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### Introduction

Polyhedral boron-containing compounds exhibit unique electronic properties, geometries, and extraordinary versatility that are of interest for a variety of applications, including medicine, health and nutrition, boron neutron capture therapy, optoelectronics, energy storage and nanomaterial.<sup>1,2</sup> This is best illustrated by the icosahedral carboranes, which have been intensively studied over the years, mainly due to their commercial availability.

Carboranes are boron-based clusters with triangular facets that incorporate carbon atoms into their structures, being, by far, the most ubiquitous members of polyhedral heteroboranes: cages that incorporate elements of the p-block of the periodic table.

## Unusual cationic rhodathiaboranes: synthesis and characterization of [8,8,8-(H)(PR<sub>3</sub>)<sub>2</sub>-9-(Py)-*nido*-8,7-RhSB<sub>9</sub>H<sub>10</sub>]<sup>+</sup> and [1,3-µ-(H)-1,1-(PR<sub>3</sub>)<sub>2</sub>-3-(Py)*isonido*-1,2-RhSB<sub>9</sub>H<sub>8</sub>]<sup>+</sup>†

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The treatment of the hydridorhodathiaboranes,  $[8,8,8-(H)(PR_3)_2-9-(Py)-nido-8,7-RhSB_9H_9]$ , where PR<sub>3</sub> = PPh<sub>3</sub> (**2**), PMePh<sub>2</sub> (**3**), PPh<sub>3</sub> and PMe<sub>2</sub>Ph (**4**), or PMe<sub>3</sub> and PPh<sub>3</sub> (**5**), and  $[8,8,8-(H)(PMePh_2)_2-9-(PMePh_2)-nido-8,7-RhSB_9H_9]$  (**6**), with TfOH affords  $[8,8,8-(H)(PR_3)_2-9-(Py)-nido-8,7-RhSB_9H_{10}]^+$  cations, where PR<sub>3</sub> = PPh<sub>3</sub> (**12**), PMePh<sub>2</sub> (**13**), PPh<sub>3</sub> and PMe<sub>2</sub>Ph (**14**), or PMe<sub>3</sub> and PPh<sub>3</sub> (**15**), and  $[8,8,8-(H)(PMePh_2)_2-9-(PMePh_2)-nido-8,7-RhSB_9H_{10}]^+$  (**16**). Compounds **13** and **14** lose H<sub>2</sub> to give  $[1,3-\mu-(H)-1,1-(PR_3)_2-3-(Py)-isonido-1,2-RhSB_9H_8]^+$ , where PR<sub>3</sub> = PMe<sub>2</sub>Ph (**18**), PPh<sub>3</sub> and PMe<sub>2</sub>Ph (**21**), or PMePh<sub>2</sub> (**22**). Similarly, the 11-vertex rhodathiaboranes,  $[1,1-(PR_3)_2-3-(Py)-1,2-RhSB_9H_8]$ , where PR<sub>3</sub> = PPh<sub>3</sub> (**7**), PMe<sub>2</sub>Ph (**8**), PMe<sub>3</sub> (**9**), or PPh<sub>3</sub> and PMe<sub>3</sub> (**10**), react with TfOH to give the corresponding cations,  $[1,3-\mu-(H)-1,1-(PR_3)_2-3-(Py)-isonido-1,2-RhSB_9H_8]^+$ , where PR<sub>3</sub> = PPh<sub>3</sub> (**17**), PMe<sub>2</sub>Ph (**18**), PMe<sub>3</sub> (**19**), or PPh<sub>3</sub> and PMe<sub>3</sub> (**20**). Four conformers of **20** are studied by X-ray diffraction methods and DFT-calculations, identifying packing motifs that stabilize different metal-thiaborane linkages, and energy variations that are involved in these conformational changes. It is demonstrated that the proton induces nonrigidity on these clusters as well as an enhancement of their Lewis acidity.

The deltahedral structures of polyhedral boron clusters are supported by a highly delocalized three-dimensional bonding that leads to cluster aromaticity.<sup>3,4</sup> The resulting three-dimensional geometries of these molecules provide precise directional control at their vertices, which can be functionalized with a vast variety of organic substituents. In addition, heteroboranes can accommodate in their structures metal elements from almost all of the periodic table, leading to the synthesis of a huge number of metallaheteroboranes, in which, many times, the heteroborane fragment can be regarded as a subrogate of well-known organic ligands.<sup>5-14</sup>

Bearing in mind that tunable ligands for transition metals constitute a broad field that centers on the idea that one can engender novel reactivity, the flexibility of heteroboranes as face-bound ligands affords interesting possibilities for the design of new systems with potential in the activation of unreactive bonds and ultimately in catalysis.<sup>2,15</sup> In addition, heteroboranes can act as substituents changing the steric and/ or electronic properties of classical ligands.<sup>16–20</sup>

It is clear, therefore, that heteroboranes have a huge potential for creating catalysts tailored to specific needs. In this regard, the use of carboranes as ligands of transition metal complexes has been extensively explored with very interesting results.<sup>2,16,21–23</sup> Of special interest to our work is the intensely

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studied hydridorhodathiaborane,  $[3,3,3-(H)(PPh_3)_2-3,1,2-RhC_2B_9H_{11}]$ ,<sup>24</sup> which undergoes rapid and reversible *closo-nido* tautomerism that is the key to its catalytic activity in, for example, the hydrogenation and isomerization of olefins. This illustrates an interesting dichotomy when dealing with polyhedral boron-containing compounds: clusters such as icosa-hedral carboranes and boranes are among the most thermo-dynamically stable molecules known, but the incorporation of a transition metal centre in the cage can lead to non-rigid systems that can generate interesting chemistry.<sup>25,26</sup>

Although the possibility of utilizing the structural flexibility of metallaboranes in catalytic reactions has been investigated,<sup>24,27</sup> polyhedral boron-containing compounds show a marked lack of examples in which the stereochemical nonrigidity of the cluster leads to bond activation and ultimately to catalysis, the most studied system being the commented hydridorhodathiaborane reported by Hawthorne and coworkers.<sup>24,28,29</sup> Therefore, an interesting goal in metallaheteroborane chemistry is to develop systems that combine the oxidative and coordinative flexibility of transition metal centres with the capability of boron clusters to exhibit oxidative/reductive flexibility in their classical *closo-nido-arachno* structural transformation.

In our recent work dealing with the reaction chemistry of the unsaturated 11-vertex rhodathiaborane,  $[8,8,8-(PPh_3)_2-nido-8,7-RhSB_9H_{10}]$  (1), we have demonstrated that the *nido-closo* structural and redox flexibility of pyridine-bound rhodathiaboranes,  $[8,8,8-(H)(PPh_3)_2-9-(Py)-nido-8,7-RhSB_9H_9]$  (2) and  $[1,1-(PPh_3)_2-3-(Py)-isonido-1,2-RhSB_9H_8]$ , is the key in the heterolytic H–H bond splitting and subsequent catalytic hydrogenation of olefins, as well as in the oxidative addition of sp-C–H bonds to the clusters.<sup>30-32</sup>

In an attempt to modify the reactivity of these clusters, we have already carried out substitution of the *exo*-polyhedral PPh<sub>3</sub> ligands in **1** and **2** with the more basic (less bulky) monodentate phosphines, PMe<sub>3</sub>, PMe<sub>2</sub>Ph and PPh<sub>2</sub>Me. This substitutional chemistry has provided a series of new hydridorhodathiaboranes of the general formulation, [8,8,8-(H)(PR<sub>3</sub>)<sub>2</sub>-9-(Py)-*nido*-8,7-RhSB<sub>9</sub>H<sub>9</sub>], where PR<sub>3</sub> = PPh<sub>3</sub> (2),<sup>31</sup> PMePh<sub>2</sub> (3),<sup>33</sup> PPh<sub>3</sub> and PMe<sub>2</sub>Ph (4),<sup>33</sup> or PPh<sub>3</sub> and PMe<sub>3</sub> (5).<sup>33</sup> The PMePh<sub>2</sub>-substituted analogue, [8,8,8-(H)(PMePh<sub>2</sub>)<sub>2</sub>-9-(PMePh<sub>2</sub>)-*nido*-8,7-RhSB<sub>9</sub>H<sub>9</sub>] (6),<sup>34</sup> is available from the reaction of **1** with PMePh<sub>2</sub>.<sup>34</sup> The thermal dehydrogenation of **2**–5 affords *isonido*-derivatives, [1,1-(L)<sub>2</sub>-3-(Py)-1,2-RhSB<sub>9</sub>H<sub>8</sub>], where  $L = PPh_3$  (7),  $PMe_2Ph$  (8),  $PMe_3$  (9),  $PPh_3$  and  $PMe_3$  (10), or  $PPh_3$  and  $PMe_2Ph$  (11).

As yields are generally good, these 11 vertex *nido*- and *isonido*-rhodathiaboranes constitute subjects for further reaction chemistry. Most recently, treatment of **2**, **7**, **9** and **10** with Brønsted acids has been found to yield polyhedral cations that exhibit remarkable reactivity, including a significant case of proton-assisted hydrogen activation *via* metal-thiaborane cooperation by *closo-nido* cluster transformations (Scheme 1).<sup>35,36</sup>

It is interesting to note that although protonation of transition metal complexes is fundamental chemistry that induces an enhancement of the Lewis acidity of the metal centres,<sup>37–39</sup> and it is relevant to many catalytic processes, to our knowledge, there are few examples of cationic metallaheteroboranes formed upon treatment with Brønsted acids.<sup>40</sup> In fact, the large majority of cationic metallaheteroboranes are based on charge-compensated heteroborane fragments, which act as face-bound ligands and which are somewhat different in nature from the polyhedral cations we describe in the present work.<sup>41–46</sup>

Herein, we build upon protonation reactions of the abovepresented series of 11-vertex rhodathiaboranes, reporting a unique set of polyhedral cations that represent some of the few examples of cationic boron-based clusters of any type.

Given the unique properties of polyhedral boron-containing compounds, commented in the Introduction, and our recent discovery that protonation of rhodathiaboranes leads to an enhancement of non-rigidity in the metal-thiaborane linkage,<sup>35</sup> this series of cationic rhodathiaboranes represents a potentially rich source of polyhedral Lewis acids that can lead to new opportunities for bond activation *via* cooperation between the metal and the thiaborane cage ligand.

### **Results and discussion**

The treatment of 2–6 with triflic acid (TfOH) leads to protonation of the *nido*-cage to give the corresponding polyhedral cations,  $[8,8,8-(H)(PR_3)_2-9-(Py)-nido-8,7-RhSB_9H_{10}]^+$ , where PR<sub>3</sub> = PPh<sub>3</sub> (12),<sup>36</sup> PMePh<sub>2</sub> (13), PPh<sub>3</sub> and PMe<sub>2</sub>Ph (14), PPh<sub>3</sub> and PMe<sub>3</sub> (15), and  $[8,8,8-(H)(PMePh_2)_2-9-(PMePh_2)-nido-8,7-RhSB_9H_{10}]^+$  (16) (Scheme 2).

These polyhedral *nido*-cations have been characterized by multinuclear NMR spectroscopy, mass spectrometry,



combined with DFT calculations. Table 1 shows <sup>11</sup>B and <sup>1</sup>H NMR data of compounds **12**, **15** and **16**. Additional <sup>1</sup>H and <sup>31</sup>P–{<sup>1</sup>H} NMR data, assigned to *exo*-polyhedral ligands, can be found in the Experimental section.

The <sup>11</sup>B{<sup>1</sup>H} NMR spectra of the *nido*-cations, **12–16**, show peaks in the interval  $\delta$ (<sup>11</sup>B) 16 to –26 ppm. Some signals exhibit relative intensities too, and these correspond to accidentally coincident resonances, which were indirectly resolved by <sup>1</sup>H–{<sup>11</sup>B} decoupling experiments that identified two separate proton resonances and also established nine cage <sup>11</sup>B–<sup>1</sup>H (terminal) related pairs for the cluster B–H(*exo*) units. These data reveal that the 11-vertex cationic *nido*-rhodathiaboranes maintain an asymmetric structure in solution, which is in agreement with the presence of two <sup>31</sup>P resonances in the <sup>31</sup>P–{<sup>1</sup>H} spectra of these compounds.

The main difference that can be noted in the <sup>11</sup>B NMR spectra of the cationic *nido*-clusters *versus* their neutral parent counterparts is an overall deshielding of the boron resonances. This is particularly so for the resonances that are assigned to the boron atoms at positions 2 and 5 in the cluster (Fig. 1), suggesting that there has been an important change in the {Rh(H)(L)<sub>2</sub>}–{ $\eta^4$ -SB<sub>9</sub>H<sub>9</sub>(Py)} bonding interaction upon protonation of the cluster (*vide infra*). The effect in the <sup>13</sup>P–{<sup>1</sup>H}



Fig. 1 Diagram that represents the chemical shifts in the <sup>11</sup>B NMR spectra. Hatched lines connect equivalent positions. Assignments were made based on <sup>1</sup>H-{<sup>11</sup>B(sel)} experiments and DFT calculations.

spectra with respect to the neutral counterparts depends on the nature of the  $PR_3$  ligands (see ESI, Fig. S1 and S2†); thus, the methyl-containing phosphines,  $PMe_2Ph$  and  $PMe_3$ , suffer a high frequency shift of ~14 ppm in compounds **14** and **15**, whereas the  $PPh_3$  resonances are slightly shielded (~2 ppm). These significant changes are also suggestive of a strong influence of the proton on the *exo*-polyhedral ligands.

In the negative region of the  ${}^{1}H{-}{{}^{11}B}$  NMR spectra, the *nido*-cations exhibit three signals (Fig. 2). The lowest frequency multiplet, which is not affected by broad-band boron decoupling, can be safely assigned to the Rh–H hydride ligand. In contrast, the singlet at the highest frequency and the doublet at intermediate frequencies broaden when the boron broadband decoupling is turned off, indicating that these resonances are due to boron-bound protons and, therefore, they may be assigned to B–H–B (high frequency) and Rh–H–B (intermediate frequency) bridging hydrogen atoms. Together, the NMR data demonstrate that the *nido*-hydridorhodathiaboranes are protonated on the pentagonal faces.

**Table 1** <sup>11</sup>B and <sup>1</sup>H NMR data for  $[8,8,8-(H)(PPh_3)_2-9-(Py)-nido-8,7-RhSB_9H_{10}]^+$  (12) and  $[8,8,8-(H)(PMe_3)(PPh_3)-9-(Py)-nido-8,7-RhSB_9H_{10}]^+$  (15), and  $[8,8,8-(H)(PMePh_2)_2-9-(PMePh_2)-nido-8,7-RhSB_9H_{10}]^+$  (16) in CD<sub>2</sub>Cl<sub>2</sub> compared to the corresponding DFT/GIAO-calculated <sup>11</sup>B-nuclear shield-ing values [in brackets]

Assign. <sup>a</sup>	12		15		16	
	$\delta(^{11}B)$	$\delta(^{1}H)$	$\delta(^{11}B)$	$\delta(^{1}H)$	$\delta(^{11}B)$	$\delta(^{1}H)$
5	15.7 [16.7]	3.79	15.3 [16.5]	3.89	14.8 [14.5]	3.62
3	8.9 [11.9]	3.14	7.9 [11.3]	2.87	7.8 [9.6]	2.78
9	[5.7]	_	[4.8]	_	-8.5 [-8.5]	_
4	-8.2 [-2.3]	1.65	-11.5 [-9.4]	1.42	-7.1 $[-2.1]$	2.77
2	-10.1 $[-7.1]$	2.61	[-8.2]	2.67	-5.9 [-1.5]	2.92
11	-11.5 [-9.8]	2.12	-15.4 [-9.6]	1.49	-9.8 [-9.0]	2.62
6	-12.4 [-12.7]	2.47	-21.9 [-13.9]	2.34	-13.2 [-12.3]	2.51
10	-20.3 [-19.3]	1.43	-23.3 [-20.6]	0.35	-21.9 $[-22.4]$	1.75
1	-22.2 $[-22.1]$	1.53	-25.9 $[-22.7]$	0.61	-20.9 $[-22.1]$	1.65
$\mu(11, 10)$	L 3	-4.32	L 3	-4.41	L 3	-4.19
μ(9, 8)		$-7.9^{b}$		$-7.13^{c}$		$-8.70^{d}$
Rh(8)–H		$-9.84^{e}$		$-10.28^{f}$		$-10.98^{g}$

<sup>*a*</sup> Assignments based on <sup>1</sup>H-{<sup>11</sup>B} selective experiments and DFT calculations. <sup>*b*</sup> Broad doublet: 60 Hz. <sup>*c*</sup> Broad doublet: 57 Hz. <sup>*d*</sup> Broad doublet: 58 Hz. <sup>*e*</sup> Apparent quartet: <sup>1</sup>J(<sup>103</sup>Rh-<sup>1</sup>H) + <sup>2</sup>J(<sup>31</sup>P<sub>A</sub>-<sup>1</sup>H) + <sup>2</sup>J(<sup>31</sup>P<sub>B</sub>-<sup>1</sup>H) \approx 15 Hz, <sup>1</sup>J(<sup>103</sup>Rh-<sup>1</sup>H) = 16.3 Hz. <sup>*f*</sup> Apparent quartet: <sup>1</sup>J(<sup>103</sup>Rh-<sup>1</sup>H) + <sup>2</sup>J(<sup>31</sup>P<sub>A</sub>-<sup>1</sup>H) + <sup>2</sup>J(<sup>31</sup>P<sub>B</sub>-<sup>1</sup>H) \approx 15 Hz, <sup>1</sup>J(<sup>103</sup>Rh-<sup>1</sup>H) = 16.3 Hz. <sup>*f*</sup> Apparent quartet: <sup>1</sup>J(<sup>103</sup>Rh-<sup>1</sup>H) + <sup>2</sup>J(<sup>31</sup>P<sub>A</sub>-<sup>1</sup>H) = 17.1 Hz.



Fig. 2 Negative region of  ${}^{1}H-{}^{11}B$  spectra. From top to bottom: 12, 14, 15 and 16. The third trace from the bottom shows a mixture of protonated *nido*-conformers, 14a and 14b, together with the cationic *isonido*-clusters, 18 and 21 (*vide infra*), a result of protonation and dehydrogenation.



Fig. 3 DFT-optimized structures at the B3LYP/6-31G\*/LANL2DZ level for (left) [8,8,8-(H)(PMe\_3)(PPh\_3)-9-(Py)-*nido*-8,7-RhSB\_9H\_{10}]^+ (15) and (right) [8,8,8-(H)(PMePh\_2)\_2-9-(PMePh\_2)-*nido*-8,7-RhSB\_9H\_{10}]^+ (16).

The final configuration of the B–H–B bridging hydrogen atoms is ambiguous, because the initial hydrogen atom along the B(9)–B(10) edge in the neutral hydridorhodathiaboranes could shift to the adjacent B(10)–B(11) edge. Thus, we carried out DFT-optimizations starting from *nido*-clusters that exhibited two contiguous bridging hydrogen atoms along the B(9)–B(10) and Rh(8)–B(9) edges. In all cases, the optimization ended with the bridging hydrogen atoms along the B(10)–B(11) and Rh(8)–B(9) edges (Fig. 3). The calculated <sup>11</sup>B chemical shifts, presented in Table 1 for **12**, **15** and **16**, agree well with the experimental data, supporting that this energetically favorable configuration of bridging hydrogen atoms is reasonable.

We have recently reported that the 11-vertex *isonido*rhodathiaboranes,  $[1,1-(PR_3)_2-3-(Py)-1,2-RhSB_9H_8]$ , where PR<sub>3</sub> = PPh<sub>3</sub> (7), PMe<sub>3</sub> (9), or PPh<sub>3</sub> and PMe<sub>3</sub> (10), react with TfOH to give 11-vertex cations of the formulation  $[1,3-\mu-(H)-1,1-(PR_3)_2-3-(Py)-isonido-1,2-RhSB_9H_8]^+$ , where PR<sub>3</sub> = PPh<sub>3</sub> (17), PMe<sub>3</sub> (19), or PPh<sub>3</sub> and PMe<sub>3</sub> (20) (Scheme 3).<sup>35</sup> From [8,8,8-(H)(PMe\_2Ph)-(PPh<sub>3</sub>)-9-(Py)-*nido*-8,7-RhSB<sub>9</sub>H<sub>9</sub>] (4), the corresponding neutral *isonido*-cluster,  $[1,1-(PMe_2Ph)(PPh_3)-3-(Py)-1,2-RhSB_9H_8]$  (11), is





Scheme 3 Protonation of *isonido*-rhodathiaboranes to give *isonido*-cations.

always formed in a mixture with its bis-(PMe<sub>2</sub>Ph)-ligated counterpart,  $[1,1-(PMe_2Ph)_2-3-(Py)-isonido-1,2-RhSB_9H_8]$  (8), complicating, therefore, the isolation of these compounds and of their protonated derivatives,  $[1,3-\mu-(H)-1,1-(PR_3)_2-3-(Py)-isonido-1,2-RhSB_9H_8]^+$ , where PR<sub>3</sub> = PPh<sub>3</sub> and PMe<sub>2</sub>Ph (21) or PMe<sub>2</sub>Ph (18) (Scheme 3). This can be inferred from Fig. 2 where is shown the negative region of a <sup>1</sup>H–{<sup>11</sup>B} NMR spectrum that was measured a few minutes after the addition of TfOH to a solution of 4: the second trace from the top. This spectrum shows the formation of a mixture of cationic bis-(PPh<sub>3</sub>)(PMe<sub>2</sub>Ph)-ligated *nido*-conformers, **14a** (red triangles) and **14b** (blue triangles), together with the *isonido*-polyhedral cations, **21** (red ellipsoid) and **18** (blue ellipsoid).

However, the bis-(PMe<sub>2</sub>Ph)-ligated rhodathiaborane, **8**, can be synthesized selectively by treatment of the mixed (PMe<sub>2</sub>Ph)-(PPh<sub>3</sub>)-ligated *nido*-parent compound, **4**, with excess of PMe<sub>2</sub>Ph. This reaction entails that the cationic cluster, **18**, is available by direct protonation of its parent neutral compound, **8**, leading to its quantitative formation and subsequent characterization as a single product. In contrast, its bis-(PPh<sub>3</sub>)-(PMe<sub>2</sub>Ph)-ligated counterpart, **21**, was characterized by multinuclear NMR spectroscopy in mixtures such as those illustrated in Fig. 2.

The bis-(PMePh<sub>2</sub>)-ligated *isonido*-rhodathiaborane, an analogue of 7–9, is not available from the thermal treatment of  $[8,8,8-(H)(PMePh_2)_2-9-(Py)-nido-8,7-RhSB_9H_9]$  (3), precluding the formation of the *isonido*-cation,  $[1,3-\mu-(H)-1,1-(PMePh_2)_2-3-(Py)-1,2-RhSB_9H_8]^+$  (22), by direct protonation of its hypothetical conjugate base,  $[1,1-(PMePh_2)_2-3-(Py)-isonido-1,2-RhSB_9H_8]$ . However, treatment of **3** with TfOH affords selectively the product of protonation and H<sub>2</sub> lost, compound **22** (see Fig. S3 included in the ESI† for this paper).

The <sup>11</sup>B and <sup>1</sup>H NMR data of the cluster atoms for the *isonido*-cations, **18**, **19**, **20** and **22**, are listed in Table 2 together with GIAO calculated nuclear magnetic chemical shieldings for some of them. Overall the pattern of <sup>11</sup>B spectra of the protonated *isonido*-cluster suffers a slight deshielding with respect to the neutral parent *isonido*-compounds, but maintaining a clear resemblance. Characteristic of this family of neutral and cationic **11**-vertex *isonido*-rhodathiaboranes is the presence

**Table 2** <sup>11</sup>B and <sup>1</sup>H NMR data for  $[1,3-\mu-(H)-1,1-(PMe_2Ph)_2-3-(Py)-isonido-1,2-RhSB_9H_8]^+$  (18),  $[1,3-\mu-(H)-1,1-(PMe_3)_2-3-(Py)-isonido-1,2-RhSB_9H_8]^+$  (19),  $[1,3-\mu-(H)-1,1-(PMe_3)_2-3-(Py)-isonido-1,2-RhSB_9H_8]^+$  (20), and  $[1,3-\mu-(H)-1,1-(PMePh_2)_2-3-(Py)-isonido-1,2-RhSB_9H_8]^+$  (22) in CD<sub>2</sub>Cl<sub>2</sub> compared to the corresponding DFT/GIAO-calculated <sup>11</sup>B-nuclear shielding values [in brackets]

Assign. <sup>a</sup>	18		19		20		22	
	$\delta(^{11}B)$	$\delta(^{1}H)$	$\delta(^{11}\mathrm{B})$	$\delta(^{1}H)$	$\delta(^{11}B)$	$\delta(^{1}H)$	$\delta(^{11}B)$	$\delta(^{1}H)$
3	58.1		58.3 [60.9]		57.9 [60.1]		58.3	_
9	30.0	4.71	29.7 31.1	4.70	29.6 29.4	4.65	29.8	4.67
5	9.6	2.95	9.0 [17.2]	2.87	10.8 [16.9]	0.97	10.9	2.79
4			[15.0]		8.9 [14.9]	2.87		
8	-13.1	2.43	-13.2 [-13.6]	1.46	-13.6 [-13.8]	1.32	-12.9	0.80
7			[-14.2]		-23.8 [-15.3]	0.90		
11			[-15.9]		-21.8 [-15.2]	0.82		
6	-23.4	0.35	-23.6 [-20.7]	0.40	-19.9 [-14.4]	-0.13	-21.8	0.21
10	-24.3	0.74	-24.9 [-21.5]	0.75	-26.2 [-21.2]	0.58	-22.5	2.27
1,3-µ-(H)		$-6.40^{b}$		$-6.70^{\circ}$		$-5.45^{d}$		$-5.28^{e}$

<sup>*a*</sup> Assignments based on <sup>1</sup>H{<sup>11</sup>B} selective experiments and DFT calculations. <sup>*b*</sup> dt, <sup>1</sup>J(<sup>103</sup>Rh-<sup>1</sup>H) = 25 Hz, <sup>2</sup>J(<sup>31</sup>P-<sup>1</sup>H) = 16 Hz. <sup>*c*</sup> dt, <sup>1</sup>J(<sup>103</sup>Rh-<sup>1</sup>H) = 25 Hz, <sup>2</sup>J(<sup>31</sup>P-<sup>1</sup>H) = 16 Hz. <sup>*c*</sup> dt, <sup>1</sup>J(<sup>103</sup>Rh-<sup>1</sup>H) = 12 Hz, <sup>2</sup>J(<sup>31</sup>P-<sup>1</sup>H) = 11 Hz. <sup>*e*</sup> dt, <sup>1</sup>J(<sup>103</sup>Rh-<sup>1</sup>H) = 25 Hz, <sup>2</sup>J(<sup>31</sup>P-<sup>1</sup>H) = 16 Hz.

of a high-frequency resonance of relative intensity 1 around  $\delta(^{11}B)$  60 ppm, which is assigned to the pyridine-substituted B(3) vertex. This signal is well separated from the rest of the peaks, which are in the range  $\delta(^{11}B)$  30 to -28 ppm. The  $^{31}P-{}^{1}H$  spectra demonstrate the presence of the *exo*-polyhedral ligands in each of the cationic *isonido*-clusters (Fig. S4†). It is interesting to note that upon protonation the Me-containing phosphine ligands, PMe<sub>3</sub> and PMe<sub>2</sub>Ph, suffer a shift to higher frequencies whereas the PPh<sub>3</sub> ligand shifts towards lower frequencies. As commented above, the same effect is observed for the protonated *nido*-clusters *versus* their neutral conjugated *nido*-bases.

The  ${}^{1}H - {}^{11}B$  and  ${}^{1}H$  NMR spectra provide decisive data for the characterization of the proton site on the clusters. Thus, all the *isonido*-cations exhibit a multiplet in the range  $\delta^{(1)}$ -5.0 to -7.0 ppm, which broadens when the boron broadband decoupling is turned off (Fig. 4). <sup>1</sup>H-{<sup>11</sup>B(sel)} experiments that relate  $\delta({}^{1}H)$  to corresponding directly bound  $\delta({}^{11}B)$ demonstrated that these protons bind the pyridine-substituted boron atom at the 3-position. This fact together with the multiplicity of the peaks demonstrate clearly that protonation takes place along the Rh(1)-B(3) edge. Therefore, the presence of these low-frequency multiplets in the  ${}^{1}H{-}{{}^{11}B}$  NMR spectra is diagnostic of the formation of the isonido-cations. The chemical shift of this resonance moves towards low frequencies as the phenyl rings on the PR<sub>3</sub> ligands are substituted by methyl groups (Fig. 4). This effect could be related to an increase in the basicity of the phosphine ligands, to anisotropic effects of the aromatic rings or to a combination of these and other factors. It should be noted that the Rh-H-B resonance in the bis-PPh<sub>3</sub> species, 17, is only seen at low temperatures.<sup>35</sup>

# X-ray diffraction analysis of [1,3- $\mu$ -(H)-1,1-(PMe<sub>3</sub>)(PPh<sub>3</sub>)-3-(Py)-1,2-RhSB<sub>9</sub>H<sub>8</sub>]<sup>+</sup> (20)

Two crystals of this cationic rhodathiaborane were grown by slow diffusion of hexane into TfOH acidified solutions of the neutral parent compound,  $[1,1-(PMe_3)(PPh_3)-3-(Py)-1,2-RhSB_9H_8]$  (10), in dichloromethane and in acetone. The crystal



Fig. 4  $^{1}H-{^{11}B}$  NMR spectra showing the low-frequency resonance assigned to the Rh(1)-H-B(3) bridging hydrogen atom. From top to bottom: 17 (at -50 °C), 22, 20, 18 and 19.

obtained from CH<sub>2</sub>Cl<sub>2</sub>-hexane, **20a**, showed an uncommon case of conformational isomerism.<sup>47</sup> This feature was commented in a previous publication,<sup>35</sup> and herein we give a rationale based on the intermolecular interactions in the lattice. The results are compared with new structural data from the crystal grown in Me<sub>2</sub>CO-hexane, **20b**. This crystallographic analysis is combined with DFT-calculations to estimate energy variations driven by {Rh(PR<sub>3</sub>)<sub>2</sub>}-{ $\eta^{n}$ -SB<sub>9</sub>H<sub>8</sub>(Py)} conformational changes.

The X-ray diffraction analysis of crystals **20a** and **20b** has given rise to four  $[1,3-\mu-(H)-1,1-(PMe_3)(PPh_3)-3-(Py)-1,2-RhSB_9H_8]^+$  structural isomers: three in the unit cell of **20a**, labeled as *isonido-***20a**<sub>1</sub>, *isonido-***20a**<sub>2</sub> and *nido-***20a**<sub>3</sub> and one in crystal **20b**, labeled *isonido-***20b** (Fig. 5). Of special relevance are the distances that define the rhodium-thiaborane interaction in these conformational isomers. The interatomiclength pattern of this linkage is illustrated in Fig. 6 for: (a) the cationic cluster, *isonido*-**20b**, (b) its DFT-optimized structure, (c) the conformer, *nido*-**20a**<sub>3</sub>, (d) compound **10**, (e) cluster 7, and (f) the parent rhodathiaborane, **1**. Table 3 shows additional Rh-B distances and angles for these compounds.

The first noticeable difference of the protonated clusters *versus* the neutral counterparts is an elongation of the distances that involve the { $Rh(PMe_3)(PPh_3)$ -{ $SB_9H_8(Py)$ } interaction as well as the *exo*-polyhedral Rh–P lengths. In particular, the conformers *isonido*-**20a**<sub>1</sub>, *isonido*-**20a**<sub>2</sub> and *isonido*-**20b** exhibit long Rh(1)-B(5) distances at 2.617(9), 2.7171(11) and 2.607(5) Å, respectively: the second being significantly longer than the other two. A bonding Rh(1)-B(5) distance



**Fig. 5** ORTEP-type drawing of  $[1,3-\mu-(H)-1,1-(PMe_3)(PPh_3)-3-(Py)-isonido-1,2-RhSB_9H_8]^+$  in crystal **20b**. Only the *ipso*-carbon atoms on the phenyl rings of the PPh\_3 ligand are included to aid clarity. Ellipsoids are shown at the 50% probability level.

would be of the order of 2.4 to 2.5 Å; therefore in these cationic conformational isomers, the Rh–B length can be viewed as non-bonding, rendering a quadrilateral open face.

This structural motif can be formed by a simple diamond-square process in a canonical *closo*-structure based on an octa-dodecahedron, giving a more open structure that is usually classified as *isonido*.<sup>48-54</sup>

In the neutral cluster [Fig. 6(d)], the Rh–B lengths of boron vertices, 4 and 5, flanking the sulfur atom, lie just on the upper part of the bonding limit that leads to the generation of a triangular *closo*-face. However, the bis-PPh<sub>3</sub>-ligated analogue,  $[1,1-(PPh_3)_2-3-(Py)-1,2-RhSB_9H_8]$  (7) [Fig. 6(e)], exhibits a Rh(1)–B(5) distance at 2.562 Å that falls just outside of what may be considered as bonding. Thus previously reported by us as a *closo*, this rhodathiaborane is perhaps better described as *isonido*.

In marked contrast, the third conformer in crystal **20a**, *nido*-**20a**<sub>3</sub>, shows a {Rh(1)S(2)B(3)B(4)B(7)} pentagonal face [Rh(1)-B(5) 3.5187(9) Å] distinctive of an 11-vertex polyhedral boron-containing compound with a *nido* structure. This structural feature is clear from the comparison of the conformer *nido*-**20a**<sub>3</sub> with crystallographically determined [8,8-(PPh<sub>3</sub>)<sub>2</sub>*nido*-8,7-RhSB<sub>9</sub>H<sub>10</sub>] (1) [Fig. 6(*c*) and (*f*), respectively].

These structural changes found in the cationic conformers with respect to the neutral counterparts indicate that the metal-thiaborane linkage is non-rigid and that conformational changes can be produced at a low energy cost in this system. In order to evaluate this fact, we carried out DFT-optimizations starting from the X-ray determined structure of *isonido*-20b, adding a hydrogen atom along the Rh(1)–B(3) edge (*closo/isonido*-labeling) as inferred by the spectroscopic NMR characterization. The initial structure of the *isonido*-cluster exhibited a hydrogen atom in a bridging position at 1.698 Å from the



Fig. 6 Details of  $[1,3-\mu-(H)-1,1-(PMe_3)(PPh_3)-3-(Py)-1,2-RhSB_9H_8]^+$ : (a) crystallographically determined, cationic *isonido*-20b, (b) DFT-calculated cationic *isonido*-20b, and (c) crystallographically determined, cationic *nido*-20a<sub>3</sub>. (d) Neutral  $[1,1-(PMe_3)(PPh_3)-3-isonido-(Py)-1,2-RhSB_9H_8]$  (10), (e) neutral  $[1,1-(PPh_3)_2-3-(Py)-isonido-1,2-RhSB_9H_8]$  (7) and (f) neutral  $[8,8-(PPh_3)_2-nido-8,7-RhSB_9H_{10}]$  (1).

**Table 3** Selected lengths [Å] and angles [°] of crystallographically determined neutral parent compounds  $[1,1-(PPh_3)_2-3-(Py)-isonido-1,2-RhSB_9H_8]$ (7) and  $[1,1-(PMe_3)(PPh_3)_2-3-(Py)-isonido-1,2-RhSB_9H_8]$  (10), together with the crystallographically determined  $[1,3-\mu-(H)-1,1-(PMe_3)(PPh_3)-3-(Py)-1,2-RhSB_9H_8]^+$ , *isonido-20b*, and DFT-calculated  $[1,3-\mu-(H)-1,1-(PPh_3)_2-3-(Py)-1,2-RhSB_9H_8]^+$  (7a)<sup>a</sup>

	7	7a	10	isonido-20b
Rh(1)-P(1)	2.3012(12)	2.4852	2.2889(10) [2.3529]	2.3228(11) [2.4107]
Rh(1) - P(2)	2.3278(13)	2.5081	2.2710(9) [2.36203]	2.3505(10) [2.4662]
Rh(1)-S(2)	2.3997(14)	2.4685	2.3841(9) [2.4895]	2.3761(11) [2.4622]
Rh(1) - B(3)	2.085(6)	2.092	2.087(4) [2.096]	2.098(4) [2.103]
Rh(1) - B(4)	2.400(6)	2.592	2.401(4) [2.504]	2.475(5) [2.581]
Rh(1) - B(5)	2.562(6)	2.850	2.471(4) [2.628]	2.607(5) [2.813]
Rh(1) - B(6)	2.387(6)	2.473	2.380(4) [2.438]	2.445(5)[2.501]
Rh(1) - B(7)	2.344(6)	2.415	2.354(4) [2.393]	2.374(4) [2.398]
P(1) - Rh(1) - P(2)	96.97(4)	99.81	96.68(4) [97.55]	96.28(4) [98.14]
P(1) - Rh(1) - S(2)	110.83(5)	95.34	103.17(4) [103.60]	98.21(4) [97.30]
P(2) - Rh(1) - S(2)	102.32(5)	102.50	110.92(3) [107.05]	98.53(4) [96.67]
P(1) - Rh(1) - B(3)	112.42(16)	120.74	114.79(11) [116.81]	122.33(13) [125.11]
P(2) - Rh(1) - B(3)	112.65(17)	122.51	108.42(11) [114.00]	119.58(13) [121.80]
B(3) - Rh(1) - S(2)	119.02(16)	111.38	120.32(11) [115.77]	116.97(14)[111.97]

<sup>a</sup> DFT-calculated values in brackets.



**Fig. 7** DFT-calculated energies and structures, computed at the B3LYP/ 6-31G\*/LANL2DZ level for B-H-B containing *nido*- and Rh-H ligated *isonido*-isomers, [(PMe<sub>3</sub>)(PPh<sub>3</sub>)(Py)RhSB<sub>9</sub>H<sub>9</sub>]<sup>+</sup>.

Rh(1) center and at 1.330 Å from the B(3) vertex, which after optimization at the B3LYP/6-31G\*/LANL2DZ level ended as a hydride ligand *trans* to the sulphur vertex, with a distance of 2.094 Å to B(3) [Fig. 6(*b*) and Fig. 7].

Note that in the calculated structures the Rh(1)–B(4) and Rh(1)–B(5) lengths are substantially elongated with respect to the experimental values (Fig. 6 and Table 3), suggesting that there is an important withdrawal of skeletal electronic density from the B(4)S(3)B(5) side to the B(6)B(3)B(7) side where the cluster is protonated. This supports the commented experimental data, giving a further indication that the Rh(1)–H–B(3) bridging-bound hydrogen atom, fully characterized in solution, exerts a strong influence on the rhodium–thiaborane bonding interaction. In this regard, it is also important to note that the P(1)–Rh(1)–S(2) and P(2)–Rh(1)–S(2) angles decrease significantly upon protonation (Table 3), proving the strong effect brought about by the presence of a proton along the

Rh(1)-B(3) edge. This structural change and the observed anion/cation packing motifs commented below are clear proof of the presence of a Rh(1)-H-B(3) bridging hydrogen atom in the crystalline structures of compound **20**.

Interestingly, the optimization of *nido*-**20a**<sub>3</sub>, starting with a hydrogen atom along the Rh(8)–H–B(9) edge, ended with a *nido*-structure that shows a bridging hydrogen atom along the B(9)–B(10) edge on the pentagonal face, resembling the structure of the crystallographically determined  $[8,8-(PPh_3)_2-8,7-RhSB_9H_{10}]$  [Fig. 6(*f*)], which is isoelectronic with the cationic pyridine adduct. This suggests that in the solid state the *nido*-conformer, **20a**<sub>3</sub>, could exhibit the hydrogen atom, arising from protonation, at the B(9)–B(10) edge rather than along the Rh(8)–B(9) edge, as suggested by the *isonido*-configuration (Fig. 7).

In any event, the DFT-calculated energy difference between the optimized nido-structure and the isonido-cation is 2.5 kcal  $mol^{-1}$  (Fig. 7). To put this energy into perspective, we should bear in mind that the barrier to rotation about the single bond of ethane is about  $2.8 \text{ kcal mol}^{-1}$ , that hydrogen bond strengths are generally estimated to be in the range 1 to 10 kcal mol<sup>-1</sup>, and that the differences in lattice energy among different polymorphic forms is expected to be in the range 1 to 2 kcal mol<sup>-1.47</sup> Therefore, the DFT-calculated *nido-* and isonido-energy minima for the polyhedral cation [(PMe<sub>3</sub>)(PPh<sub>3</sub>)- $RhSB_{9}H_{9}(Py)$ <sup>+</sup> demonstrate that these conformers are thermodynamically accessible, providing a rationale for this significant case of conformational isomorphism in crystal 20a (different conformers in the same crystal), nicely complemented by the existence of a different isonido-conformer in crystal 20b.

To analyze possible packing motifs leading to crystal environments that may favor the predominance of one conformation *versus* another, we need to discuss in more detail the crystal structures of **20a** and **20b**. Both structures are based on a matrix of rhodathiaborane cations and triflate anions, which assimilates solvent molecules. In the extended structure of



**Fig. 8** Dimer of *nido*-conformers, **20** $a_3$ , stabilized by pyridine  $\pi$ - $\pi$  interactions.



Fig. 9 Crystal packing of 20a along the *a* axis: in red the layer of *nido*-conformers,  $20a_3$ ; in blue and green the *isonido*-conformers,  $20a_1$  and  $20a_2$ .

crystal **20a**, the *nido*-cations, **20a**<sub>3</sub>, form dimers *via*  $\pi$ - $\pi$  interactions between the pyridine rings. The configuration of the pyridine rings in the dimer falls into the category of parallel-displaced,<sup>55</sup> and an inversion centre relates both pyridine-substituted clusters (Fig. 8). These dimers pack along the crystallographic *a* direction forming ribbons that are repeated down the *b* direction leading to the formation of a layer of cationic *nido*-clusters (Fig. 9). There is one crystallographically independent triflate anion at 3.780 Å from the pyridine rings, following the *nido*-rhodathiaborane cations along the *a* axis.

Alternatively, both *isonido*-conformers,  $20a_1$  and  $20a_2$ , associate in pairs through sextuple phenyl embrace (SPE) interactions (Fig. 10). The P…P separation and the Rh–P…P–Rh colinearity are 6.9 Å and 173°, respectively, and fall in the range reported for this attractive edge-to-face interaction (Fig. 10).<sup>56</sup> The resulting rhodathiaborane dimers pack along the *a*-axis, forming two crystallographically independent ribbons (blue and green in Fig. 9). Each dimer interleaves between two {RhSB<sub>9</sub>-heads of dimers on adjacent ribbons,



Fig. 10 Details of the intermolecular SPE involving the  $PPh_3$  ligands of two *isonido*-conformers in 20a.



**Fig. 11** Crystal packing of **20b** along the *c* axis, showing the zigzag ribbon-like structure running along the *b* axis.

leading to relatively short cage contacts (4.136 Å the shortest) that are reminiscent of the interdigitated protruding teeth of a zip fastener. The overall effect is the formation of zigzag ribbon-like layers in the *ab* plane: two of these layers sandwich a layer of *nido*-cages (Fig. 9).

Similarly, the *isonido*-clusters found in the crystal **20b** exhibit attractive interactions of the phenyl groups of adjacent clusters forming dimers. This basic supramolecular motif packs in the same fashion as their *isonido*-congeners above, leading to a zigzag ribbon-like structure that runs along the *b* axis. This packing forms large rhombohedral channels that are filled with the triflate anions as well as co-crystallized solvent molecules of hexane and acetone (Fig. 11).

It is interesting to note that in both crystals, **20a** and **20b**, the triflate anions lie close to the pyridine rings of the polyhedral cations (shortest N····O length at 3.278 Å). As illustrated in Fig. 12, the anion/cation packing motif involving the *isonido*-clusters is virtually the same, being, as expected, different for the *nido*-isomer. These packing motifs agree well with the fact that there is a region of net positive charge along the Rh(1)–B(3) edge of the polyhedral cations, where, as demonstrated by NMR spectroscopy, the neutral *isonido*-rhodathiaboranes are protonated.



Fig. 12 View of *isonido*-cation/triflate packing motifs in crystals 20a and 20b, and the *nido*-cation/triflate packing recognition.

After this analysis, it is clear that there are two packing motifs that play an important role in the stabilization of different conformers in the unit cell of crystal 20a. Thus,  $\pi$ - $\pi$ pyridine dimer formation brings about a distortion of the 11 vertex rhodathiaborane cage to give a nido-structure with a pentagonal face, whereas attractive edge-to-face interactions of phenyl groups favor a closer isonido-conformation with a pseudo- $C_s$  symmetry. We should bear in mind that  $\pi$ - $\pi$  pyridine binding energies have been calculated to be in the range 2.2 to 3.8 kcal mol<sup>-1</sup>,<sup>55</sup> and that an edge-to-face attractive interaction of a phenyl ring within a SPE is estimated to be 2.4 kcal  $mol^{-1}$  to 3.3 kcal  $mol^{-1}$ .<sup>56</sup> It is clear that given the proximity of cluster conformational energies between the nido- and isonidorhodathiaborane cations, these intermolecular forces are sufficient to stabilize both isomers. Thus, the creation of different crystal environments within the lattice leads to the formation of different conformers in the same unit cell.

# General considerations and conclusions

11-Vertex *nido-* and *isonido-*rhodathiaboranes are easily protonated by TfOH to afford *nido-* and *isonido-*cations. Since the yields of these neutral 11-vertex rhodathiaboranes are generally good, this is a convenient entry into the area of polyhedral boron-containing cations which is scarcely explored with only a small number of reported cationic boranes and metallaheteroboranes.<sup>39–46,57–63</sup> It is important to recall that the majority of reported cationic metallaheteroboranes generally contain charge-compensating ligands;<sup>41–46</sup> and the number of cationic polyhedral boron clusters formed by simple protonation is very small indeed.<sup>39,40</sup> The herein reported reactions with TfOH together with previous results with HCl<sup>36,64</sup> give an overall view of the reactivity of this family of rhodathiaboranes with Brønsted acid (Scheme 4).

The reactions start by protonation of the cages along Rh-B edges. The proton induces an enhancement of the Lewis acidity of the clusters, which undergo further transformations depending on the nature of the *exo*-polyhedral ligands and on the anion: Cl<sup>-</sup> versus TfO<sup>-</sup>. Thus, upon protonation with HCl, the putative cationic species suffer an attack of the chlorine anion, leading to the formal incorporation of HCl into the cluster framework, which in the case of the isonido-clusters results in the opening of the structure to nido-species with pentagonal faces; in addition, for the PPh3-ligated species, phosphine release is also found (Scheme 4). In a similar fashion, the neutral nido-reagents undergo formal HCl addition and H<sub>2</sub> liberation, followed, in some cases, by PPh<sub>3</sub> extrusion (Scheme 4). The reactions with TfOH involve the same protonated intermediates, which are more stable in the presence of weakly coordinating triflate anions than in the presence of strong coordinating chlorine anions. However, upon protonation with TfOH, some of the nidoclusters undergo  $H_2$  lost and *nido*  $\rightarrow$  *isonido* transformations; but more spectacular is the lability of the bis-PPh<sub>3</sub>ligated isonido-rhodathiaborane, 7, that with TfOH leads to an equilibrium between cationic and neutral OTf-ligated species.35

The herein reported crystallographic and DFT studies demonstrate that the high degree of flexibility associated with the metal-thiaborane linkage upon protonation enables the formation of different structural isomers that in the case of the cation,  $[1,3-\mu-(H)-1,1-(PMe_3)(PPh_3)-3-(Py)-isonido-1,2-RhSB_9H_8]^+$ , are stabilized in the solid state by common intermolecular interactions. This proton-induced cluster non-rigidity can lead to new ways of reactivity by polyhedral boroncontaining compounds, which may be useful in the activation of unreactive bonds.

We are currently developing these and other aspects, dealing with the reaction chemistry of these unique rhodathiaboranes.

### **Experimental section**

### General

All reactions were carried out under an argon atmosphere using standard Schlenk-line techniques. Solvents were obtained from an Innovative Technology Solvent Purification System. All commercial reagents were used as received without further purification. The rhodathiaboranes [ $8,8,8-(H)(PR_3)_2-9-(Py)-nido-8,7-RhSB_9H_9$ ], where PR<sub>3</sub> = PPh<sub>3</sub> (2), PMePh<sub>2</sub> (3), PPh<sub>3</sub> and PMe<sub>2</sub>Ph (4), PPh<sub>3</sub> and PMe<sub>3</sub> (5); [ $8,8,8-(H)(PMePh_2)_2-9-(PMePh_2)-nido-8,7-RhSB_9H_9$ ] (6), and [1,1-(PR3)2-3-(Py)-1,2-RhSB9H8] where PR<sub>3</sub> = PPh<sub>3</sub> (7), PMe<sub>2</sub>Ph (8), PMe<sub>3</sub> (9), PPh<sub>3</sub> and PMe<sub>3</sub> (10), or PPh<sub>3</sub> and PMe<sub>2</sub>Ph (11), were prepared by published methods.<sup>30,33,34</sup> The synthesis and characterization



of the cationic rhodathiaboranes,  $[8,8,8-(H)(PPh_3)_2-9-(Py)-nido-8,7-RhSB_9H_{10}]^+$  (12) and  $[1,3-\mu-(H)-1,1-(PR_3)_2-3-(Py)-isonido-1,2-RhSB_9H_9]^+$ , where PR<sub>3</sub> = PPh<sub>3</sub> (17), PMe<sub>3</sub> (19), PPh<sub>3</sub> and PMe<sub>3</sub> (20), were reported previously.<sup>35,36</sup>

NMR spectra were recorded on Bruker Avance 300 MHz and AV 400 MHz spectrometers, using <sup>11</sup>B, <sup>11</sup>B–<sup>{1</sup>H}, <sup>1</sup>H, <sup>1</sup>H{<sup>11</sup>B}, <sup>1</sup>H{<sup>11</sup>B(selective)} and <sup>31</sup>P–<sup>{1</sup>H} techniques. <sup>1</sup>H chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative to tetramethylsilane. <sup>11</sup>B chemical shifts were measured relative to [BF<sub>3</sub>(OEt)<sub>2</sub>)]. <sup>31</sup>P (121.48 MHz) chemical shifts were measured relative to H<sub>3</sub>PO<sub>4</sub> (85%). Mass spectrometry data were recorded using a VG Autospec double focusing mass spectrometer, a microflex MALDI-TOF, and a ESQUIRE 3000+ API-TRAP, operating in either positive or negative mode. In each case there was excellent correspondence between the calculated and measured isotopomer envelopes. A well-matched isotope pattern may be taken as a good criterion of identity.<sup>65</sup>

#### X-ray structure analysis of crystals 20a and 20b

Crystal **20a** was grown by slow diffusion of hexane into a dichloromethane solution, and its structure has been previously reported (CCDC 907304). Crystal **20b** was obtained by slow diffusion of hexane into an acetone solution (CCDC 937675). In both cases, the studied crystals, **20a** and **20b**, were coated with perfluoropolyether, mounted on a glass fiber and fixed in a cold nitrogen stream (T = 100(2) K) to the goniometer

head. Data collection was performed using a Bruker Kappa APEX DUO CCD area detector diffractometer with monochromatic radiation  $\lambda(Mo_{K\alpha}) = 0.7107073$  Å, using narrow frames  $(0.3^{\circ} \text{ in } \omega)$ . The data were reduced (SAINT)<sup>66</sup> and corrected for absorption effects by multiscan methods (SADABS).<sup>67</sup> The structure was solved using the SHELXS-86 program,<sup>68</sup> and refined against all  $F^2$  data by full-matrix least-squares techniques (SHELXL-97).<sup>69</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined with a positional and thermal riding model.

CCDC 907304 (20a) and 937675 (20b) contains the supplementary crystallography data for this paper.

 $[8,8,8-(H)(PMePh_2)_2-9-(Py)-nido-8,7-RhSB_9H_{10}]^+$ (13). In a 5 mm NMR tube, a solution of [8,8,8-(H)(PMePh<sub>2</sub>)<sub>2</sub>-9-(Py)-nido-8,7-RhSB<sub>9</sub>H<sub>9</sub>] (3) (0.0054 mg, 0.0075 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.3 mL) under argon was treated with triflic acid (0.66 mL, 0.075 mmol). The resulting light orange sample was studied by NMR spectroscopy. The data revealed the formation of a mixture formed by the nido-cluster, 13, and its dehydrogenation isonido-product, 22 (see below), in a 1:0.5 ratio. As time passes, this mixture of compounds changes to give 22 as a single product. This reactivity precluded the isolation of 13, and its characterization was carried out in situ in samples that contained mixtures of this cationic hydridorhodathiaborane (two conformers, see Fig. S3 ESI<sup>†</sup>) and its isonido-derivative. NMR data: the A label corresponds to the major conformer and B to the minor. <sup>11</sup>B (128 MHz;  $CD_2Cl_2$ ; 298 K):  $\delta$  15.6, 12.8,

6.8, 4.5, -11.2, -14.9, -21.0, -23.6. NMR <sup>1</sup>H-{<sup>11</sup>B} (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$  10.64 (2H, d, <sup>3</sup>*J*<sub>HH</sub> = 4.8 Hz, *H*<sub>oA</sub>-NC<sub>5</sub>H<sub>5</sub>), 10.36 (1H, t,  ${}^{3}J_{HH}$  = 8.1 Hz,  $H_{pA}$ -NC<sub>5</sub>H<sub>5</sub>), 10.19 (2H, d,  ${}^{3}J_{HH}$  = 5.2 Hz,  $H_{oB}$ -NC<sub>5</sub>H<sub>5</sub>), 10.02 (1H, t,  ${}^{3}J_{HH} = 7.9$  Hz,  $H_{pB}$ -NC<sub>5</sub>H<sub>5</sub>), 9.66 (2H, t,  ${}^{3}J_{HH} = 6.7$  Hz,  $H_{mA}$ -NC<sub>5</sub>H<sub>5</sub>), 9.50 (2H, m,  $H_{mB}$ -NC<sub>5</sub>H<sub>5</sub>), 9.6 to 8.7 (40H, m, PMePh<sub>2</sub>), 3.88 (1H, s, BH), 2.58 (1H, s, BH), 2.36 (1H, s, BH), 2.29 (3H, d,  ${}^{2}J_{HP}$  = 10.9 Hz,  $PMe_{A}Ph_{2}$ ), 2.16 (3H, d,  ${}^{2}J_{HP}$  = 10.9 Hz,  $PMe_{B}Ph_{2}$ ), 1.90 (3H, d,  ${}^{2}J_{\text{HP}} = 9.6 \text{ Hz}, \text{PM}e_{\text{B}}\text{Ph}_{2}$ , 1.81 (3H, d,  ${}^{2}J_{\text{HP}} = 10.9 \text{ Hz}, \text{PM}e_{\text{A}}\text{Ph}_{2}$ ), 1.62 (1H, s, BH), 1.12 (1H, s, BH), -4.28 (1H, s, BH<sub>A</sub>B), -4.54 (1H, s, B-H<sub>B</sub>-B), -5.18 (1H, m, Rh-H<sub>B</sub>-B), -7.49 (1H, d br,  ${}^{1}J_{\text{HRh}} \approx {}^{2}J_{\text{PH}} = 60$  Hz, Rh-H<sub>A</sub>-B), -10.16 (1H, apparent q,  ${}^{1}J_{\text{HRh}} \approx {}^{2}J_{\text{HP}} = 20.5 \text{ Hz}, \text{ Rh-H}_{\text{A}}$ , -10.64 (1H, m, Rh-H<sub>B</sub>). NMR <sup>31</sup>P-{<sup>1</sup>H} (162 MHz; CD<sub>2</sub>Cl<sub>2</sub>; 298 K):  $\delta$  30.5 (1P, dd,  ${}^{1}J_{PRh} = 121$  Hz,  ${}^{2}J_{PP} = 25$  Hz,  $P_{A}MePh_{2}$ ), 27.7 (1P, dd,  ${}^{1}J_{PRh} =$ 136 Hz,  ${}^{2}J_{PP}$  = 22 Hz, P<sub>B</sub>MePh<sub>2</sub>), 15.7 (1P, d-br,  ${}^{1}J_{PRh}$  = 117 Hz,  $P_AMePh_2$ ), 12.5 (1P, dd,  ${}^{1}J_{PRh} = 100$  Hz,  ${}^{2}J_{PP} = 25$  Hz, P<sub>A</sub>MePh<sub>2</sub>).

 $[8,8,8-(H)(PMe_2Ph)(PPh_3)-9-(Py)-nido-8,7-RhSB_9H_9]^+$  (14). A 5 mm NMR tube was charged with 5.4 mg (0.0075 mmol) of [8,8,8-(H)(PMe<sub>2</sub>Ph)(PPh<sub>3</sub>)-9-(Py)-nido-8,7-RhSB<sub>9</sub>H<sub>9</sub>] (4), 0.3 mL of CD<sub>2</sub>Cl<sub>2</sub> and 0.66 µL (0.075 mmol) of TfOH. The resulting orange solution was studied by NMR spectroscopy. The data demonstrated the formation of a mixture of protonated 14,  $[1,3-\mu-(H)-1,1-(PMe_2Ph)(PPh_3)-3-(Py)-isonido-1,2-RhSB_9H_8]^+$  (21) and  $[1,3-\mu-(H)-1,1-(PMe_2Ph)_2-3-(Py)-closo-1,2-RhSB_9H_8]^+$  (18) in a 1:1:0.5 ratio, respectively. After several hours, the system evolves to give a mixture that contains the isonidoderivatives, 21 and 18, in a 1:0.3 ratio. 14:  ${}^{1}H - {}^{11}B$  NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$  2.25 (6H, overlapped t, <sup>2</sup>J<sub>HP</sub> = 13.6 Hz, PMe<sub>2</sub>Ph), -4.42 (1H, s, B-H-B), -7.38 (1H, d, <sup>1</sup>J<sub>HRh</sub> = 56.6 Hz, B–H–Rh), –10.1 (1H, q,  ${}^{1}J_{HRh} \approx {}^{2}J_{PP}$  = 22 Hz, Rh–H). <sup>31</sup>P–{<sup>1</sup>H} NMR (162 MHz; CDCl<sub>3</sub>; 298 K):  $\delta$  32.9 (1P, dd, <sup>1</sup>J<sub>PRh</sub> = 97 Hz,  ${}^{2}J_{PP}$  = 22 Hz, PPh<sub>3</sub>), 14.4 (1P, d br,  ${}^{1}J_{PRh}$  = 116 Hz, PMe<sub>2</sub>Ph).

[8,8,8-(H)(PMe<sub>3</sub>)(PPh<sub>3</sub>)-9-(Py)-nido-8,7-RhSB<sub>9</sub>H<sub>10</sub>]<sup>+</sup> (15). A Schlenk tube, immersed in an isopropanol/dry ice bath at -15 °C, was charged (under an atmosphere of argon) with 20 mg (0.030 mmol) of [8,8,8-(H)(PMe<sub>3</sub>)(PPh<sub>3</sub>)-9-(Py)-nido-8,7-RhSB<sub>9</sub>H<sub>9</sub>] (5), 10 mL of CD<sub>2</sub>Cl<sub>2</sub> and 2.69 µL (0.030 mmol) of TfOH. The reaction mixture was stirred for 15 minutes. The solvent was then removed in vacuo and the residue was washed three times with hexane to yield 16.0 mg of 15 (0.019 mmol, 66%).  ${}^{1}H{-}{}^{11}B$  NMR (400 MHz,  $CD_2Cl_2$ , 300 K):  $\delta$  8.86 (2H, d, <sup>2</sup>*J*<sub>HH</sub> = 5.5 Hz, *H*<sub>o</sub>-NC<sub>5</sub>H<sub>5</sub>), 8.32 (1H, t, *H*<sub>p</sub>-NC<sub>5</sub>H<sub>5</sub>), 7.85 (2H, t, H<sub>m</sub>-NC<sub>5</sub>H<sub>5</sub>), 7.62 and 7.20 (15H, m, PPh<sub>3</sub>), 1.42 (6H, d,  ${}^{2}J_{HP}$  = 11.1 Hz, PMe<sub>3</sub>).  ${}^{31}P-{}^{1}H$  NMR (162 MHz; CDCl<sub>3</sub>; 298 K):  $\delta$  33.9 (1P, dd, <sup>1</sup>*J*<sub>PRh</sub> = 110 Hz, <sup>2</sup>*J*<sub>PP</sub> = 22 Hz,  $PPh_3$ ), 6.3 (1P, dd,  ${}^{1}J_{PRh} = 104$  Hz,  ${}^{2}J_{PP} = 22$  Hz,  $PMe_3$ ). NMR <sup>19</sup>F-{<sup>1</sup>H} (282 MHz; CD<sub>2</sub>Cl<sub>2</sub>; 300 K):  $\delta$  -78.2 (3F, s, OTf). LRMS (MALDI<sup>+</sup>/DIT): m/z calcl. for C<sub>26</sub>H<sub>40</sub>B<sub>9</sub>NP<sub>2</sub>RhS: 659  $[M - 2H]^+$ ; found 659. Calcl. for C<sub>23</sub>H<sub>29</sub>B<sub>9</sub>NPRhS: 583 [M - (2H + $PMe_3$ ]<sup>+</sup>; found 58. Isotope envelopes match those calculated from the known isotopic abundances of the constituent elements.

 $[8,8,8-(H)(PMePh_2)_2-9-(PMePh_2)-nido-8,7-RhSB_9H_{10}]^+$  (16). To 7 mL of a dichloromethane solution of  $[8,8,8-(H)(PMePh_2)_2-$  9-(PMePh<sub>2</sub>)-*nido*-8,7-RhSB<sub>9</sub>H<sub>10</sub>] (6) (45.6 mg; 0.054 mmol) was added 5 µL (0.054 mmol) of triflic acid (HOTf). After 30 min of stirring at -30 °C under an argon atmosphere, the solvent was removed under vacuum and the residue was washed three times with hexane to afford 41.7 mg of compound **16** (0.072 mmol, 78%). NMR <sup>1</sup>H-{<sup>11</sup>B} (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$  7.80 to 6.65 (30H, m, PMePh<sub>2</sub>), 2.24 (3H, d, <sup>2</sup>J<sub>HP</sub> = 13.2 Hz, PMePh<sub>2</sub>), 2.11 (3H, d, <sup>2</sup>J<sub>HP</sub> = 11.2 Hz, PMePh<sub>2</sub>), 2.07 (3H, d, <sup>2</sup>J<sub>HP</sub> = 10.0 Hz, PMePh<sub>2</sub>). NMR <sup>31</sup>P-{<sup>1</sup>H} (202 MHz; CD<sub>2</sub>Cl<sub>2</sub>; 298 K):  $\delta$  28.8 (1P, d, <sup>1</sup>J<sub>PRh</sub> = 121 Hz, PMePh<sub>2</sub>), 10.0 (1P, dd, <sup>1</sup>J<sub>PRh</sub> = 99.5 Hz, <sup>2</sup>J<sub>PP</sub> = 28 Hz, PMePh<sub>2</sub>), 2.6 (1P, q, B-PMePh<sub>2</sub>). LRMS (MALDI<sup>+</sup>/DIT): *m*/*z* calcl. for C<sub>39</sub>H<sub>50</sub>B<sub>9</sub>P<sub>3</sub>RhS: 843 [M]<sup>+</sup>; found 843, the isotope envelope matches that calculated from the known isotopic abundances of the constituent elements.

 $[1,3-\mu-(H)-1,1-(PMe_2Ph)_2-3-(Py)-isonido-1,2-RhSB_9H_8]^+$ (18). To 0.3 mL of a CD<sub>2</sub>Cl<sub>2</sub> solution of neutral [1,1-(PMe<sub>2</sub>Ph)<sub>2</sub>-3-(Py)-isonido-1,2-RhSB<sub>9</sub>H<sub>8</sub>] (8) (3.8 mg; 0.064 mmol) in a 5 mm NMR tube was added 0.57 µL of TfOH. The initial red colour of the solution turned into yellow upon addition of the strong acid. The reaction was studied by multinuclear NMR spectroscopy, showing a quantitative protonation of 8 to give 18. Spectral data of **18**: NMR  ${}^{1}H - \{{}^{11}B\}$  (300 MHz; CD<sub>2</sub>Cl<sub>2</sub>; 298 K):  $\delta$  9.23 (2H, d,  ${}^{3}J_{HH}$  = 5.4 Hz,  $H_{o}$ -NC<sub>5</sub>H<sub>5</sub>), 8.58 (1H, t,  ${}^{3}J_{HH}$  = 7.8 Hz,  $H_p$ -NC<sub>5</sub>H<sub>5</sub>), 8.14 (2H, t,  ${}^{3}J_{HH} = 7.8$  Hz,  $H_m$ -NC<sub>5</sub>H<sub>5</sub>), 1.55 (6H,  $[AX_3]_2$  spin system, N =  ${}^2J_{HP} + {}^4J_{HP} = 10.5$  Hz, PMe<sub>2</sub>Ph), 1.48 (6H,  $[AX_3]_2$  spin system, N =  ${}^2J_{HP}$  +  ${}^4J_{HP}$  = 10.2 Hz, PMe<sub>2</sub>Ph). <sup>31</sup>P NMR (121 MHz;  $CD_2Cl_2$ ; 298 K):  $\delta$  0.51 (2P, d,  ${}^{1}J_{PRh} = 100$  Hz, PMe<sub>2</sub>Ph). NMR  ${}^{19}F-\{{}^{1}H\}$  (282 MHz; CD<sub>2</sub>Cl<sub>2</sub>; 300 K):  $\delta$  -78.8 (3F, s, OTf). LRMS (MALDI<sup>+</sup>/DIT): m/z calcl. for  $C_{21}H_{36}B_9NP_2RhS$ : 597  $[M]^+$ ; found 597. Calcl. for  $C_{13}H_{25}B_9NPRhS$ : 458 [M – PMe<sub>2</sub>Ph]<sup>+</sup>; found 521. Isotope envelopes match those calculated from the known isotopic abundances of the constituent elements.

[1,3- $\mu$ -(H)-1,1-(PMe<sub>2</sub>Ph)(PPh<sub>3</sub>)-3-(Py)-*isonido*-1,2-RhSB<sub>9</sub>H<sub>8</sub>]<sup>+</sup> (21). Obtained in the reaction of 14 with TfOH as described above, it was characterized *in situ*. <sup>1</sup>H–{<sup>11</sup>B} NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$  1.59 (3H, d, <sup>2</sup>J<sub>HP</sub> = 10.5 Hz, PMe<sub>2</sub>Ph), 1.39 (3H, d, <sup>2</sup>J<sub>HP</sub> = 10.6 Hz, PMe<sub>2</sub>Ph), -5.51 (1H, ddd, <sup>1</sup>J<sub>HRh</sub> = 23 Hz, <sup>2</sup>J<sub>HP</sub> = 14 Hz, <sup>2</sup>J<sub>HP</sub> = 17 Hz, B–H–Rh). <sup>31</sup>P–{<sup>1</sup>H} NMR (162 MHz; CD<sub>2</sub>Cl<sub>2</sub>; 298 K):  $\delta$  35.9 (1P, dd, <sup>1</sup>J<sub>PRh</sub> = 110 Hz, <sup>2</sup>J<sub>PP</sub> = 20 Hz, PPh<sub>3</sub>), -1.5 (1P, dd, <sup>1</sup>J<sub>PRh</sub> = 100 Hz, <sup>2</sup>J<sub>PP</sub> = 20 Hz, PMe<sub>2</sub>Ph).

[1,3-μ-(H)-1,1-(PMePh<sub>2</sub>)<sub>2</sub>-3-(Py)-*isonido*-1,2-RhSB<sub>9</sub>H<sub>8</sub>]<sup>+</sup> (22). A 14.6 mg (0.02 mmol) amount of [8,8,8-(H)(PMePh<sub>2</sub>)<sub>2</sub>-9-(Py)*nido*-8,7-RhSB<sub>9</sub>H<sub>9</sub>] (3) was dissolved in 10 mL of dichloromethane in a Schlenk tube immersed in a dry-ice bath at –25 °C. Then TfOH (1.8 μL, 0.020 mmol) was added, and the reaction mixture was stirred for 1 h at –25 °C. The solvent was then removed *in vacuo* and the residue was washed three times with hexane to yield 11.0 mg of 22 (0.013 mmol, 63%). NMR <sup>1</sup>H–{<sup>11</sup>B} (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 9.05 (2H, d, <sup>2</sup>J<sub>HH</sub> = 5.6 Hz, *H*<sub>0</sub>-NC<sub>5</sub>H<sub>5</sub>), 8.61 (1H, t, *H*<sub>p</sub>-NC<sub>5</sub>H<sub>5</sub>), 8.14 (2H, t, *H*<sub>m</sub>-NC<sub>5</sub>H<sub>5</sub>), 7.83 a 6.89 (20H, m, PMePh<sub>2</sub>), 1.84 (6H, [AX<sub>3</sub>]<sub>2</sub> spin system, N = <sup>2</sup>J<sub>HP</sub> + <sup>4</sup>J<sub>HP</sub> = 8.6 Hz n, 2PMePh<sub>2</sub>). NMR <sup>31</sup>P–{<sup>1</sup>H} (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ 12.3 (2P, d, <sup>1</sup>J<sub>PRh</sub> = 141 Hz, PMePh<sub>2</sub>). NMR <sup>19</sup>F-{<sup>1</sup>H} (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$  -78.5 (3F, s, OTf). LRMS (MALDI<sup>+</sup>/DIT): *m/z* calcl. for C<sub>31</sub>H<sub>40</sub>B<sub>9</sub>NP<sub>2</sub>RhS: 721 [M]<sup>+</sup>; found 721. Calcl. for C<sub>18</sub>H<sub>27</sub>B<sub>9</sub>NPRhS: 521 [M – PMePh<sub>2</sub>]<sup>+</sup>; found 521. Isotope envelopes match those calculated from the known isotopic abundances of the constituent elements.

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