Unusual Cationic Rhodathiaboranes: Synthesis
and Characterization of $[8,8,8-(H)(PR_3)_2-9-(Py)-nido-8,7-RhSB_9H_{10}]^+$ and $[1,3-\mu-(H)-1,1-(PR_3)_2-3-(Py)-isonido-1,2-RhSB_9H_8]^+$

Beatriz Calvo, Ramón Macías,* Maria Jose Artigas, Fernando J. Lahoz
and Luis A. Oro

ISQCH, Universidad de Zaragoza-CSIC, C/Pedro Cerbuna 12, 50009 Zaragoza, Spain; E-mail:
King Fahd University of Petroleum and Minerals, KFUPM, Visting professor, Dhahran, 31261,
Saudi Arabia.

Departamento de Química Física-BIFI, Universidad de Zaragoza, 50009-Zaragoza, Spain.

E-mail: rmacias@unizar.es

28 September 2014

GRAPHICAL ABSTRACT

A unique set of polyhedral boron-based clusters is reported to exhibit remarkable structural non-rigidity with potential in bond activation.

ABSTRACT

The treatment of the hydridorhodathiaboranes, $[8,8,8-(\text{H})(\text{PR}_3)_2-9-(\text{Py})\text{-}n\text{id}\text{o}-8,7\text{-RhSB}_9\text{H}_9]$, where $\text{PR}_3 = \text{PPh}_3$ (**2**), PMePh_2 (**3**), PPh_3 and PMe_2Ph (**4**), or PMe_3 and PPh_3 (**5**), and $[8,8,8-(\text{H})(\text{PMePh}_2)_2-9-(\text{PMePh}_2)\text{-}n\text{id}\text{o}-8,7\text{-RhSB}_9\text{H}_9]$ (**6**), with TfOH affords $[8,8,8-(\text{H})(\text{PR}_3)_2-9-(\text{Py})\text{-}n\text{id}\text{o}-8,7\text{-RhSB}_9\text{H}_{10}]^+$ cations, where $\text{PR}_3 = \text{PPh}_3$ (**12**), PMePh_2 (**13**), PPh_3 and PMe_2Ph (**14**), or PMe_3 and PPh_3 (**15**), and $[8,8,8-(\text{H})(\text{PMePh}_2)_2-9-(\text{PMePh}_2)\text{-}n\text{id}\text{o}-8,7\text{-RhSB}_9\text{H}_{10}]^+$ (**16**). Compounds **13** and **14** lose H_2 to give $[1,3\text{-}\mu\text{-(H)-}1,1\text{-(PR}_3)_2\text{-}3\text{-(Py)-}i\text{sonido-}1,2\text{-RhSB}_9\text{H}_8]^+$, where $\text{PR}_3 = \text{PMe}_2\text{Ph}$ (**18**), PPh_3 and PMe_2Ph (**21**), or PMePh_2 (**22**). Similarly, the 11-vertex rhodathiaboranes, $[1,1\text{-(PR}_3)_2\text{-}3\text{-(Py)-}1,2\text{-RhSB}_9\text{H}_8]$, where $\text{PR}_3 = \text{PPh}_3$ (**7**), PMe_2Ph (**8**), PMe_3 (**9**), or PPh_3 and PMe_3 (**10**), react with TfOH to give the corresponding cations, $[1,3\text{-}\mu\text{-(H)-}1,1\text{-(PR}_3)_2\text{-}3\text{-(Py)-}i\text{sonido-}1,2\text{-RhSB}_9\text{H}_8]^+$, where $\text{PR}_3 = \text{PPh}_3$ (**17**), PMe_2Ph (**18**), PMe_3 (**19**), or PPh_3 and PMe_3 (**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.

INTRODUCTION

Polyhedral boron-containing compounds exhibit unique electronic properties, geometries, and extraordinary versatility that are interesting for a variety of applications, including medicine, health and nutrition, boron neutron capture therapy, optoelectronics, energy storage and nanomaterial.^{1, 2} 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 in their structures, being, by far, the most ubiquitous members of polyhedral heteroboranes: cages that incorporate elements of the p-block of the Periodic Table.

The deltahedral structures of polyhedral boron clusters are supported by a highly delocalized three-dimensional bonding that leads to cluster aromaticity.^{3, 4} The resulting three-dimensional geometries of these molecules provide a 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 the Periodic Table, leading to the synthesis of a huge number of metallaheteroboranes, in which many times the heteroborane fragment can be regarded a surrogate of well-known organic ligands.⁵⁻¹⁴

Bearing in mind that tunable ligands for transition metals is 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.^{2, 15} In addition, heteroboranes can act as substituents changing the steric and/or electronic properties of classical ligands.¹⁶⁻²⁰

It is clear, therefore, that heteroboranes have a huge potential for creating catalysts tailored to

specific needs. In this regards, the use of carboranes as ligands of transition metal complexes has been extensively explored with very interesting results.^{2, 16, 21-23} And of special interest to our work is the intensely studied hydridorhodathiaborane, $[3,3,3-(H)(PPh_3)_2-3,1,2-RhC_2B_9H_{11}]$,²⁴ which undergoes rapid and reversible *closo-nido* tautomerism that is the key of its catalytic activity in, for example, the hydrogenation and isomerization of olefins. This illustrates an interesting dichotomy dealing with polyhedral boron-containing compounds: clusters such as icosahedral carboranes and boranes are among the most thermodynamically 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.^{25, 26}

Although the possibility of utilizing the structural flexibility of metallaboranes in catalytic reactions has been investigated,^{24, 27} polyhedral boron-containing compounds show a marked lack of examples in which the stereochemical non-rigidity of the cluster leads to bond activation and ultimately to catalysis, the most studied system being the commented hydridorhodathiaborane reported by Hawthorne and co-workers.^{24, 28, 29}

Scheme 1 Proton assisted hydrogen activation.

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-aracno* structural transformation.

In our recent work dealing with the reaction chemistry of the unsaturated 11-vertex

rhodathiaborane, [8,8,8-(PPh₃)₂-*nido*-8,7-RhSB₉H₁₀] (**1**), we have demonstrated that the *nido-closo* structural and redox flexibility of pyridine-bound rhodathiaboranes, [8,8,8-(H)(PPh₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] (**2**) and [1,1-(PPh₃)₂-3-(Py)-*isonido*-1,2-RhSB₉H₈] 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.³⁰⁻³²

In an attempt to modify the reactivity of these clusters, we have already carried out substitution of the *exo*-polyhedral PPh₃ ligands in **1** and **2** with the more basic (less bulky) monodentate phosphines, PMe₃, PMe₂Ph and PPh₂Me. This substitutional chemistry has provided a series of new hydridorhodathiaboranes of general formulation, [8,8,8-(H)(PR₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉], where PR₃ = PPh₃ (**2**),³¹ PMePh₂ (**3**),³³ PPh₃ and PMe₂Ph (**4**),³³ or PPh₃ and PMe₃ (**5**).³³ The PMePh₂-substituted analogue, [8,8,8-(H)(PMePh₂)₂-9-(PMePh₂)-*nido*-8,7-RhSB₉H₉] (**6**),³⁴ is available from the reaction of **1** with PMePh₂.³⁴ The thermal dehydrogenation of **2-5** affords *isonido*-derivatives, [1,1-(L)₂-3-(Py)-1,2-RhSB₉H₈], where L = PPh₃ (**7**), PMe₂Ph (**8**), PMe₃ (**9**), PPh₃ and PMe₃ (**10**), or PPh₃ and PMe₂Ph (**11**).

As yields are generally good, these 11 vertex *nido*- and *isonido*-rhodathiaboranes constitute subjects for further reaction chemistry. Most recently, the 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).^{35, 36}

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,³⁷⁻³⁹ and it is relevant to many catalytic processes, to our knowledge, there are few examples of cationic metallaheteroboranes formed upon treatment with Brønsted acids.⁴⁰ In fact, the large majority of cationic metallaheteroboranes are based on charged-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.⁴¹⁻⁴⁶

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

Given the unique properties of polyhedral boron-containing compounds, commented in this introduction, and our recent discovery that protonation of rhodathiaboranes leads to an enhancement of non-rigidity in the metal-thiaborane linkage,³⁵ this series of cationic rhodathiaboranes represent 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 the protonation of the *nido*-cage to give the corresponding polyhedral cations, $[8,8,8\text{-}(\text{H})(\text{PR}_3)_2\text{-}9\text{-(Py)-}nido\text{-}8,7\text{-RhSB}_9\text{H}_{10}]^+$, where $\text{PR}_3 = \text{PPh}_3$ (**12**),³⁶ PMePh_2 (**13**), PPh_3 and PMe_2Ph (**14**), PPh_3 and PMe_3 (**15**), and $[8,8,8\text{-}(\text{H})(\text{PMePh}_2)_2\text{-}9\text{-(PMePh}_2\text{)-}nido\text{-}8,7\text{-RhSB}_9\text{H}_{10}]^+$ (**16**) (Scheme 2).

Scheme 2 Protonation of 11-vertex *nido*-rhodathiaboranes.

These polyhedral *nido*-cations have been characterized by multinuclear NMR spectroscopy, mass spectrometry, combined with DFT-calculations. Table 1 gathers ^{11}B and ^1H NMR data of compounds, **12**, **15** and **16**. Additional ^1H and $^{31}\text{P}\{-^1\text{H}\}$ NMR data, assigned to *exo*-polyhedral ligands, can be found in the experimental section.

Fig. 1 Diagram that represents 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.

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

Table 1 ^{11}B and ^1H NMR data for $[\text{8,8,8-(H)(PPh}_3)_2\text{-9-(Py)-nido-8,7-RhSB}_9\text{H}_{10}]^+$ (**12**) and $[\text{8,8,8-(H)(PMe}_3\text{)(PPh}_3\text{)-9-(Py)-nido-8,7-RhSB}_9\text{H}_{10}]^+$ (**15**), and $[\text{8,8,8-(H)(PMePh}_2)_2\text{-9-(PMePh}_2\text{)-nido-8,7-RhSB}_9\text{H}_{10}]^+$ (**16**) in CD_2Cl_2 compared to the corresponding DFT/GIAO-calculated ^{11}B -nuclear shielding values [in brackets]

Assign. ^a	12			15			16		
	$\delta(^{11}\text{B})$	$\delta(^1\text{H})$		$\delta(^{11}\text{B})$	$\delta(^1\text{H})$		$\delta(^{11}\text{B})$	$\delta(^1\text{H})$	
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
$\mu(11, 10)$			-4.32			-4.41			-4.19
$\mu(9, 8)$			-7.9 ^b			-7.13 ^c			-8.70 ^d
Rh(8)-H			-9.84 ^e			-10.28 ^f			-10.98 ^g

^a Assignments based on $^1\text{H}\{-^{11}\text{B}\}$ selective experiments and DFT calculations. ^b Broad doublet: 60 Hz. ^c Broad doublet: 57 Hz. ^d Broad doublet: 58 Hz. ^e Apparent quartet: $^1J(^{103}\text{Rh}-^1\text{H}) + ^2J(^{31}\text{P}_\text{A}-^1\text{H}) + ^2J(^{31}\text{P}_\text{B}-^1\text{H}) \approx 15$ Hz. ^f $^1J(^{103}\text{Rh}-^1\text{H}) = 16.3$ Hz. ^g Apparent quartet: $^1J(^{103}\text{Rh}-^1\text{H}) + ^2J(^{31}\text{P}_\text{A}-^1\text{H}) + ^2J(^{31}\text{P}_\text{B}-^1\text{H}) \approx 19$ Hz, $^1J(^{103}\text{Rh}-^1\text{H}) = 20.2$ Hz. ^h Apparent quartet: $^1J(^{103}\text{Rh}-^1\text{H}) + ^2J(^{31}\text{P}_\text{A}-^1\text{H}) + ^2J(^{31}\text{P}_\text{B}-^1\text{H}) \approx 18$ Hz, $^1J(^{103}\text{Rh}-^1\text{H}) = 17.1$ Hz

The main difference that can be noted in the ^{11}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 the positions 2 and 5 in the cluster (Figure 1), suggesting that there has been an important change in the $\{\text{Rh(H)(L)}_2\}-\{\eta^4\text{-SB}_9\text{H}_9(\text{Py})\}$ bonding interaction upon protonation of the cluster (*vide infra*). The effect in the $^{13}\text{P}\{-^1\text{H}\}$ spectra with respect the neutral counterparts depends on the nature of the PR_3 ligands (see Supporting Information, Figures 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 strong influence of the proton on the *exo*-polyheral ligands.

Fig. 2 Negative region of $^1\text{H}\{-^{11}\text{B}\}$ 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*), result of protonation and dehydrogenation.

In the negative region of the $^1\text{H}\{-^{11}\text{B}\}$ NMR spectra, the *nido*-cations exhibit three signals (Figure 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 broad-band 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.

Fig. 3 DFT-optimized structures at the B3LYP/6-31G*/LANL2DZ level for (left) [8,8,8-(H)(PMe₃)(PPh₃)-9-(Py)-*nido*-8,7-RhSB₉H₁₀]⁺ (**15**), and (right) [8,8,8-(H)(PMePh₂)₂-9-(PMePh₂)-*nido*-8,7-RhSB₉H₁₀]⁺ (**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 the cases, the optimization ended with the bridging hydrogen atoms along the B(10)–B(11) and Rh(8)–B(9) edges (Figure 3). The calculated ¹¹B chemical shifts, gathered 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-(PR₃)₂-3-(Py)-1,2-RhSB₉H₈], where PR₃ = PPh₃ (**7**), PMe₃ (**9**), or PPh₃ and PMe₃ (**10**), react with TfOH to give 11-vertex cations of formulation [1,3-μ-(H)-1,1-(PR₃)₂-3-(Py)-*isonido*-1,2-RhSB₉H₈]⁺, where PR₃ = PPh₃ (**17**), PMe₃ (**19**), or PPh₃ and PMe₃ (**20**).³⁵ From [8,8,8-(H)(PMe₂Ph)(PPh₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**4**), the corresponding neutral *isonido*-cluster, [1,1-(PMe₂Ph)(PPh₃)-3-(Py)-1,2-RhSB₉H₈] (**11**), is always formed in a mixture with its *bis*-(PMe₂Ph)-ligated counterpart, [1,1-(PMe₂Ph)₂-3-(Py)-*isonido*-1,2-RhSB₉H₈] (**8**), complicating,

therefore, the isolation of these compounds, and of their protonated derivatives, $[1,3-\mu\text{-(H)}-1,1\text{-(PR}_3)_2\text{-3-(Py)-isonido-1,2-RhSB}_9\text{H}_8]^+$, where $\text{PR}_3 = \text{PPh}_3$ and PMe_2Ph (**21**) or PMe_2Ph (**18**). This can be inferred from Figure 2 where it is shown the negative region of a $^1\text{H}\{-^{11}\text{B}\}$ NMR spectrum that was measured few minutes after addition of TfOH to a solution of **4**: second trace from the top. This spectrum shows the formation of a mixture of cationic *bis*-(PPh_3)(PMe_2Ph)-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_2Ph)-ligated rhodathiaborane, **8**, can be synthesized selectively by treatment of the mixed (PMe_2Ph)(PPh_3)-ligated *nido*-parent compound, **4**, with excess of PMe_2Ph . 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_3)(PMe_2Ph)-ligated counterpart, **21**, was characterized by multinuclear NMR spectroscopy in mixtures such as that illustrated in Figure 2 above.

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

The *bis*-(PMePh_2)-ligated *isonido*-rhodathiaborane, analogue of **7-9**, is not available from the

thermal treatment of [8,8,8-(H)(PMePh₂)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] (**3**), precluding the formation of the *isonido*-cation, [1,3-μ-(H)-1,1-(PMePh₂)₂-3-(Py)-1,2-RhSB₉H₈]⁺ (**22**) by direct protonation of its hypothetical conjugate base, [1,1-(PMePh₂)₂-3-(Py)-*isonido*-1,2-RhSB₉H₈]. However, treatment of **3** with TfOH affords selectively the product of protonation and H₂ lost, compound **22** (see Figure S3 included in the supporting information for this paper).

Table 2 ¹¹B and ¹H NMR data for [1,3-μ-(H)-1,1-(PMe₂Ph)₂-3-(Py)-*isonido*-1,2-RhSB₉H₈]⁺ (**18**), [1,3-μ-(H)-1,1-(PMe₃)₂-3-(Py)-*isonido*-1,2-RhSB₉H₈]⁺ (**19**), [1,3-μ-(H)-1,1-(PMe₃)(PPh₃)-3-(Py)-*isonido*-1,2-RhSB₉H₈]⁺ (**20**), and [1,3-μ-(H)-1,1-(PMePh₂)₂-3-(Py)-*isonido*-1,2-RhSB₉H₈]⁺ (**22**) in CD₂Cl₂ compared to the corresponding DFT/GIAO-calculated ¹¹B-nuclear shielding values [in brackets]

	18			19			20			22		
Assign. ^a	δ(¹¹ B)	δ(¹ H)		δ(¹¹ B)	δ(¹ H)		δ(¹¹ B)	δ(¹ H)		δ(¹¹ B)	δ(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 ^c			-5.45 ^d		-5.28 ^e	

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

The ¹¹B and ¹H 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 the ¹¹B spectra of the protonated *isonido*-cluster suffers a slight deshielding with respect the neutral parent *isonido*-compounds, but maintaining a clear resemblance. Characteristic of this family of neutral and cationic 11-vertex *isonido*-rhodathioaboranes, is the presence of a high-frequency resonance of relative intensity 1 around

$\delta(^{11}\text{B})$ 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 $\delta(^{11}\text{B})$ 30 to -28 ppm. The $^{31}\text{P}\{-^1\text{H}\}$ spectra demonstrate the presence of the *exo*-polyhedral ligands in each of the cationic *isonido*-clusters (Figure S4). It is interesting to note that upon protonation the Me-containing phosphine ligands, PMe_3 and PMe_2Ph , suffer a shift to higher frequencies whereas the PPh_3 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 $^1\text{H}\{-^{11}\text{B}\}$ and ^1H 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 $\delta(^1\text{H})$ - 5.0 to -7.0 ppm, which broadens when the boron broad-band decoupling is turned off (Figure 4). $^1\text{H}\{-^{11}\text{B}(\text{sel})\}$ experiments that relate $\delta(^1\text{H})$ to corresponding directly bound $\delta(^{11}\text{B})$, 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 the protonation takes place along the Rh(1)–B(3) edge. Therefore, the presence of these low-frequency multiplets in the $^1\text{H}\{-^{11}\text{B}\}$ NMR spectra is diagnostic of formation of the *isonido*-cations. The chemical shift of this resonance moves towards low frequencies as the phenyl rings on the PR_3 ligands are substituted by methyl groups (Figure 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_3 species, **17**, is only seen at low temperatures.³⁵

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

X-ray diffraction analysis of $[\text{1,3-}\mu\text{-(H)-1,1-(PMe}_3\text{)(PPh}_3\text{)-3-(Py)-1,2-RhSB}_9\text{H}_8\text{]}^+$ (**20**)

Two crystals of this cationic rhodathiaborane were grown by slow diffusion of hexane into TfOH acidified solutions of the neutral parent compound, $[\text{1,1-(PMe}_3\text{)(PPh}_3\text{)-3-(Py)-1,2-RhSB}_9\text{H}_8]$ (**10**), in dichloromethane and in acetone. The crystal obtained from CH_2Cl_2 / hexane, **20a**, showed an uncommon case of conformational isomerism.⁴⁷ This feature was commented in a previous publication,³⁵ 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_2CO / hexane, **20b**. This crystallographic analysis is combined with DFT-calculations to estimate energy variations driven by $\{\text{Rh}(\text{PR}_3)_2\}\text{-}\{\eta^n\text{-SB}_9\text{H}_8(\text{Py})\}$ conformational changes.

The X-ray diffraction analysis of crystals **20a** and **20b** have given rise to four $[\text{1,3-}\mu\text{-(H)-1,1-(PMe}_3\text{)(PPh}_3\text{)-3-(Py)-1,2-RhSB}_9\text{H}_8]^+$ structural isomers: three in the unit cell of **20a**, labeled as

isonido-20a₁, *isonido-20a₂* and *nido-20a₃*; and one in crystal **20b**, labeled *isonido-20b*. Of special relevance are the distances that define the rhodium–thiaborane interaction in these conformational isomers. The interatomic-length pattern of this linkage is illustrated in Figure 6 for: (a) the cationic cluster, *isonido-20b*, (b) its DFT-optimized structure, (c) the conformer, *nido-20a₃*, (d) compound **10**, (e) cluster **7**, and (f) the parent rhodathiaborane, **1**. Table 3 gathers additional Rh–B distances and angles for these compounds.

Fig. 5 ORTEP-type of drawing of $[1,3\text{-}\mu\text{-(H)}\text{-}1,1\text{-(PMe}_3\text{)}\text{(PPh}_3\text{)}\text{-}3\text{-(Py)}\text{-isonido-}1,2\text{-RhSB}_9\text{H}_8]^+$ in crystal **20b**. Only the *ipso*-carbon atoms on the phenyl rings of the PPh₃ ligand are included to aid clarity. Ellipsoids are shown at 50 % probability levels.

The first noticeable difference of the protonated clusters *versus* the neutral counterparts is an elongation of the distances that involve the $\{\text{Rh(PMe}_3\text{)}\text{(PPh}_3\text{)}\}\text{-}\{\text{SB}_9\text{H}_8\text{(Py)}\}$ interaction as well as the *exo*-polyhedral Rh–P lengths. In particular, the conformers, *isonido-20a₁*, *isonido-20a₂* 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 would be of the order 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.

Fig. 6 Detail 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*₃. Together with: (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**)

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

Table 3. Selected lengths [Å] and angles [°] of crystallographically determined neutral parent compounds [1,1-(PPh₃)₂-3-(Py)-*isonido*-1,2-RhSB₉H₈] (**7**) and [1,1-(PMe₃)(PPh₃)₂-3-(Py)-*isonido*-1,2-RhSB₉H₈] (**10**), together with the crystallographically determined, [1,3-μ-(H)-1,1-(PMe₃)(PPh₃)-3-(Py)-1,2-RhSB₉H₈]⁺, *isonido*-**20b**, and DFT-calculated [1,3-μ-(H)-1,1-(PPh₃)₂-3-(Py)-1,2-RhSB₉H₈]⁺ (**7a**).^a

	7	7a	10	<i>isonido</i> - 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]

^a DFT-calculated values in brackets.

In the neutral cluster [Figure 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*-PPh₃-ligated analogue, [1,1-(PPh₃)₂-3-(Py)-1,2-RhSB₉H₈] (**7**) [Figure 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*-**20a₃**, 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 conformer *nido*-**20a₃** with crystallographically determined [8,8-(PPh₃)₂-*nido*-8,7-RhSB₉H₁₀] (**1**) [Figure 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 Rh(1) center and at 1.330 Å from the B(3) vertex, which after the 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) [Figure 6 (b) and Figure 7].

Notice that in the calculated structures the Rh(1)–B(4) and Rh(1)–B(5) lengths are substantially elongated with respect the experimental values (Figure 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) where the cluster is protonated. This supports the commented experimental data, giving further indication that the Rh(1)–H–B(3) bridging-bound hydrogen atom, fully characterized in solution, exerts a strong influence to 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 changes and the observed anion / cation packing motifs commented below, are clear proofs 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-20a₃*, 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 crystallographically determined, [8,8-(PPh₃)₂-8,7-RhSB₉H₁₀] [Figure 6 (f)], which is isoelectronic with the cationic

pyridine adduct. This suggests that in the solid state the *nido*-conformer, **20a₃**, could exhibit the hydrogen atom, arising from protonation, at the B(9)–B(10) edge rather than along the Rh(8)–B(9), as suggested by the *isonido*-configuration (Figure 7).

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, $[(\text{PMe}_3)(\text{PPh}_3)(\text{Py})\text{RhSB}_9\text{H}_9]^+$.

In any event, the DFT-calculated energy difference between the optimized *nido*-structure and the *isonido*-cation is 2.5 kcal/mol (Figure 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 kcal/mol, that hydrogen bond strengths are generally estimated to be in the range 1 to 10 kcal/mol, and that the differences in lattice energy among different polymorphic forms is expected to be in the range 1 to 2 kcal/mol.⁴⁹ Therefore, the DFT-calculated *nido*- and *isonido*-energy minima for the polyhedral cation, $[(\text{PMe}_3)(\text{PPh}_3)\text{RhSB}_9\text{H}_9(\text{Py})]^+$, 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 crystal **20a**, the *nido*-cations, **20a₃**, form dimers via π - π interactions between the pyridine rings. The configuration of the pyridine rings in the dimer fall into the category of parallel-displaced,⁵⁵ and an inversion centre relates both pyridine-substituted clusters (Figure 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 (Figure 9). There is one crystallographically independent triflate anion at 3.780 Å from the pyridine rings, following the *nido*-rodathiaborane cations alongside the *a* axis.

Alternatively, both *isonido*-conformers, **20a₁** and **20a₂**, associate in pairs through sextuple phenyl embrace (SPE) interactions (Figure 10). The P $\cdots$ P separation and the Rh-P $\cdots$ P-Rh colinearity are 6.9 Å and 173°, respectively, and fall in the range reported for this attractive edge-to-face interaction (Figure 10).⁵⁶ The resulting rhodathiaborane dimers pack along the *a*-axis, forming two crystallographically independent ribbons (blue and green in Figure 9). Each dimer interleaves between two {RhSB₉}-heads of dimers on adjacent ribbons, leading to relative 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 on the *ab* plane: two of these layers sandwich a layer of *nido*-cages (Figure 9).

Fig. 8 Dimer of *nido*-conformers, **20a₃**, stabilized by pyridine π - π interactions.

Fig. 9 Crystal packing of **20a** along the *a* axis: in red the layer of *nido*-conformers, **20a₃**; in blue and green the *isonido*-conformers, **20a₁** and **20a₂**

Similarly, the *isonido*-clusters found in the crystal **20b** exhibit the attractive interactions of the phenyl groups of adjacent clusters forming dimers. This basic supramolecular motif packs

in the same fashion than 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 (Figure 11).

Fig. 10 Detail of the intermolecular SPE involving the PPh₃ 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.

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 $\cdots$ O length at 3.278 Å). As illustrated in Figure 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, π - π 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 *pseudo*- C_s symmetry. We should bear in mind that π - π pyridine binding energies have been calculated to be in the range 2.2 to 3.8 kcal/mol,⁵⁵ and that an edge-to-face attractive interaction of a phenyl ring within a SPE is estimated to be 2.4 kcal/mol to 3.3 kcal/mol.⁵⁶ It is clear that given the proximity of cluster conformational energies between the *nido*- and *isonido*-rhodathiaborane 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.

Scheme 4 Stepwise reactions of 11-vertex rhodathiaboranes with HCl and TfOH.

General considerations Conclusions

11-vertex *nido*- and *izonido*-rhodathiaboranes are easily protonated by TfOH to afford *nido*- and *izonido*-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.^{39-46, 57-63} It is important to recall that the majority of reported cationic metallaheteroboranes generally contain charge-compensating ligands,⁴¹⁻⁴⁶ and the number of cationic polyhedral boron clusters formed by simple protonation is very small indeed.^{39, 40}

The herein reported reactions with TfOH together with previous results with HCl,^{36, 64} 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[−] *versus* TfO[−]. Thus, upon protonation with HCl, the putative cationic species suffer the attack of the chlorine anion, leading to the formal incorporation of HCl in the cluster framework, which in the case of the *isonido*-clusters results in an 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 similar fashion, the neutral *nido*-reagents undergo formal HCl addition and H₂ liberation, followed, in some cases, by PPh₃ 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 *nido*-clusters undergo H₂ lost and *nido*→*isonido* transformations; but more spectacular is the lability of the *bis*-PPh₃-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–tiaborane linkage upon protonation enables the formation of different structural isomers that in the case of the cation, [1,3-μ-(H)-1,1-(PMe₃)(PPh₃)-3-(Py)-*isonido*-1,2-RhSB₉H₈]⁺, 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 boron-containing compounds, which may be useful in the activation of un-reactive 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)(PR₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉], where PR₃ = PPh₃ (**2**), PMePh₂ (**3**), PPh₃ and PMe₂Ph (**4**), PPh₃ and PMe₃ (**5**); [8,8,8-(H)(PMePh₂)₂-9-(PMePh₂)-*nido*-8,7-RhSB₉H₉] (**6**), and [1,1-(PR₃)₂-3-(Py)-1,2-RhSB₉H₈] where PR₃ = PPh₃ (**7**), PMe₂Ph (**8**), PMe₃ (**9**), PPh₃ and PMe₃ (**10**), or PPh₃ and PMe₂Ph (**11**), were prepared by published methods.^{30, 33, 34} The synthesis and characterization of the cationic rhodathiaboranes, [8,8,8-(H)(PPh₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₁₀]⁺ (**12**), and [1,3-μ-(H)-1,1-(PR₃)₂-3-(Py)-*isonido*-1,2-RhSB₉H₉]⁺, where PR₃ = PPh₃ (**17**), PMe₃ (**19**), PPh₃ and PMe₃ (**20**), were reported previously.^{35, 36}

NMR spectra were recorded on Bruker Avance 300-MHz and AV 400-MHz spectrometers, using ¹¹B, ¹¹B-{¹H}, ¹H, ¹H{¹¹B}, ¹H{¹¹B(selective)} and ³¹P-{¹H} techniques. ¹H chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative to tetramethylsilane. ¹¹B chemical shifts were measured relative to [BF₃(OEt)₂]. ³¹P (121.48 MHz) chemical shifts were measured relative to H₃PO₄ (85%). Mass spectrometry data were recorded on a VG Autospec double focusing mass spectrometer, on a microflex MALDI-TOF, and on a ESQUIRE 3000+ API-TRAP, operating in either positive or negative modes. In each case there was an excellent correspondence between the calculated and measured isotopomer envelopes. A well-matched isotope pattern may be taken as a good criterion of

identity.⁶⁵

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 was 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 were performed on a Bruker Kappa APEX DUO CCD area detector diffractometer with monochromatic radiation $\lambda(\text{MoK}\alpha) = 0.7107073 \text{ \AA}$, using narrow frames (0.3° in ω). The data were reduced (SAINT)⁶⁶ and corrected for absorption effects by multiscan methods (SADABS).⁶⁷ The structure was solved using the SHELXS-86 program,⁶⁸ and refined against all F² data by full-matrix least-squares techniques (SHELXL-97).⁶⁹ 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- contains the supplementary crystallography data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

[8,8,8-(H)(PMePh₂)₂-9-(Py)-*nido*-8,7-RhSB₉H₁₀]⁺ (13**):** In a 5 mm NMR tube, a solution of **[8,8,8-(H)(PMePh₂)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] (**3**)** (0.0054 mg, 0.0075mmol) in CD₂Cl₂ (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. With time, this mixture of compound 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 hydridorhoadathiaborane (two conformers, see Figure S Supporting Information) and its *isonido*-derivative. NMR data: the A label corresponds to the major conformer and B to the minor. ^{11}B (128 MHz; CD_2Cl_2 ; 298 K): δ 15.6, 12.8, 6.8, 4.5, -11.2, -14.9, -21.0, -23.6. NMR $^1\text{H}\{-^{11}\text{B}\}$ (400 MHz, CD_2Cl_2 , 300 K): δ 10.64 (2H, d, $^3J_{\text{HH}} = 4.8$ Hz, $H_{\text{oA}}\text{-NC}_5\text{H}_5$), 10.36 (1H, t, $^3J_{\text{HH}} = 8.1$ Hz, $H_{\text{pA}}\text{-NC}_5\text{H}_5$), 10.19 (2H, d, $^3J_{\text{HH}} = 5.2$ Hz, $H_{\text{oB}}\text{-NC}_5\text{H}_5$), 10.02 (1H, t, $^3J_{\text{HH}} = 7.9$ Hz, $H_{\text{pB}}\text{-NC}_5\text{H}_5$), 9.66 (2H, t, $^3J_{\text{HH}} = 6.7$ Hz, $H_{\text{mA}}\text{-NC}_5\text{H}_5$), 9.50 (2H, m, $H_{\text{mB}}\text{-NC}_5\text{H}_5$), 9.6 to 8.7 (40H, m, PMePh_2), 3.88 (1H, s, BH), 2.58 (1H, s, BH), 2.36 (1H, s, BH), 2.29 (3H, d, $^2J_{\text{HP}} = 10.9$ Hz, $\text{PMe}_\text{A}\text{Ph}_2$), 2.16 (3H, d, $^2J_{\text{HP}} = 10.9$ Hz, $\text{PMe}_\text{B}\text{Ph}_2$), 1.90 (3H, d, $^2J_{\text{HP}} = 9.6$ Hz, $\text{PMe}_\text{B}\text{Ph}_2$), 1.81 (3H, d, $^2J_{\text{HP}} = 10.9$ Hz, $\text{PMe}_\text{A}\text{Ph}_2$), 1.62 (1H, s, BH), 1.12 (1H, s, BH), -4.28 (1H, s, BH_AB), -4.54 (1H, s, B-H_B-B), -5.18 (1H, m, Rh-H_B-B), -7.49 (1H, d br, $^1J_{\text{HRh}} \approx ^2J_{\text{PH}} = 60$ Hz, Rh-H_A-B), -10.16 (1H, apparent q, $^1J_{\text{HRh}} \approx ^2J_{\text{HP}} = 20.5$ Hz, Rh-H_A), -10.64 (1H, m, Rh-H_B). NMR $^{31}\text{P}\{-^1\text{H}\}$ (162 MHz; CD_2Cl_2 ; 298 K): δ 30.5 (1P, dd, $^1J_{\text{PRh}} = 121$ Hz, $^2J_{\text{PP}} = 25$ Hz, $\text{P}_\text{A}\text{MePh}_2$), 27.7 (1P, dd, $^1J_{\text{PRh}} = 136$ Hz, $^2J_{\text{PP}} = 22$ Hz, $\text{P}_\text{B}\text{MePh}_2$), 15.7 (1P, d-br, $^1J_{\text{PRh}} = 117$ Hz, $\text{P}_\text{A}\text{MePh}_2$), 12.5 (1P, dd, $^1J_{\text{PRh}} = 100$ Hz, $^2J_{\text{PP}} = 25$ Hz, $\text{P}_\text{A}\text{MePh}_2$).

[8,8,8-(H)(PMe₂Ph)(PPh₃)-9-(Py)-*nido*-8,7-RhSB₉H₉]⁺ (14): A 5 mm NMR tube was charged with 5.4 mg (0.0075 mmol) of [8,8,8-(H)(PMe₂Ph)(PPh₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**4**), 0.3 mL of CD_2Cl_2 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- μ -(H)-1,1-(PMe₂Ph)(PPh₃)-3-(Py)-*isonido*-1,2-RhSB₉H₈]⁺ (**21**) and [1,3- μ -(H)-1,1-(PMe₂Ph)₂-3-(Py)-*closio*-1,2-RhSB₉H₈]⁺ (**18**) in a 1:1:0.5, respectively. After several hours, the system evolves to give a mixture that contains the *isonido*-derivatives, **21** and **18** in a 1:0.3 ratio. **14**: $^1\text{H}\{-^{11}\text{B}\}$ NMR (400 MHz, CD_2Cl_2 , 300 K): δ 2.25 (6H, overlapped t, $^2J_{\text{HP}} = 13.6$ Hz, PMe_2Ph), -4.42 (1H, s, B-H-B), -7.38 (1H, d, $^1J_{\text{HRh}} = 56.6$ Hz, B-H-Rh), -10.1 (1H, q, $^1J_{\text{HRh}}$

$\approx {}^2J_{\text{PP}} = 22$ Hz, Rh-H). $^{31}\text{P}\{-^1\text{H}\}$ NMR (162 MHz; CDCl_3 ; 298 K): δ 32.9 (1P, dd, ${}^1J_{\text{PRh}} = 97$ Hz, ${}^2J_{\text{PP}} = 22$ Hz, PPh_3), 14.4 (1P, d br, ${}^1J_{\text{PRh}} = 116$ Hz, PMe_2Ph).

[8,8,8-(H)(PMe₃)(PPh₃)-9-(Py)-nido-8,7-RhSB₉H₁₀]⁺ (15): A Schlenk tube, immersed in an isopropanol/dry ice bath at -15 °C, was charged (under and atmosphere of argon) with 20 mg (0.030 mmol) of [8,8,8-(H)(PMe₃)(PPh₃)-9-(Py)-nido-8,7-RhSB₉H₉] (5), 10 mL of CD_2Cl_2 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 %). $^1\text{H}\{-^{11}\text{B}\}$ NMR (400 MHz, CD_2Cl_2 , 300 K): δ 8.86 (2H, d, ${}^2J_{\text{HH}} = 5.5$ Hz, $H_o\text{-NC}_5\text{H}_5$), 8.32 (1H, t, $H_p\text{-NC}_5\text{H}_5$), 7.85 (2H, t, $H_m\text{-NC}_5\text{H}_5$), 7.62 a 7.20 (15H, m, PPh_3), 1.42 (6H, d, ${}^2J_{\text{HP}} = 11.1$ Hz, PMe_3),. $^{31}\text{P}\{-^1\text{H}\}$ NMR (162 MHz; CDCl_3 ; 298 K): δ 33.9 (1P, dd, ${}^1J_{\text{PRh}} = 110$ Hz, ${}^2J_{\text{PP}} = 22$ Hz, PPh_3), 6.3 (1P, dd, ${}^1J_{\text{PRh}} = 104$ Hz, ${}^2J_{\text{PP}} = 22$ Hz, PMe_3]. NMR $^{19}\text{F}\{-^1\text{H}\}$ (282 MHz; CD_2Cl_2 ; 300 K): δ -78.2 (3F, s, OTf). LRMS (MALDI⁺/DIT): m/z calcl for $\text{C}_{26}\text{H}_{40}\text{B}_9\text{NP}_2\text{RhS}$: 659 $[\text{M}-2\text{H}]^+$; found 659. Calcl for $\text{C}_{23}\text{H}_{29}\text{B}_9\text{NPRhS}$: 583 $[\text{M}-(2\text{H}+\text{PMe}_3)]^+$; found 58. Isotope envelopes match those calculated from the known isotopic abundances of the constituent elements.

[8,8,8-(H)(PMePh₂)₂-9-(PMePh₂)-nido-8,7-RhSB₉H₁₀]⁺ (16): To 7 mL of a dichloromethane solution of [8,8,8-(H)(PMePh₂)₂-9-(PMePh₂)-nido-8,7-RhSB₉H₁₀] () (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 argón atmosphere, the solvent was removed under vacuo and the residue washed three time with hexane to afford 41.7 mg of compound **16** (0.072 mmol, 78 %). NMR $^1\text{H}\{-^{11}\text{B}\}$ (500 MHz, CD_2Cl_2 , 300 K): δ 7.80 to 6.65 (30H, m, PMePh_2), 2.24 (3H, d, ${}^2J_{\text{HP}} = 13.2$ Hz, PMePh_2), 2.11 (3H, d, ${}^2J_{\text{HP}} = 11.2$ Hz, PMePh_2), 2.07 (3H, d, ${}^2J_{\text{HP}} = 10.0$ Hz, PMePh_2). NMR $^{31}\text{P}\{-^1\text{H}\}$ (202 MHz; CD_2Cl_2 ; 298 K): δ 28.8 (1P, d, ${}^1J_{\text{PRh}} = 121$ Hz, PMePh_2), 10.0 (1P, dd, ${}^1J_{\text{PRh}} = 99.5$ Hz, ${}^2J_{\text{PP}} = 28$ Hz, PMePh_2), 2.6 (1P, q, B- PMePh_2). LRMS (MALDI⁺/DIT): m/z calcl for $\text{C}_{39}\text{H}_{50}\text{B}_9\text{P}_3\text{RhS}$: 843 $[\text{M}]^+$; found 843, isotope envelope matching that calculated from

the known isotopic abundances of the constituent elements.

[1,3- μ -(H)-1,1-(PMe₂Ph)₂-3-(Py)-isonido-1,2-RhSB₉H₈]⁺ (18): To 0.3 mL of a CD₂Cl₂ solution of neutral [1,1-(PMe₂Ph)₂-3-(Py)-isonido-1,2-RhSB₉H₈] (**8**) (3.8 mg; 0.064 mmol) in a 5 mm NMR tube, was added 0.57 μ L 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 ¹H-¹¹B} (300 MHz; CD₂Cl₂; 298 K): δ 9.23 (2H, d, ³J_{HH} = 5.4 Hz, H_o-NC₅H₅), 8.58 (1H, t, ³J_{HH} = 7.8 Hz, H_p-NC₅H₅), 8.14 (2H, t, ³J_{HH} = 7.8 Hz, H_m-NC₅H₅), 1.55 (6H, [AX₃]₂ spin system, N = ²J_{HP} + ⁴J_{HP} = 10.5 Hz, PMe₂Ph), 1.48 (6H, [AX₃]₂ spin system, N = ²J_{HP} + ⁴J_{HP} = 10.2 Hz, PMe₂Ph),. ³¹P NMR (121 MHz; CD₂Cl₂; 298 K): δ 0.51 (2P, d, ¹J_{PRh} = 100 Hz, PMe₂Ph). NMR ¹⁹F-¹H} (282 MHz; CD₂Cl₂; 300 K): δ -78.8 (3F, s, OTf). LRMS (MALDI⁺/DIT): *m/z* calcd for C₂₁H₃₆B₉NP₂RhS: 597 [M]⁺; found 597. Calcd for C₁₃H₂₅B₉NPRhS: 458 [M-PMe₂Ph]⁺; found 521. Isotope envelopes match those calculated from the known isotopic abundances of the constituent elements.

[1,3- μ -(H)-1,1-(PMe₂Ph)(PPh₃)-3-(Py)-isonido-1,2-RhSB₉H₈]⁺ (21): Obtained in the reaction of **14** with TfOH as described above, it was characterized *in situ*. ¹H-¹¹B} NMR (400 MHz, CD₂Cl₂, 300 K): δ 1.59 (3H, d, ²J_{HP} = 10.5 Hz, PMe₂Ph), 1.39 (3H, d, ²J_{HP} = 10.6 Hz, PMe₂Ph), -5.51 (1H, ddd, ¹J_{HRh} = 23 Hz, ²J_{HP} = 14 Hz, ²J_{HP} = 17 Hz, B-H-Rh). ³¹P-¹H} NMR (162 MHz; CD₂Cl₂; 298 K): δ 35.9 (1P, dd, ¹J_{PRh} = 110 Hz, ²J_{PP} = 20 Hz, PPh₃), -1.5 (1P, dd, ¹J_{PRh} = 100 Hz, ²J_{PP} = 20 Hz, PMe₂Ph).

[1,3- μ -(H)-1,1-(PMePh₂)₂-3-(Py)-isonido-1,2-RhSB₉H₈]⁺ (22): A 14.6 mg (0.02 mmol) amount of [8,8,8-(H)(PMePh₂)₂-9-(Py)-nido-8,7-RhSB₉H₉] (**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 μ L, 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 ^1H - $\{^{11}\text{B}\}$ (500 MHz, CD_2Cl_2 , 298K): δ 9.05 (2H, d, $^2J_{\text{HH}} = 5.6$ Hz, $H_o\text{-NC}_5\text{H}_5$), 8.61 (1H, t, $H_p\text{-NC}_5\text{H}_5$), 8.14 (2H, t, $H_m\text{-NC}_5\text{H}_5$), 7.83 a 6.89 (20H, m, PMePh_2), 1.84 (6H, $[\text{AX}_3]_2$ spin system, $N = ^2J_{\text{HP}} + ^4J_{\text{HP}} = 8.6$ Hz n, 2PMePh_2). NMR ^{31}P - $\{^1\text{H}\}$ (202 MHz, CD_2Cl_2 , 298 K): δ 12.3 (2P, d, $^1J_{\text{PRh}} = 141$ Hz, PMePh_2). NMR ^{19}F - $\{^1\text{H}\}$ (282 MHz, CD_2Cl_2 , 300 K): δ -78.5 (3F, s, OTf). LRMS (MALDI $^+$ / DIT): m/z calcl for $\text{C}_{18}\text{H}_{27}\text{B}_9\text{NPRhS}$: 522 $[\text{M-PMePh}_2]^+$; found 522, isotope envelope matching that calculated from the known isotopic abundances of the constituent elements. LRMS (MALDI $^+$ /DIT): m/z calcl for $\text{C}_{31}\text{H}_{40}\text{B}_9\text{NP}_2\text{RhS}$: 721 $[\text{M}]^+$; found 721. Calcl for $\text{C}_{18}\text{H}_{27}\text{B}_9\text{NPRhS}$: 521 $[\text{M-PPh}_3]^+$; found 521. Isotope envelopes match those calculated from the known isotopic abundances of the constituent elements.

Notes and references

^a *Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea-ISQCH, Universidad de Zaragoza-CSIC, C/Pedro Cerbuna 12, 50009 Zaragoza, Spain; E-mail: rmacias@unizar.es*

†Electronic Supplementary Information (ESI) available: Additional NMR spectra, and DFT-calculated details and coordinates. Deposition numbers at the Cambridge Crystallographic Data Centre: CCDC-907304 for **20a** and CCDC-937675 for **20b**. See DOI: 10.1039/b000000x/

1. *Boron Science: New Technologies and Applications*, ed. N. S. Hosmane, CRC Press, Boca Raton, FL, 2012.
2. R. N. Grimes, *Carboranes*, Academic Press, Elsevier Inc., Amsterdam, 2011.
3. R. B. King, *J. Math. Chem.*, 1990, **4**, 69-85.
4. J. Aihara, *J. Am. Chem. Soc.*, 1978, **100**, 3339-3342.

5. L. Wesemann, in *Comprehensive Organometallic Chemistry*, eds. D. M. P. Mingos and R. H. Crabtree, Elsevier, Oxford, 2007, vol. 3, pp. 113-131.
6. N. S. Hosmane and J. A. Maguire, in *Comprehensive Organometallic Chemistry*, eds. R. H. Crabtree and D. M. P. Mingos, Elsevier, Oxford, 2007, vol. 3, Chap. 3.05, pp. 175-264.
7. T. Onak, in *Comprehensive Organometallic Chemistry*, eds. E. W. Abel, F. G. A. Stone and G. Wilkinson, Elsevier Science Ltd., Oxford, 1995, vol. 1, pp. 217-255.
8. R. N. Grimes, in *Comprehensive Organometallic Chemistry II*, eds. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 1, pp. 373-430.
9. L. T. Todd, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press Ltd., Oxford, 1982, vol. 1, pp. 534-553.
10. T. Onak, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Ltd., Oxford, 1982, vol. 1, pp. 411-457.
11. R. N. Grimes, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press Ltd., Oxford, 1982, vol. 1, pp. 459-542.
12. Z. Xie, *Acc. Chem. Res.*, 2003, **36**, 1, 9.
13. Z. Xie, *Coord. Chem. Rev.*, 2002, **231**, 23-46.
14. J. Zhang and Z. W. Xie, *Pure Appl. Chem.*, 2013, **85**, 661-670.
15. S. Hao and X. Zuowei, in *Boron Science*, ed. N. S. Hosmane, CRC Press, 2011, pp. 517-528.
16. S. Bauer and E. Hey-Hawkins, in *Boron Science*, ed. N. S. Hosmane, CRC Press, 2011, pp. 529-578.
17. A. M. Spokoyny, C. W. Machan, D. J. Clingerman, M. S. Rosen, M. J. Wiester, R. D. Kennedy, C. L. Stern, A. A. Sarjeant and C. A. Mirkin, *Nat Chem*, 2011, **3**, 590-596.
18. A. M. Spokoyny, C. D. Lewis, G. Teverovskiy and S. L. Buchwald, *Organometallics*, 2012, **31**, 8478-8481.

19. M. E. El-Zaria, H. Arii and H. Nakamura, *Inorg. Chem.* 2011, **50**, 4149-4161.
20. A. M. Spokoyny, M. G. Reuter, C. L. Stern, M. A. Ratner, T. Seideman and C. A. Mirkin, *J. Am. Chem. Soc.*, 2009, **131**, 9482-9483.
21. S. Liu, Y.-F. Han and G.-X. Jin, *Chem. Soc. Rev.*, 2007, **36**, 1543-1560.
22. X. Wang, S. Liu, L.-H. Weng and G.-X. Jin, *Chem. Eur. J.*, 2007, **13**, 188-195.
23. N. P. E. Barry and P. J. Sadler, *Chem. Soc. Rev.*, 2012, **41**, 3264-3279.
24. J. A. Belmont, J. Soto, R. E. King, A. J. Donaldson, J. D. Hewes and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1989, **111**, 7475-7486.
25. J. D. Kennedy and B. Stíbr, in *Current Topics in the Chemistry of Boron*, ed. G. Kabalka, The Royal Society of Chemistry, Cambridge, 1994, pp. 285-292.
26. J. D. Kennedy, in *The Borane, Carborane, Carbocation Continuum*, ed. J. Casanova, Wiley, New York, 1998, pp. 85-116.
27. C. W. Jung and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1980, **102**, 3024-3032
28. P. E. Behnken, D. C. Busby, M. S. Delaney, R. E. King, C. W. Kreimendahl, T. B. Marder, J. J. Wilczynski and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1984, **106**, 7444-7450.
29. P. E. Behnken, J. A. Belmont, D. C. Busby, M. S. Delaney, R. E. King, C. W. Kreimendahl, T. B. Marder, J. J. Wilczynski and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1984, **106**, 3011-3025.
30. Á. Álvarez, R. Macías, J. Bould, C. Cunchillos, F. J. Lahoz and L. A. Oro, *Chem. Eur. J.*, 2009, **15**, 5428-5431.
31. Á. Álvarez, R. Macías, M. J. Fabra, F. J. Lahoz and L. A. Oro, *J. Am. Chem. Soc.*, 2008, **130**, 2148-2149.
32. Á. Álvarez, R. Macías, J. Bould, M. J. Fabra, F. J. Lahoz and L. A. Oro, *J. Am. Chem. Soc.*, 2008, **130**, 11455-11466.

33. B. Calvo, Á. Álvarez, R. Macías, P. García-Orduña, F. J. Lahoz and L. A. Oro, *Organometallics*, 2012, **31**, 2986-2995.
34. B. Calvo, M. Kess, R. Macias, C. Cunchillos, F. J. Lahoz, J. D. Kennedy and L. A. Oro, *Dalton Trans.*, 2011, **40**, 6555-6564.
35. B. Calvo, R. Macías, M. J. Artigas, F. J. Lahoz and L. A. Oro, *Chem. Eur. J.*, 2013, **19**, 3905-3912.
36. B. Calvo, R. Macías, C. Cunchillos, F. J. Lahoz and L. A. Oro, *Organometallics*, 2012, **31**, 2526-2529.
37. G. J. Kubas, *Metal Dihydrogen and σ -Bond Complexes: Structure, Theory and Reactivity*, Kluwer Academic/Plenum, New York, 2001.
38. E. T. Papish, M. P. Magee and J. R. Norton, in *Recent Advances in Hydride Chemistry*, eds. M. Peruzzini and R. Poli, Elsevier, London, 2001, ch. 2, pp. 39-74.
39. O. Bondarev, Y. V. Sevryugina, S. S. Jalisatgi and M. F. Hawthorne, *Inorg. Chem.*, 2012, **51**, 9935-9942.
40. W. C. Kalb, Z. Demidowicz, D. M. Speckman, C. Knobler, R. G. Teller and M. F. Hawthorne, *Inorg. Chem.*, 1982, **21**, 4027-4036.
41. A. R. Kudinov, P. Zanello, R. H. Herber, D. A. Loginov, M. M. Vinogradov, A. V. Vologzhanina, Z. A. Starikova, M. Corsini, G. Giorgi and I. Nowik, *Organometallics*, 2010, **29**, 2260-2271.
42. G. Ferguson, J. Pollock, P. A. McEneaney, D. P. Oconnell, T. R. Spalding, J. F. Gallagher, R. Macías and J. D. Kennedy, *Chem. Commun.*, 1996, 679-681.
43. D. D. Ellis, P. A. Jelliss and F. G. A. Stone, *Dalton*, 2000, 2113-2122.
44. R. Núñez, O. Tutusaus, F. Teixidor, C. Viñas, R. Sillanpää and R. Kivekäs, *Chem. Eur. J.*, 2005, **11**, 5637-5647.

45. J. G. Planas, C. Viñas, F. Teixidor, M. E. Light, M. B. Hursthouse and H. R. Ogilvie, *Eur. J. Inorg. Chem.*, 2005, **2005**, 4193-4205.
46. J. P. Sheehan, T. R. Spalding, G. Ferguson, J. F. Gallagher, B. Kaitner and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1993, 35-42.
47. J. Bernstein, *Polymorphism in Molecular Crystals*, Oxford University Press, Oxford, 2002.
48. K. Nestor, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, J. Plešek, B. Štíbr and M. Thornton-Pett, *Inorg. Chem.*, 1989, **28**, 2219-2221.
49. M. Bown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *Organometallics*, 1987, **6**, 2254-2255.
50. M. Bown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1990, 3039-3049.
51. K. Nestor, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1989, **0**, 455-456.
52. J. Bould, N. P. Rath and L. Barton, *Acta. Crystallogr. Sect. C*, 1997, **53**, 416-419.
53. O. Volkov, R. Macias, N. P. Rath and L. Barton, *J. Organomet. Chem.*, 2002, **657**, 40-47.
54. J. Bould, C. Cunchillos, F. J. Lahoz, L. A. Oro, J. D. Kennedy and R. Macías, *Inorg. Chem.*, 2010, **49**, 7353-7361.
55. Q. A. Smith, M. S. Gordon and L. V. Slipchenko, *J. Phys. Chem. A*, 2011, **115**, 4598-4609.
56. I. Dance and M. Scudder, *J. Chem. Soc., Chem. Commun.*, 1995, 1039-1040.
57. J. J. Solomon and R. F. Porter, *J. Am. Chem. Soc.*, 1972, **94**, 1443-1450.
58. E. L. Muetterties, *Pure Appl. Chem.*, 1965, **10**, 53.

59. P. Brint, E. F. Healy, T. R. Spalding and T. Whelan, *J. Chem. Soc., Dalton Trans.*, 1981, 2515-2522.
60. E. J. M. Hamilton, H. T. Leung, R. G. Kultyshev, X. Chen, E. A. Meyers and S. G. Shore, *Inorg. Chem.*, 2012, **51**, 2374-2380.
61. M. Kameda, M. Shimoï and G. Kodama, *Inorg. Chem.*, 1984, **23**, 3705-3709.
62. M. Kameda and G. Kodama, *Inorg. Chem.*, 1985, **24**, 2712-2714.
63. M. Kameda and G. Kodama, *J. Am. Chem. Soc.*, 1980, **102**, 3647-3649.
64. B. Calvo, R. Macías, M. J. Artigas, F. J. Lahoz and L. A. Oro, *Inorg. Chem.*, 2012, **52**, 211-221.
65. W. Henderson and J. S. McIndoe, *Mass Spectrometry of Inorganic and Organometallic Compounds*, John Wiley & Sons Ltd., 2005.
66. Z. Otwinowski and W. Minor, in *Methods Enzymol.*, ed. J. R. M. S. C. W. Carter, Academic Press, New York, 1997, vol. 276, pp. 307-326.
67. R. H. Blessing, *Acta Cryst.*, 1995, **A51**, 33.
68. G. M. Sheldrick, University of Göttingen: Göttingen, Germany, 1997.
69. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.