Reactions of 11-vertex Rhodathiaboranes with HCl: Synthesis and Reactivity of New Cl-ligated Clusters

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December 10, 2012

GRAPHICAL ABSTRACT AND SYNOPSIS

Reactions of 11-vertex rhodathiaboranes with HCl are presented. The clusters accommodate the acid, undergoing structural and electronic *closo*-to-*nido* transformations that demonstrate the bifunctional character of these compounds. Two new examples of stoichiometric cycles driven by Brønsted acid / base chemistry are described.

ABSTRACT

Reactions of $[8,8,8\text{-(H)(PPh}_3)_2\text{-9-(Py)-nido-8,7-RhSB}_9\text{H}_9]$ (**1**), $[1,1\text{-(PPh}_3)_2\text{-3-(Py)-closo-1,2-RhSB}_9\text{H}_8]$ (**2**) and $[1,1\text{-(CO)(PPh}_3)_2\text{-3-(Py)-closo-1,2-RhSB}_9\text{H}_8]$ (**4**), where Py = Pyridine, with HCl to give the Cl-ligated clusters, $[8,8\text{-(Cl)(PPh}_3)_2\text{-9-(Py)-nido-8,7-RhSB}_9\text{H}_9]$ (**3**) and $[8,8,8\text{-(Cl)(CO)(PPh}_3)_2\text{-9-(Py)-nido-8,7-RhSB}_9\text{H}_8]$ (**5**), have recently demonstrated the remarkable *nido*-to-*closo* redox flexibility and bifunctional character of this class of 11-vertex rhodathiaboranes. To get a sense of the scope of this chemistry, we report here the reactions of PR_3 -ligated analogues, $[8,8,8\text{-(H)(PR}_3)_2\text{-9-(Py)-nido-8,7-RhSB}_9\text{H}_9]$, where $\text{PR}_3 = \text{PMePh}_2$ (**6**), or PPh_3 and PMe_3 (**7**); and $[1,1\text{-(PR}_3)_2\text{-3-(Py)-closo-1,2-RhSB}_9\text{H}_8]$, where $\text{PR}_3 = \text{PPh}_3$ and PMe_3 (**8**), PMe_3 (**9**) or PMe_2Ph (**10**), with HCl to give Cl-ligated clusters. The results demonstrate that in contrast to the PPh_3 -ligated compounds, **1**, **2** and **3**, the reactions with **6-10** are less selective, giving rise to the formation of mixtures that contain monophosphine species, $[8,8\text{-(Cl)(PR}_3)_2\text{-9-(Py)-nido-8,7-RhSB}_9\text{H}_9]$, where $\text{PR}_3 = \text{PMe}_3$ (**11**), PMe_2Ph (**12**) or PMePh_2 (**15**), and bis-ligated derivatives, $[8,8,8\text{-(Cl)(PR}_3)_2\text{-9-(Py)-nido-8,7-RhSB}_9\text{H}_9]$, where $\text{PR}_3 = \text{PMe}_3$ (**13**) or PMe_2Ph (**14**). The $\{\text{RhCl(PR}_3)_2\}$ -containing compounds, **3**, **11**, **12** and **15**, are formally unsaturated 12 skeletal electron pair (sep) clusters with *nido*-structures. DFT-calculations demonstrate that the *nido*-structure is more stable than the predicted *closo*-isomers. In addition, it has been carried out studies that involve the reactivity of **3** with Lewis bases. Thus, it is reported that **3** interacts with MeCN in solution and it reacts with CO and pyridine to give the corresponding Rh-L adducts, $[8,8,8\text{-(Cl)(L)(PPh}_3)_2\text{-9-(Py)-nido-8,7-RhSB}_9\text{H}_9]$, where L = CO (**5**) or Py (**20**). On the other hand, the treatment of **3** and **5** with Proton Sponge (PS) promotes the abstraction of HCl, as $[\text{PSH}]\text{Cl}$, from the *nido*-clusters, and the regeneration of the parent *closo*-species, completing two new stoichiometric cycles that are driven by Brønsted acid / base chemistry.

MAIN TEXT

Introduction

In polyhedral boron chemistry, it has long been a goal to develop catalytic cycles by combining the oxidative and coordinative richness of transition metal elements with the capability of boron clusters to exhibit oxidative/reductive flexibility in their classical *closo* - *nido* - *arachno* transformations. In this regard, we have shown that the 11-vertex rhodathiaborane system, [8,8,8-(H)(PPh₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] (**1**) / [1,1-(PPh₃)₂-3-(Py)-*closo*-1,2-RhSB₉H₈] (**2**) exhibits a remarkable *nido*-to-*closo* redox reactivity that can operate in the hydrogenation of alkenes (Py = pyridine).¹ In this system, the {SB₉H₈(Py)} fragment can be regarded as a non-innocent ligand that cooperates with the metal vertex in the reactions, conferring a bifunctional nature to these rhodathiaboranes.

Reactions of **1** and **2** with hydrochloric acid have recently demonstrated further the remarkable lability and bifunctional character these 11-vertex rhodathiaboranes.² These reactions are new convenient routes to Cl-ligated rhodathiaboranes; thus, air-stable yellow [8,8-(Cl)(PPh₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**3**) can be synthesized in high yield from [RhCl(PPh₃)₃] and readily available Cs[*arachno*-6-SB₉H₁₂], carrying out three steps (Scheme 1).

Scheme 1: Synthesis of **3**

Alternatively, compound **3** can be prepared in 75% yield from the reaction of the *closo*-derivative, **2**, with HCl. Similarly, the CO-ligated counterpart, [1,1-(CO)(PPh₃)-9-(Py)-*closo*-1,2-RhSB₉H₈] (**4**), reacts with HCl to give orange-yellow [8,8,8-(Cl)(CO)(PPh₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**5**). Building upon the reactivity of **1** and **2** with hydrochloric acid, we have extended our studies to the PR₃-ligated analogues, [8,8,8-(H)(PR₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉], where PR₃ = PMePh₂ (**6**), or PPh₃ and PMe₃ (**7**);³ and [1,1-(PR₃)₂-3-(Py)-*closo*-1,2-RhSB₉H₈], where PR₃ = PPh₃ and PMe₃ (**8**), PMe₃ (**9**) or PMe₂Ph (**10**),³ discussing trends and differences within this family of 11-vertex clusters.

Results and Discussion

Reactions of *closo*- and *nido*-rhodathiaboranes with HCl

Scheme 2 can be used as a guide to the following sections. The synthesis of **3** and its reactivity with CO has been described earlier.² Now we explore the reactivity of the 11-vertex *nido*- and *closo*-rhodathiaboranes, **6-10**, which are PR₃-ligated derivatives of the *nido*- and *closo*-counterparts, **1** and **2**. As commented in the introduction, the treatment of the *closo*-derivative, **2**, with aqueous HCl, followed by filtration and drying over magnesium sulfate, affords **3** in good yields (Scheme 1).² Similarly, the reactions of the *bis*-PR₃-ligated *closo*-counterparts, **9** and **10**, with HCl yield new mono-phosphine *nido*-clusters, [8,8-(Cl)(PR₃)-9-(Py)-*nido*-8,7-RhSB₉H₉], where PR₃ = PMe₃ (**11**) or PMe₂Ph (**12**), in moderate to high yields. However, when these reactions were carried out in NMR scale, the solvent was evaporated and the resulting residue washed with hexane, the NMR data showed the formation of mixtures that contained the mono-phosphine-ligated clusters, **11** and **12**, together with the bis-phosphine derivatives, [8,8,8-(Cl)(PR₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉], where PR₃ = PMe₃ (**13**), PMe₂Ph (**14**), with higher ratios of the bis-phosphine to the mono-phosphine compounds.

In contrast to **9** and **10**, the reaction of the mixed PR₃-ligated analogue **8** with HCl affords a mixture of **3** and **11** in a 1:2 ratio. Alternatively, **3** is also available from the reaction of **1** and hydrochloric acid;² likewise, the treatment of the *nido*-hydridorhodathiaboranes, [8,8,8-(H)(PR₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉], where PR₃ = PMePh₂ (**6**), or PPh₃ and PMe₃ (**7**), with HCl affords the corresponding chloro-derivatives, [8,8,8-(Cl)(PR₃)-9-(Py)-*nido*-8,7-RhSB₉H₉], where PR₃ = PMe₃ (**11**) or PMePh₂ (**15**).

Scheme 2

Structural Aspects.—The structures of **3** and **5** were reported in an earlier communication,² and now these are analyzed in more detail, together with the new Cl-ligated clusters, [8,8,8-(Cl)(PMe₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] (**13**) and [8,8,8-(Cl)(PMe₂Ph)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] (**14**). It should be noticed that for **13** a static disorder was observed in the thiaborane fragment and the phosphine ligands. This disorder has been modeled with two sets of positions with complementary occupancy factors (0.92/0.08). The distances and angles discussed below deal with the major occupancy cluster.

These compounds have a *nido* 11-vertex cluster geometry with a five-membered {RhSB₃} open face (schematic II, Figure 1). This structure is now well represented with examples that show different combinations of *exo*-polyhedral ligands either at the B(9) vertex or at the Rh(8) center. In compound **3**, the pentagonal open face has a pyridine-bound vertex at the B(9) position and a {Rh(Cl)(PPh₃)} fragment, which renders this cluster isoelectronic with [8,8-(L)₂-*nido*-8,7-RhSB₉H₁₀], where L = PPh₃ (**16**),⁴ (CH₂)₃(PPh₂)₂,⁵: rhodathiaboranes that exhibit a B(9)-H(9) vertex and {RhP₂} fragments as part of the open face (schematic cluster structure I).

Figure 1 ORTEP-type of drawing of compounds **3** (left) and **14** (right), and detail of the rhodium-to-cluster coordination sphere (below the clusters). Ellipsoids are shown at 50 % probability levels.

Compounds **5**, **13** and **14** are based on the same pyridine-substituted $\{\eta^4\text{-SB}_9\text{H}_9(\text{Py})\}$ fragment than **3**, but with rhodium vertices that bear a third *exo*-polyhedral ligand to form the organometallic fragments, $\{\text{Rh}(\text{Cl})(\text{CO})(\text{PPh}_3)\}$, $\{\text{Rh}(\text{Cl})(\text{PMe}_3)_2\}$ and $\{\text{Rh}(\text{Cl})(\text{PMe}_2\text{Ph})_2\}$, respectively (schematic cluster structure II, Figure 1). These rhodium units are reminiscent of **1**,⁶ which contains a $\{\text{Rh}(\text{H})(\text{PPh}_3)_2\}$ fragment at the 8-position. Thus, for comparison, important interatomic distances and angles in **1**, **3**, **5**, **13** and **14** are given in Table 2.

Figure 2 Drawings of compounds **3**, **5** and **2**, respectively, illustrating the angle θ between the $\{\text{Rh}(8)\text{S}(7)\text{B}(9)\}$ and $\{\text{S}(7)\text{B}(2)\text{B}(5)\text{B}(9)\}$, which is virtually zero for the 11-vertex octadecahedral *closo*-structure of **2**, and 50° for the *nido*-cages of **3** and **5**. For an 11-vertex fragment of a regular icosahedron it would be 62° .

A common structural feature of **3** and **16** is that the $\{\text{RhCl}(\text{PPh}_3)\}$ and $\{\text{Rh}(\text{PPh}_3)_2\}$ units are twisted away from a reference plane through $\text{Rh}(8)\text{B}(1)\text{B}(6)$. The dihedral angles Φ between the planes formed by $\text{P}(1)\text{Rh}(8)\text{Cl}$ and $\text{P}(1)\text{Rh}(8)\text{P}(2)$, in **3** and **16**, and the $\text{S}(7)\text{Rh}(8)\text{B}(9)$ plane are 53° and 59° , respectively. Table 1 gathers this structural facet that is found in 11-vertex metallaheteroboranes that incorporate $\{\text{M}(\text{L})_2\}$ - and $\{\text{MCIL}\}$ -fragments, where $\text{M} = \text{Rh}, \text{Ir}, \text{or Pt}$. Also listed in Table 1 are the angles between the $\{\text{M}(8)\text{E}(7)\text{B}(9)\}$ and $\{\text{E}(7)\text{B}(2)\text{B}(5)\text{B}(9)\}$, where $\text{E} = \text{C}, \text{N}$ or S , planes in different 11-vertex metallaheteroboranes (Figure 2). This dimension is appropriate to examine for intermediacy of structure between conventionally *nido* compounds **1**, **3**, **5**, **6**, **13** and **14**, and *closo*-cages **2**, **8**, **9** and **10**. The data indicate that conventional *nido*-structures exhibit a θ angle close to 50° , whereas, in 11-vertex metallaheteroboranes that incorporate $\{\text{ML}_2\}$ units, there is some shift from the *nido* structure towards the closed octadecahedral cage. As expected for 11-vertex *isonido*-clusters, which exhibit a quadrilateral

open face, the θ angles are closer to pure 11-vertex octadodecahedral *closo*-cages than to 11-vertex icosahedral *nido*-clusters, but clearly shifted toward the *nido*-cage when compared to typical 11-vertex *closo*-cages (see Table 1).

Table 1 Angles Φ and θ for 11-vertex metallaheteroboranes

Compound	Φ^a	θ^b	ref
[8,8-(PPh ₃) ₂ - <i>nido</i> -8,7-RhSB ₉ H ₁₀] (16)	59°	46 °	4
[8,8-(PPh ₃) ₂ -9-(OEt)- <i>nido</i> -8,7-RhSB ₉ H ₉]	63°	48 °	7
[8,8-(η^2 -dppe)- <i>nido</i> -8,7-RhSB ₉ H ₁₀]	69°	48 °	8
[8,8-(η^2 -dppp)- <i>nido</i> -8,7-RhSB ₉ H ₁₀]	69°	47 °	5
[8,8-(η^2 -dppp)-9-(OEt)- <i>nido</i> -8,7-RhSB ₉ H ₉]	77°	46 °	5
[8,8-(Cl)(PPh ₃) ₂ -9-(Py)- <i>nido</i> -8,7-RhSB ₉ H ₉] (3)	53°	49°	2
[1,1-(PPh ₃) ₂ -3-(Py)- <i>closo</i> -1,2-RhSB ₉ H ₈] (2)	85°	2°	6
[1,1-(PMe ₂ Ph) ₂ -3-(Py)- <i>closo</i> -1,2-RhSB ₉ H ₈] (10)	83°	6°	3
[1,1-(PMe ₃)(PPh ₃)-3-(Py)- <i>closo</i> -1,2-RhSB ₉ H ₈] (8)	85°	2°	3
[1,1,1-(H)(PMe ₃) ₂ - <i>isonido</i> -1,2-IrSB ₉ H ₉]	81°	13°	9
[1,1,1-(H)(PPh ₃) ₂ - <i>isonido</i> -1,2-IrC ₂ B ₈ H ₁₀]	88°	14°	10
[8,8-(PPh ₃) ₂ - <i>nido</i> -8,7-RhNB ₉ H ₁₁]	31°	38°	11
[8,8-(PMe ₂ Ph) ₂ - <i>nido</i> -8,7-PtCB ₉ H ₁₁]	36°	37°	12
[8,8-(PMe ₂ Ph) ₂ -9-(OMe)- <i>nido</i> -8,7-PtCB ₉ H ₁₀]	44°	36°	11
[8,8,8-(H)(PPh ₃) ₂ -9-(Py)- <i>nido</i> -8,7-RhSB ₉ H ₉] (1)	–	52°	1b
[8,8,8-(H)(PMePh ₂) ₂ -9-(Py)- <i>nido</i> -8,7-RhSB ₉ H ₉] (6)	–	50°	3
[8,8,8-(Cl)(CO)(PPh ₃) ₂ -9-(Py)- <i>nido</i> -8,7-RhSB ₉ H ₉] (5)	–	50°	2
[8,8,8-(Cl)(PMe ₂ Ph) ₂ -9-(Py)- <i>nido</i> -8,7-RhSB ₉ H ₉] (14)		51°	this work
[8,8,8-(CO)(η^2 -dppe)- <i>nido</i> -8,7-RhSB ₉ H ₁₀]	–	50°	13
[8,8,8-(η^2 -dppe)(NCMe)- <i>nido</i> -8,7-RhSB ₉ H ₁₀]	–	50°	13
[8,8,8-(PMe ₂ Ph) ₃ - <i>nido</i> -8,7-RhSB ₉ H ₁₀]	–	50°	14
[8,8,8-(η^1 -dppm)(η^2 -dppm)- <i>nido</i> -8,7-RhSB ₉ H ₁₀]	–	50°	5
[8,8,8-(k^2 -bpy)(PPh ₃)- <i>nido</i> -8,7-RhSB ₉ H ₁₀]	–	52°	15
[8,8,8-(CO)(PMe ₃) ₂ - <i>nido</i> -8,7-IrSB ₉ H ₁₀]	–	51°	9

^aDihedral angles between {L(1)M(8)L(2)} and {E(7)M(8)B(9)} planes. ^bDihedral angles between {M(8)E(7)B(9)} and {E(7)B(2)B(5)B(9)}. *Nido* numbering is used to define the planes.

The $\{\text{RhCl}(\text{PPh}_3)\}$ unit is an unusual moiety in rhodaheteroboranes, which, within the polyhedral environment of a $\{\eta^4\text{-SB}_9\}$ -to-Rh interaction as in **3**, has only been crystallographically characterized in the dirhodadithiaborane, $[(\text{PPh}_3)_2\text{HRh}(\text{PPh}_3)\text{ClRhS}_2\text{B}_7\text{H}_7]$ (**17**; schematic cluster structure III).¹⁶ A similar rhodium-to-thiaborane interaction is found in $[\text{8-Cl-}\{8,9-(\mu\text{-dppm})\}\text{-10-PPh}_3\text{-}nido\text{-}8,7\text{-RhSB}_9\text{H}_7]$ (**18**),¹⁷ in which a diphenylphosphinemethane ligand, dppm, is bridging the Rh(8) atom and the 9-position in the open face of the cage (Schematics IV). The chlorine atom in **3** is attached to the rhodium center at a distance of 2.354(2) Å, which is shorter than the rhodium–chlorine bonds, 2.3710(10) and 2.370(2) Å, in **17** and **18**, respectively, but close to the value of 2.356(2) Å found in $[\text{2,3-}(\text{PPh}_3)_2\text{-3-Cl-}\mu\text{-2;3-Cl-2-(Ph}_2\text{PC}_6\text{H}_4)\text{-}closo\text{-}2,3,1\text{-Rh}_2\text{SB}_9\text{H}_8]$.⁴ In the bis-PR₃-ligated clusters, **13** and **14**, the Rh–Cl distance is markedly longer at 2.5196(7) and 2.5116(8) Å, respectively (the mean of Rh–Cl distances found in the CSD is 2.403(3) Å). It is interesting to point out that in the herein crystallographically studied Cl-ligated clusters, **3**, **5**, **13** and **14**, and other previously reported Cl-ligated rhodathiaboranes, the chlorine ligand is *trans* to boron vertices, contrasting with the preference of the hydride ligand to lie *trans* to the sulfur vertex (*vide infra*).

Comparative NMR studies.— The mono-phosphine-ligated 11-vertex rhodathiaboranes, **3**, **11**, **12** and **15**, have been characterized by multinuclear NMR spectroscopy. The $^{11}\text{B}\{-^1\text{H}\}$ NMR spectra show seven resonances in a 2:2:1:1:1:1:1 relative intensity ratio for **3**, **12** and **15**, whereas for the PMe_3 -ligated analogue **11**, there are eight signals in the ratio 2:1:1:1:1:1:1:1, indicating that the clusters are asymmetric in solution (Figure 3). This asymmetry is further confirmed by the $^1\text{H}\{-^{11}\text{B}\}$ spectra that exhibit nine proton resonances of hydrogen atoms bound to boron atoms, resolving, therefore, the peaks of intensity two that correspond to overlapping ^{11}B resonances. The similarity of the ^{11}B NMR spectra in this series of Cl-ligated 11-vertex rhodathiaboranes is remarkable, suggesting that the substitution of PPh_3 in the crystallographically determined cluster, **3**, by the more basic phosphines, PMe_3 , PMe_2Ph and PMePPh_2 , does not have a significant effect in the electronic distribution within the $\{\eta^4\text{-SB}_9\text{H}_9(\text{Py})\}$ moiety.

Figure 3 Diagrams representing the chemical shifts in the ^{11}B NMR spectra. Hatched lines connect equivalent positions. Assignments were made based on $^1\text{H}\{-^{11}\text{B}(\text{sel})\}$ experiments and DFT-calculations on the PH_3 model, $[\text{8,8-(Cl)(PH}_3\text{)-9-(Py)-nido-8,7-RhSB}_9\text{H}_9]$ (**3a**).

The four chloro-ligated clusters, **3**, **11**, **12** and **15**, exhibit a sharp doublet in the corresponding $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra at room temperature. This sharpness suggests that $^{31}\text{P}\text{-}^{11}\text{B}$ coupling is small, supporting an *exo*-polyhedral ligand orientation with the PR_3 ligands lying *trans* to the S(7) vertex. Thus, the $\{\text{Rh}(\text{Cl})\text{PR}_3\}\text{-to-}\{\eta^4\text{-SB}_9\text{H}_9(\text{Py})\}$, where $\text{PR}_3 = \text{PMe}_3$, PMe_2Ph , PMePPh_2 or PPh_3 , configuration in solution appears to resemble that found in the solid state for **3** (Figure 1). The ^{31}P resonances shift from the low-field value of $\delta+32.2$ in **3**, through the values of $\delta+18.1$ and $+12.3$ in **15** and **12**, respectively, to the high-field resonance of $\delta+7.8$ in **11**. The $^1J(^{103}\text{Rh}\text{-}^{31}\text{P})$ coupling constant is 8 Hz smaller in the PMe_3 -ligated cluster, **11**, than in the PPh_3 analogue **3**.

The bis-phosphine-ligated clusters, **13** and **14**, were characterized *in situ* by NMR in samples that contained the mono-phosphine parent species, **11** and **12**, as minor components. Although the assignment of the resonances has some ambiguity due to overlapping peaks, the $^1\text{H}\{-^{11}\text{B}\}$ and ^{11}B NMR data indicate that the pattern of the spectra do not change significantly upon coordination of a second phosphine ligand at the rhodium centre (Figure 5 below). The $^{31}\text{P}\{-^1\text{H}\}$ spectra exhibit two principal

resonances, which correspond to two different phosphine ligands. It is noteworthy that the highest field peak is broad in both species even at low temperature.

Bonding Considerations.—Application of the electron-counting rules to compounds **3**, **11**, **12** and **15** gives a formal 12 sep. This number predicts a *closo*-structure based on an octadodecahedron.¹⁸ In compound **3**, the rhodium centre could be tentatively described as having a distorted square-planar environment, with bonding vectors directed toward the two *exo*-polyhedral ligands, and the S(7) and B(4) vertices of the {SB₉H₉(Py)}-fragment, which in **3** are situated *trans* to the PPh₃ and Cl ligands, respectively (Figure 1).

A discrepancy between the electron-counting rules and the structure is common among polyhedral molecules that incorporate C_{2v} fragments such as {RhL₂} or {PtL₂}. This problem has been long recognized and rationalized,¹⁹ and it has been dealt with in the literature several times.^{11,16,20} Alternatively, it has been suggested¹³ that two CH...Rh agostic interactions with two *ortho*-C-H bonds of the PPh₃ ligands of the {Rh(PPh₃)₂} unit in the formally unsaturated 11-vertex rhodathiaborane, **16**, play an important and decisive role in the stabilization of *nido* versus *closo* geometries in this type of compound. Incidentally, there are two CH...Rh contacts at 2.75 and 3.27 Å in the molecular structure of **3**, which could stabilize the *nido*-structure by providing the additional electron pair to the cluster framework. In order to evaluate this hypothesis, we decided to undertake DFT-calculations on the PH₃ model, [8,8-(Cl)(PH₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**3a**), and its hydrido isomer [1,1,1-(Cl)(H)(PH₃)-3-(Py)-*isonido*-8,7-RhSB₉H₈] (**3b** and **3c**). The calculated structural and nuclear shielding properties of **3a** agree well with the experimental data of the Cl-ligated *nido*-clusters, **3**, **11**, **12** and **15** (see supporting information, Table S1) suggesting that **3a** is a reasonable model for these 11-vertex unsaturated clusters. The energy of the optimized minima for the *nido*-isomer, **3a**, lies 57 kJ/mol lower in energy than the isomer **3b** (Figure 4) which exhibits an *isonido*-structure. This structure, with a {Rh(1)S(2)B(4)B(7)} quadrilateral open face, resembles calculated intermediates along the fluxional pathway of compound **16**¹¹ as well as the crystallographically determined hydrido-iridathiaborane, [1,1,1-(H)(PMe₃)₂-*isonido*-1,2-IrSB₉H₉] (**19**).⁹ It is interesting to note that a {η⁴-SB₉H₈(Py)}-to-{Rh(Cl)(H)(PH₃)} conformational

change from **3b** to **3c** implies an increase of 50 kJ/mol in the energy of the PH₃-model, indicating that there is a clear preference of the hydride ligand to occupy the position *trans* to the sulphur vertex *versus* to a boron vertex of the hexagonal {S(1)B(3)B(4)B(5)B(6)B(7)} face. Since the boron vertex in metallaheteroboranes has a stronger *trans* influence than the cage heteroatoms,²¹ the final *exo*-polyhedral orientation of the metal ligands with respect to the {SB₉H₈(Py)} fragment is controlled by the sulfur vertex with the hydride ligand, which have a stronger *trans* influence than chlorine and PR₃ ligands, lying *trans* to the cage S atom. This effect, therefore, stabilizes the calculated *isonido*-conformer **3b** *versus* **3c**, however it is not strong enough to stabilize the *isonido* structure *versus* the *nido*; in other words, in **3** a B-H-B bridging position for the hydrogen atom is more stable than the formation of a Rh-H bond *trans* to the sulphur vertex. This contrasts with compound **19** in which an 11-vertex *isonido*-structure with a S(2)-to-{Ir(1)H} *trans* configuration is more stable than the B-H-B *nido*-isomer.⁹ In this regard, a boron vertex-to-metal hydride destabilizing effect is also directing the exopolyhedral ligand orientation in the previously reported hydridometallathiaboranes [8,8,8-(H)(PR₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉], where PR₃ = PPh₃ (**1**),^{1a} PMePh₂ (**6**),³ [8,8,8-(H)(PMePh₂)₂-9-(PMePh₂)-*nido*-8,7-RhSB₉H₉],³ [8,8,8-(H)(PPh₃)₂-*nido*-8,7-RhS₂B₈H₈],²² [8,8,8-(H)(PPh₃)₂-*nido*-8,7-RhCSB₈H₁₀],²³ [8,8,8-(H)(PPh₃)₂-*nido*-8,7,12-IrS₂B₉H₉],²² [2,2,2-(H)(PMe₃)₂-*nido*-2,6-IrSB₈H₁₀]²⁴ and [2,2,2-(H)(PMe₃)₂-*closo*-2,1-IrSB₈H₈],²⁴ in which invariably the hydride ligand lies *trans* to the sulfur vertex.

Figure 4 DFT-calculated energies and structures, computed at the B3LYP/6-31G*/LANL2DZ level for the PH_3 model [8,8-(Cl)(PH_3)-9-(Py)-*nido*-8,7-RhSB $_9$ H $_9$] (**3a**) and two rhodium-hydride ligated isomers, [1,1-(Cl)(H)(PH_3)-3-(Py)-*isonido*-8,7-RhSB $_9$ H $_8$] (**3b** and **3c**).

In conclusion, the calculations presented here for the Cl-ligated species, with PH_3 ligands, demonstrate that the *nido* structure is more stable in the ground state, *i.e.* as isolated molecules. Therefore, without any possible contribution from *agostic* interactions from P-aryl hydrogen atoms or from other molecules, there is no need to invoke $\text{CH}\cdots\text{Rh}$ agostic interactions to account for the molecular structures of **3**, **11**, **12** and **15**. These results conform to analogous DFT-analysis performed on the isoelectronic 11-vertex rhodathiaborane, [8,8-(PPh_3) $_2$ -*nido*-8,7-RhSB $_9$ H $_{10}$] (**16**).¹¹

Reactions with Lewis Bases

The electronic unsaturation of the 11-vertex Cl-ligated rhodathiaboranes augurs a rich reaction chemistry with Lewis bases. The following sections describe the interaction of **3** with CH₃CN, and the reactions with CO, pyridine and Proton Sponge.

As illustrated in Figures S10 to S12, the addition of 8 equivalents of acetonitrile to a solution of **3** in dichloromethane results in significant changes of the NMR spectra. Thus, ¹¹B resonances corresponding to the B(9), B(3) and B(5) vertices shift towards high field, the B(6) and B(11) peaks, which overlap in CD₂Cl₂ (top trace of Figure S10), split upon addition of CH₃CN to separate clearly in neat CD₃CN (bottom trace of Figure S10), whereas the peaks corresponding to B(1) and B(10) overlap to split again in neat CD₃CN. Changes are also significant in the ¹H resonances of the boron-bound hydrogen atoms (Figure S11). The effect is clear in the high field shift of the H(1), H(3), H(10) and μ-H(9,10) proton resonances, whereas those corresponding to H(4), H(5), H(6) and H(11) appear to approach to each other, suffering a shielding. Finally, the ³¹P-¹H spectrum exhibits a slight shift of the sharp doublet to low fields, and a change of the ¹J(¹⁰³Rh-³¹P) coupling constant from 153 Hz in CD₂Cl₂ to 140 Hz in CD₃CN (Figure S12).

In addition to the above-noted changes, in neat CD₃CN, there is formation of minor species, inferred from new low intensity peaks in the ¹¹B-¹H NMR spectrum and the existence of a new broad peak at +15.0 ppm in the ³¹P-¹H. Interestingly, when the sample is evaporated to dryness and dissolved in CD₂Cl₂, the NMR spectra correspond to the Cl-ligated cluster, **3**, demonstrating that the behavior in acetonitrile is reversible.

These results are consistent with the existence of an equilibrium between **3**, free acetonitrile and a CH₃CN-ligated species of formulation [8,8,8-(Cl)(NCCH₃)(PPh₃)-9-(Py)-*nido*-8,7-RhSB₉H₉], with the equilibrium shifted to the left of equation 1 below. Under this rationale, the low intensity NMR resonances found in the ¹¹B-¹H and ³¹P-¹H in CD₃CN (Figures S10 to S12) should correspond to the acetonitrile adduct, which upon evaporation of the solvent gives **3**.

PGSE NMR diffusion experiments reveal that the self-diffusion coefficient, D , of free acetonitrile (10 mM) in CD_2Cl_2 at 300 K, changes from a value of $3.73 \times 10^{-9} \text{ m}^2/\text{s}$ to $3.26 \times 10^{-9} \text{ m}^2/\text{s}$ when the chloro-derivative, **3**, is added to give mixture of 4:1 ratio of CH_3CN to rhodathioborane. D -values of 4.29×10^{-9} , 4.34×10^{-9} and $5.4 \times 10^{-9} \text{ m}^2/\text{s}$ have been published for acetonitrile.²⁵ A decrease in the D -value is consistent with the interaction of acetonitrile with the polyhedral cluster, which due to its bigger size should have lower D -values, slowing down, therefore, the diffusion of the smaller CH_3CN molecules.

Figure 5 Diagrams representing the chemical shifts in the ^{11}B NMR spectra. Hatched lines connect equivalent positions.

The reaction between **3** and carbon monoxide gives **5** in high yield.² Related to this reaction, the treatment of **3** with pyridine affords a new rhodathiaborane that has been characterized by multinuclear NMR spectroscopy and mass spectrometry as $[\mathbf{8,8,8-(Cl)(Py)(PPh_3)-9-(Py)-nido-8,7-RhSB_9H_9}]$ (**20**). A comparison of the ^{11}B NMR spectrum shows that the pattern is very similar to those of the CO and *bis*- PMe_3 -ligated adducts, **5** and **13** (Figure 5); and to the mono-phosphine derivative, **3**. Since shielding patterns provide potential information regarding the cluster bonding, this comparative NMR work suggests that the $\{\eta^4\text{-SB}_9\text{H}_9(\text{Py})\}$ -to-rhodium interaction in the formally unsaturated $\{\text{RhCl}(\text{PR}_3)\}$ -

ligated species, **3**, **11**, **12** and **15**, is fundamentally the same than in the saturated $\{\text{RhCl}(\text{PR}_3)_2\}$ -ligated derivatives, **13**, **14** and **20**. These species may, therefore, be regarded as sixteen-electron $\{\text{RhCl}(\text{PR}_3)\}$ and eighteen-electron $\{\text{RhCl}(\text{PR}_3)_2\}$ complexes with the $\{\text{nido-SB}_9\text{H}_9(\text{Py})\}$ moiety, which is acting as a *tetrahapto* ligand with bidentate character: this would imply a basic four-orbital square-planar and five-orbital square-pyramidal metal co-ordination sphere (see Figure 1).

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of **20** exhibits a sharp doublet at $\delta +30.5$, suggesting that the PPh_3 ligand of the pyridine adduct remains *trans* to the S(7) vertex. This contrasts to the CO adduct, **5**, which shows a very broad resonance at room temperature, and a configuration in the solid state with the PPh_3 ligand *trans* to the B(9) vertex. Interestingly, the best agreement between the measured ^{11}B NMR chemical shift values and the boron nuclear shielding properties, as calculated *via* the GIAO approach (Figures S7-S9, and Table S11), corresponds to the PH_3 model in which the phosphine ligand is *trans* to the S(7) vertex, the pyridine *trans* to the B(3)-B(4) edge and the chlorine *trans* to the B(9) vertex (Figure S9).

Scheme 3

A general characteristic of boranes, heteroboranes, and their metal derivatives metallaboranes and metallaheteroboranes, is that B-H-B bridging hydrogen atoms are relative acidic. This allows, for example, the deprotonation of polyhedral boron-containing compounds such as *nido*- $\text{B}_{10}\text{H}_{14}$,²⁶ *aracho*-4- CB_8H_{14} ,²⁷ *aracho*-4- SB_8H_{12} ,²⁸ *nido*-4- NB_9H_{12} ,¹¹ $[\text{8,8-(PPh}_3)_2\text{-nido-8,7-RhSB}_9\text{H}_{10}]^4$ or $[\text{8,8-}$

(PMe₂Ph)₂-*nido*-8,7-PtB₁₀H₁₂]²⁹ by treatment with the strong bases. Following this approach, the reaction of the rhodathiaborane, **3**, with the non-nucleophilic base N,N,N',N'-tetramethylnaphthalene-1,8-diamine, commonly known as Proton Sponge (PS), in dichloromethane afforded small amounts of the *bis*-PPh₃-ligated *closo*-parent cluster, **2**, and the salt [PSH]Cl. However, when the reaction was carried out in the presence of one equivalent of PPh₃, the reaction is quantitative. Similarly, the treatment of the CO-ligated cluster, **5**, with PS affords the CO-ligated *closo*-cluster, [1,1-(CO)(PPh₃)-3-(Py)-1,2-RhSB₉H₈] (**4**).

As summarized in Scheme 3, the reactions of **3** and **5** with PS permit two reaction cycles to be constructed. For both rhodathiaboranes, HCl leads to a *closo*-to-*nido* transformation of the clusters, whereas the PS induces the reverse *nido*-to-*closo* change and the consequent regeneration of **2** and **5**. The reactions are, therefore, connected by HCl addition and [PSH]Cl salt release. If we consider the cycles with species “in” balanced against species “out”, the net reactions are equations 2 and 3:

These two new stoichiometric cycles are, therefore, driven by simple Brønsted acid/base chemistry.

Conclusions

The PPh₃-ligated rhodathiaboranes, **1**, **2** and **4**, react readily with aqueous HCl to give new Cl-ligated clusters in high yields. Similarly, the PR₃-ligated analogues, **6-10**, react with hydrochloric acid to give Cl-ligated clusters. In contrast to the PPh₃-counterparts, these reactions are less selective, giving rise to the formation of mixtures that contain [8,8-(Cl)(PR₃)-9-(Py)-*nido*-8,7-RhSB₉H₉], where PR₃ = PMe₃ (**11**), PMe₂Ph (**12**) or PMePh₂ (**15**), and [8,8-(Cl)(PR₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉], where PR₃ = PMe₃ (**13**) or PMe₂Ph (**14**). For the {RhCl(PR₃)₂}-containing compounds, **13** and **14**, the reaction implies the addition of HCl to the 11-vertex *closo*-clusters and the transformation of the structure to *nido*. This structural opening is consistent with the thesis that the introduction of one electron pair into a *closo* cluster opens the cage to a *nido* framework. However, the formation of the mono-PR₃-ligated species, **3**, **11** and **12**, from the corresponding *closo*-compounds, takes place with the loss of a phosphine ligand to

give formally unsaturated 12 sep clusters with *nido*-structures, rather than the predicted *closo*-isomers. DFT-calculations demonstrate that the *nido*-structure is more stable than the *closo*, without the need to invoke intramolecular Rh^{III}CH agostic interactions.

The unsaturated nature of the mono-PR₃-ligated species, **3**, **11**, **12** and **15**, is further demonstrated by (i) experiments that show interaction between the PPh₃ derivative, **3**, and MeCN in solution, (ii) the formation of *bis*-PR₃-ligated species, **13** and **14**, and (iii) the reactions of **3** with carbon monoxide and pyridine that afford the corresponding Rh-CO and Rh-Py adducts, **5** and **20**.

Irrespective of the mechanism, the clusters can accommodate the Brønsted acid, HCl, demonstrating the bifunctional acid / base nature of these 11-vertex rhodathiaboranes. In addition, the use of a weak nucleophile and strong base such as PS, promotes the extrusion of HCl (as the [PSH]Cl salt) from the *nido*-clusters, and their consequent structural transformation to *closo*, closing stoichiometric cycles that are driven by acid / base chemistry (scheme 3). Sustainable chemical transformations are reliant on reversible processes, based on catalytic and stoichiometric cycles. The *closo*→*nido* interconversions of 11-vertex rhodathiaboranes via addition / elimination of HCl, are new examples of stoichiometric cycles that may find their way into some synthetic applications. We are exploring these and other aspects arising from the chemistry of these polyhedral clusters.

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 of Innovative Technology Inc. The 11-vertex rhodathiaboranes **1**, **2**, **4**, **6**, **7**, **8**, **9** and **10** were prepared according to the literature methods.¹ Proton Sponge was purchased from Aldrich and used as received. 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 × 20 cm and dried in air at 25 °C. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer, using a Universal ATR Sampling Accessory. NMR spectra were recorded on Bruker Avance 300-MHz and AV 400-MHz spectrometers, using ³¹P-{¹H}, ¹¹B, ¹¹B-{¹H},

^1H , $^1\text{H}\{-^{11}\text{B}\}$ and $^1\text{H}\{-^{11}\text{B}(\text{selective})\}$ techniques. Residual solvent protons were used as reference (δ , ppm, CDCl_3 , 7.26; CD_2Cl_2 , 5.33; CD_3CN , 1.96). ^{11}B chemical shifts are quoted relative to $[\text{BF}_3(\text{OEt})_2]$ and ^{31}P chemical shifts are quoted relative to 85% aqueous H_3PO_4 . 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 of purity for the Cl-ligated species **11**, **12**, **13**, **14** and **15** were clean multinuclear NMR spectra allied with mass spectrometric fragmentation patterns.

X-ray crystallography

The structures of **3** and **5** were reported in reference 2. Crystals of compounds **13** and **14** suitable for X-ray diffraction analysis were grown by slow diffusion of hexane into a concentrated solution of each rhodathiaborane in dichloromethane. X-ray diffraction data were collected at low temperature (100(2) K) on an automatic Bruker Kappa APEX DUO CCD area detector diffractometer equipped with graphite-monochromatic Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$) using narrow frames (0.3° in ω). In all cases, single crystals were mounted on a fiber and were covered with a protective perfluoropolyether. Intensities were integrated including Lorentz and polarization effect with SAINT-Plus program³⁰ and corrected for absorption using multi-scan methods applied with SADABS program.³¹ The structures were solved using the SHELXS-97 program.³² Refinements were carried out by full-matrix least-squares on F^2 with SHELXL-97,³³ including isotropic and subsequent anisotropic displacement parameters for all non-hydrogen atoms. Experimental diffraction parameters and crystal data are gathered in Table 3.

Calculations

All calculations were performed using the Gaussian 03 package.³⁴ 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 rhodium 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 ^{11}B shielding values were related to chemical shifts by comparison with the computed value for B_2H_6 , which was taken to be $\delta(^{11}\text{B}) + 16.6$ ppm relative to the $\text{BF}_3(\text{OEt}_2) = 0.0$ ppm standard.

DOSY experiments

The ^1H DOSY experiments were performed on a Bruker Avance 400 MHz spectrometer. During the DOSY experiments, the temperature was set to 300 K and maintained with an air flow of 400 L h^{-1} . The experiments were acquired with the pulse program, “stepppg1s”, in Bruker software with spinning of the sample to avoid convection influence. The diffusion time (D20) and gradient duration (P30) were optimized with the “stepppg1s” sequence by observation of progressive decay of the signal intensities of the acetonitrile peak in CD_2Cl_2 for each measurement until 1 to 5% of the residual signal with maximum strength (95%). The value of D20 employed in the ^1H DOSY experiments was set to 100 ms and the spoil gradient (P19) to 0.6 ms, while P30' s of 2.5 and 1.2 ms were optimized for a solution of **3** (20.1 mg, 0.033 mmol) in 0.4 mL of CD_2Cl_2 with 6.8 μL of CH_3CN ; and for free CH_3CN (in the same molar ratio as in the presence of **3**) in CD_2Cl_2 . The gradient strength was varied between 2% and 95% in 16 square spaced increments. $\text{AQ} = 5.4$ s, 8 scans, and a relaxation delay, D1, of 1 were used. The raw data were processed using the Bruker DOSY package and T_1/T_2 relaxation module. The fitting curves for free acetonitrile and acetonitrile in the presence of compound **3** are presented as supplementary material in Figure S13.

[8,8-(Cl)(PMe₃)-9-(Py)-nido-8,7-RhSB₉H₉] (11): A solution of [1,1-(PMe₃)₂-3-(Py)-*clos*o-1,2-RhSB₉H₈] (**9**) (35.4 mg, 0.075 mmol) in dichloromethane was treated with aqueous HCl (37 % wt). The reaction mixture was stirred for 30 min at room temperature under argon. Then, the solution was filtered through Celite using a cannula. The resulting orange filtrate was dried over MgSO_4 for two hours. After the removal of the magnesium sulfate, the solvent was evaporated and the resulting solid washed three times with hexane to give **11** (39.7 mg, 0.064 mmol, 87 %). IR (ATR): ν 2530 vs (BH). IR (ATR): ν 2530 vs (BH). ^{11}B NMR (96 MHz, CD_2Cl_2 , 300 K): δ +15.4 (2B, s, BH, B-py), +4.1 (2B, br, BH), +1.4

(1B, d, $^1J_{\text{BH}} = 131$ Hz, BH), -5.1 (1B, d, $^1J_{\text{BH}} = 141$ Hz, BH), -11.7 (1B, d, $^1J_{\text{BH}} = 135$ Hz, BH), -22.5 (1B, d, $^1J_{\text{BH}} = 144$ Hz, BH), -25.4 (1B, d, $^1J_{\text{BH}} = 116$ Hz, BH), -28.7 (1B, br, BH). ^1H - $\{^{11}\text{B}\}$ NMR (300 MHz, CDCl_3 , 300 K): δ +9.48 (2H, s, $H_o\text{-NC}_5\text{H}_5$), +8.20 (1H, m, $H_p\text{-NC}_5\text{H}_5$), +7.73 (2H, m, $H_m\text{-NC}_5\text{H}_5$), +4.18 (1H, s, BH), +3.41 (1H, s, BH), +3.24 (1H, s, BH), +2.74 (1H, s, BH), +2.64 (1H, s, BH), +1.41 (1H, s, BHB), +1.12 (3H, d, $^2J_{\text{HP}} = 10.9$ Hz, PMe_3) +0.80 (2H, s, BH). ^{31}P - $\{^1\text{H}\}$ NMR (121 MHz, CDCl_3 , 300 K): δ +7.8 (d, $^1J_{\text{RHP}} = 145$ Hz). Anal. Calcd. for $\text{C}_8\text{H}_{23}\text{B}_9\text{ClNPRhS}\cdot(\text{HCl})$: C, 20.51; H, 5.16; N, 2.99. Found: C, 19.95; H, 5.15; N, 2.69. LRMS (MALDI): m/z 396 [$\text{M}^+-(\text{Cl}+\text{H})$, isotope envelope. $\text{B}_9\text{C}_8\text{H}_{23}\text{NPRhS}$ requires 396; $\text{B}_9\text{C}_8\text{ClH}_{24}\text{NPRhS}$ requires 432], 472 [$\text{M}^++\text{PMe}_3-(\text{Cl}+\text{H})$, isotope envelope. $\text{B}_9\text{C}_{11}\text{H}_{31}\text{NPRhS}$ requires 472].

[8,8-(Cl)(PMe₂Ph)-9-(Py)-*nido*-8,7-RhSB₉H₉] (12): A solution of [1,1-(PMe₂Ph)₂-3-(Py)-*closo*-1,2-RhSB₉H₈] (**10**) (20 mg, 0.034 mmol) in dichloromethane was treated with aqueous HCl (37 % wt). The reaction mixture was stirred for 2 h at room temperature under argon. Then, the solution was filtered through Celite using a cannula. The resulting orange filtrate was dried over MgSO_4 for two hours. After the removal of the magnesium sulfate, the solvent was evaporated and the resulting solid washed three times with hexane to give **12** (11 mg, 0.021 mmol, 64 %). ^{11}B - $\{^1\text{H}\}$ NMR (128 MHz; CD_2Cl_2 ; 298K): δ +14.9 (2B, s, B-py, BH), +1.9 (2B, br, BH), -11.8 (1B, d, $^1J_{\text{BH}} = 124$ Hz, BH), -22.8 (1B, d, $^1J_{\text{BH}} = 157$ Hz, BH), -24.9 (1B, br, BH), -28.5 (1B, br, BH). ^1H - $\{^{11}\text{B}\}$ NMR (400 MHz; CD_2Cl_2 ; 298K): δ +8.86 (2H, s, $H_o\text{-NC}_5\text{H}_5$), +8.14 (1H, t, $^3J_{\text{HH}} = 7.6$ Hz, $H_p\text{-NC}_5\text{H}_5$), +7.55 (2H, t, $H_m\text{-NC}_5\text{H}_5$), +7.39 to 7.30 (5H, m, PMe_2Ph), +4.22 (1H, s, BH), +3.32 (1H, s, BH), +3.18 (1H, s, BH), +2.92 (1H, s, BH), +2.54 (1H, s, BH), +1.77 (1H, s, BHB), +1.67 (3H, br, PMe_2Ph), +1.58 (3H, d, $^2J_{\text{HP}} = 10.2$ Hz, PMe_2Ph), +1.22 (1H, s, BH), +0.74 (1H, s, BH). ^{31}P - $\{^1\text{H}\}$ NMR (161 MHz; CD_2Cl_2 ; 193 K): δ +15.7 ($^1J_{\text{RHP}} = 140$ Hz). LRMS (MALDI): m/z 458.2 [$\text{M}^+-(\text{Cl}+\text{H})$, isotope envelope. $\text{B}_9\text{C}_{13}\text{ClH}_{25}\text{NPRhS}$ requires 494], 596 [$\text{M}^++(\text{PMe}_2\text{Ph})-(\text{Cl}+\text{H})$, isotope envelope. $\text{B}_9\text{C}_{21}\text{H}_{35}\text{NP}_2\text{RhS}$ requires 596].

[8,8,8-(Cl)(PMe₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] (13): 5 mg of **9** (0.011 mmol) was dissolved in 0.3 mL of CDCl_3 in a 5 mm NMR tube, and then 0.2 mL of HCl (37 % wt) was added. The resulting red solution was examined by NMR spectroscopy at room temperature. The NMR data corresponded to **11**;

however, evaporation of the CDCl_3 solvent and washing (three times) with hexane, afforded an orange solid that showed the mono- PMe_3 -ligated cluster, **11**, together with the *bis*- PMe_3 -ligated derivative, [**13**] in a 1:1.3 relative intensity ratio, respectively. The $^{11}\text{B}\{-^1\text{H}\}$ NMR spectrum showed overlapping resonances that made difficult the assignment of the resonances among the two Cl-ligated clusters. Of these, the following may be individually assigned to **13**: IR (ATR): ν 2522 vs (BH), 1069 m 945 s. ^{11}B NMR (96 MHz, CD_2Cl_2 , 300 K): δ +12.9 (1B, s, B-Py), +11.7 (1B, br, BH), +5.8 (1B, d, $^1J_{\text{BH}} = 136$ Hz, BH), -1.1 (1B, d, $^1J_{\text{BH}} = 108$ Hz, BH), -2.1 (1B, d, $^1J_{\text{BH}} = 122$ Hz, BH), -15.3 (1B, d, $^1J_{\text{BH}} = 134$ Hz, BH), -21.6 (1B, d, $^1J_{\text{BH}} = 128$ Hz, BH), -24.4 (1B, d, $^1J_{\text{BH}} = 142$ Hz, BH), -30.1 (1B, d, $^1J_{\text{BH}} = 142$ Hz, BH). $^1\text{H}\{-^{11}\text{B}\}$ NMR (300 MHz, CD_2Cl_2 , 300 K): δ +9.48 (2H, s, $H_o\text{-NC}_5\text{H}_5$), +8.20 (1H, m, $H_p\text{-NC}_5\text{H}_5$), +7.73 (2H, m, $H_m\text{-NC}_5\text{H}_5$), +3.90 (1H, s, BH), +3.55 (1H, s, BH), +3.08 (1H, s, BH), +3.02 (1H, s, BH), +2.20 (1H, s, BH), 1.66 (1H, s, BHB), +1.40 (3H, d, $^2J_{\text{HP}} = 8.4$ Hz, PMe_3) +0.96 (2H, s, BH), +0.96 (3H, d, $^2J_{\text{HP}} = 11.8$ Hz, PMe_3). $^{31}\text{P}\{-^1\text{H}\}$ RMN (161MHz, CD_2Cl_2 , 183 K): δ -2.2 (1P, dd, $^1J_{\text{RHP}} = 131$ Hz, $^2J_{\text{PP}} = 28$ Hz, PMe_3), -24.2 (1P, br. d, $^1J_{\text{RHP}} \approx 86$ Hz, PMe_3). LRMS: m/z (MALDI) 473 [$\text{M}^+\text{-Cl}$ isotope envelope $\text{B}_9\text{C}_9\text{H}_{32}\text{NP}_2\text{RhS}$; $\text{B}_9\text{C}_9\text{ClH}_{32}\text{NP}_2\text{RhS}$ requires 508].

[8,8-(Cl)(PMe₂Ph)₂-9-(Py)-nido-8,7-RhSB₉H₉] (14): 8 mg of **10** (0.012 mmol) was dissolved in 0.3 mL of CDCl_3 in a 5 mm NMR tube, and then 0.2 mL of HCl (37 % wt) was added. The resulting red solution was examined by NMR spectroscopy at room temperature. The NMR data corresponded to the above-characterized chloro-ligated derivative **12**; however, evaporation of the CDCl_3 solvent and washing (three times) with hexane, afforded an orange solid that showed the mono- PMe_2Ph -ligated cluster, **12**, and the *bis*- PMe_2Ph -ligated derivative, [8,8-(Cl)(PMe₂Ph)₂-9-(Py)-nido-8,7-RhSB₉H₉] (**14**), in a 0.3:1 relative intensity ratio, respectively. The $^{11}\text{B}\{-^1\text{H}\}$ NMR spectrum showed overlapping resonances that made difficult the assignment of the resonances among the two Cl-ligated clusters. Of these, the following may be individually assigned to **14**: $^{11}\text{B}\{-^1\text{H}\}$ NMR (96 MHz, CD_2Cl_2 , 300 K): δ +12.4 (1B, s, B-Py), +8.3 (1B, br, BH), +2.7 (1B, d, $^1J_{\text{BH}} = 117$ Hz, BH), -3.0 (1B, d, $^1J_{\text{BH}} = 119$ Hz, BH), -11.5 (1B, d, $^1J_{\text{BH}} = 137$ Hz, BH), -13.3 (1B, br, BH), -18.1 (1B, d, $^1J_{\text{BH}} = 139$ Hz, BH), -22.0 (1B, d, $^1J_{\text{BH}} = 148$ Hz, BH), -29.5 (1B, br, BH). $^1\text{H}\{-^{11}\text{B}\}$ NMR (300 MHz; CD_2Cl_2 ; 298K): (300 MHz,

CD₂Cl₂, 300 K): δ +9.48 (2H, s, *H_o*-NC₅H₅), +8.06 (1H, m, *H_p*-NC₅H₅), +7.74 (2H, m, *H_m*-NC₅H₅), +7.51 to 7.05 (10H, m, PMe₂Ph), +3.92 (1H, s, BH), +3.70 (1H, s, BH), +2.90 (1H, s, BH), +2.72 (1H, s, BH), +1.94 (1H, s, BH), +1.65 (3H, d, ²J_{HP} = 8.9 Hz, PMe₂Ph) +1.58 (1H, s, BHB), +1.44 (3H, d, ²J_{HP} = 8.2 Hz, PMe₂Ph), +1.00 (1H, s, BH), +0.92 (3H, d, ²J_{HP} = 10.6 Hz, PMe₂Ph), +0.65 (3H, d, ²J_{HP} = 9.3 Hz, PMe₂Ph), +0.28 (1H, s, BH). ³¹P-{¹H} NMR (161MHz, CD₂Cl₂, 183 K): δ +8.4 (1P, d, ¹J_{RhP} = 140 Hz, ²J_{PP} = 26 Hz), -17.3 (1P, d, ¹J_{RhP} = 78 Hz). LRMS: *m/z* (MALDI) 596 [M⁺-(Cl+H), isotope envelope. B₉C₂₁H₃₅NP₂RhS requires 596; B₉C₂₁ClH₃₆NP₂RhS requires 632].

[8,8-(Cl)(PMePh₂)-9-(Py)-*nido*-8,7-RhSB₉H₉] (15): A solution of [8,8,8-H(PMePh₂)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] (6) (30 mg, 0.041 mmol) in dichloromethane was treated with aqueous HCl (37 % wt). The reaction mixture was stirred for 2 h at room temperature under argon. Then, the solution was filtered through Celite using a cannula. The resulting orange filtrate was dried over MgSO₄ for two hours. After the removal of the magnesium sulfate, the solvent was evaporated and the resulting solid washed three times with hexane to give **15** (12.2 mg, 0.022 mmol, 53 %). IR (ATR): ν 2524 vs (BH), 1259 m, 1017 m, 797 s, 691 s. ¹¹B-{¹H} NMR (96 MHz; CD₂Cl₂; 298K): δ +15.2 (2B, s, BH, B-py), +2.6 (2B, d, ¹J_{BH} = 140 Hz, BH), -4.1 (1B, d, ¹J_{BH} = 120 Hz, BH), -12.2 (1B, d, ¹J_{BH} = 148 Hz, BH), -22.3 (1B, d, ¹J_{BH} = 151 Hz, BH), -23.9 (1B, d, ¹J_{BH} = 140 Hz, BH), -29.2 (1B, br, BH). ¹H-{¹¹B} NMR (300 MHz; CD₂Cl₂; 298K): δ +8.59 (2H, m, *H_o*-NC₅H₅), +7.94 (1H, m, *H_p*-NC₅H₅), +7.60 (2H, m, *H_m*-NC₅H₅), +7.54 to 6.95 (10H, m, PMePh₂), +4.71 (1H, s, BH), +4.33 (1H, s, BH), +3.45 (1H, s, BH), +3.03 (1H, s, BH), +1.81 (1H, s, BH), +1.79 (3H, d, ²J_{HP} = 10.2 Hz, PMePh₂), +1.13 (1H, s, BHB). ³¹P-{¹H} NMR (161 MHz; CD₂Cl₂; 300 K): δ +18.1 (1P, d, ¹J_{RhP} = 149 Hz). Anal. Calcd. for C₁₈H₂₇B₉ClNP₂Rh: C, 38.88; H, 4.89; N, 2.52. Found: C, 38.95; H, 4.25; N, 1.57. LRMS (MALDI): *m/z* 554 [M-(H), isotope envelope. B₉C₁₈ClPH₂₆NRhS requires 554; B₉C₂₁ClH₂₇NP₂RhS requires 556], 520 [M-(Cl+H), isotope envelope. B₉C₁₈PH₂₆NRhS requires 520; B₉C₂₁ClH₂₇NP₂RhS requires 556]. HRMS (MALDI): *m/z* calc. for B₉C₁₈ClPH₂₆NRhS 554.1075, found 554.1051. HRMS (MALDI): *m/z* calc. for B₉C₁₈PH₂₆NRhS 521.1415, found 521.1432.

[8,8,8-(Cl)(Py)(PPh₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] (20): 14.3 mg of **3** (0.023 mmol) was dissolved in 10 mL of CH₂Cl₂ in a Schlenk tube, and then 7.48 μ L (7.32 mg, 0.093 mmol) of pyridine was added to the orange solution in dichloromethane (10 mL). The solvent was evaporated and the resulting solid washed three times with hexane to give [8,8,8-(Cl)(PPh₃)(Py)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**20**) (9.8 mg, 0.014 mmol, 61 %). ¹¹B NMR (128 MHz, CDCl₃, 300 K): δ +11.6 (2B, br, BH, B-Py), +8.1 (1B, br, BH), -0.3 (1B, br, BH), -1.8 (1B, br, BH), -14.8 (1B, d, ¹J_{BH} = 142 Hz, BH), -16.9 (1B, d, ¹J_{BH} = 125 Hz, BH), -22.3 (1B, d, d, ¹J_{BH} = 125 Hz, BH), -29.5 (1B, br, BH). ¹H-¹¹B NMR (400 MHz, CDCl₃, 300 K): δ +8.82 (2H, d, ³J_{HH} = 8.8 Hz, *H_o*-NC₅H₅-B), +8.71 (2H, br, *H_o*-NC₅H₅-Rh), 7.97 (1H, br, *H_p*-NC₅H₅-Rh), +7.83 (1H, t, ³J_{HH} = 7.7 Hz, *H_p*-NC₅H₅-B), +7.58 (2H, t, ³J_{HH} = 7.7 Hz, *H_m*-NC₅H₅-B), +7.50-7.06 (15H, m, PPh₃), +3.94 (1H, s, BH), +3.81 (1H, s, BH), +3.76 (1H, s, BH), +3.00 (1H, s, BH), +2.89 (1H, s, BH), +2.06 (1H, s, BH), +1.86 (1H, s, BH), +1.75 (1H, s, BHB). ³¹P-¹H NMR (161 MHz, CDCl₃, 300 K): δ +30.5 (d, ¹J_{RhP} = 146 Hz).

Reaction of [1,1-(PPh₃)(PMe₃)-3-(Py)-*closo*-1,2-RhSB₉H₉] (8) with HCl: 5 mg, 0.0076 mmol) of **8** was dissolved in 0.3 mL of CD₂Cl₂ in a 5 mm NMR tube, and was treated with aqueous HCl (37 % wt). The resulting solution was examined by NMR spectroscopy at room temperature. The NMR data revealed the formation of the Cl-ligated mono-phosphine rhodathiaboranes, [8,8-(Cl)(PPh₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**3**) and [8,8-(Cl)(PMe₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**11**) in a 1:2 ratio, respectively.

[8,8,8-(H)(PMe₃)(PPh₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] (7) with HCl: A solution of **7** (13.7 mg, 0.021 mmol) in dichloromethane was treated with aqueous HCl (37 % wt). The reaction mixture was stirred for 2 h at room temperature under argon. Then, the solution was filtered through Celite using a cannula. The resulting orange filtrate was dried over MgSO₄ for two hours. After the removal of the magnesium sulfate, the solvent was evaporated and the resulting solid washed three times with hexane. NMR spectroscopy showed that the solid was mainly compound **3**, together with small amounts of unidentified species.

Study of the Interaction of 3 with MeCN: A 5.5 mg of **3** (0.0089 mmol) was dissolved in 0.3 mL of CDCl₃ in a 5 mm NMR tube, and then 4 μ L of CH₃CN (0.076 mmol) was added to the orange solution.

The resulting solution was examined by NMR spectroscopy at room temperature. ^{11}B NMR (96 MHz, CDCl_3 , 300 K): δ +14.9 (2B, broad, BH, B-Py), +4.9 (1B, d, $^1J_{\text{BH}} = 132$ Hz, BH), +2.5 (1B, broad, BH), -2.1 (1B, d, $^1J_{\text{BH}} = 107$ Hz, BH), -13.5 (1B, d, $^1J_{\text{BH}} = 137$ Hz, BH), -21.3 (1B, d, $^1J_{\text{BH}} = 130$ Hz, BH), -29.2 (1B, broad, BH). $^1\text{H}\{-^{11}\text{B}\}$ NMR (300 MHz, CDCl_3 , 300 K): δ +8.83 (1H, m, $H_o\text{-NC}_5\text{H}_5$), +7.91 (1H, m, $H_p\text{ NC}_5\text{H}_5$), +7.42 (2H, m, $H_m\text{ NC}_5\text{H}_5$), +7.39-7.28 (15H, m, PPh_3), +4.58 (1H, s, BH), +3.55 (1H, s, BH), +3.23 (1H, s, BH), +2.96 (1H, s, BH), +2.71 (1H, s, BH), +1.96 (1H, s, BH), +1.71 (1H, s, BHB), +1.23 (1H, s, BH), +1.04 (1H, s, BH). $^{31}\text{P}\{-^1\text{H}\}$ NMR (121MHz, CDCl_3 , 300 K): δ +32.1 (1P, d, $^1J_{\text{RHP}} = 149$ Hz).

Figures S10 to S12 illustrate the variation of the $^{11}\text{B}\{-^1\text{H}\}$, $^1\text{H}\{-^{11}\text{B}\}$ and $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of **3** in CDCl_3 in the presence of different amounts of free acetonitrile, and in neat CD_3CN . The NMR data in CD_3CN is as follow: ^{11}B NMR (160 MHz, 300 K): δ +14.9 (minor, 1B, s, B-py), +12.1 (1B, s, B-py), +7.6 (1B, d, $^1J_{\text{BH}} = 135.3$ Hz, BH), +4.9 (minor, 1B, d, $^1J_{\text{BH}} = 119.2$ Hz, BH), +0.1 (1B, d, $^1J_{\text{BH}} = 132.9$ Hz, BH), -2.6 (1B, d, $^1J_{\text{BH}} = 126.0$ Hz, BH), -16.6 (1B, d, $^1J_{\text{BH}} = 139.9$ Hz, BH), -18.6 (1B, d, $^1J_{\text{BH}} = 112.6$ Hz, BH), -22.0 (1B, d, $^1J_{\text{BH}} = 134.6$ Hz, BH), -22.9 (1B, d, $^1J_{\text{BH}} = 141.0$ Hz, BH), -29.9 (1B, d, $^1J_{\text{BH}} = 106.9$ Hz, BH). $^1\text{H}\{-^{11}\text{B}\}$ NMR (500 MHz, 300 K): δ +8.95 (2H, m, $H_o\text{ NC}_5\text{H}_5$), +8.25 (1H, m, $H_p\text{ NC}_5\text{H}_5$), +7.90 (2H, m, $H_m\text{ NC}_5\text{H}_5$), +7.53-7.18 (15H, m, PPh_3), +4.20 (1H, s, BH), +3.84 (minor, 1H, s, BH), +3.61 (1H, s, BH), +3.49 (1H, s, BH), +2.94 (1H, s, BH), +1.80 (1H, s, BH), +1.15 (1H, s, BH), +1.02 (1H, s, BH), +0.60 (1H, s, BH). $^{31}\text{P}\{-^1\text{H}\}$ NMR (202 MHz, 300 K): δ +32.4 (d, $^1J_{\text{RHP}} = 142.9$ Hz, PPh_3), +15.54 (minor, 1P, s, PPh_3), ratio 1:0.23.

Reaction of [8,8-(Cl)(PPh₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] (3) with Proton Sponge (PS): 7.1 mg of **3** (0.012 mmol) was dissolved in 0.3 mL of CD_2Cl_2 in a 5 mm NMR tube together with stoichiometric amounts of free PPh_3 ; then 2.50 mg of Proton Sponge (0.012 mmol) was added to the orange solution. The resulting reaction mixture was examined by NMR spectroscopy at room temperature. The NMR data demonstrated the quantitative formation of the parent *closo*-compound, [1,1-(PPh₃)₂-3-(Py)-*closo*-1,2-RhSB₉H₈] (**2**), together with the [PSH]Cl salt. $^1\text{H}\{-^{11}\text{B}\}$ NMR data for [PSH]Cl (400 MHz; CD_2Cl_2 ;

298K): δ 18.68 (1H, s, $H^+N_2C_{14}H_{18}$), 7.94 (2H, m, $Ho-H^+N_2C_{14}H_{18}$), 7.75 (2H, m, $Hp-H^+N_2C_{14}H_{18}$), 7.65 (1H, m, $Hm-H^+N_2C_{14}H_{18}$), 3.23 (12H, s, $CH_3-H^+N_2C_{14}H_{18}$).

Reaction of [8,8,8-(Cl)(CO(PPh₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] (5) with Proton Sponge (PS): An NMR tube was charged with 6.3 mg (0.01 mmol) of **5**, which was dissolved in 0.3 mL of CD₂Cl₂. Then, 2.5 mg (0.012 mmol) of PS was added to the solution under an argon atmosphere. The reaction was shaken 5 minutes at room temperature, and studied by NMR. The spectroscopic demonstrated the quantitative formation of the parent *closo*-compound, [1,1-(CO)(PPh₃)-3-(Py)-*closo*-1,2-RhSB₉H₈] (**4**), together with the [PSH]Cl salt.

ACKNOWLEDGMENTS. We acknowledge the Spanish Ministry of Science and Innovation (CTQ2009-10132, CONSOLIDER INGENIO, CSD2009-00050, MULTICAT and CSD2006-0015, Crystallization Factory) for support of this work. B.C. thanks the “Diputación General de Aragón” for a pre-doctoral scholarship.

Table 2. Selected interatomic distances (Å) for [8,8,8-(H)(PPh₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] **1**, [8,8-(Cl)(PPh₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] **3**, [8,8,8-(Cl)(CO)(PPh₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] **5**, [8,8,8-(Cl)(PMe₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] **13**, [8,8,8-(Cl)(PMe₂Ph)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] **14** and [8,8-(PPh₃)₂-*nido*-8,7-RhSB₉H₁₀] **16**.

	1	3	5	13	14	16
Rh(8)–S(7)	2.431(2)	2.361(2)	2.4060(16)	2.3654(7)	2.3574(7)	2.3769(12)
Rh(8)–P(1)	2.354(2)	2.294(2)	2.4091(7)	2.2830(6)	2.2990(7)	2.2906(11)
Rh(8)–P(2)	2.341(2)	–	–	2.3635(7)	2.3868(7)	2.4198(11)
Rh(8)–H(1)	1.54(6)	–	–	–	–	–
Rh(8)–Cl(1)	–	2.354(2)	2.4295(9)	2.5196(6)	2.5116(8)	–
Rh(8)–B(9)	2.220(9)	2.099(8)	2.211(2)	2.166(2)	2.179(3)	2.145(4)
Rh(8)–B(3)	2.201(11)	2.202(10)	2.206(18)	2.270(9)	2.230(3)	2.243(4)
Rh(8)–B(4)	2.217(10)	2.198(9)	2.223(4)	2.211(2)	2.218(3)	2.236(4)
Rh(8)–C(1)	–	–	1.833(3)	–	–	–
C(1)–O(1)	–	–	1.130(5)	–	–	–
B(9)–N(1)	1.547(11)	1.548(12)	1.546(3)	1.566(2)	1.566(4)	–
S(7)–B(2)	1.980(9)	1.975(10)	1.970(3)	1.995(2)	1.985(3)	1.986(5)
S(7)–B(3)	2.059(11)	2.056(9)	2.07(2)	2.073(9)	2.102(3)	2.035(4)
S(7)–B(11)	1.953(9)	1.909(6)	1.899(10)	1.914(2)	1.914(3)	1.908(5)
B(2)–B(3)	1.906(14)	1.886(14)	1.964(19)	1.893(9)	1.925(5)	1.886(6)
B(3)–B(4)	1.772(15)	1.799(13)	1.788(17)	1.798(9)	1.800(5)	1.766(5)
B(2)–B(6)	1.745(14)	1.776(14)	1.756(4)	1.746(3)	1.758(5)	1.744(7)
B(4)–B(9)	1.819(16)	1.791(13)	1.807(5)	1.809(3)	1.786(4)	1.785(5)
B(9)–B(10)	1.856(13)	1.847(14)	1.825(4)	1.880(3)	1.898(4)	1.864(6)
B(10)–B(11)	1.784(14)	1.894(14)	1.817(4)	1.805(3)	1.808(5)	1.863(7)
P(1)–Rh(8)–C(1)	–	–	86.63(11)	–	–	–
P(1)–Rh(8)–P(2)	100.27(7)	–	–	95.96(2)	101.88(3)	98.50(3)
P(1)–Rh(8)–H(1)	71(2)	–	–	–	–	–
P(2)–Rh(8)–H(1)	98(2)	–	–	–	–	–
P(1)–Rh(8)–Cl(1)	–	90.62(7)	92.08(2)	82.91(2)	83.08(2)	–
P(2)–Rh(8)–Cl(1)	–	–	–	91.13(2)	84.29(2)	–
P(1)–Rh(8)–S(7)	96.38(7)	163.83(7)	93.95(4)	163.30(2)	160.88(3)	170.05(4)
P(2)–Rh(8)–S(7)	102.05(8)	–	–	94.98(2)	91.85(2)	85.88(3)
P(1)–Rh(8)–B(4)	114.3(3)	92.9(2)	128.67(9)	89.62(6)	85.74(8)	89.46(10)
P(1)–Rh(8)–B(9)	162.4(3)	102.0(3)	175.97(6)	102.04(5)	100.96(8)	93.08(10)
S(7)–Rh(8)–Cl(1)	–	87.4(4)	86.73(7)	84.31(2)	85.15(2)	–
Cl(1)–Rh(8)–B(4)	–	176.1(2)	139.16(9)	122.44(6)	123.71(9)	–
Cl(1)–Rh(8)–B(9)	–	128.2(3)	91.30(7)	169.26(5)	169.69(8)	–
B(9)–Rh(8)–S(7)	87.1(3)	92.1(3)	88.37(7)	84.91(5)	88.36(8)	92.30(11)
Cl(1)–Rh(8)–C(1)	–	–	105.48(11)	–	–	–
Rh(8)–B(9)–N(1)	120.6(5)	120.60(6)	117.22(15)	126.17(12)	126.7(2)	–

Table 3 Crystallographic Data and Structure Refinement Information for **13** and **14**.

Compound	13	14
Chemical formula	C ₁₄ H ₃₈ B ₉ ClNOP ₂ RhS	C ₂₂ H ₃₈ B ₉ Cl ₃ NP ₂ RhS
Formula Mass	566.11	717.08
Crystal system	Monoclinic	Orthorhombic
<i>a</i> /Å	24.184(5)	14.6864(11)
<i>b</i> /Å	15.085(3)	16.7403(13)
<i>c</i> /Å	14.588(3)	26.010(2)
α /°	90.00	90.00
β /°	93.002(3)	90.00
γ /°	90.00	90.00
Unit cell volume/Å ³	5314.8(18)	6394.8(8)
Temperature/K	100(2)	100(2)
Space group	<i>C2/c</i>	<i>Pbca</i>
No. of formula units per unit cell, <i>Z</i>	8	8
Radiation type	MoK α	MoK α
Absorption coefficient, μ /mm ⁻¹	0.951	0.967
No. of reflections measured	28762	83840
No. of independent reflections	6964	6284
<i>R</i> _{int}	0.0220	0.0788
Final <i>R</i> _I values (<i>I</i> > 2 σ (<i>I</i>))	0.0258	0.0304
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2 σ (<i>I</i>))	0.0677	0.0672
Final <i>R</i> _I values (all data)	0.0276	0.0531
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.0685	0.0725
Goodness of fit on <i>F</i> ²	1.130	1.028

SUPPORTING INFORMATION PARAGRAPH. DFT-calculated NMR data; spectra of **3** in the presence of CH₃CN; DOSY experiments; and cif files for **13** and **14**.

FIGURE CAPTIONS

Fig. 1 ORTEP representation of the structure of **3** and **14**; only the ipso-carbon atoms of the Ph rings are showed for clarity. Selected distances [Å] and angles [°]:

Figure 2 Drawings of compounds **3**, **5** and **2**, respectively, illustrating the angle θ between the {Rh(8)S(7)B(9)} and {S(7)B(2)B(5)B(9)}, which is zero for the 11-vertex octadecahedral *closo*-structure of **2**, and 50° for the *nido*-cages of **3** and **5**. For an 11-vertex fragment of a regular icosahedron it would be 62°.

Figure 3 Diagrams representing the chemical shifts in the ¹¹B NMR spectra. Hatched lines connect equivalent positions. Assignments were made based on ¹H-¹¹B(sel)} experiments and DFT-calculations on the PH₃ model, [8,8-(Cl)(PH₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**3a**).

Figure 4 DFT-calculated energies and structures, computed at the B3LYP/6-31G*/LANL2DZ level for the PH₃ model [8,8-(Cl)(PH₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**3a**) and two rhodium-hydride ligated isomers, [1,1-(Cl)(H)(PH₃)-3-(Py)-*isonido*-8,7-RhSB₉H₈] (**3b** and **3c**).

Figure 5 Diagrams representing the chemical shifts in the ¹¹B NMR spectra. Hatched lines connect equivalent positions.

TABLE CAPTIONS

Table 1 Angles Φ and θ for 11-vertex metallaheteroboranes

Table 2. Selected interatomic distances (Å) for [8,8,8-(H)(PPh₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] **1**, [8,8-(Cl)(PPh₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] **3**, [8,8,8-(Cl)(CO)(PPh₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] **5** [8,8,8-(Cl)(PMe₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] **13**, [8,8,8-(Cl)(PMe₂Ph)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] **14** and [8,8-(PPh₃)₂-*nido*-8,7-RhSB₉H₁₀] **16**.

Table 3 Crystallographic Data and Structure Refinement Information for **3**, **5**, **13** and **14**.

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