (see Table 1) show eight peaks in a 1:1:2:1:1:1:1:1 intensity ratio, slightly shielded [mean  $\delta(^{11}\text{B})$  *ca.* -6 ppm] with respect to compound **1** [mean  $\delta(^{11}\text{B})$  *ca.* -4 ppm.]. The signal of relative intensity 2 results from the accidental coincidence of resonances from two chemically different boron sites: these are effectively distinguished individually by  $^1\text{H}$ - $\{^{11}\text{B}(\text{selective})\}$  experiments. In contrast, the expected nine signals are all resolved in the  $^{11}\text{B}$  spectra of the *bis*-( $\text{PMePh}_2$ ) species **4** and they exhibit the largest overall shielding in the series [mean  $\delta(^{11}\text{B})$  *ca.* -10 ppm], which may reflect a different electron contribution of the two  $\text{PPh}_2\text{Me}$  ligands in **4** compared to the mixed pairs of phosphines,  $\{(\text{PPh}_3)(\text{PMe}_3)\}$  and  $\{(\text{PPh}_3)(\text{PMe}_2\text{Ph})\}$  in the monosubstituted counterparts **5** and **6**. The  $^1\text{H}$ -{Dossett #200} spectra of these new  $\text{PR}_3$ -ligated rhodathiaboranes show that there is also a shielding of the BHB bridging-hydrogen atom with respect to the  $\text{PPh}_3$  derivative **1**, with the higher shielding [at  $\delta(^1\text{H})$  -0.46 ppm] being that of compound **4**. It has been suggested that higher-field shifts of the BHB proton resonances in *nido* eleven-vertex rhodathiaboranes of this type correlate with a negative charge build-up on the metal centers.<sup>7</sup> Thus, the trend of high-field shifts found in the series of rhodathiaboranes, **1**, **4**, **5** and **6** could be related, at least in part, to an increase in the electron density at the rhodium

centre:  $\{\text{Rh}(\text{PPh}_3)_2\} < \{\text{Rh}(\text{PPh}_3)(\text{PMe}_2\text{Ph})\} < \{\text{Rh}(\text{PPh}_3)(\text{PMe}_3)\} < \{\text{Rh}(\text{PMePh}_2)_2\}$ .

**Table 1.**  $^{11}\text{B}$  and  $^1\text{H}\{-^{11}\text{B}\}$  NMR data for the *bis*-phosphine compounds **5** and **6** in  $\text{CDCl}_3$  at room temperature. In brackets are the DFT/GIAO-calculated  $^{11}\text{B}$  nuclear shielding values for **6**

Assignment <sup>a</sup>	<b>5</b>		<b>6</b>	
	$\delta(^{11}\text{B})$	$\delta(^1\text{H})$	$\delta(^{11}\text{B})$ [DFT]	$\delta(^1\text{H})$
3	+15.5	+3.65	+15.8 [+21.9]	+3.74
9	+10.6	+3.20	+10.3 [+19.6]	+3.10
11	+2.6 <sup>b</sup>	+3.24	+2.2 [+9.8]	+3.22
6		+2.37	[+8.3]	+2.29
4	-1.3	+3.09	-1.3 [+1.5]	+3.02 <sup>e</sup>
5	-8.5	+2.29	-8.2 [-10.5]	+2.39 <sup>e</sup>
1	-18.5 <sup>c</sup>	+0.83	-23.2 [-14.2]	+1.55 <sup>e</sup>
10	-24.4	+1.14	-25.6 [-18.2]	+0.91
2	-28.2 <sup>d</sup>	+0.83	-27.7 [-28.8]	+0.70
$\mu$ -(9,10)		-1.30		-1.33

<sup>a</sup> Assignments based on  $^1\text{H}\{-^{11}\text{B}\}$  selective experiments and comparison with **1**. <sup>b</sup> Accidentally coincident  $^{11}\text{B}$  resonances for B(6) and B(11). <sup>c</sup>  $^1J(^{11}\text{B}\text{-}^1\text{H})$  *ca.* 150 Hz. <sup>d</sup>  $^1J(^{11}\text{B}\text{-}^1\text{H})$  *ca.* 141 Hz.

The  $^{31}\text{P}\{-^1\text{H}\}$  spectra of the  $\text{PMe}_3$  and  $\text{PMe}_2\text{Ph}$  mixed-ligand  $\text{PPh}_3$  compounds **5** and **6** at room temperature exhibit two doublets of doublets, which conform to the asymmetric structure of these cluster compounds. The signals around  $\delta(^{31}\text{P})$  *ca.* +25 ppm correspond to the  $\text{PPh}_3$  ligands, whereas the resonances of the methyl-ligated phosphines are at higher field. In contrast, the *bis*-( $\text{PMePh}_2$ )-ligated rhodathiaborane **4** exhibits a very broad signal in the  $^{31}\text{P}\{-^1\text{H}\}$  spectrum at room temperature: this

signal splits into two doublets of doublets at lower temperatures, resembling the pattern of **5** and **6**. The  $^1\text{H}$  NMR spectrum of **4** also shows a temperature-dependent behaviour that at high temperatures renders equivalent the two resonances of the  $\text{PMePh}_2$  ligands, and leads to the coalesce in pairs of some of the BH terminal hydrogen resonances. Therefore, the NMR data for **4** at different temperatures are suggestive of an intramolecular dynamic process, which resembles the fluxional behavior of other analogous *nido*-structured eleven-vertex metallaheteroboranes  $\{\text{MEB}_9\}$  where M = Pt or Rh and E = S, N or C (see Table 2). The activation energies for these processes are readily estimated from the temperatures at which peak-coalescences are observed in the NMR spectra. This type of non-rigid behaviour has become increasingly recognised in eleven-vertex metallaheteroboranes that incorporate formally unsaturated pseudo-square-planar Rh(I) or Pt(II) vertices; and recent DFT calculations have revealed that *isonido*- and *closo*-shaped clusters are points along the reaction coordinate of this inter-enantiomeric fluxional process.<sup>8</sup>

**Table 2.** Activation energies for the fluxional process of eleven-vertex *nido*-metallaheteroboranes

Compound	$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )	Reference
$[(\text{PPh}_3)_2\text{RhSB}_9\text{H}_{10}]$ ( <b>1</b> )	58	1
$[(\text{PPh}_2\text{Me})_2\text{RhSB}_9\text{H}_{10}]$ ( <b>4</b> )	52	this work
$[(\text{dppp})\text{RhSB}_9\text{H}_{10}]$	53	5
$[(\text{dppp})\text{RhSB}_9\text{H}_9(\text{OEt})]^{\text{a}}$	>64	5
$[(\text{PPh}_3)_2\text{RhNB}_9\text{H}_{11}]$	46	8
$[(\text{PMe}_2\text{Ph})_2\text{PtCB}_9\text{H}_{11}]$	62	8
$[(\text{PMe}_2\text{Ph})_2\text{PtCB}_9\text{H}_{10}(\text{OEt})]$	>75	9

<sup>a</sup>  $\text{dppp} = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$

The *tris*-( $\text{PMe}_2\text{Ph}$ )-ligated *nido*-rhodathiaborane **7** has been reported previous to this work,<sup>10</sup> but for

convenience of comparison its spectroscopic data are described here together with those of **8**. The molecular structure of **7** was also determined by single-crystal X-ray diffraction in the previous work.<sup>10</sup> We now report the crystallographic analysis of the new *tris*-(PMe<sub>3</sub>)-ligated analogue **8** (*vide infra*). The <sup>11</sup>B and <sup>1</sup>H NMR data for both compounds are listed in Table 3. The proton spectra of each cluster exhibits nine signals in the positive region that can be assigned to the nine BH units of the cluster, and a singlet at the highest-field that corresponds to the BHB hydrogen atom. Due to the overlapping of some resonances, the <sup>11</sup>B spectra do not show the separated nine-peak pattern expected for the asymmetric structure of these clusters; however, selective <sup>1</sup>H-<sup>11</sup>B} decoupling experiments enabled the indirect resolution of the individual components of the broad signals of relative intensity 2 and 3 in the spectra of **7** and **8**, respectively (Table 3). Although **7** and **8** each bear a third phosphine ligand on the metal centre, there is no overall significant shift toward higher fields [mean δ(<sup>11</sup>B) –6 ppm] with respect the monosubstituted *bis*-(phosphine) parent compounds **5** and **6**, suggesting that the additional electron density donated by the third ligand is highly localized at the rhodium centre and that the electronic structures within the clusters of **5**, **6**, **7** and **8** are all very similar. In this regard, and according to the rationale described above, the shift to higher field of more than 2.6 p.p.m. in the <sup>1</sup>H NMR resonance of the BHB hydrogen atoms in **7** and **8** may reflect an increase in the electron density at the rhodium centre; differential neighbouring-group magnetic anisotropic effects arising from P-phenyl *versus* P-methyl substituents on the phosphines may also play a rôle. In any event, this large high-field shift in the BHB bridging proton resonance is diagnostic of formation of {RhL<sub>3</sub>} *tris*-ligated eleven-vertex rhodathiaboranes *versus* their {RhL<sub>2</sub>} *bis*-ligated counterparts. For **7** and **8**, the presence of three phosphine ligands bound to the rhodium atom is clear in the <sup>31</sup>P-<sup>1</sup>H} NMR spectra that show three signals in a 1:1:1 relative intensity ratio. For compound **8**, the comparison of the spectrum at 223 K with that at 300 K is a nice illustration of the “thermal decoupling” of the boron nuclei,<sup>11</sup> which leads



to a resolution of the coupling constants  ${}^2J({}^{31}\text{P}-{}^{31}\text{P})$  at low temperature that are not manifest at room temperature (see Figure S3 in the supporting information).

**Table 3.**  ${}^{11}\text{B}$  and  ${}^1\text{H}$  NMR data for the *tris*-phosphine compounds **7** and **8** in  $\text{CDCl}_3$  at room temperature. In brackets are the DFT/GIAO-calculated  ${}^{11}\text{B}$  nuclear shielding values for **8**.

Assignment	<b>7</b>		<b>8</b>	
	$\delta({}^{11}\text{B})$	$\delta({}^1\text{H})$	$\delta({}^{11}\text{B})$ [DFT]	$\delta({}^1\text{H})$
6	+13.5	+4.03	+13.0 [+13.8]	+3.95
9	+7.1	+3.79	+6.1 [+12.2]	+3.29
3	+7.1	+2.14	+6.1 [+11.9]	+3.12
4	+5.3	+3.55	+6.1 [+8.1]	+1.93
11	-1.1	+2.40	-2.3 [+1.8]	+2.83
10	-14.1	+2.40	-15.4 [-14.0]	+1.84
5	-15.5	+1.97	-15.5 [-15.7]	+1.70
1	-21.2	+1.93	-22.9 [-20.9]	+1.70
2	-27.0	+1.24	-27.1 [-28.6]	+1.20
$\mu$ -(9,10)		-3.98		-3.75

The characterization of the new B-ligated hydridorhodathiaborane **9** has also been carried out by X-ray diffraction analysis (*vide infra*) and by NMR spectroscopy. The  ${}^{11}\text{B}$ - $\{{}^1\text{H}\}$  NMR spectrum shows eight peaks in a 2:1:1:1:1:1:1:1 intensity ratio, with the peak of relative intensity 2 resulting from an accidental overlap of two resonances. These latter two are effectively distinguished by  ${}^1\text{H}$ - $\{{}^{11}\text{B}\}$  selective decoupling experiments as mentioned above. Diagnostic of the formation of the eleven-vertex hydrido-*nido*-rhodathiaborane are the  ${}^1\text{H}$ - $\{{}^{11}\text{B}\}$  NMR signals at  $\delta({}^1\text{H})$  -1.82 and -12.13 ppm,

which correspond to the BHB bridging hydrogen atom and the Rh-H hydride ligand, respectively. In the  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum, compound **9** exhibits three resonances with the highest-field signal being significantly broader than the other two, and, therefore, assigned to the  $\text{PPh}_2\text{Me}$  ligand directly bound to the boron vertex B(9).

**Table 4**  $^{11}\text{B}$ ,  $^1\text{H}$  and  $^{31}\text{P}$  NMR data for compound **9** in  $\text{CDCl}_3$  at room temperature compared with the corresponding DFT-calculated chemical shifts

Assignment <sup>a</sup>	Cluster data			$^1J(^{11}\text{B}\text{-}^1\text{H})/\text{Hz}$
	$\delta(^{11}\text{B})$ (ppm)		$\delta(^1\text{H})$ (ppm)	
	measured	calculated		
3, 6	+4.2	+8.3, +7.7	+2.81, +3.58	122
4	-0.8	+2.7	+3.01	127
11	-2.8	+0.5	+3.11	
9	-4.0	-0.9	[B- $\text{PPh}_2\text{Me}$ ]	
5	-7.5	-11.3	+1.86	122
2, 10	-21.2	-22.3, -22.8	+1.31	
1	-25.1	-24.5	+1.58	132
$\mu$ (9, 10)			-1.79	
8		[Rh-H]	-12.10	

<sup>a</sup> Based on  $^1\text{H}\{-^{11}\text{B}(\text{sel})\}$  experiments and DFT calculations

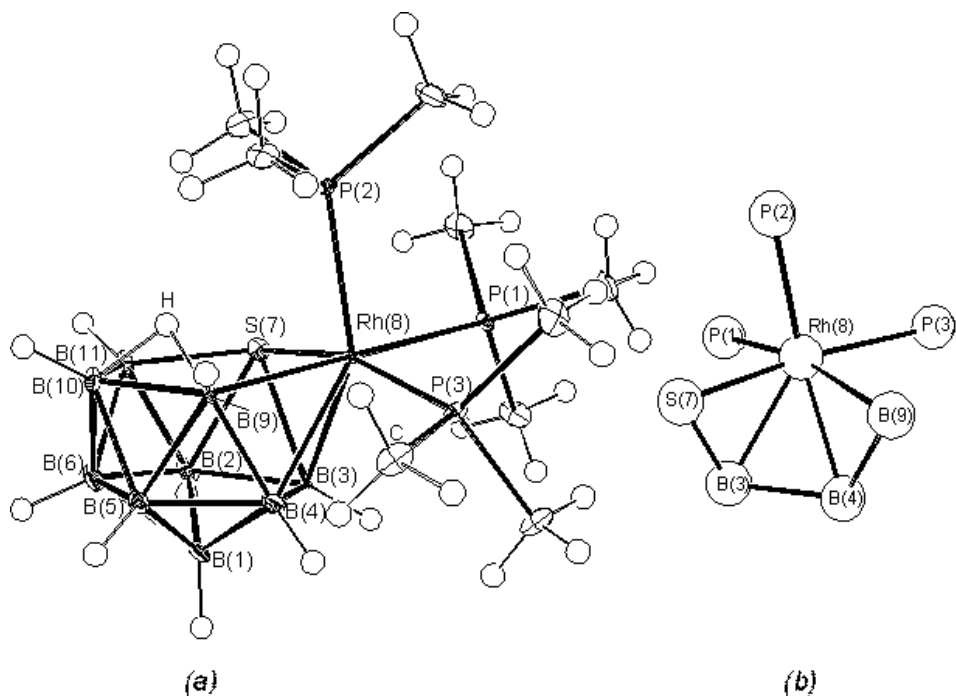
PPh<sub>2</sub>Me data in CDCl<sub>3</sub> solution<sup>a</sup>

Assignment <sup>b</sup>	$\delta(^{31}\text{P})$ (ppm)		$^1J(^{103}\text{Rh}-^{31}\text{P})$	$\delta(^1\text{H})$ (ppm)	$^2J(^{31}\text{P}-^1\text{H})/\text{Hz}$
	measured <sup>c</sup>	calcd.	Hz		
P(1)	+15.3	+14.7	85	+1.72	7.4
P(2)	+9.6	+10.6	128	+1.64	6.8
P(3)	-2.9 <sup>d</sup>	-7.5	-	+1.67	11.2

<sup>a</sup> Measured at 273 K. <sup>b</sup> Based on <sup>1</sup>H-<sup>31</sup>P(selective) experiments and DFT-calculations. <sup>c</sup> Broad signals: <sup>2</sup>J(<sup>31</sup>P-<sup>31</sup>P) coupling constants not observed <sup>1</sup>J(<sup>31</sup>P-<sup>11</sup>B) = 129 Hz

**Molecular structures of [(PMe<sub>3</sub>)<sub>3</sub>RhSB<sub>9</sub>H<sub>10</sub>] **8** and [(PMePh<sub>2</sub>)<sub>2</sub>(H)RhSB<sub>9</sub>H<sub>9</sub>(MePh<sub>2</sub>)] **9****

The crystal and molecular structures of **8** and **9** were established by single-crystal *X*-ray crystallography. A summary of selected derived interatomic distances and angles for these two rhodathiaboranes are in Table 5, and drawings of these molecules are in Figures 1 and 2. The molecular structure of each compound is based on an eleven-vertex open *nido*-arrangement that has a pentagonal open face, formally obtained by the removal of one vertex from an icosahedron. Both **8** and **9** are formally (11+2) skeletal-electron-pair (sep) *nido*-rhodathiaborane analogues of the hypothetical parent borane B<sub>11</sub>H<sub>15</sub>: three bridging hydrogen atoms and three BH groups on the pentagonal open face of B<sub>11</sub>H<sub>15</sub> are formally replaced by a sulphur atom, a {B(PMePh<sub>2</sub>)} vertex and the {RhH(PMePh<sub>2</sub>)<sub>2</sub>} fragment to give **9**; two BH groups and three of the four bridging hydrogen atoms of B<sub>11</sub>H<sub>15</sub> are formally replaced by a sulphur atom and the {Rh(PPh<sub>2</sub>Me)<sub>3</sub>} fragment in **8**.

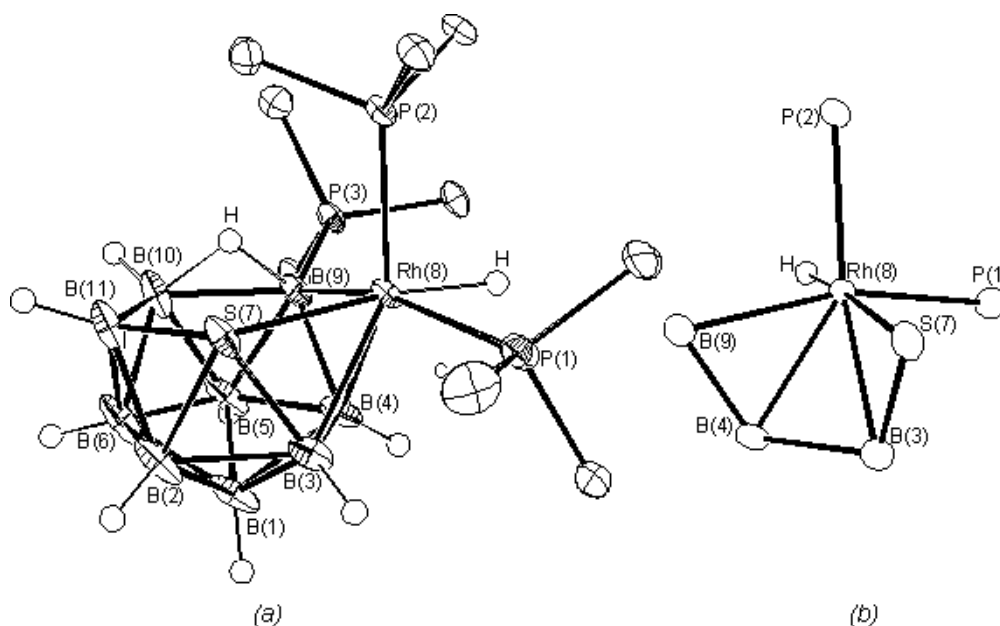


**Figure 1** (a) ORTEP-type of drawing of compound **8** (50 % thermal ellipsoids for non-hydrogen atoms); (b) Detail of the {Rh(PMe<sub>3</sub>)<sub>3</sub>}-to-{SB<sub>9</sub>H<sub>10</sub>} metal-to-cluster coordination sphere.

**Table 5.** Selected interatomic distances (Å) and angles (°) between interatomic vectors for **8** and **9** with standard uncertainties (s.u) in parentheses.

	<b>8</b>	<b>9</b>
Rh(8)-S(7)	2.3736(7)	2.4172(5)
Rh(8)-P(1)	2.4016(4)	2.3206(6)
Rh(8)-P(2)	2.3619(4)	2.3175(5)
Rh(8)-P(3)	2.2869(4)	n/a
Rh(8)-B(3)	2.291(3)	2.238(2)
Rh(8)-B(4)	2.2517(18)	2.224(2)
Rh(8)-B(9)	2.2339(17)	2.218(2)
S(7)-B(2)	2.0012(19)	1.970(3)
S(7)-B(3)	2.047(3)	2.062(2)
S(7)-B(11)	1.9140(19)	1.930(3)
P(3)-B(9)	n/a	1.943(2)
B(6)-B(11) (shortest)	1.739(3)	1.742(4)
B(2)-B(3) (longest)	1.885(4)	1.907(4)
B-B (average)	1.795(1)	1.796(1)
P(1)-Rh(8)-P(2)	96.256(14)	100.810(19)
P(1)-Rh(8)-P(3)	93.443(15)	n/a
P(1)-Rh(8)-B(9)	174.29(5)	159.43(6)
P(1)-Rh(8)-H(1)	n/a	80.3(12)
P(2)-Rh(8)-P(3)	97.946(15)	n/a
P(2)-Rh(8)-B(3)	148.61(8)	147.57(6)

P(2)-Rh(8)-B(4)	133.44(5)	144.25(6)
P(2)-Rh(8)-H(1)	n/a	89.1(12)
S(7)-Rh(8)-P(1)	86.400(15)	99.077(19)
S(7)-Rh(8)-P(2)	98.40(2)	95.149(18)
S(7)-Rh(8)-P(3)	163.57(2)	n/a
S(7)-Rh(8)-B(9)	88.04(4)	88.79(5)
Rh(8)-B(9)-P(3)	n/a	124.17(11)



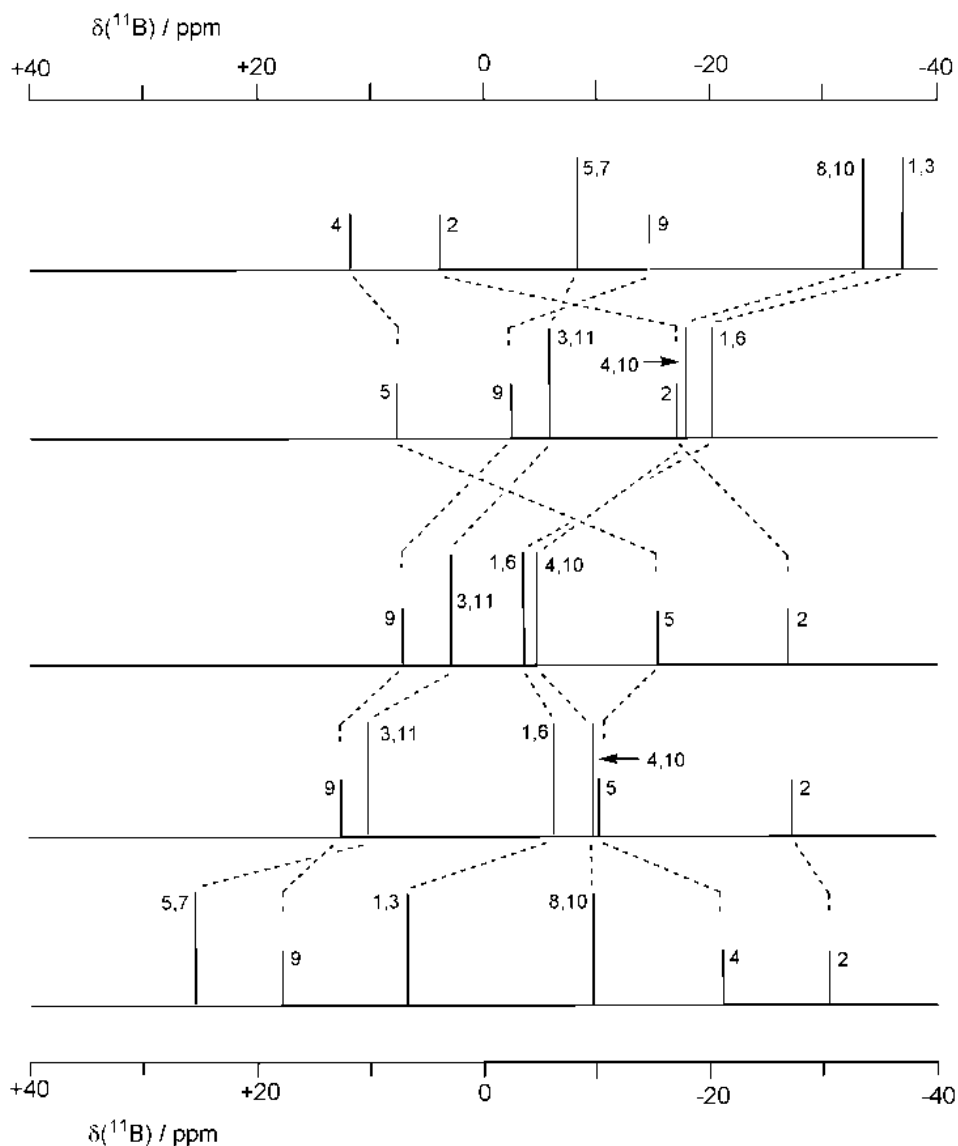
**Figure 2.** (a) ORTEP-type of drawing of compound **9** (50 % thermal ellipsoids for non-hydrogen atoms); (b) Detail of the {Rh(PMePh<sub>2</sub>)<sub>2</sub>H}-to-{SB<sub>9</sub>H<sub>9</sub>(PMePh<sub>2</sub>)} metal-to-cluster coordination sphere

The interboron distances are all within normal ranges for polyhedral boron-containing clusters, although the larger distances in excess of 1.9 Å for the B(2)-B(3) vectors that flank the sulphur atoms should perhaps be noted. The Rh-P distances across the whole series of eleven-vertex rhodathiaboranes **1**, **2**, **7**, **8** and **9** vary from the shortest in compound **8** at 2.2868(5) Å to the longest in **7** at 2.4539(8) Å.<sup>10</sup> In each of these compounds, the longest Rh-P linkage is with the phosphine ligand

that is *trans* to a boron vertex: B(9) for compounds **2**, **7**, **8** and **9**, and B(4) for compound **1**; the shortest is assigned to the PR<sub>3</sub> ligand that is *trans* to the S(7) vertex, whereas the intermediate Rh-P distances correspond to the phosphine groups that occupy positions *transoid* to the B(3)-B(4) edge of the cluster. This trend suggests that a boron vertex has a stronger *trans*-effect than either a B-B edge or a sulphur vertex in metallathiaboranes. Overall, there are no significant differences in the corresponding distances and angles among the five {RhSB<sub>9</sub>H<sub>9</sub>L} clusters [where L = H (**1**), NC<sub>5</sub>H<sub>5</sub> (**2**) or PMePh<sub>2</sub> (**9**)], although it may be noted that the Rh(8)-S(7) length in the hydridorhodathiaboranes **2** and **9** is *ca.* 0.05 Å longer than in the other derivatives, suggesting a higher structural *trans*-effect of the hydride ligand compared to the phosphines, PPh<sub>3</sub>, PMePh<sub>2</sub>, PMe<sub>2</sub>Ph and PMe<sub>3</sub>.

### **Bonding considerations**

In view of the relevance of this set of compounds to the catalytic potential of the {RhSB<sub>9</sub>} system,<sup>2,3,4</sup> the electronic constitution of the clusters, particularly with regard to the rhodium centre, merits consideration. The *bis*-(PR<sub>3</sub>)-ligated rhodathiaboranes, **1**, **4**, **5** and **6**, could be regarded as formally ‘unsaturated’ clusters, with the “unsaturation” arising from the tendencies of rhodium to adopt square-planar 16-electron metal configuration.<sup>8, 12,13</sup>



**Figure 3.** Stick diagrams representing the chemical shifts and relative intensities in the  $^{11}\text{B}$  NMR spectra of *nido*-6- $\text{SB}_9\text{H}_{11}$  (lowest trace), the *bis*(ligand) species  $[\text{8,8}-(\text{PPh}_3)_2\text{-nido-8,7-RhSB}_9\text{H}_{10}]$  **1** (low centre trace), the *tris*(ligand) species  $[\text{8,8,8}-(\text{PMe}_2\text{Ph})_3\text{-nido-8,7-RhSB}_9\text{H}_{10}]$  **7** (centre trace),  $[\text{8}-(\eta^5\text{-C}_5\text{Me}_5)\text{-nido-8,7-IrSB}_9\text{H}_{10}]$  **10** (upper centre trace), and the  $[\text{arachno-6-SB}_9\text{H}_{12}]^-$  anion



(uppermost trace). The values for **1**, **7** and **10** are averaged across the pseudo-mirror-plane of the {SB<sub>9</sub>} fragment for purposes of comparison. Hatched lines connect equivalent positions. Note the inversion of cluster nuclear shielding characteristics between **7** and **10** (see text).

Thus, these species could be described as Rh(I) complexes of {RhL<sub>2</sub>}<sup>+</sup> with {*nido*-SB<sub>9</sub>H<sub>10</sub>}<sup>-</sup> fragments acting as bidentate ligands in a *tetrahapto* fashion, with the rhodium centre contributing two orbitals into the cluster bonding scheme. Bearing in mind the basic synthesis of **1** from [RhCl(PPh<sub>3</sub>)<sub>3</sub>], it is reasonable to consider the {SBH<sub>10</sub>} fragment in compound **1** as an LX ligand that formally replaces both the PPh<sub>3</sub> and the chlorine ligand in the [RhCl(PPh<sub>3</sub>)<sub>3</sub>]. Therefore, the attribution of the oxidation state +1 to the rhodium centre in these *bis*-(PR<sub>3</sub>)-ligated clusters is reasonable. In accord with this, the <sup>11</sup>B NMR shielding pattern in compound **1** and its *bis*(ligand) congeners **4**, **5** and **6** is clearly related to that of *nido*-6-SB<sub>9</sub>H<sub>11</sub> itself (Figure 3, bottom two traces).<sup>14</sup> With three *exo*-polyhedral ligands on the metal centre, the situation in the *tris*-(PR<sub>3</sub>)-ligated compounds **7** and **8** is potentially somewhat different. In principle, Wade's Rules<sup>15, 16</sup> would allocate to a {RhL<sub>3</sub>} fragment a contribution of three orbitals and three electrons to the cluster framework. If this were the case, then the stereochemistry around the metal centre could be described as pseudo-octahedral, with three bonding vectors mainly directed towards the sulphur vertex, the boron atom B(9), and the B(3)-B(4) edge, and with the other three to the three *exo*-polyhedral ligands [Figure 1 (b)]. Therefore, a description of **7** and **8** as Rh(III) octahedral complexes of {RhL<sub>3</sub>}<sup>3+</sup>, with a tridentate tetrahapto *arachno*-type {SB<sub>9</sub>H<sub>10</sub>}<sup>3-</sup> ligand, might at first sight be reasonable from the electron-counting rules approach as well as from a metal-to-ligand coordinative interaction. However, this would imply that the clusters of these *tris*(ligand) species would have quite different electronic structures from the *bis*(ligand) species, which would not be consistent with the similarities (a) of the cluster <sup>11</sup>B NMR shielding patterns (Figure 3, centre trace)

and (b) of the cluster dimensions among all the *bis* and *tris* ligated compounds **1**, **4**, **5**, **6**, **7** and **8**. These last two considerations suggest closely related electronic structures, and thence imply that **7** and **8** are best regarded as eighteen-electron rhodium(I) species, with five implied bonding vectors, two directed into the cluster as with compounds **1**, **4**, **5**, and **6**, with the other three directed towards the three phosphine ligands. This conclusion is supported by comparison of the  $^{11}\text{B}$  nuclear shielding patterns with that of a cluster compound of the eleven-vertex  $\{\text{nido-8,7-MSB}_9\}$  configuration that does have a three-orbital cluster contribution from the metal centre, *e.g.*  $[\text{8-(}\eta^5\text{-C}_5\text{Me}_5\text{)-nido-8,7-IrSB}_9\text{H}_{10}]$  (**10**)<sup>17</sup> with an octahedral Ir(III) centre (Figure 3, upper centre trace). It can be seen that, comparing compound **10** to compounds **1**, **4**, **5**, **6**, **7** and **8**, there is a fundamental change in the cluster electronic structure, as manifested in the cluster  $^{11}\text{B}$  shielding characteristics - an essential inversion of the overall shielding pattern. This inversion is characteristic of *nido* versus *arachno* ten-vertex cluster species,<sup>18</sup> and it can be seen (Figure 3, top trace) that the pattern of the cluster shielding of the  $\{\text{SB}_9\}$  unit of compound **10** clearly relates to that of the *arachno*  $[\text{6-SB}_9\text{H}_{12}]^-$  anion, rather than that of *nido*- $\text{6-SB}_9\text{H}_{11}$ .

The electronic structure within the cluster of the B-ligated hydridorhodathiaborane **9** is closely related to those of compounds **7** and **8**. Wade's Rules<sup>16</sup> could be taken to describe the  $\{\text{RhH}(\text{PMePh}_2)_2\}$  fragment as a three-orbital two-electron contributor to the cluster bonding, which would leave the rhodium centre with a formal oxidation state of three. The stereochemistry [Figure 2 (b)] could thence be viewed in terms of a quasi-octahedral Rh(III) complex of an *arachno*-type  $\{\text{SB}_9\text{H}_9(\text{PMePh}_2)\}^{2-}$  fragment with a  $\{\text{RhH}(\text{PMePh}_2)_2\}^{2+}$  centre. Alternatively, however, the  $\{\text{nido-SB}_9\text{H}_9(\text{PMePh}_2)\}$  fragment in **9** could be regarded as a 'charge-compensated' neutral ligand acting in a bidentate *tetrahapto* fashion, resulting in a Rh(I) species. In view of the arguments enunciated in the previous

paragraph, we favour this second interpretation. The  $^{11}\text{B}$  nuclear magnetic shielding pattern is consistent with this.

### Ligand-Exchange Processes and Mechanistic Considerations

In order to obtain some mechanistic insights about the substitutional chemistry of  $[8,8-(\text{PPh}_3)_2\text{-nido-}8,7\text{-RhSB}_9\text{H}_{10}]$  (**1**) with monodentate phosphines, the reactions (small scale) were studied at low temperatures by NMR spectroscopy. The reaction of two equivalents of  $\text{PMe}_3$  with the rhodathiaborane **1** at 223 K immediately forms the *bis*(ligand) monosubstituted derivative **6** and the *tris*-( $\text{PMe}_3$ )-ligated cluster **8**. Reaction of **1** with  $\text{PMe}_2\text{Ph}$  similarly gives mixed-ligand *bis*(phosphine) **5** and *tris*(ligand) **7**. The relative temperature-dependent broadenings of the signals in the  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra of **5** and **6**, together with GIAO nuclear-shielding calculations, suggest that the substitution in **1** takes place selectively by the displacement of the  $\text{PPh}_3$  ligand that is trans to the S(7) vertex (Scheme 1). The formation of  $\{\text{RhL}_3\}$ -containing species indicates that the addition of a third phosphine ( $\text{PMe}_3$  or  $\text{PMe}_2\text{Ph}$ ) to the rhodium centre in the presumed  $[8,8-(\text{PR}_3)_2\text{-nido-}8,7\text{-RhSB}_9\text{H}_{10}]$  intermediates (where  $\text{PR}_3$  is  $\text{PMe}_3$  or  $\text{PMe}_2\text{Ph}$ ) is faster than the substitution reaction of  $\text{PPh}_3$  in **5** and **6**. The results suggest that the presence of more basic and less sterically demanding phosphine ligands on the rhodium centre, facilitates the substitution of the second  $\text{PPh}_3$  ligand in **5** and **6**, and that the resulting supposed di-substituted intermediates react faster with free  $\text{PR}_3$  than the mono-substituted compounds (Scheme 2).

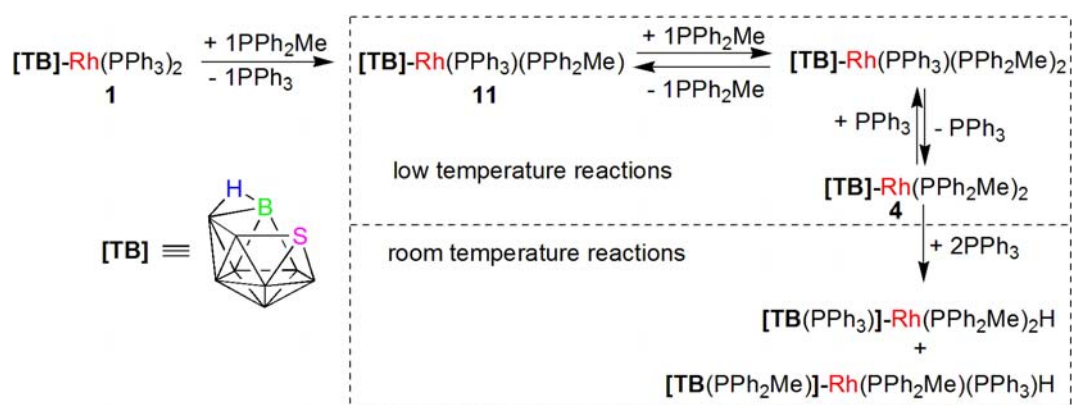


at *ca.* +5 ppm, overall resembling the spectrum of compound **4**. In addition, the signal from free PMePh<sub>2</sub> is virtually lost on the base line. The corresponding <sup>1</sup>H-<sup>11</sup>B} NMR spectra show a significant broadening in the signals at δ(<sup>1</sup>H) -2.00 and -3.00 ppm, and a final coalescence to give a single peak at -2.28 ppm. These observations suggest strongly that, at low temperatures, the monosubstituted {(PPh<sub>3</sub>)(PMePh<sub>2</sub>)} intermediate **11** and the *bis*-(PMePh<sub>2</sub>)-substituted species **4** are in equilibrium with the free phosphines and a *tris*-(PR<sub>3</sub>)-ligated cluster compound (Scheme 3). In this regard, as commented in the previous sections, a shift to higher field of around 2.00 ppm in the proton NMR signal of the BHB hydrogen atom in eleven-vertex *nido*-rhodathiaboranes is diagnostic of formation of the *tris*(phosphine) {RhL<sub>3</sub>} species.

At room temperature, the equilibrium is completely shifted toward the disubstituted species **4**, but a lowering of the temperature back to 188 K reproduces the spectrum discussed above, demonstrating the reversibility of the system. However, at room temperature overnight, the system evolves to a mixture of two hydridorhodathiaboranes: one of them readily resembles **9** and the other is also very similar, with small differences in the chemical shifts in the NMR spectra (Figure S6). This indicates that the presence of free PPh<sub>3</sub> in the media leads to formation of mixed-phosphine species [8,8,8-(PR<sub>3</sub>)<sub>2</sub>(H)-*nido*-8,7-RhSB<sub>9</sub>H<sub>9</sub>-(PR<sub>3</sub>)], in which the phosphine ligands can be combinations of PPh<sub>3</sub> and PMePh<sub>2</sub>.

The temperature-dependent behaviour of B-ligated [(PMePh<sub>2</sub>)<sub>2</sub>(H)RhSB<sub>9</sub>H<sub>9</sub>(PMePh<sub>2</sub>)] **9** in the presence of one equivalent of PPh<sub>3</sub> was also studied. As the temperature decreases, the signals in the <sup>31</sup>P-<sup>1</sup>H} NMR spectrum broaden significantly. At 223 K, this behaviour is accompanied with formation of small amounts of free PMePh<sub>2</sub> (Figure S7). The corresponding <sup>1</sup>H-<sup>11</sup>B} spectrum shows concomitant broadening of the signals that arise from the BHB bridging hydrogen atom and the Rh-H hydride ligand. As the temperature is decreased further, to 188 K, some of the signals sharpen in <sup>31</sup>P-

$\{^1\text{H}\}$  spectrum, and there is formation of new peaks; the  $^1\text{H}\text{-}\{^{11}\text{B}\}$  NMR spectrum reflects these changes, showing now two BHB proton signals and three Rh-H hydride resonances with different relative intensity ratios (Figure S8). At room temperature, the NMR data show only the signals of compound **9**. These observations are consistent with chemical exchange reactions involving free  $\text{PPh}_3$  and the  $\text{PMePh}_2$  ligands in the hydridorhodathiaborane **9** (Scheme 4).



**Scheme 3**

The observations described above permit a rudimentary reaction pathway to be described. In the conditions used for this work, the reaction rates of **1** with the more basic phosphines,  $\text{PMePh}_2$ ,  $\text{PMe}_2\text{Ph}$  and  $\text{PMe}_3$ , to give the corresponding monosubstituted *bis*-(phosphine) derivatives, **4**, **5** and **6** by the displacement of the  $\text{PPh}_3$  group *transoid* to the sulphur atom, appear to be similar. However the subsequent outcome of the reaction depends on the nature of the entering monodentate phosphine. Thus, the reaction rates of  $\text{PMe}_2\text{Ph}$  and  $\text{PMe}_3$  with the supposed *bis*-substituted rhodathiaborane intermediates,  $[8,8\text{-}(\text{PR}_3)_2\text{-nido-}8,7\text{-RhSB}_9\text{H}_{10}]$ , where  $\text{PR}_3 = \text{PMe}_3$  or  $\text{PMe}_2\text{Ph}$ , are faster than with the monosubstituted precursors **5** and **6**, leading to the formation of the *tris*-( $\text{PR}_3$ )-ligated species **7** and **8**. Since at low temperature we have not observed any stepwise formation of products that could indicate a rate-determining step, the rate of monosubstitution in **1** and the subsequent formation of the

*tris*(phosphine)  $\{\text{Rh}(\text{PR}_3)_3\}$ -containing species appear to be of the same order of magnitude. In contrast, the reaction rate of the monosubstituted *bis*-(ligand)  $\{\text{Rh}(\text{PPh}_3)(\text{PMePh}_2)\}$  intermediate **11** with more  $\text{PMePh}_2$  to give **4** is slower, and the NMR data suggest that a possible step for the substitution of the second  $\text{PPh}_3$  phosphine in **11** is the formation of a *tris*(ligand) rhodathiaborane species, *viz.*  $[(\text{PPh}_3)(\text{PMePh}_2)_2\text{-nido-RhSB}_9\text{H}_{10}]$ , in equilibrium with compound **4** and free ligand (Scheme 3). This conclusion implies that the most plausible mechanism for the reactions of **1** with monodentate phosphines is associative, *i.e.* addition of phosphine to the *bis*(phosphine) species **1**, followed by loss of phosphine to give the observed *bis*(ligand) products.

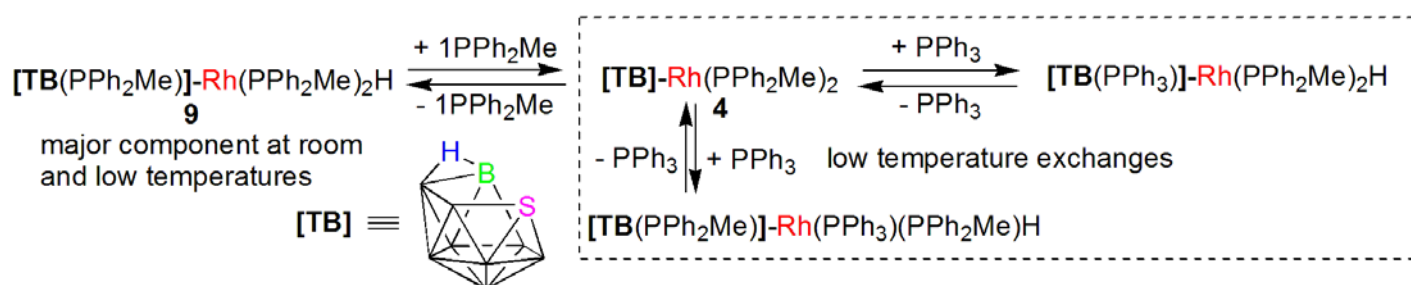
On the other hand, although the NMR data reveal an interesting chemical lability for **9**, it is not clear whether the formation of this hydridorhodathiaborane is also driven by the formation of a Rh-centred adduct that could promote the exchange of a Rh-bound  $\text{PMePh}_2$  ligand with the terminal hydrogen atom at the boron B(9) position; or whether, alternatively, the B- $\text{PMePh}_2$  bond undergoes incipient dissociation, partially opening coordination sites on the cluster that could facilitate the exchange processes.

## Conclusions

The series of compounds **4-9** illustrates nicely that the reactivity of the parent rhodathiaborane **1** with monodentate phosphines, and the composition and configuration of the resulting derivatives, are ultimately controlled by the nature of the phosphine. Thus the treatment of **1** with  $\text{PPh}_3$  does not form *tris*- $\text{PPh}_3$ -ligated species analogous to **7** and **8**, and the cluster remains formally unsaturated in the presence of triphenylphosphine.<sup>1,6</sup> In contrast, the less bulky and more basic phosphines,  $\text{PMePh}_2$  and  $\text{PMe}_3$ , afford  $\{\text{Rh}(\text{L})_3\}$ -vertices that confer one additional electron pair to the resulting eleven-vertex clusters compared with **1**. Interestingly,  $\text{PMePh}_2$  exhibits an alternative behaviour: too bulky to form an stable  $\{\text{Rh}(\text{PMePh}_2)_3\}$ -fragment in this system, it has sufficient Lewis basicity to bind the boron

B(9) vertex and to form a stable hydridorhodathiaborane. Variable-temperature experiments demonstrate the chemical lability of these eleven-vertex rhodathiaboranes, suggesting strongly that the most plausible mechanism for the substitution of the phosphine ligands is associative, implying the binding of a third phosphine at the rhodium centre. Likewise, the chemical lability exhibited by the hydridorhodathiaborane **9** could take place by associative processes at the  $\{\text{Rh}(\text{PMePh}_2)_2(\text{H})\}$  metal centre, which could be linked with an incipient partial dissociation of the B(9)-bound phosphine.

The treatment of **1** with monodentate phosphines is a convenient synthetic route for the alteration of the *exo*-polyhedral ligand sphere, confirming the tailorability of this eleven-vertex rhodathiaborane system. Following the synthetic approach used for the preparation of **2**,<sup>2</sup> the *bis*-PR<sub>3</sub>-ligated clusters, **4-6**, can (*a priori*) be easily modified by the treatment with pyridine, thus opening the door to the synthesis of hydridorhodathiaboranes that may exhibit an enhancement of the catalytic activity with respect **2**. In the case of PMePh<sub>2</sub>, the reaction with **1** affords directly a new hydridorhodathiaborane with an interesting ligand non-rigidity, which augurs for a rich chemistry to complement and extend the reported reactivity of the pyridine-ligated rhodathiaborane **2** with unsaturated organic molecules.



Scheme 4



## Experimental

### General Procedures

Reactions were carried out under an argon atmosphere using standard Schlenk-line techniques. Solvents were obtained dried from a Solvent Purification System marketed by Innovative Technology Inc. The commercially available phosphines  $\text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$  and  $\text{PMePh}_2$  were used as received without further purification. The eleven-vertex rhodathiaborane  $[8,8-(\text{PPh}_3)_2\text{-nido-}8,7\text{-RhSB}_9\text{H}_{10}]$  (**1**) was prepared according to the literature method.<sup>6</sup> Preparative thin-layer chromatography (TLC) was carried out using 1 mm layers of silica gel G (Fluka, type GF254) made from water slurries on glass plates of dimensions  $20 \times 20$  cm and dried in air at 25 °C. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer, using an Universal ATR Sampling Accessory. NMR spectra were recorded on Bruker Avance 300-MHz AV 400-MHz and 500 MHz spectrometers, using  $^{31}\text{P}\{-^1\text{H}\}$ ,  $[^{31}\text{P}\text{-}^1\text{H}]\text{-HMBC}$ ,  $^{11}\text{B}$ ,  $^{11}\text{B}\{-^1\text{H}\}$ ,  $^1\text{H}$ ,  $^1\text{H}\{-^{11}\text{B}\}$  and  $^1\text{H}\{-^{11}\text{B}(\text{selective})\}$  techniques.  $^1\text{H}$  NMR chemical shifts were measured relative to residual proton resonances in the deuterated solvents used, and are reported in ppm relative to tetramethylsilane.  $^{11}\text{B}$  chemical shifts are quoted relative to  $[\text{BF}_3(\text{OEt})_2]$  and  $^{31}\text{P}$  chemical shifts are quoted relative to 85% aqueous  $\text{H}_3\text{PO}_4$ . Note that the values for  $^1J(^{11}\text{B}\text{-}^1\text{H})$  quoted are from the measured doublet maximum-to-maximum peak separation at room temperature in the solvents specified, and, for broader resonances in particular, will generally be smaller than the real coupling constant  $^1J(^{11}\text{B}\text{-}^1\text{H})$ . Mass spectrometric data were recorded on a MICROFLEX instrument operating in either positive or negative modes, using matrix-assisted laser desorption/ionization (MALDI). A nitrogen laser of 337 nm (photon energy of 3.68 eV) was used for the ionization processes, and the molecules under study were protected with a matrix of *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB).

Criteria for purity for the *bis*(ligand) species **4**, **5** and **6**, which are straightforward analogues of the

well-characterised species **1** were clean multinuclear NMR spectra allied with mass spectrometric confirmation of the molecular ions.

### **X-ray crystallography**

*X*-ray diffraction data for compounds **8** and **9** were collected on the BM16 CRG beam line at the ESRF. We mounted single crystals of both complexes on micro Mount supports and were covered with perfluoropolyether. Data were measured in a single axis HUBER diffractometer, equipped with Oxford 600 Cryosystem open-flow nitrogen cryostat (100(1) K), using Silicon(111) monochromated synchrotron radiation ( $\lambda = 0.73780 \text{ \AA}$ ). Intensities were integrated with HKL2000 suite<sup>19</sup> and corrected for absorption using a multiscan method applied with SORTAV program.<sup>20</sup> The structures were solved and refined using the programs SHELXS-86<sup>21</sup> and SHELXL-97<sup>22</sup> respectively. Anisotropic displacement parameters were used in both refinements for all non-disordered atoms. In the case of **8**, a minor disorder (0.917 & 0.083(2) occupancy factors) affected the coordination of the sulphur atom to the metal. In the case of **9**, a clear situation of disorder involved a phenyl ring of one of the metal-bonded phosphines; this disorder was modelled on the base of two slightly displaced phenyl rings with similar occupancy factors (0.422 & 0.578(9)). Additionally, in the crystal structure of **9**, the presence of a highly disordered solvent molecule –interpreted as n-hexane– was also identified. The electronic density in the solvent region was estimated with PLATON/SQUEEZE program,<sup>23, 24</sup> and eventually five residual peaks with complementary occupancies were included in the refinement to compensate the presence of half an hexane molecule. For both structures, hydrogen atoms of the phosphine ligands were included in calculated positions and allowed to refine riding on their parent carbon atoms; the hydrogen atoms of the borane cluster in both structures, and the hydride ligand in **9**, were included from the difference Fourier maps and refined as free isotropic atoms.

Crystal data for **8**: C<sub>9</sub>H<sub>37</sub>B<sub>9</sub>P<sub>3</sub>RhS, *M* = 450.56, crystal size 0.105 x 0.056 x 0.049 mm<sup>3</sup>, orthorhombic,

$P_{bca}$ ,  $a = 16.3060(10)$ ,  $b = 15.5790(10)$ ,  $c = 17.4840(10)$  Å,  $V = 4441.5(5)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.407$  g cm<sup>-3</sup>,  $\mu = 1.088$  mm<sup>-1</sup>, 74697 measured, 5464 independent reflections (5211 observed), 261 parameters,  $R_{int} = 0.058$ ,  $R_1 = 0.0252$ ,  $wR(F^2) = 0.0693$ . Crystal data for **9**: C<sub>39</sub>H<sub>49</sub>B<sub>9</sub>P<sub>3</sub>RhS · ½ C<sub>6</sub>H<sub>14</sub>,  $M = 886.04$ , crystal size 0.10 x 0.08 x 0.02 mm<sup>3</sup>, triclinic,  $P-1$ ,  $a = 11.4960(10)$ ,  $b = 12.6030(10)$ ,  $c = 17.1240(10)$  Å,  $\alpha = 75.9350(10)$ ,  $\beta = 82.6070(10)$ ,  $\gamma = 65.0700(10)^\circ$ ,  $V = 2181.4(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.349$  g cm<sup>-3</sup>,  $\mu = 0.577$  mm<sup>-1</sup>, 43398 measured, 11291 independent reflections (10602 observed), 576 parameters,  $R_{int} = 0.0412$ ,  $R_1 = 0.0402$ ,  $wR(F^2) = 0.1105$ . Full crystallographic details of both complexes have been deposited with the Cambridge Crystallographic Data Centre with CCDC reference numbers 814662 (**8**) & 814663 (**9**).

### Calculations

All calculations were performed using the Gaussian 03 package.<sup>25</sup> Structures were initially optimized using standard methods with the STO-3G\* basis-sets for C, B, P, S, and H with the LANL2DZ basis-set for the metal atom. The final optimizations, including frequency analyses to confirm the true minima, together with GIAO nuclear-shielding calculations, were performed using B3LYP methodology, with the 6-31G\* and LANL2DZ basis-sets. The GIAO nuclear shielding calculations were performed on the final optimized geometries, and computed <sup>11</sup>B and <sup>31</sup>P shielding values were related to chemical shifts by comparison with the computed value for B<sub>2</sub>H<sub>6</sub> and H<sub>3</sub>PO<sub>4</sub>, which were taken to be  $\delta(^{11}\text{B}) + 16.6$  ppm relative to the BF<sub>3</sub>(OEt<sub>2</sub>) = 0.0 ppm standard, and  $\delta(^{31}\text{P}) = 0.0$  ppm, respectively.

### Synthesis of [8,8-(PMePh<sub>2</sub>)<sub>2</sub>-nido-8,7-RhSB<sub>9</sub>H<sub>10</sub>] (**4**)

**Compound 4**: A Schlenk tube equipped with a magnetic stirrer was charged with [(PPh<sub>3</sub>)<sub>2</sub>RhSB<sub>9</sub>H<sub>10</sub>] (**1**, 180 mg, 0.24 mmol). The rhodathiaborane was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL), and PMePh<sub>2</sub> (89 µL,

0.48 mmol) was added (with a syringe) to the tube. The resulting orange solution was stirred at room temperature under an atmosphere of argon for 16 hours. The reaction mixture was concentrated to *ca.* 0.5 mL. Slow addition of hexane produced an orange solid that was separated by decantation, washed with hexane, and dried *in vacuo* (0.129 g, 84 %).  $^{11}\text{B}$  NMR (160 MHz;  $\text{CDCl}_3$ ; 298 K):  $\delta$  10.6 (1B, br, BH), -1.8 (1B, br, BH), -9.1 (1B, d, BH), -27.6 (1B, br, BH);  $^1\text{H}$ - $\{^{11}\text{B}\}$  NMR (300 MHz;  $\text{CDCl}_3$ ; 298 K):  $\delta$  7.89–6.86 (20 H, m, Ph), 2.15 (1H, br s, BH), 1.81 (1H, br s, BH), 1.78 (1H, br s, BH), -1.61 (1H, br s, BHB);  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR (161 MHz;  $\text{CDCl}_3$ ; 202 K):  $\delta$  21.8 (dd,  $^1J_{\text{RHP}} = 149$  Hz,  $\text{PMePh}_2$ ,  $^2J_{\text{PP}} = 38$  Hz), 5.8 (dd,  $^1J_{\text{RHP}} = 137$  Hz,  $^2J_{\text{PP}} = 38$  Hz,  $\text{PMePh}_2$ ), at 296 K these two doublet of doublets coalesce;  $^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ; 202 K):  $\delta$  2.27 (3H, s,  $^2J_{\text{PH}} = 9.7$  Hz,  $\text{PPh}_2\text{Me}$ ), 1.38 (3H, s,  $^2J_{\text{PH}} = 7$  Hz,  $\text{PMePh}_2$ ), at 279 K these two singlets coalesce;  $^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ; 327 K):  $\delta$  1.81 (6H, s,  $^2J_{\text{PH}} = 7.5$  Hz,  $\text{PMePh}_2$ );  $\Delta G^\ddagger = 52 \pm 3$  kJ mol $^{-1}$ .

Synthesis of [8,8-( $\text{PPh}_3$ )(L)-*nido*-8,7-RhSB $_9$ H $_{10}$ ] [L =  $\text{PMe}_2\text{Ph}$  (5),  $\text{PMe}_3$  (6)]

**Compound 5:**  $\text{PMe}_2\text{Ph}$  (16.6 mL, 0.124 mmol) was added to a red solution of **1** (0.0473 g, 0.062 mmol) in dichloromethane at room temperature. The reaction mixture was stirred for 1 h. under an argon atmosphere, then reduced in volume and applied to a preparative TLC plate. The chromatogram was developed with a mixture of 4:1  $\text{CH}_2\text{Cl}_2$ /hexane, leading to the isolation an orange component of  $R_F = 0.8$  that was characterized as **5** (0.0201 g, 0.0313 mmol, 51 %); and a yellow product of  $R_F = 0.5$  that was identified as **7** (0.0093 g, 0.014 mmol, 23 %, see below). **Compound 5:**  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ; 298K):  $\delta$  8.10–6.92 (20 H, m, Ph), 1.94 (3H, d,  $^2J_{\text{PH}} = 11$  Hz,  $\text{P}(\text{CH}_3)_2\text{Ph}_2$ ), 1.29 (1H, s, BH), 1.17 (3H, d,  $^2J_{\text{PH}} = 10$  Hz,  $\text{P}(\text{CH}_3)_2\text{Ph}_2$ ).  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR (161 MHz;  $\text{CDCl}_3$ ; 298K):  $\delta$  23.8 (1P, dd,  $^1J_{\text{RHP}} = 132$  Hz,  $^2J_{\text{PP}} = 45$  Hz,  $\text{PPh}_3$ ), 10.7 (1P, dd,  $^1J_{\text{RHP}} = 150$  Hz,  $\text{P}(\text{CH}_3)_2\text{Ph}_2$ ). Cluster  $^{11}\text{B}$  and  $^1\text{H}$  NMR data are summarized in Table 1.

**Compound 6:** Following the same procedure than above, 0.037 mg (0.048 mmol) of **1** was treated

with 36.8  $\mu\text{L}$  (0.097 mmol), and the resulting reaction mixture was separated by TLC, using a 3:2 ratio of  $\text{CH}_2\text{Cl}_2$ /hexane. The chromatogram gave two bands: red,  $R_F = 0.5$ , and yellow  $R_F = 0.2$ . The red component was characterized as compound **6** (0.0173 g, 0.030 mmol, 62 %) and the yellow product was identified as **8** (0.0106 g, 0.018 mmol, 38 %). Compound **6**:  $\nu_{\text{max}}(\text{ATR})/\text{cm}^{-1}$  2918 m, 2849 m, 2517 s (BH), 2159 s, 2030 s, 1996 s.  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ; 298K):  $\delta$  7.67–6.79 (15 H, m, Ph), 1.30 (9H, d,  $^2J_{\text{PH}} = 10$  Hz,  $\text{P}(\text{CH}_3)_3$ ).  $^{31}\text{P}\{-^1\text{H}\}$  NMR (161 MHz;  $\text{CDCl}_3$ ; 223K):  $\delta$  25.1 (1P, dd,  $^1J_{\text{RhP}} = 141$  Hz,  $^2J_{\text{PP}} = 38$  Hz,  $\text{PPh}_3$ ), 5.1 (1P, dd,  $^1J_{\text{RhP}} = 107$  Hz,  $^2J_{\text{PP}} = 38$  Hz,  $\text{P}(\text{CH}_3)_3$ ). Cluster  $^{11}\text{B}$  and  $^1\text{H}$  NMR data are summarized in Table 1.

### Synthesis of [8,8,8-(L)<sub>3</sub>-nido-8,7-RhSB<sub>9</sub>H<sub>10</sub>] [L = $\text{PMe}_2\text{Ph}$ (**7**), $\text{PMe}_3$ (**8**)]

**Compound 7**: 58 mg of **1** (0.076 mmol) was dissolved in 15 mL of  $\text{CH}_2\text{Cl}_2$  in a Schlenk tube. 3.37 mL (0.23mmol) of  $\text{PMe}_2\text{Ph}$  was added to the orange solution of the rhodathiaborane, and the reaction mixture was stirred at room temperature under an atmosphere of argon for 4 h. The reaction mixture was concentrated to *ca.* 0.5 mL. Slow addition of hexane produced an orange solid that was separated by decantation, washed with hexane, and dried *in vacuo* to give 0.0479 g of **6** (96 %). Elemental analysis: found: C, 42.5; H, 6.5; P, 14.2 %.  $\text{C}_{24}\text{H}_{43}\text{B}_9\text{P}_3\text{Rh}_1\text{S}_1$  requires C, 43.9; H, 6.6; P, 14.2 %.  $\nu_{\text{max}}(\text{ATR})/\text{cm}^{-1}$  3055m, 2915m, 2545w, 2345m, 2117w, 1992w (BH), 1432w, 1296m, 1280m, 1001m, 933w and 895w.  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ; 298K):  $\delta$  7.93–6.84 (aromatic), 2.01 (9H, d,  $^2J_{\text{PH}} = 3$  Hz,  $\text{P}(\text{CH}_3)_3$ ), 1.91 (9H, d,  $^2J_{\text{PH}} = 3$  Hz,  $\text{P}(\text{CH}_3)_3$ ), 1.68 (9H, d,  $^2J_{\text{PH}} = 5$  Hz,  $\text{P}(\text{CH}_3)_3$ ), 1.59 (9H, d,  $^2J_{\text{P,H}} = 10$  Hz,  $\text{P}(\text{CH}_3)_3$ ), 1.56 (9H, d,  $^2J_{\text{PH}} = 7$  Hz,  $\text{P}(\text{CH}_3)_3$ ), 1.33 (9H, d,  $^2J_{\text{PH}} = 8$  Hz,  $\text{P}(\text{CH}_3)_3$ ).  $^{31}\text{P}\{-^1\text{H}\}$  NMR (202 MHz;  $\text{CDCl}_3$ ; 300K):  $\delta$  +11.6 (1P, dt,  $^1J_{\text{RhP}} = 145$  Hz,  $^2J_{\text{PP}} = 27$  Hz), -11.8 (1P, dt,  $^1J_{\text{RhP}} = 145$  Hz,  $^2J_{\text{PP}} = 20$  Hz), -24.2 (1P, d, br,  $^1J_{\text{Rh-P}} = 81$  Hz); cluster  $^{11}\text{B}$  and  $^1\text{H}$  NMR data are summarized in Table 3. *m/z* (MALDI) 381  $\{\text{M-PMe}_2\text{Ph}\}^+$  isotope envelope:  $\text{P}_1\text{C}_8\text{H}_{21}\text{Rh}_1\text{S}_1\text{B}_9$  requires 381 and complete molecule  $\text{P}_2\text{C}_{16}\text{H}_{32}\text{Rh}_1\text{S}_1\text{B}_9$  requires 519).

**Compound 8:** Following the same procedure than with **6** above, 141.3 mg (0.18 mmol) of **1** were treated with 42.0mg (0.55 mmol) of  $\text{PMe}_3$ . Yield: 70.6 mg, 0.15 mmol, 82%. Elemental analysis: found: C, 22.9; H, 7.9; P, 19.6%.  $\text{C}_9\text{H}_3\text{B}_9\text{P}_3\text{Rh}_1\text{S}_1$  requires C, 22.9; H, 7.9; P, 19.7%). IR(ATR):  $\nu_{\text{max}}/\text{cm}^{-1}$  3422w, 2927w, 2909w, 2551m, 2503w, 2474m (BH), 1645s, 1433m, 1418w, 1303m, 1282w, 1261m, 1093m, 1038m, 957s, 910w, 722m.  $^{31}\text{P}\{-^1\text{H}\}$  ( $\text{CDCl}_3$ ; 223 K) and  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ; 300 K) ordered as  $\delta(^{31}\text{P})$  (intensity, multiplicity,  $^1J_{\text{Rh-P}}$ ,  $^2J_{\text{P-P}}$ ) [ $\delta(^1\text{H})$  of directly bound  $\text{CH}_3$  groups,  $^2J_{\text{P-H}}$ ]: +3.2 (1P, dt,  $^1J_{\text{Rh-P}} = 124$  Hz,  $^2J_{\text{PP}} = 25$  Hz) [1.54, d,  $^2J_{\text{P-H}} = 10$  Hz], -25.3 (1P, ddd,  $^1J_{\text{RhP}} = 127$  Hz,  $^2J_{\text{PP}} = 25$  Hz,  $^2J_{\text{P-P}} = 33\text{Hz}$ ) [1.59, d,  $^2J_{\text{PH}} = 10$  Hz], -30.6 (1P, broad d,  $^1J_{\text{Rh-P}} = 87$  Hz) [1.45, d,  $^2J_{\text{PH}} = 7$  Hz]; cluster  $^{11}\text{B}$  and  $^1\text{H}$  NMR data are summarized in Table 3.  $m/z$  (MALDI $^+$ ) 471 ( $\text{M}^+$  isotope envelope;  $\text{P}_3\text{C}_9\text{H}_3\text{Rh}_1\text{S}_1\text{B}_9$  requires 471).

### Synthesis of [8,8,8-(PMePh $_2$ ) $_2$ (H)-nido-8,7-RhSB $_9$ H $_9$ -9-(PMePh $_2$ )] (**9**)

0.608g (0.79 mmol) of **1** in 15mL of  $\text{CH}_2\text{Cl}_2$  were treated with 0.44 mL (2.38 mmol) of  $\text{PPh}_2\text{Me}$  in a Schlenk tube under argon at room temperature. After two hours of vigorous stirring, hexane was added and the resulting solid was separated by decantation, washed with hexane, and dried in vacuum to give 0.615g (0.73 mmol; 93%) of **8**. Elemental analysis: found: C, 51.8; H, 5.54; P, 11.0%.  $\text{C}_{39}\text{H}_{49}\text{B}_9\text{P}_3\text{Rh}_1\text{S}_1$  requires C, 55.6; H, 5.9; P, 11.0%. IR(ATR):  $\nu_{\text{max}}/\text{cm}^{-1}$  3054w, 2921w, 2852w, 2519m (BH), 2050sh (RhH), 1585s, 1572s, 1481m, 1433w, 1093m, 1026m, 999m, 881w, 738w, 690w.  $^1\text{H}\{-^{11}\text{B}\}$  NMR (500 MHz;  $\text{CDCl}_3$ ; 298K)  $\delta$  7.69–6.90 (aromatic); other NMR data are summarized in Table 3.  $m/z$  (MALDI $^+$ ) 641  $\{\text{M}-2\text{HPMePh}_2\}^+$  isotope envelope.  $\text{P}_2\text{C}_{26}\text{H}_{34}\text{Rh}_1\text{S}_1\text{B}_9$  requires 641).

### Variable-temperature NMR studies

The reaction of **1** with  $\text{PMePh}_2$  was studied at low temperature by NMR spectroscopy. 15 mg of the rhodathiaborane was put in a 5 mm NMR tube, and dissolved in 0.6 mL of  $\text{CD}_2\text{Cl}_2$  under an argon atmosphere. To the resulting orange solution, 1 equivalent of  $\text{PMePh}_2$  was added at the temperature of

liquid nitrogen. The tube was transported immersed in liquid nitrogen and it was inserted into an NMR probe head with the temperature set to 188 K. The  $^1\text{H}$ - $\{^{11}\text{B}\}$  and  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectra was then measured; the sample was then heated to 223 K and the  $^1\text{H}$  and  $^{31}\text{P}$ - $\{^1\text{H}\}$  spectra measured at this temperature. The sample tube was removed from the NMR instrument and transported (immersed in liquid nitrogen) to the Schlenk line, where a second equivalent of phosphine was added at low temperature. The resulting reaction mixture was studied at different temperatures (see supplementary material: Figures S4-S6).

Following the same procedure, 15 mg of the hydridorhodathiaborane **9** was dissolved in 0.6 mL of  $\text{CD}_2\text{Cl}_2$  with 1 equivalent of free  $\text{PPh}_3$ , and the resulting yellow solution was studied over a range of temperatures by  $^1\text{H}$ - $\{^{11}\text{B}\}$  and  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectroscopy (Figures S7-S8).

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### **Notes and references**

Electronic Supplementary Information (ESI) available: Experimental and DFT-calculated NMR data for **1**, **6** and **8**; NMR spectra of the reaction of **1** with  $\text{PPh}_2\text{Me}$  at different temperature, as well as **9** with  $\text{PPh}_3$ ; DFT-calculated coordinates for **1**, **6**, **8** and **9**.

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