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# Coordination and cluster compounds of ruthenium with the $[hypho-1,2-S_2B_6H_9]^-$ ligand<sup>†</sup>

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The reaction between [tmndH][*hypho*-1,2-S<sub>2</sub>B<sub>6</sub>H<sub>9</sub>] (tmnd = *N*,*N*,*N*',*N*'-tetramethylnaphthalene-1,8-diamine) and [RuCl(PPh<sub>3</sub>)<sub>2</sub>( $\eta^{5}$ -Cp)] in CH<sub>2</sub>Cl<sub>2</sub> at room temperature afforded two ruthenathiaboranes, [5-( $\eta^{5}$ -Cp)-5-(PPh<sub>3</sub>)-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>9</sub>], **1**, and [Ru( $\eta^{1}$ -1,2-S<sub>2</sub>B<sub>6</sub>H<sub>9</sub>)(PPh<sub>3</sub>)<sub>2</sub>( $\eta^{5}$ -Cp)], **2**, in 6 and 48% yields, respectively. The heating of a solution of [Ru( $\eta^{1}$ -1,2-S<sub>2</sub>B<sub>6</sub>H<sub>9</sub>)(PPh<sub>3</sub>)<sub>2</sub>( $\eta^{5}$ -Cp)], **2** in CH<sub>2</sub>Cl<sub>2</sub> at reflux temperature afforded **1** in 59% yield. Compound **1** could be described as either a *hypho* nine-vertex {RuS<sub>2</sub>B<sub>6</sub>} cluster or a coordination compound of ruthenium which contains a bidentate  $\eta^{2}$ -dithiaborate cluster ligand; the latter description is preferred. Compound **2** contains an eight-atom *hypho*-type {1,2-S<sub>2</sub>B<sub>6</sub>} cage bonded to the ruthenium atom of the {Ru(PPh<sub>3</sub>)<sub>2</sub>( $\eta^{5}$ -Cp)} unit by one sulfur atom and may be described as a compound of ruthenium coordinated  $\eta^{1}$ - to the dithiaborate cluster ligand. The reaction between [tmndH][*hypho*-1,2-S<sub>2</sub>B<sub>6</sub>H<sub>9</sub>] and [RuCl<sub>2</sub>( $\eta^{6}$ -MeC<sub>6</sub>H<sub>4</sub>Pr<sup>1</sup>)-*arachno*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>], **3**, in 94% yield. Further reaction of **3** and PMePh<sub>2</sub> afforded another *arachno* {RhS<sub>2</sub>B<sub>6</sub>} cluster, [5-( $\eta^{6}$ -MeC<sub>6</sub>H<sub>4</sub>Pr<sup>1</sup>)-*arachno*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>], **3**, an 94% sield. Further reaction of **3** and PMePh<sub>2</sub> afforded another *arachno* {RhS<sub>2</sub>B<sub>6</sub>} cluster, [5-( $\eta^{6}$ -MeC<sub>6</sub>H<sub>4</sub>Pr<sup>1</sup>)-*arachno*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>], **3**, an 94% sield. Further reaction of **3** and PMePh<sub>2</sub> afforded another *arachno* {RhS<sub>2</sub>B<sub>6</sub>} cluster, [5-( $\eta^{6}$ -MeC<sub>6</sub>H<sub>4</sub>Pr<sup>1</sup>)-*arachno*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>], **3**, an 94% sield. Further reaction of **3** and PMePh<sub>2</sub> afforded another *arachno* {RhS<sub>2</sub>B<sub>6</sub>} cluster, [5-( $\eta^{6}$ -MeC<sub>6</sub>H<sub>4</sub>Pr<sup>1</sup>)-*arachno*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>], **3**, an 94% sield. Further reaction of **3** and PMePh<sub>2</sub> afforded another *arachno* {RhS<sub>2</sub>B<sub>6</sub>} cluster, [5-( $\eta^{6}$ -MeC<sub>6</sub>H<sub>4</sub>Pr<sup>1</sup>)-*arachno*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>], **4**, in 25% yield. Compounds **1**, **2** and **4** were characterised with sin

## Introduction

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We have investigated transition-element compounds of heteroborane ligands from the viewpoints of (a) the coordination of a hetero-atom to the transition element by a single bond<sup>1</sup> and (b) the incorporation of the transition element as a cluster vertex with several multicentre bonds between the transition element and heteroborane unit.1-3 Most of the reaction chemistry used to synthesise borane cluster complexes of transition elements involves reactions between cluster-based anions and transition-element compounds that contain easily removable ligands such as anionic halide and hydride, or neutral ligands such as carbonyls and phosphines.<sup>4</sup> The mechanisms of formation of transition-element heteroborane clusters are not well understood but it is reasonable to assume that in many cases the initial steps involve the expulsion of a labile ligand from the transition-element coordination sphere and its replacement by a coordinate bond between the transition element and the heteroborane. Further condensation resulting in a more intimate incorporation of the metal-centre into the boron-containing matrix may then occur. Two questions arise: "Can examples of coordination compounds that are initially formed be isolated?" And "can they then be converted into the more condensed transition-element heteroborane cluster complexes?" If cluster ligands with "open" architectures are used, for example hypho clusters, an ancillary question may arise, "at what stage do the initially formed compounds become clusters?" In order to investigate these questions, we have prepared some ruthenium complexes of the [hypho-1,2-S<sub>2</sub>B<sub>6</sub>H<sub>9</sub>]<sup>-</sup> anion. Whilst there are many reports of  $\eta^1$  and  $\eta^2$  Ru–S bonded coordination complexes with a variety of sulfur ligands,<sup>6</sup> the number of ruthenium derivatives of thiaboranes is relatively small. As far as we are aware, only six ruthenathiaboranes have been

reported, namely,  $[2,3-(\eta^6-MeC_6H_4Pr^i)_2$ -*closo*-2,3,1-Ru<sub>2</sub>SB<sub>9</sub>H<sub>9</sub>] **5**,  $[7-Cl-2,3-(\eta^6-MeC_6H_4Pr^i)_2$ -*closo*-2,3,1-Ru<sub>2</sub>SB<sub>9</sub>H<sub>8</sub>] **6**,  $[2-(\eta^6-C_6Me_6)$ -*closo*-2,1-RuSB<sub>8</sub>H<sub>8</sub>] **7**,  $[11-Cl-7-(\eta^6-MeC_6H_4Pr^i)$ -*nido*-7,8-RuSB<sub>9</sub>H<sub>10</sub>] **8**,  $^7$  [5-( $\eta^6-C_6Me_6$ )-*arachno*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>] **9** and [5-( $\eta^6-C_6Me_6$ )-5-Cl-*hypho*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>9</sub>] **10**.<sup>8</sup> Of these, the two compounds which have the {RuS<sub>2</sub>B<sub>6</sub>} skeleton, **9** and **10**, were structurally characterised by single crystal X-ray analyses.<sup>8</sup> The ruthenium-to-cage interactions in **9** and **10** were of the  $\eta^4$  (Ru to S<sub>2</sub>B<sub>2</sub>) and  $\eta^2$  (Ru to S,S') types, respectively, see diagrams I and II.



<sup>†</sup> Metallaheteroborane chemistry. Part 17.<sup>1</sup>

Numerous compounds with monohapto  $(\eta^1) \sigma$ -bonds between transition elements and heteroborane ligands containing B, C, P, As and Ge have been previously reported. Examples include [Fe( $\eta^1$ -PB<sub>10</sub>H<sub>12</sub>)(CO)<sub>2</sub>( $\eta^5$ -Cp)], [Fe( $\eta^1$ -1,2-GeCHB<sub>10</sub>H<sub>10</sub>)-(CO)<sub>2</sub>( $\eta^5$ -Cp)]<sup>9</sup> and, [Fe( $\eta^1$ -As<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(CO)<sub>2</sub>( $\eta^5$ -Cp)].<sup>1,9</sup> However, the only previously reported metallathiaborane in which one sulfur cluster atom acts solely as the donor site is [Ir( $\eta^1$ -S<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(PPh<sub>3</sub>)<sub>3</sub>(H)<sub>2</sub>], **11**, prepared by the treatment of [*arachno*-2,3-S<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>-</sup> with [IrCl(PPh<sub>3</sub>)<sub>3</sub>] in dichloromethane solution at room temperature.<sup>2</sup>

In the present work we describe the synthesis of four new ruthenathiaboranes  $[5-(\eta^5-Cp)-5-(PPh_3)-hypho-5,4,6-RuS_2B_6H_9]$  1,  $[\operatorname{Ru}(\eta^{1}-hypho-1,2-S_{2}B_{6}H_{9})(\operatorname{PPh}_{3})_{2}(\eta^{5}-\operatorname{Cp})]$  **2**,  $[5-(\eta^{6}-\operatorname{MeC}_{6}H_{4}\operatorname{Pr}^{i})$ arachno-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>], 3, and  $[5-(\eta^6-MeC_6H_4Pr^i)-8-(PMePh_2)-8-(P$ arachno-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>6</sub>], 4. Compound 2 is the first reported ruthenathiaborane in which the only interaction between the ruthenium centre and the thiaborane ligand is a monohapto Ru–S  $\sigma$  bond. The conversion of the monohapto bonding mode in 2 into a dihapto bonding mode in 1 is demonstrated and the alternative descriptions of 1 either as a coordination complex, or as a cluster, are examined. The effect of changing the ruthenium reagent from [RuCl(PPh<sub>3</sub>)<sub>2</sub>( $\eta^{5}$ -Cp)] to [RuCl<sub>2</sub>( $\eta^{6}$ -MeC<sub>6</sub>H<sub>4</sub>Pr<sup>i</sup>)]<sub>2</sub> is to generate an  $\eta^4$ -{S<sub>2</sub>B<sub>2</sub>}-ligating *arachno* {RuS<sub>2</sub>B<sub>6</sub>} cluster compound, 3, directly. Compounds 2, 1 and 3/4, respectively, thereby represent successive steps in the incorporation of a metal centre into a cluster, ultimately to form a condensed contiguous metalladihtiaborane skeleton. (Note. The  $\eta^6$ -MeC<sub>6</sub>H<sub>4</sub>Pr<sup>i</sup> ligand will be represented by '*p*-cym' in all further formulae).

# **Results and discussion**

#### Syntheses

Compounds  $[5-(\eta^5-Cp)-5-(PPh_3)-5,4,6-RuS_2B_6H_9]$  **1** and  $[Ru(\eta^1-1,2-S_2B_6H_9)(PPh_3)_2-(\eta^5-Cp)]$  **2** were synthesised by the reaction between the  $[1,2-hypho-S_2B_6H_9]^-$  anion and  $[RuCl(PPh_3)_2(\eta^5-Cp)]$ . The reaction of equimolar amounts of  $[1,2-hypho-S_2B_6H_9]^$ and  $[RuCl(PPh_3)_2(\eta^5-Cp)]$  in dichloromethane for five days afforded  $[5-(\eta^5-Cp)-5-(PPh_3)-5,4,6-RuS_2B_6H_9]$  **1** and  $[Ru(\eta^1-1,2-S_2B_6H_9)(PPh_3)_2(\eta^5-Cp)]$  **2** in 6% and 48% yields, respectively. Both **1** and **2** were purified by preparative t.l.c. and crystallised from dichloromethane–hexane and toluene–hexane solutions, respectively. When compound **2** was heated in dichloromethane solution at reflux temperature for three weeks it was converted to **1** in 59% yield. This conversion was accompanied by loss of PPh<sub>3</sub> and suggests that the formation of **1** may be a stepwise process in which compound **2** is the intermediate (Scheme 1).

 $[RuCl(PPh_3)_2(\eta^5-Cp)] + [tmndH][1,2-hypho-S_2B_6H_9] \rightarrow$ 

$$\begin{array}{rcl} [tmndH]Cl &+ [Ru(\eta^{1}-1,2-S_{2}B_{6}H_{9})(PPh_{3})_{2}(\eta^{5}-Cp)] \rightarrow \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & &$$

Scheme 1 Syntheses of compounds 1 and 2 near here.

Compound **3**,  $[5-(p-cym)-arachno-5,4,6-RuS_2B_6H_8]$ , was isolated in 94% yield from the reaction between the  $[hypho-1,2-S_2B_6H_9]^-$  anion and  $[RuCl_2(\eta^6-p-cym)]_2$  in CH<sub>2</sub>Cl<sub>2</sub> for five days at room temperature. When **3** was treated with a tenfold excess of PMePh<sub>2</sub> in solution in refluxing toluene for three weeks, it afforded  $[5-(p-cym)-8-(PMePh_2)-arachno-5,4,6-RuS_2B_6H_6]$ , **4**, in 25% yield.

### Crystal and molecular structures

(a)  $[Ru(\eta^1-1,2-S_2B_6H_9)(PPh_3)_2(\eta^5-Cp)]$  2. The molecular structure of compound 2 (Fig. 1), as determined by single-crystal X-ray diffraction analysis, shows that there is a single



**Fig. 1** ORTEP plot of the major part of  $[\text{Ru}(\eta^1-1,2-S_2B_6H_9)-(\text{PPh}_3)_2(\eta^5-\text{Cp})]$  **2**, showing the numbering scheme; for clarity, only the first carbon is shown for each phenyl ring and the minor occupancy sites (S2A, S2B) of S(2) are omitted. Ellipsoids are shown at the 30% probability level. Selected interatomic distances (Å) and angles (°): Ru1–S1 2.4017(9), Ru1–P1 2.3576(9), Ru1–P2 2.3319(9), S1–B5 1.879(5), S1–B6 1.888(4), S2–B3 1.852(7), S2–B7 1.866(6), B3–B4 1.798(9), B3–B8 1.813(7), B3–B7 1.947(8), B4–B8 1.733(7), B4–B5 1.796(8), B5–B8 1.828(7), B5–B6 2.000(7), B6–B8 1.791(6), B6–B7 1.814(7), B7–B8 1.794(7); S1–Ru1–P2 87.19(3), S1–Ru1–P1 92.88(3), P1–Ru1–P2 99.51(3), B5–S1–Ru1 116.98(17), B5–S1–B6 64.1(2), B6–S1–Ru1 114.67(4), B3–S2–B7 63.2(2). There are no unusual distances or angles within the PPh<sub>3</sub> or Cp ligands and the Ru to Cp parameters are normal.

bond between one sulfur atom of the thiaborane cage and the ruthenium atom. Important interatomic distances and angles for **2** are given in the legend to Fig. 1. Compound **2** is only the second example of a compound in which a sulfur atom in a thiaborane cage is involved in an unsupported donor–acceptor bond to the transition element. The previously reported compound was  $[Ir(\eta^1-S_2B_9H_{10})(PPh_3)_3H_2]$  **11**.<sup>2</sup>

In this diffraction analysis, it should be noted that, whereas the S1 atom in compound **2** was located on a single crystallographic site, the other sulfur atom was found to be disordered unequally over three positions, *i.e.* S2, S2A and S2B, but only S2 is shown in Fig. 1. The Ru1–S1 distance, of 2.4017(9) Å, is significantly longer ( $3 \times su$ ) than the Ru–S distance in several other {Ru(PPh<sub>3</sub>)<sub>2</sub>( $\eta^{5}$ -Cp)}-containing compounds, *e.g.* in [Ru(C<sub>3</sub>H<sub>6</sub>S)(PPh<sub>3</sub>)<sub>2</sub> ( $\eta^{5}$ -Cp)][CF<sub>3</sub>SO<sub>3</sub>] at 2.3459(20) Å,<sup>10</sup> and in [Ru(PhCH<sub>2</sub>CH<sub>2</sub>SH)(PPh<sub>3</sub>)<sub>2</sub>( $\eta^{5}$ -Cp)][BF<sub>4</sub>] at 2.369(2) Å,<sup>11</sup> but similar to that in [Ru(C<sub>6</sub>H<sub>11</sub>SH)(PPh<sub>3</sub>)<sub>2</sub>( $\eta^{5}$ -Cp)][BF<sub>4</sub>] at 2.389(2) Å.<sup>12</sup>

The S1-B5 and S1-B6 distances in compound 2 are 1.879(5) and 1.888(4) Å, respectively. These values are at the lower end of the range of S–B distances in previously studied  $\{RuS_2B_6\}$  ruthenathiaboranes, i.e. in [5-(n<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)-arachno-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>] **9** at 1.880(10) to 1.939(9) Å and in [5-(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)-5-(Cl)-hypho-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>9</sub>] 10 at 1.887(25) to 1.943(19) Å.<sup>8</sup> As is common for metal derivatives of boranes and heteroboranes, a large range of distances was observed for the B-B interactions in compound 2, varying from 1.733(7) to 2.000(7) Å.<sup>1-4</sup> As mentioned below for compound 1, the largest interboron distance of 2.000(7) Å is approaching the bonding limit. The ruthenium-phosphorus distances in  $[Ru(\eta^{1}-1, 2-S_{2}B_{6}H_{9})(PPh_{3})_{2}(\eta^{5}-Cp)]$  2, Ru1–P1 and Ru1–P2, are significantly different from each other at 2.3574(9) and 2.3320(9) Å, respectively. Similar differential distances have been reported in compounds with non-cluster ligands, e.g., in [Ru(C<sub>3</sub>H<sub>6</sub>S)(PPh<sub>3</sub>)<sub>2</sub>(Cp)] [CF<sub>3</sub>SO<sub>3</sub>] at 2.3616(18) and 2.3576(19) Å,<sup>10</sup> in [Ru(PhCH<sub>2</sub>CH<sub>2</sub>SH)(PPh<sub>3</sub>)<sub>2</sub>(Cp)][BF<sub>4</sub>] at 2.349(2) and 2.344(2) Å,<sup>11</sup> and in [Ru(C<sub>6</sub>H<sub>11</sub>SH)(PPh<sub>3</sub>)<sub>2</sub>(Cp)][BF<sub>4</sub>] at 2.345(2) and 2.360(2) Å.12

(b) [5-( $\eta^5$ -Cp)-5-(PPh<sub>3</sub>)-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>9</sub>] 1. The results of a single-crystal X-ray diffraction analysis of 1 show that the ruthenium atom is bonded to both sulfur atoms of the S<sub>2</sub>B<sub>6</sub>H<sub>9</sub> cage but not to any boron atom (Fig. 2). The molecule may be regarded as electronically equivalent to previously reported [5-( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)-5-Cl-*hypho*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>9</sub>] 10,<sup>8</sup> *i.e.* as based on a *hypho* nine-vertex {RuS<sub>2</sub>B<sub>6</sub>} cluster system. The *hypho* nine-vertex geometry formally derives from icosahedral *closo* twelve-vertex by removal of three vertices<sup>5</sup> as shown in diagram II. Alternatively, the *hypho* eight-vertex [1,2-S<sub>2</sub>B<sub>6</sub>H<sub>9</sub>]<sup>-</sup> dithiaborane cage anion may be viewed as a chelating S,S'-ligand where each sulfur atom acts as a two-electron donor to the {Ru(PPh<sub>3</sub>)( $\eta^5$ -Cp)}<sup>+</sup> unit in a similar fashion to the [S<sub>2</sub>CX]<sup>-</sup> ligand in [Ru( $\eta^2$ -S<sub>2</sub>CX)(PPh<sub>3</sub>)( $\eta^5$ -Cp)], where X = NR<sub>2</sub>, OR,<sup>13</sup> or SPr<sup>n</sup>.<sup>14</sup>



Fig. 2 ORTEP plot of  $[5-(Cp)-5-(PPh_3)-hypho-5,4,6-RuS_2B_6H_9]$  1, showing the numbering scheme; Ellipsoids are shown at the 30% probability level. Selected interatomic distances (Å) and angles (°): Ru5–P12.3016(13), S4–B11.919(7), Ru5–S42.3977(14), S4–B91.899(6), Ru5–S6 2.3945(15), S6–B2 1.908(7), S6–B7 1.897(7), B1–B2 1.795(9), B1–B3 1.779(9), B1–B9 1.968(10), B2–B3 1.800(9), B2–B7 1.969(10), B3–B7 1.825(10), B3–B8 1.732(10), B3–B9 1.822(9), B7–B8 1.788(11), B8–B9 1.782(9); P1–Ru5–S4 91.88(5), P1–Ru5–S6 92.09(5), S4–Ru5–S6 91.46(5), Ru5–S4–B1 108.1(2), Ru5–S4–B9 107.3(2), Ru5–S6–B7 107.5(2), Ru5–S6–B2 109.0(2), B2–B1–S4 115.8(4), B1–B2–S6 114.8(4), S6–B7–B8 125.5(4), S4–B9–B8 125.7(4), B7–B8–B9 108.3(5). There are no unusual distances or angles within the PPh<sub>3</sub> or Cp ligands and the Ru to Cp parameters are normal.

Important interatomic distances and angles for 1 are given in the legend to Fig. 2. The Ru5-S4 and Ru5-S6 distances in compound 1 are 2.3977(14) and 2.3945(15) Å, respectively. These distances are the same within  $3 \times su$  as those of 2.409(4) and 2.402(4) Å in [5-(n<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)-5-Cl-hypho-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>9</sub>] 10, but longer than those in  $[5-(\eta^6-C_6Me_6)-arachno-5,4,6-RuS_2B_6H_8]$ 9, where Ru7-S6 is 2.369(2) Å and Ru7-S8 is 2.367(2) Å.<sup>8</sup> The latter, smaller, values may be compared with Ru-S distances in the ruthenium-chelated xanthate compound [Ru( $\eta^2$ - $S_2CSPr^n$ )(PPh<sub>3</sub>)( $\eta^5$ -Cp)], Ru–S1, 2.374(4) Å and Ru–S2, 2.362(2) Å.<sup>14</sup> The S–B interatomic distances in 1 range from 1.897(7) to 1.919(7) Å. Similar variations were also found in  $[5-(\eta^6-C_6Me_6)-$ 5-Cl-hypho-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>9</sub>] 10, *i.e.* from 1.89(3) to 1.943(19) Å.<sup>8</sup> A large range of B-B distances is observed in compound 1, from 1.732(10) to 1.969(10) Å, typical of borane species,<sup>1-4</sup> although the highest value, of 1.969(10) Å, is somewhat long, and nears the arbitrary 2.0 Å distance often taken as the limit of a significant covalent interboron bonding interaction. A similar situation exists in compound 2 above. These long interboron distances involve the boron atoms which are also bonded to sulfur atoms.

(c) [5-(p-cym)-8-(PMePh<sub>2</sub>)-5,4,6-*arachno*-RuS<sub>2</sub>B<sub>6</sub>H<sub>6</sub>], 4. The structural analysis of crystals of compound 4 revealed that it has a typical nine-vertex *arachno* structure with the ruthenium atom occupying a position adjacent to both sulfur atoms, Fig. 3. Formally, its *arachno* nine-vertex geometry derives from a *closo* eleven-vertex structure by the removal of two adjacent vertices<sup>5</sup> as shown in diagram I. Important interatomic distances and angles are given in the legend to Fig. 3.

Some asymmetry is observed among the Ru–S distances in compound **4**, with Ru5–S4 at 2.3649(12) Å and Ru5–S6 at 2.3786(12) Å, but these distances are similar to those of 2.369(2) and 2.367(2) Å in  $[5-(\eta^6-C_6Me_6)$ -*arachno*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>]**9**, the only other *arachno* nine-vertex {RuS<sub>2</sub>B<sub>6</sub>} cluster compound that has been structurally defined.<sup>8</sup> The two Ru–B distances in **4**, of 2.283(5) Å for Ru5–B1 and of 2.294(5) Å for Ru5–B2, also compare with the values of 2.235(8) and 2.246(9) Å in compound **9**. The B–B distances in **4** range from 1.724(8) to 1.888(7) Å. A similar variation exists in  $[5-(\eta^6-C_6Me_6)-5,4,6$ -*arachno*-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>] **9**, where the B–B distances range from 1.735(14) to 1.951(12) Å.<sup>8</sup> It is noteworthy that in both **4** and **9** the B–B interactions that are flanked by a sulfur atom or a ruthenium fragment are the longest. The S–B interactions bridged by the {Ru(*p*-cym)} unit, *i.e.* S4–B1 at 1.936(5) and S6–B2 at 1.914(5) Å,



**Fig. 3** ORTEP plot of  $[5-(p-cym)-8-(PMePh_2)-arachno-5,4,6-RuS_2B_6H_6]$  **4**, showing the numbering scheme. Ellipsoids are shown at the 30% probability level. Selected interatomic distances (Å) and angles (°): Ru5–S4 2.3649(11), Ru5–S6 2.3786(12), Ru5–B1 2.283(5), Ru5–B2 2.294(5), P1–B8 1.903(5), S4–B1 1.936(5), S4–B9 1.885(5), S6–B2 1.914(5), S6–B7 1.889(6), B1–B2 1.848(7), B1–B3 1.782(7), B1–B9 1.888(7), B2–B3 1.782(7), B2–B7 1.889(8), B3–B7 1.724(8), B3–B8 1.764(7), B3–B9 1.740(7), B7–B8 1.787(8), B8–B9 1.752(7); S4–Ru5–S6 101.47(4), S4–Ru5–B1 49.20(13), S6–Ru5–B2 48.32(13), B1–Ru5–B2 47.63(18), Ru5–S4–B9 109.79(16), Ru5–S6–B7 109.61(18), P1–B8–B3 114.8(3), P1–B8–B7 118.0(3), P1–B8–B9 113.4(3), B7–B8–B9 110.3(4). There are no unusual distances or angles within the PPh<sub>2</sub>Me or *p*-cym ligands and the Ru to *p*-cym parameters are normal.

are longer than those bridged by boron atoms, *i.e.* S(4)–B(9) at 1.885(5) and S(6)–B(7) at 1.889(6) Å. Also noteworthy is that the range of S–B distances in compound **4**, from 1.884(5) to 1.936(5) Å, was similar to those observed for compound **9**, 1.880(10) to 1.939(9) Å, and for [5-( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)-5-Cl-*hypho*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>9</sub>] **10**, from 1.89(3) to 1.936(5) Å.<sup>8</sup>

An additional noteworthy point is the location of the *endo*terminal hydrogen atom on B(8) in compound **4**. This is as found for many analogues such as the 4-L-*arachno*-B<sub>9</sub>H<sub>13</sub> series that have all-boron clusters, in which L is a two-electron donor ligand in the equivalent position to that of PMePh<sub>2</sub> in compound **4**.<sup>15</sup> In the species [5-(*p*-cym)-*arachno*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>] **3**, which does not have a two-electron ligand on a cluster boron atom, there is no such *endo*-terminal hydrogen atom, even though *arachno* nine-vertex cluster character also obtains. Instead, there are two bridging hydrogen atoms to the B(8) position, from the B(7) and B(9) positions that flank it, approximately disposed as in the *hypho*-type species **2** (Fig. 1). This is consistent with the behaviour in all-boron *arachno* nine-vertex clusters.<sup>15</sup>

# Comments on the description of species 1 either as a coordination compound or as a hypho $RuS_2B_6$ cluster compound

Whereas compound 2,  $[Ru(\eta^1-hypho-1,2-S_2B_6H_9)(PPh_3)_2(\eta^5-1)]$ Cp)], is readily described as an  $\eta^1$ -mode coordination complex between the eight-vertex cluster ligand  $[hypho-1, 2-S_2B_6H_9]^-$ , and a ruthenium centre, compound 1, [5-(n<sup>5</sup>-Cp)-5-(PPh<sub>3</sub>)-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>9</sub>], can be described either as a coordination compound of the bidentate  $\eta^2$ -bonded eight vertex [hypho-1,2-S<sub>2</sub>B<sub>6</sub>H<sub>9</sub>]<sup>-</sup> ligand and a ruthenium centre, or as a nine-vertex hypho cluster compound in which the  $\{RuS_2B_6\}$  unit defines the nine-vertex core. It is not possible to choose between these descriptions on the basis of the evidence from the solid state structure analysis or the NMR spectroscopic results, vide infra. Comparison of the Ru-S distances in 1, of 2.3978(14) and 2.3941(15) Å, with Ru-S distances in coordination compounds such as the bidentate xanthate derivative  $[Ru(\eta^2-S_2CSPr^n)(PPh_3)(\eta^5-Cp)]$  at 2.374(4) and 2.362(2) Å,14 or monodentate sulfur-ligand species such as [Ru(C<sub>3</sub>H<sub>6</sub>S)(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-Cp)][CF<sub>3</sub>SO<sub>3</sub>] at 2.3459(20) Å<sup>10</sup> and  $[Ru(PhCH_2CH_2SH)(PPh_3)_2(\eta^5-Cp)][BF_4]$  at 2.369(2) Å},<sup>11</sup> and in the arachno cluster  $[(\eta^6-C_6Me_6)-arachno-5,4,6-RuS_2B_6H_8]$  9 at 2.369(2) and 2.367(2) Å<sup>8</sup> shows the distances in 1 are somewhat longer. However, the distance in 1 is similar to that in  $[Ru(C_6H_{11}SH)(PPh_3)_2(\eta^5-Cp)][BF_4]$  at 2.389(2) Å<sup>12</sup> and the compound [Ru( $\eta^1$ -1,2-S<sub>2</sub>B<sub>6</sub>H<sub>9</sub>)(PPh<sub>3</sub>)<sub>2</sub>( $\eta^5$ -Cp)] **2** at 2.4021(9) Å. Thus no distinction can be made between coordinate bonds and cluster bonds on the basis of bond length.

Since compound 1 does not necessarily require the descriptor "cluster" for the bonding between the ruthenium and  $S_2B_6$  atoms, it can be described as a coordination complex of ruthenium and the  $\eta^2$ -[*hypho*-1,2-S\_2B\_6H\_9]<sup>-</sup> ligand similar to the bidentate xanthate derivative [Ru( $\eta^2$ -S\_2CSPr<sup>n</sup>)(PPh\_3)( $\eta^5$ -Cp)].<sup>14</sup> Likewise compound 10, [5-( $\eta^6$ -C<sub>6</sub>Me\_6)-5-Cl-*hypho*-5,4,6-RuS\_2B\_6H\_9], could be equally described as a coordination complex rather than as a contiguous {RuS\_2B\_6} cluster compound, *i.e.* as [RuCl( $\eta^2$ -S,S'-*hypho*-1,2-S\_2B\_6H\_9)( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)]. While both "coordination complex" and "cluster" descriptions appear equally valid for 1 and 10, a description of [Ru( $\eta^2$ -S\_2CSPr<sup>n</sup>)(PPh\_3)( $\eta^5$ -Cp)] as a {RuS\_2C} *arachno* cluster would not be regarded as helpful by most chemists even though it is recognized that delocalized bonding exists in the xanthate ligand.

However, whereas compound 2 is clearly a coordination complex, compounds 3 and 4 are definitely clusters. Thus the sequence of compounds  $2 \rightarrow 1 \rightarrow 3/4$  shows a progressive increase in the amount of metal-to-cluster bonding as the orbital availability on the metal centre increases as the number of phosphine ligands on the {M(Ar)(PR<sub>3</sub>)<sub>n</sub>} fragments is reduced from two to zero. Where does the complex-to-cluster change occur? In the present work, the answer would appear to be between the structures represented in compounds 1 and 3/4.

#### NMR spectroscopy

For compounds 1, 2 and 4 the results of multinuclear and multiple resonance spectroscopy, as recorded for the individual compounds in the relevant experimental sections below, were entirely consistent with the solid-state structures established from the single-crystal X-ray diffraction analyses (Figs. 1, 2 and 3, respectively), confirming that the crystals selected in each case were representative of the bulk samples. Comparison with previously reported NMR data<sup>8</sup> for its  $\{Ru(C_6Me_6)\}$  analogue similarly supported the [5-(p-cym)-5,4,6-arachno-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>] constitution of compound 3. Salient points of comparison or of other interest are summarized in the following three paragraphs. For all compounds it may be noted that there was a general absence of [11B-11B] correlations between pairs of boron atoms flanked by heteroatoms or by hydrogen bridges. This is a well-recognized phenomenon, and signifies a smaller coupling  ${}^{1}J({}^{11}B-{}^{11}B)$  for such environments, and is consistent with the longer interboron distances often observed for these positions, and therefore weaker direct interboron bonding, and concurs with the structural discussion section above. These small  ${}^{1}J({}^{11}B-{}^{11}B)$  couplings implicit here are generally parallelled by small vicinal couplings  ${}^{3}J({}^{1}H-{}^{1}H)$  between any hydrogen atoms bound to the two boron atoms in question, similarly reducing the incidence of observations of interproton correlations in [<sup>1</sup>H–<sup>1</sup>H]-COSY work.

For  $[5-(\eta^5-Cp)-5-(PPh_3)-5,4,6-RuS_2B_6H_9]$  1 the symmetrical mirror-plane structure was readily apparent from the relative intensities of the cluster 11B and 1H resonance signals, as was its overall similarity with its previously described Ru-chlorinated ruthenadithiaborane congener [5-(n<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)-5-Cl-hypho-5,4,6- $RuS_2B_6H_9$ ] 10.<sup>8</sup> The principal difference from 10 was the <sup>11</sup>B(7,9) resonance at  $\delta(^{11}B)$  +8.4 ppm, which is at significantly lower field, by over 10 ppm, other differences at less than 5.4 ppm not being remarkable. For  $[Ru(\eta^1-1,2-S_2B_6H_9)(PPh_3)_2(\eta^5-Cp)]$  2 the <sup>11</sup>B and <sup>1</sup>H spectra were somewhat more complex, consistent with the less symmetrical molecular structure (Fig. 2), but readily assignable by comparison with the data for the free  $[hypho-1, 2-S_2B_6H_9]^-$  anionic ligand, for the neutral species [5- $(\eta^5$ -Cp)-5-(PPh<sub>3</sub>)-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>9</sub>] 1 just mentioned, and for [5- $(\eta^6-C_6Me_6)-Cl-hypho-5,4,6-RuS_2B_6H_9$ ] 10.<sup>8</sup> In particular, data were very similar to those of the free  $[hypho-1,2-S_2B_6H_9]^-$  anion, consistent with a description as a simple coordination complex of this anion, as discussed in the text above. Thus, the <sup>11</sup>B resonances at ca. +5.0 ppm due to the B(3)B(5) pair are only slightly upfield, by ca. 2.0 ppm, compared with the resonance for the free anion,<sup>16</sup> and the B(4) and B(8) resonances at  $\delta$ <sup>(11</sup>B) -26.6 and -54.5 ppm, respectively, in compound 2 are similarly only at slightly higher field than those of the corresponding resonances in the free anion: these high similarities adduce to the conclusion that compound 2 can be best regarded as a metal-ligand complex as discussed below.

For [5-(p-cym)-*arachno*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>] **3**, as with compound **1** above, the mirror-plane symmetry is manifest in the relative intensity patterns for the cluster <sup>11</sup>B and <sup>1</sup>H resonances. The assignment of the bridging hydrogen resonances to their positions, as summarized in the experimental section, is noteworthy. In particular, and in contrast to compound **4** (Fig. 3; see also structural and NMR and discussions above and below, respectively), bridging hydrogen atoms were apparent between B(7) and B(8), and between B(8) and B(9). Overall, the NMR parameters measured for **3** are in clear parallel to the corresponding parameters reported for the closely related and previously characterised {Ru(C<sub>6</sub>Me<sub>6</sub>)} analogue,<sup>8</sup> clearly confirming the [5-(p-cym)-*arachno*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>] constitution and configuration.

The compound [5-(p-cym)-8-(PMePh<sub>2</sub>)-*arachno*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>6</sub>] **4** similarly had <sup>11</sup>B and <sup>1</sup>H NMR spectra consistent with the molecular plane of symmetry (Fig. 3). Even though its gross *arachno* nine-vertex {5,4,6-RuS<sub>2</sub>B<sub>6</sub>} description is as that for compound **3** above, there are in this case substantial differences in cluster-atom shielding. The most notable difference between **3** and **4** is the substantial downfield shift of the <sup>11</sup>B(3) resonance, of over 35 ppm, from -49.2 ppm in **3** to -12.4 ppm in **4**. This difference is associated with the contrasting differences in the disposition of the inner-sphere *endo*/bridging hydrogen atoms about the open-face B(7), B(8) and B(9) positions, as mentioned in the structural discussion above. The phenomenon is categorised by Heřmáneks 'µ-H Rule',<sup>17</sup> and is classically manifested in the *ca*. 30 ppm difference in <sup>11</sup>B shielding at the B(2) and B(4) positions when *nido*-B<sub>10</sub>H<sub>14</sub> and the [*arachno*-B<sub>10</sub>H<sub>14</sub>]<sup>2–</sup> anion are compared. In the more directly relevant ninevertex *arachno* system, the phenomenon is exhibited by the [*arachno*-B<sub>9</sub>H<sub>14</sub>]<sup>–</sup> anion itself, which exhibits both types of site.<sup>15</sup>

# Conclusions

What is seen in the results from the present work is the progression from coordination complex to cluster as electrons are removed from the transition-element site. The structural sequence  $2 \rightarrow 1 \rightarrow 3/4$  illustrates the Wadian principles<sup>5</sup> of successive effective removal of electrons resulting in the formation of more closed species, *viz*,



Successive removal of both two-electron phosphine ligands can be regarded as the successive removal of two electron pairs from the cluster count, so the core nine-atom assembly goes from coordination complex or 'pre-*hypho*' cluster, **2** to coordination complex/*hypho* cluster **1** and thence to an *arachno* cluster, examples of which are seen in **3** and **4**. Wade's rules are also an effective count of orbital availability: successive removal of the two phosphine ligands releases one and then two ruthenium orbitals for bonding into the cluster, resulting in successively more condensed species.

# Experimental

# General procedures

The compounds  $[RuCl(PPh_3)_2(\eta^5-Cp)]$  and  $[Ru(p-cym)Cl_2]_2$  were used as supplied by the Aldrich Chemical Co. The dithiaborate salt [tmndH][hypho-1,2- $S_2B_6H_9$ ], (tmnd = N,N,N',N'tetramethylnaphthalene-1,8-diamine), was a generous gift from Prof. B. Štíbr and coworkers and is gratefully acknowledged. Purification of solvents and products, and manipulative procedures for recording spectra used in this work have been described in previous Parts of this series.1 Infrared spectra were recorded as KBr discs on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Carbon and hydrogen elemental analyses were performed at University College Cork on a Perkin-Elmer 240C microanalyser. NMR spectra were recorded on Bruker ARX 250 and DRX 500 spectrometers, using  ${}^{11}B$ ,  ${}^{11}B$ -{ ${}^{1}H(broadband)$ },  ${}^{1}H$ ,  ${}^{1}H$ - ${^{11}B(broadband)}, {^{1}H-{^{11}B(selective)}}, {^{11}B-{^{11}B}-COSY}-{^{1}H},$  $[^{1}H-^{1}H]$ -COSY- $\{^{11}B\}$  and  ${}^{31}P\{^{1}H\}$  techniques in combined analytical procedures as described in previous Parts of this series.<sup>1</sup> Chemical shifts  $\delta$  are expressed in parts per million (ppm) to high frequency (low field) relative to  $\Xi$  100 MHz for <sup>1</sup>H (nominally internal SiMe<sub>4</sub>),  $\Xi$  32.083972 MHz for <sup>11</sup>B (nominally internal [BF<sub>3</sub>(OEt<sub>2</sub>)]) and  $\Xi$  40.480 730 MHz for <sup>31</sup>P (nominally 85% H<sub>3</sub>PO<sub>4</sub>), using deuterated solvent <sup>2</sup>D resonances as internal secondary standards. Splittings arising from couplings  ${}^{1}J({}^{11}B-{}^{1}H)$  are taken from resolution-enhanced (linenarrowed) <sup>11</sup>B spectra with digital resolution 4 Hz. For broadened <sup>11</sup>B resonances, the splitting observed will be smaller than the coupling constant  $J({}^{11}B-{}^{1}H)$  from which the splitting arises.

[5-(Cp)-5-(PPh<sub>3</sub>)-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>9</sub>], 1, and [Ru(η<sup>1</sup>-1,2-S<sub>2</sub>B<sub>6</sub>H<sub>9</sub>)-(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-Cp)] 2. To a solution of [tmndH][hypho-1,2- $S_2B_6H_9$ ] (0.050 g, 0.138 mmol) in dichloromethane (15 ml) was added [RuCl(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-Cp)] (0.100 g, 0.138 mmol). The orange reaction mixture was stirred for 5 days at room temperature. It was concentrated under reduced pressure and subjected to preparative t.l.c. (CH<sub>2</sub>Cl<sub>2</sub>-hexane) (6 : 4). Two yellow bands were extracted into dichloromethane. Crystallisation of the first yellow compound ( $R_{\rm F}$  0.9) from CH<sub>2</sub>Cl<sub>2</sub>-hexane (1 : 1) afforded orange crystals of [5-(n<sup>5</sup>-Cp)-5-(PPh<sub>3</sub>)-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>9</sub>] 1 (0.005 g, 6.4%). (Found: C, 48.9; H, 5.2. C<sub>23</sub>H<sub>29</sub>B<sub>6</sub>PRuS<sub>2</sub> requires C, 48.8; H 5.2%). IR: v<sub>max</sub> (KBr) 2568(s)(BH), 2558(s), 2539(s), 2521(vs), 2508(s) (BH) cm<sup>-1</sup>. <sup>11</sup>B and <sup>1</sup>H NMR data (CDCl<sub>3</sub>, 298 K) ordered as assignment  $\delta$ <sup>(11</sup>B) [ $\delta$ <sup>(1</sup>H) of directly attached proton]: BH(7,9) +8.4 [+3.74], BH(1,2) -22.7 [+1.41], BH(8) -23.9 [+2.37], BH(3) -50.4 [-0.34]. Additional data are as follows:  $\delta({}^{1}H)$ (phenyl) +7.27 to +7.59,  $\delta({}^{1}H)(C_{5}H_{5})$  +4.15,  $\delta({}^{1}\text{H})(\mu$ -7,8 and 8,9) -1.55,  $\delta({}^{1}\text{H})(\mu$ -1,2) -1.79;  $\delta({}^{31}\text{P})(\text{PPh}_{3})$ +49.8.

Crystallisation of the second yellow band ( $R_{\rm F}$  0.5) from toluene–hexane (1 : 1) yielded orange crystals of [Ru(η<sup>1</sup>-1,2-S<sub>2</sub>B<sub>6</sub>H<sub>9</sub>)(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-Cp)] **2** (0.055 g, 48.2%). (Found: C, 59.8; H, 5.6. C<sub>41</sub>H<sub>44</sub>B<sub>6</sub>P<sub>2</sub>RuS<sub>2</sub> requires C, 59.4; H 5.6%). IR:  $\nu_{\rm max}$ (KBr) 2552(s), 2528(s,sh), 2514(s), 2493(s) (BH) cm<sup>-1</sup>. <sup>11</sup>B and <sup>1</sup>H NMR data (CD<sub>2</sub>Cl<sub>2</sub> 298 K) ordered as assignment  $\delta$ (<sup>11</sup>B)[ $\delta$ (<sup>1</sup>H) of directly attached proton]: BH(7/9) +5.0 [+3.47] and [+3.45], BH(1/2) -21.3 [+1.76], BH(1/2) -23.6 [+1.90], BH(8) -26.6 [+2.24], BH(3) -54.5 [-0.48]. Additional data are as follows:  $\delta$ (<sup>1</sup>H)(phenyl) +6.87 to +7.72,  $\delta$ (<sup>1</sup>H)(C<sub>3</sub>H<sub>5</sub>) +4.35,  $\delta$ (<sup>1</sup>H)( $\mu$ -7,8 and 8,9) -1.11 and -1.65,  $\delta$ (<sup>1</sup>H)( $\mu$ -1,2) +0.44;  $\delta$ (<sup>31</sup>P)(PPh<sub>3</sub>)(294 K) +41.9 (doublet) and +37.7 (doublet), <sup>2</sup>J(<sup>31</sup>P-<sup>31</sup>P) 37.5 Hz.

# Reaction of $[Ru(\eta^1-1,2-S_2B_6H_9)(PPh_3)_2(\eta^5-Cp)]$ 2 in refluxing dichloromethane solution

A sample of  $[\text{Ru}(\eta^1-1,2\text{-}S_2\text{-}B_6\text{H}_9)(\text{PPh}_3)_2(\eta^5\text{-}\text{Cp})]$  **2** (0.05 g, 0.060 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) and the solution heated to reflux temperature for 3 weeks. The yellow reaction mixture was concentrated under reduced pressure and subjected to preparative t.l.c. (CH<sub>2</sub>Cl<sub>2</sub>-hexane) (6 : 4). A yellow band ( $R_F$  0.9) was extracted into dichloromethane. This was identified spectroscopically (IR and NMR) as [5-( $\eta^5$ -Cp)-5-(PPh\_3)-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>9</sub>] **1** (0.020 g, 58.5%).

[5-(p-cym)-arachno-5,4,6-RuS2B6H8]. 3. To a solution of [tmndH][hypho-1,2-S<sub>2</sub>B<sub>6</sub>H<sub>9</sub>] (0.025 g, 0.069 mmol) was added  $[\operatorname{Ru}(p-\operatorname{cym})\operatorname{Cl}_2]_2$  (0.021 g, 0.034 mmol). The orange mixture was stirred for 2 h at room temperature whereupon it was concentrated under reduced pressure and subjected to preparative t.l.c. (CH<sub>2</sub>Cl<sub>2</sub>-hexane) (7 : 3). A single yellow band ( $R_{\rm F}$ 0.9) was extracted into CH<sub>2</sub>Cl<sub>2</sub>. Crystallisation from CH<sub>2</sub>Cl<sub>2</sub>hexane afforded orange crystals of [5-(p-cym)-arachno-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>] 3 (0.024 g, 93.7%). (Found: C, 32.5; H, 5.9. C10H22B6RuS2 requires C, 32.3; H, 6.0%). IR: vmax (KBr) 2574(m), 2556(m), 2543(s), 2527(vs), 2507(s), 2494(m))(BH) cm<sup>-111</sup>B and <sup>1</sup>H NMR data (CDCl<sub>3</sub> 300 K) ordered as assignment  $\delta$ (<sup>11</sup>B)  $[\delta(^{1}H)$  of directly attached proton] {observed splitting from  $^{1}J^{11}B^{-1}H)/Hz$ : BH(7,9) +3.7 [+3.65]{150}, BH(1,2) -13.9 [+2.33]{165}, BH(8) -33.8 [+1.82]{ca. 145}, BH(3) -49.2 [+0.40]{145}. Additional data are as follows:  $\delta({}^{1}H)$ [(CH<sub>3</sub>)<sub>2</sub>-CHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>] +5.65 (2H, doublet) and +5.48 [2H, doublet,  ${}^{3}J({}^{1}H-{}^{1}H)$  5.4 Hz],  $\delta({}^{1}H)[(CH_{3})_{2}CHC_{6}H_{4}CH_{3}]$  +2.75. (1H, septet),  $\delta({}^{1}\text{H})[(CH_{3})_{2}CHC_{6}H_{4}CH_{3}] + 2.17$  (3H, singlet),  $\delta({}^{1}\text{H})[(CH_{3})_{2}\text{CHC}_{6}\text{H}_{4}\text{CH}_{3}] + 1.31[6\text{H}, \text{doublet}, {}^{3}J({}^{1}\text{H}-{}^{1}\text{H})$ 6.8 Hz],  $\delta({}^{1}\text{H})[(\mu-7,8) \text{ and } (\mu-8,9)] - 1.49$ .

#### Reaction of [5-(p-cym)-arachno-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>8</sub>] with PMePh<sub>2</sub>

To a solution of  $[5-(p-cym)-arachno-5,4,6-RuS_2B_6H_8]$  **3** (0.05 g, 0.134 mmol) in toluene (10 ml) was added PMePh<sub>2</sub> (0.25 ml,

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1.34 mmol). The mixture was stirred at reflux temperature for 16 h whereupon it was concentrated under reduced pressure and subjected to preparative t.l.c. with  $CH_2Cl_2$ -hexane solvent (6:4). An orange band ( $R_{\rm F}$  0.5) was extracted into dichloromethane. Crystallisation from toluene-heptane (1:1) afforded orange crystals of [5-(p-cym)-8-(Ph<sub>2</sub>MeP)-arachno-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>6</sub>] 4 (0.019 g, 24.8%). (Found C, 48.6; H, 5.8.  $C_{23}H_{33}B_6PRuS_2$ requires C, 48.4; H, 5.8%). IR: v<sub>max</sub> (KBr) 2521(vs), 2491(s), 2458(vs)(BH) cm<sup>-1</sup>. <sup>11</sup>B and <sup>1</sup>H NMR data (CDCl<sub>3</sub> 297 K) ordered as assignment  $\delta(^{11}B)$  [ $\delta(^{1}H)$  of directly attached proton]  $\{{}^{1}J{}^{11}B{}^{-1}H)/Hz\}$ : BH(7,9) +10.8 [+3.96] $\{ca.145\}$ , BH(3) -12.4 [+1.52]{*ca.* 141}, BH(1,2) -20.8 [+1.73]{*ca.* 158}, BH(8) -47.9 [-1.28]{ca. 134}. Additional data are as follows:  $\delta({}^{1}\text{H})$ [phenyl(PPh<sub>2</sub>Me)] +7.42 to +7.64, aromatic  ${}^{1}\text{H}$ resonances from cym C<sub>6</sub>H<sub>4</sub> at +5.53 [doublet,  ${}^{3}J({}^{1}H-{}^{1}H)$ 5.8 Hz] and +5.37 [doublet],  $\delta({}^{1}\text{H})[\text{Me}_2\text{C}H]$  +2.79 [septet,  $^{3}J(^{1}\text{H}-^{1}\text{H})$  7.0 Hz], methyl resonances at  $\delta(^{1}\text{H})$  +2.14 [singlet], +1.92 [doublet,  ${}^{2}J({}^{31}P-{}^{1}H)$  11.0 Hz] and +1.30 ppm. [doublet];  $\delta({}^{31}P)(PPh_2Me)(300 \text{ K}) + 12.6, {}^{1}J({}^{11}B-{}^{31}P) \text{ ca. } 115 \text{ Hz.}$ 

#### Crystal structure analyses

Data for compounds **1**, **2** and **4** were collected with an Enraf-Nonius CAD4 diffractometer. The data were corrected for absorption using psi-scans or ABSORB;<sup>18</sup> structure solution used NRCVAX<sup>18</sup> and refinement was with SHELXL-97.<sup>19</sup> PLATON<sup>20</sup> was used for the molecular graphics. Full details in CIF format for the three structures are available from the CCDC (reference numbers 264502, 264503 and 264504 for compounds **1**, **2** and **4**, respectively). Accurate cell dimensions and crystal orientation were determined by least squares procedure from 25 reflections obtained using graphite-monochromatised Mo-K $\alpha$ radiation ( $\lambda = 0.71073$  Å) following a procedure described in detail elsewhere.<sup>1</sup>

X-Ray analysis of [5-( $\eta^5$ -Cp)-5-(PPh<sub>3</sub>)-hypho-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>9</sub>]

**1.** Crystal Data.  $C_{23}H_{29}B_6PRuS_2$ , M = 566.50, monoclinic, Pc, a = 9.482(2), b = 14.275(5), c = 9.753(2) Å,  $\beta = 93.49(2)^\circ$ , Z = 2,  $D_c = 1.428$  g cm<sup>-3</sup>, U = 1317.7(6) Å<sup>3</sup>, F(000) = 576,  $\lambda$ (Mo-Ka) = 0.71073 Å,  $\mu = 0.825$  mm<sup>-1</sup>, T = 294 (1) K, R = 0.0348 for 2707 observed reflections,  $R_w = 0.0863$  for all 3036 unique reflections. Space group Pc or P2/c from the systematic absences; Pc assumed and confirmed by the analysis.

Flack value -0.02(4). The bridging H atoms in the boron cage were refined with restraints [B–H 1.24(4) Å] and the terminal B–H atoms were refined with B–H 1.10(4) Å restraints. All other H atoms were allowed for as riding with the normal SHELXL-97 constraints.

X-Ray analysis of  $[Ru(\eta^1-1,2-S_2B_6H_9)(PPh_3)_2(\eta^5-Cp)]$  2. Crystal Data.  $C_{41}H_{44}B_6P_2RuS_2$ , M = 828.75, monoclinic,  $P2_1/c$ , a = 11.0113(9), b = 18.7264(16), c = 19.840(2) Å, β = 95.546(10)°, Z = 4, D<sub>c</sub> = 1.352 g cm<sup>-3</sup>, U = 4072.0(7) Å<sup>3</sup>, F(000) = 1704, λ(Mo-Kα) = 0.71073 Å,  $\mu$  = 0.596 mm<sup>-1</sup>, T = 294(1) K, R = 0.0418, for 5438 observed reflections.  $R_w = 0.0974$  for all 8839 unique reflections. It became obvious during the structure determination that there was some disorder in the structure. Two small peaks (approximately 1 e  $Å^{-3}$ ) corresponding with other orientations for S atom S(2) were visible and labelled as S(2A) and S(2B). Coordinates for these two sites were determined from difference maps and included (with a  $U_{iso}$  value of 0.05 Å<sup>2</sup>) but not refined in subsequent calculations. Occupancy factor refinement using the SUMP control in SHELXL97 led to occupancy values of 0.906(3), 0.051(2) and 0.043(2) for S(2), S(2A) and S(2B), respectively. It was not possible to locate any other atoms corresponding with the disordered low-occupancy S(2A) and S(2B) atoms and all other atoms were refined with unit-occupancy. The bridging H atoms in the boron cage were refined with restraints [B-H

1.24(4) Å] and the terminal B–H atoms were refined with B–H 1.10(4) Å restraints. All other H atoms were allowed for as riding with the normal SHELXL-97 constraints

X-Ray analysis of [5-(*p*-cym)-8-(Ph<sub>2</sub>MeP))-*arachno*-5,4,6-RuS<sub>2</sub>B<sub>6</sub>H<sub>6</sub>] 4. Crystal Data. C<sub>23</sub>H<sub>33</sub>B<sub>6</sub>PRuS<sub>2</sub>, M = 570.51, monoclinic,  $P2_1/c$ , a = 11.0430(10), b = 10.1578(7), c = 24.528(2) Å,  $\beta = 94.168(7)^{\circ}$ , Z = 4,  $D_x = 1.381$  g cm<sup>-3</sup>, U = 2744.1(4) Å<sup>3</sup>, F(000) = 1168,  $\lambda$ (Mo-K $\alpha$ ) = 0.7107 Å,  $\mu = 0.793$  mm<sup>-1</sup>, T = 294(1) K, R = 0.0432 for 4115 observed reflections,  $R_w = 0.1036$  for all 6264 unique reflections. Boron cage H atoms were located from a difference synthesis and their coordinates normalised to give a B–H distances of 1.10 Å; these H atom contributions were then included but not refined in the final calculations. All other H atoms were allowed for as riding with the normal SHELXL-97 constraints.

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