Modification of [8,8,8-(PPh₃)₂(H)-9-(Py)-*nido*-8,7-RhSB₉H₉], Py = NC₅H₅, with Monodentate Phosphines: Reactivity and Mechanistic Insights

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ABSTRACT

The [8,8,8-(PPh₃)₂(H)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**2**) / [1,1-(PPh₃)₂-3-(Py)-*closo*-1,2-RhSB₉H₈] (**3**) pair catalyzes the hydrogenation of olefins through *nido*-to-*closo* transformations. Substitution of the phosphine ligands can lead to an improvement of the catalytic activity of this system. Therefore, the substitutional chemistry of **2** with PMePh₂, PMe₂Ph and PMe₃ has been studied, leading to the formation of [8,8,8-(PPh₃)(PR₃)(H)-9-(Py)-*nido*-8,7-RhSB₉H₉], where R₃ = Me₂Ph (**5**) and Me₃ (**6**), and [8,8,8-(PR₃)₂(H)-9-(Py)-*nido*-8,7-RhSB₉H₉], where R₃ = MePh₂ (**4**) or Me₂Ph (**7**). Kinetic studies on the reaction of PMe₂Ph with **2** indicate that the substitutions follow a dissociative mechanism. The thermal dehydrogenation of **5-7** affords the corresponding *closo*-derivatives, [1,1-(PPh₃)(L)-3-(Py)-*closo*-1,2-RhSB₉H₈], where L = PMe₂Ph (**9**) or PMe₃ (**10**), and [1,1-(L)₂-3-(Py)-*closo*-1,2-RhSB₉H₈], where L = PMe₂Ph (**11**) or PMe₃ (**12**). The substitution of PPh₃ by the more basic less bulky phosphines facilitates hydrogen loss and consequent *nido*-to-*closo* transformations. The reaction of **5** and **6** with C₂H₄ promotes a *nido*-to-*closo* cluster change, and the consequent formation of **10** and **11** together with small amounts of C₂H₄-ligated [1,1-(L)(η²-C₂H₄)-3-(Py)-*closo*-1,2-RhSB₉H₈], where L = PPh₃ (**13**) or PMe₃ (**15**), characterized *in situ* by ¹H NMR spectroscopy. In the reactions with ethylene, ethane is detected *in situ*, indicating that the olefin is hydrogenated. The reactions of **5** and **6** with CO afford the CO-ligated

[1,1-(L)(CO)-3-(Py)-*closo*-1,2-RhSB₉H₈], where L = PMe₂Ph (**16**) or PMe₃ (**17**). The reactivity of the new PR₃-ligated *nido*-clusters *versus* H₂, C₂H₄ and CO is not improved with the phosphines studied in this work; however, the changes found in the chemical behaviour of this system are dramatic, confirming the tailorability of these eleven-vertex rhodathiboranes and the potential optimization of its catalytic activity by the adequate choice of the *exo*-polyhedral ligands.

Introduction

In recent years, we have developed the chemistry of pyridine-ligated 11-vertex rhodathiaboranes that are synthesized from [8,8-(PPh₃)₂-*nido*-8,7-RhSB₉H₁₀] (**1**).¹ In particular, the system formed by [8,8,8-(PPh₃)₂(H)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**2**) and [1,1-(PPh₃)₂-3-(Py)-*closo*-1,2-RhSB₉H₈] (**3**) has been found to give rise to an interesting reaction chemistry that embraces: (i) *nido*-to-*closo* deshydrogenation, (ii) dihydrogen promoted *closo*-to-*nido* transformations, (iii) oxidative addition of *sp* C–H bonds, and (iv) catalysis of hydrogenation and isomerization of olefins (Scheme 1).²

Scheme 1 Formation of **2**, and ethylene dihydrogen mediated *nido* → *closo* → *nido* conversion.

These 11-vertex clusters are easily prepared, versatile and stable, and, in view of the reactivity above-commented, they are compounds with potential as homogeneous catalyst precursors. Therefore, in an attempt to modify the reactivity of these clusters, we have already carried out substitution of the *exo*-polyhedral PPh₃ ligands in **1** with the more basic (less bulky) monodentate phosphines, PMe₃, PMe₂Ph and PPh₂Me.³ The results of this work have provided new rhodathiaboranes [8,8-(PPh₃)(PR₃)-*nido*-8,7-RhSB₉H₁₀], where R₃ = Me₃ and Me₂Ph, and [8,8-(PMePh₂)₂-*nido*-8,7-RhSB₉H₁₀], which (*a priori*) were convenient starting materials for the synthesis of new hydridorhodathiaboranes derived from **2**; however, as these compounds are obtained as mixtures with the corresponding *tris*-PR₃ ligated species,

[8,8,8-(PR₃)₃-*nido*-8,7-RhSB₉H₁₀], separatory work was necessary for the isolation of the clusters in moderate to low yields. In view of these results,³ and as a continuation of our systematic tailoring of the 11-vertex rhodathiaborane system **2** / **3**, we decided to study the substitutional chemistry of **2**.

Here we describe the reactivity of compound **2** with PMePh₂, PMe₂Ph and PMe₃, the subsequent preparation of new 11-vertex hydrido-Rh *nido*-clusters and the study of their reactivity with small molecules such as CO, C₂H₄ and H₂, discussing trends and differences within the new series of PR₃-ligated clusters and with the previously reported PPh₃-ligated counterparts **2** and **3**.

Results and Discussion

Reactions of [8,8,8-(PPh₃)₂(H)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**2**) with PR₃

Treatment of the *bis*-(PPh₃)-ligated compound **2** with one equivalent of phosphine PR₃ affords [8,8,8-(PPh₃)(PR₃)(H)-9-(Py)-*nido*-8,7-RhSB₉H₉] where R₃ = Me₂Ph (**5**) or Me₃ (**6**). A 1 to 4 molar ratio of **2** vs PMe₃ yields also the monosubstituted hydrido cluster **6**; whereas the reaction of **2** with 4 equivalents of PMe₂Ph affords the mixture, **5**, that contains two monosubstituted isomers (*vide infra*) **5a** and **5b**, and the disubstituted [8,8,8-(PMe₂Ph)₂(H)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**7**) (Scheme 2). In interesting contrast, the reaction of **2** with PMePh₂ in a 1:1 molar ratio gives mixtures that contain the new disubstituted species, [8,8,8-(PMePh₂)₂(H)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**4**), and the starting **2** (Scheme 2). The new 11-vertex hydridorhodathiaboranes **4-7** have been characterized by multinuclear NMR spectroscopy and mass spectrometry. In addition, a solid-state X-ray diffraction analysis confirmed the molecular structure of **4** (Figure 1).

Scheme 2

These rhodathiaboranes have an 11-vertex {RhSB₉} core geometry, formally derived from an icosahedron by the removal of a vertex, which resembles the structures of the pyridine-ligated counterpart **2**^{2a} and the PMePh₂-B(9) substituted [8,8,8-(PMePh₂)₂(H)-9-(PMePh₂)-*nido*-8,7-RhSB₉H₉] (**8**).³ The framework structures correspond exactly to what one expects for a 13-skeletal electron pair (sep) cluster with 11-vertices.⁴ This contrasts with the formal unsaturation found in the parent compound, **1**,¹ which has only 12 sep, but a *nido* structure. The discrepancy between the number of sep and the structure is an interesting feature of 11-vertex heteroborane frameworks that incorporate {Rh(L)₂} or {Pt(L)₂} (L = phosphine ligands) fragments,⁵ making them intrinsically Lewis acidic, and, therefore, potentially labile. The Rh(8)-S(7) distance of 2.4270(5) Å in **4** is close to the values found for the previously reported analogue **2** (Schemes 1 and 2) and **8** (schematics I below),^{2a,3} where the hydride ligand is also *trans* to the S(7) vertex (Table 1). In contrast, the Rh(8)-S(7) distance is *ca.* 0.05 Å shorter in *tris*-PR₃-ligated *nido*-rhodathiaboranes that bear a phosphine ligand *trans* to the sulphur atom,³ confirming the high structural *trans* influence of the hydride ligand (Table 1). It is interesting to note

that Rh-P distances in the PMePh₂-ligated cluster **4** are *ca.* 0.03 Å shorter than the corresponding values in the PPh₃ analogue **2**, reflecting the higher σ-donor capabilities of PMePh₂ and its smaller steric hindrance. In **2**, **4** and **8**, the longest Rh-P distance corresponds to the phosphine ligand *trans* to the substituted 9-position of the cluster; and the difference between the two Rh-P distances within each cluster is *ca.* 0.013(2) Å.

Figure 1 Molecular structure of compound **4**. Only the *ipso*-carbon atoms on the phenyl groups are included to aid clarity. Ellipsoids are shown at 50 % probability levels. Selected interatomic distances [Å] and angles [°]: Rh(8)-S(7) 2.4270(5), Rh(8)-P(1) 2.3224(6), Rh(8)-P(2) 2.3091(6), Rh(8)-H 1.53(3), Rh(8)-B(3) 2.230(2), Rh(8)-B(4) 2.209(2), Rh(8)-B(9) 2.214(2), B(9)-N 1.556(3); P(1)-Rh(8)-P(2) 98.10(2), P(1)-Rh(8)-S(7) 105.08(2), P(2)-Rh(8)-S(7) 97.82(2), P(1)-Rh(8)-B(9) 95.66(6), P(2)-Rh(8)-B(9) 163.22(6), P(1)-Rh(8)-B(3) 157.35(7), P(1)-Rh(8)-B(4) 141.17(6), P(2)-Rh(8)-B(3) 87.61(6), P(2)-Rh(8)-B(4) 116.59(6), S(7)-Rh(8)-H 168.2(14).

Table 1. *Trans*-effect of the hydride ligand in some 11-vertex *nido*-rhodathiaboranes.

Compound	Rh(8)-S(7) (Å)	Reference
$[(PPh_3)_2RhSB_9H_{10}]$ (1) ^a	2.3769(6)	1
$[(PMePh_2)_3RhSB_9H_{10}]$ ^a	2.3757(8)	6
$[(PMe_3)_3RhSB_9H_{10}]$ ^a	2.3736(7)	3
$[(PPh_3)_2(H)RhSB_9H_9(Py)]$ (2) ^b	2.431(2)	2b
$[(PMePh_2)_2(H)RhSB_9H_9(Py)]$ (4) ^b	2.4271(5)	this work
$[(PMePh_2)_2(H)RhSB_9H_9(PMePh_2)]$ (8) ^b	2.4172(5)	3

^aNon-hydride containing vs ^bhydride-containing clusters.

The structure of **4** is consistent with its spectroscopic data and those of the analogues, **2**, **5** (mixture of isomers), **6** and **7**. In this type of compounds, the ¹¹B NMR resonances are found in the interval between $\delta(^{11}B) +12.0$ to -28.0 ppm. The pattern does not change significantly through the series with the boron-11 resonance at the lowest field assigned to the pyridine-ligated boron atom at the 9-position. The Rh-H hydride and B-H-B bridging hydrogen resonances are quite informative, serving as diagnostic for the formation of these clusters. The hydride signal appears close to $\delta(^1H) -12.5$ ppm in the series: an apparent quartet for the *bis*-PPh₃- and *bis*-PMePh₂-ligated clusters, **2** and **4**; and a doublet of doublet of doublets for the mono-substituted analogue **6**. In contrast, the PMe₂Ph mono-substituted counterpart **5** exhibits two hydride resonances in a 1:0.6 ratio, indicating the presence of two isomers (**5a** and **5b**, Scheme 2). The resonance of the B-H-B bridging hydrogen atom in the isomers **5** (two isomers but one BHB signal) and **6** is slightly deshielded with respect to the *bis*-PPh₃-ligated rhodathiaborane, **2**; and, although the differences are small, the trend is a shift towards lower fields as the PPh₃ ligand is substituted by PMePh₂, PMe₂Ph and PMe₃ phosphines. This tendency is opposite to the shielding found in $[8,8-(PPh_3)_2-nido-8,7-RhSB_9H_{10}]$ (**1**), and its phosphine derivatives, $[8,8-(PPh_3)(PR_3)-nido-8,7-$

RhSB₉H₁₀], where R₃ = Me₃ and Me₂Ph and [8,8-(PMePh₂)₂-*nido*-8,7-RhSB₉H₁₀],³ where more basic phosphines at the metal centre yield a shielding of the B-H-B bridging resonance.

Scheme 3 depicts the shift of the hydride ¹H resonance found in **2**, **4**-**7**. Monosubstitution with PMe₂Ph and PMe₃ at the position *trans* to the B(9) vertex results in a shielding of the signal, being the shift larger for the more basic phosphine, PMe₃; however, if the substitution takes place at the position *trans* to the B(3)-B(4) edge (compound **5b**), the shift toward higher fields (from the parent compound **2**) is smaller (**5b** vs **5a**). As a first approximation, these changes in the ¹H resonance of the hydride ligands could result from a change in the basicity of the PR₃ ligands: more basic phosphines on the metal centre shift the resonance to higher fields. However, the disubstituted cluster **7** does not reflect this tendency, exhibiting a Rh-H hydride signal between those of the monosubstituted counterparts, **5a** and **5b**. From these results, it can be concluded that a PPh₃ ligand *trans* to the B(3)-B(4) edge appears to influence the shielding of the Rh-H hydride, indicating that differential neighboring-group magnetic anisotropic effects arising from P-phenyl *versus* P-methyl substituents on the phosphines play a rôle.

Scheme 3 Illustration of the ¹H chemical shift of the Rh-H hydride ligand

The ³¹P-¹H NMR spectra are very informative for the characterization of these compounds. Compound **4** exhibits two doublets of doublets separated by 4.8 ppm and shifted about 15.0 ppm to higher fields with respect the starting material, **2**. The ³¹P-¹H NMR spectrum of **6** consists of two well

separated signals at $\delta(^{31}\text{P})$ +49.2 and -15.4 ppm, assigned to the PPh_3 and PMe_3 ligands, respectively. In contrast, the mixture of compounds **5a** and **5b** shows two ^{31}P signals at high field and two at low field, which together with the presence of two hydride resonances in the ^1H NMR spectrum, demonstrate (as commented above) that the reaction of **2** with PMe_2Ph leads to the formation of two isomeric compounds with different $\{\text{Rh}(\text{L})_2\text{H}\}$ -to- $\{\text{SB}_9\text{H}_9(\text{Py})\}$ configurations: (i) PMe_2Ph *trans* to the B(9) vertex and PPh_3 *trans* to the B(3)-B(4) edge (**5a**), and (ii) PPh_3 *trans* to the B(9) vertex and PMe_2Ph *trans* to the B(3)-B(4) edge (**5b**). In addition, the *bis*- PMe_2Ph -ligated counterpart **7** exhibits a broad doublet at $\delta(^{31}\text{P})$ +3.1 ppm and a doublet of doublets at -1.8 ppm, which can be assigned to the resonances of the PMe_2Ph ligands *trans* to the B(9) and to the S(7) vertices, respectively.

An interesting characteristic that share these pyride-ligated hydridorhodathiaboranes is the temperature-dependent behavior of their ^{31}P - $\{^1\text{H}\}$ NMR spectra (see Figures S1 and S2). Thus, one of the phosphorus resonances is significantly broader than the other at room temperature (see Figure S1), and it sharpens as the temperature is decreased. First discovered for compound **2** (Figure S2), it was thought that this behavior is consistent with a dissociation of the PPh_3 ligand *trans* to the B(9) vertex.^{2b} However, this conclusion should be put into question since the broadening could be due to ^{31}P - ^{11}B couplings, which at lower temperatures are reduced due to the thermal decoupling of the quadrupolar ^{11}B ($I = 3/2$) nucleus.⁷

Substitution reactions: Mechanistic Considerations

In order to obtain some mechanistic insights about the substitutional chemistry of **2** with monodentate phosphines, small scale reactions were studied at low temperatures by NMR spectroscopy. Upon the addition of 1 equivalent of PMe_3 to a CD_2Cl_2 solution of **2** at 188 K, the ^{31}P - $\{^1\text{H}\}$ spectrum exhibits the signals of compound **2**, free PPh_3 and PMe_3 (Figure 2). The resonances of the substitution product, **6**, are not well detected in the ^{31}P - $\{^1\text{H}\}$ spectra until the temperature reaches 273 K. At room temperature, the reaction is completed [Figure 2: the broadness of the resonance close to $\delta(^{31}\text{P})$ -15.0 ppm arises most probably from $^2J(^{31}\text{P}$ - $^{11}\text{B})$ coupling as commented above]. The proton NMR spectrum reflects these results, showing the disappearance of the starting material **2** and the consequent formation of its

substitution product **6** (Figure S3). There is also a weak Rh-H hydride signal at -12.70 ppm, which may correspond to a minor $\{\text{Rh}(\text{PMe}_3)(\text{PPh}_3)(\text{H})\}$ -to- $\{\text{SB}_9\text{H}_9(\text{Py})\}$ isomer. In any event, these data reveal that the reaction of **2** with PMe_3 affords the monosubstituted product **6** with good regioselectivity: the substitution takes place at the *exo*-polyhedral position that is *trans* to the B(9) vertex. Following the same procedure, the treatment of **2** with 1 equivalent of PMe_2Ph at low temperatures neither affords significant amounts of substitution products until the temperature reaches 273 K (see Figures S4 and S5). At room temperature, there is not free PMe_2Ph left and there are two sets of major signals in the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum. As commented above, the spectrum is consistent with the presence of two $\{\text{RhH}(\text{PPh}_3)(\text{PMe}_2\text{Ph})\}$ -to- $\{\text{SB}_9\text{H}_9(\text{Py})\}$ isomers: the signals at the lowest field are assigned to the PPh_3 ligands, whereas the peaks at around $\delta(^{31}\text{P})$ -5 ppm correspond to the PMe_2Ph groups. In the same conditions, the reaction of **2** with 1 equivalent of PMePh_2 starts also to take place at significant rates above 273 K (see Figure S6 and S7); but in contrast, there is formation of the PMePh_2 disubstituted cluster, **4**.

Figure 2 Variable temperature $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra of **2** upon addition of 1 equivalent of PMe_3 at low temperature (bottom spectrum).

These results indicate clearly that the reactions of the monodentate phosphines, PMePh_2 , PMe_2Ph and PMe_3 , with **2**, occur at lower rates than with the previously studied rhodathiaborane, **1**.³ Variable-temperature experiments suggested that the most plausible mechanism for the substitution of the phosphine ligands in the parent compound **1** (Scheme 1) is associative, implying the binding of a third phosphine at the rhodium centre.³ For the herein described reactions of **2** with monodentate phosphines, however, it is not clear if, as discussed above, the broadening of one of the two ^{31}P resonances in this new series of hydridorhodathiaboranes, **4-7**, is due to $^{31}\text{P}\text{-}^{11}\text{B}$ coupling or to dissociative processes (or both).

In compound **6**, DFT-calculations have confirmed the assignment of the broad ^{31}P signal at the highest field as the PMe_3 ligand *trans* to the pyridine-substituted B(9) vertex (Table S10); in addition, previous DFT-studies revealed that elongation of the Rh-PH_3 bond *trans* to the B(9)-Py vertex in the model $[\text{8,8,8-(PH}_3)_2\text{H-9-(Py)-nido-8,7-RhSB}_9\text{H}_9]$, results in a smaller energy increase of the cluster compared with the elongation of the Rh-PH_3 bond *trans* to the B(3)-B(4) edge.^{2b} Thus, these theoretical results suggest that dissociation of the PR_3 ligand *trans* to the {B(9)-Py} vertex in **2** and **4-7**, may play an important role in the reactivity of these clusters.

Kinetic studies. The following kinetic studies try to shed more light on the reaction mechanism. The reaction between **2** and PMe_2Ph was studied by ^1H NMR spectroscopy, monitoring the decrease of the hydride integral resonance *versus* time. The concentration of PMe_2Ph was kept in excess to hold *pseudo* first-order condition. The value of k_{obs} , summarized in Table 2, is independent of the concentration of PMe_2Ph , suggesting that the substitution of one PPh_3 ligand in **2** takes place in a dissociative process. The activation parameters obtained from the Eyring plot (Figure S15), $\Delta H^\ddagger = 33 \pm 3 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = 45 \pm 9 \text{ eu}$, are consistent with dissociation of PPh_3 as the most plausible mechanism for this reaction. Therefore, although the commented-above temperature-dependent broadening in the $^{31}\text{P}\{-^1\text{H}\}$ spectra of **2-7** may arise mainly from the effects of “thermal decoupling” on the boron nuclei, dissociation of the phosphine ligand *trans* to B(9), as previously suggested by us,^{2b} appears to direct the reactivity of these clusters.

Table 2 Rate Constants for PPh₃ Substitution in Compound **2**^a

T(K)	[PMe ₂ Ph] (equivalents)	10 ² <i>k</i> _{obs} (min ⁻¹) ^b
273	5	1.4
273	20	1.4
263	10	0.13
268	10	0.27
273	10	1.4
279	10	2.5
283	10	14.3

^a[**2**] = 0.02 M in CD₂Cl₂. ^b Values obtained from three different measurements.

Reactivity Studies

The modification of the *exo*-polyhedral ligands in the 11-vertex rhodathiaboranes **2** and **3** is a reasonable approach for the fine-tuning of the reactivity of this system. The adequate combination of *exo*-polyhedral ligands bound either to the rhodium atom or to the B(9) vertex, can (*a priori*) result in an improvement of the catalytic activity of this kind of clusters. Therefore, we carried out a systematic study of the reactivity of the new PR₃-ligated clusters, **4-7**, having the PPh₃-ligated clusters **2** and **3** as reference.

Dehydrogenation. The hydridorhodathiaboranes **2**, **5-7**, are stable in solution at room temperature; however, heating at reflux temperature in dichloromethane results in the loss of dihydrogen and the concomitant *nido*-to-*closo* transformation of the clusters (Scheme 4). In contrast, the PMePh₂-ligated counterpart, **4**, does not undergo dehydrogenation. Quantitative studies on the dehydrogenation reactions were carried out by ¹H NMR spectroscopy at 50 °C in CD₂Cl₂ (Tables S4 - S6). The results were adjusted to a first-order kinetic, yielding the reaction rates and half-life constants listed in Table 3.

Table 3 Rate constants and half-life times for the dehydrogenation reactions of **2**, **5a**, **5b**, **6** and **7** in CD₂Cl₂ at 50 °C

Compound	$k \times 10^4 \text{ min}^{-1}$	$t_{1/2} \text{ (h)}$
2	26±1.4	4.4
5a	41±0.5	2.8
5b	25±0.4	4.6
6	45±1.6	2.6
7	83±1.5	1.4

These data show that the fastest rate of dehydrogenation corresponds to the *bis*-PMe₂Ph-ligated **7**: roughly three times as fast as the parent cluster **2** and the isomers **5b**. Next in the series, we find the isomer **5a** and the PMe₃ monosubstituted derivative **6**, which exhibit a rate of dehydrogenation approximately two times faster than **2** (and **5b**). This trend indicates that the substitution of PPh₃ with more basic and less bulky phosphine ligands, facilitates the dehydrogenation of the clusters and the consequent *nido-to-closo* transformation. In addition, the different rate between the isomers **5a** and **5b** suggests that a *trans* arrangement of PR₃, where R₃ = Me₂Ph (**5a** and **5b**) and Me₃ (**6**), to the B(9) vertex results in an increase of the dehydrogenation rate. It is somewhat surprising, however, that in the same conditions the hydrogen loss is completely hindered for the PMePh₂-ligated compound **4**.

Scheme 4

The thermal treatment of **5**, **6** and **7** is a convenient route to the synthesis of the mixed-ligated *closo*-derivatives [1,1-(PPh₃)(L)-3-(Py)-*closo*-1,2-RhSB₉H₈], where L = PMe₂Ph (**9**) or PMe₃ (**10**); and the *bis*-PR₃-ligated analogues, [1,1-(PR₃)₂-3-(Py)-*closo*-1,2-RhSB₉H₈], where L = PMe₂Ph (**11**) or PMe₃ (**12**). These compounds have been fully characterized by multinuclear NMR and mass spectrometry. And X-ray diffraction analysis has confirmed the molecular structures of **10** and **11** (Figure 3 and Figure S16, respectively).

Figure 3 Molecular structure of **10**. 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. Selected interatomic distances (Å) and angles (°): Rh(1)-S(2) 2.3841(9), Rh(1)-P(1) 2.2889(10), Rh(1)-P(2) 2.2710(9), Rh(1)-B(3) 2.087(4), Rh(1)-B(4) 2.401(4), Rh(1)-B(5) 2.471(4), Rh(1)-B(6), 2.380(4), Rh(1)-B(7) 2.354(4); P(1)-Rh(1)-P(2) 96.68(4).

The molecular structures of **10** and **11** are based on the canonical structure of an octadecahedron that may be rationalized by simple application of the Wade/Mingos approach.⁴ The rhodium atom occupies the apical cluster position connected to six atoms in the {SB₉} fragment with two *exo*-polyhedral metal coordination sites occupied by the PPh₃ and PR₃ ligands. Compounds **9-12** are isoelectronic with **3** and the organometallic derivatives, [1,1-(PPh₃)(η²-L)-3-(Py)-*closo*-1,2-RhSB₉H₈], where L = η²-C₂H₄ (**13**, Scheme 1 above) or η²-C₂(CO₂Me)₂,^{2c} as well as others rhodathiaboranes that have different *exo*-

polyhedral ligands on the rhodium centre and the B(3) vertex.^{2c,8} No surprising, the longest Rh-P distance [2.3278(13) Å] corresponds to **3** that bears two bulky PPh₃ ligands; however, it is interesting to notice that in **10** the P-Rh distance of the PMe₃ ligand [2.2889(10) Å] is longer than that of PPh₃ [2.2710(9) Å], suggesting that the steric effects of PPh₃ dominate against the better σ -donor capabilities of PMe₃.

Reactions with H₂(g). The *closo*-rhodathiaborane **3** reacts with dihydrogen to give the *nido*-cluster **2**.^{2a} This is a significant reaction that implies the heterolytic splitting of H₂ on the *closo*-cluster and completes an stoichiometric cycle of dehydrogenation/hydrogenation that represents the essence of the catalytic activity of the system (see Scheme 1 above).^{2b} Therefore, one of the objectives of this work was to change the phosphine ligands to optimize the activation of dihydrogen by 11-vertex *closo*-rhodathiaboranes and subsequently the transfer of the two hydrogen atoms to unsaturated organic molecules. However, in the same conditions than **3**, the 11-vertex *closo*-rhodathiaboranes **9-12** do not react with dihydrogen. Thus, although the loss of H₂ is facilitated by the presence of the more basic and less bulky PMe₂Ph and PMe₃ ligands in **5-7**, the reverse reaction with H₂ (to regenerate these *nido*-hydrido clusters) is hindered. In other words, the energy barrier for the dehydrogenation of the *nido*-clusters is lower than for the PPh₃-ligated compound **2**; whereas the activation energy of the reaction of the 11-vertex *closo*-rhodathiaboranes **9-12** with H₂, appears to be higher than for **3**, precluding the H₂ addition to the *closo*-clusters. In this context, once more, it is noteworthy that **4** does not undergo hydrogen loss in the same conditions than **2** and **5-7**, indicating that for the PMePh₂-ligated counterpart the activation energy barrier towards the formation of the hypothetical *closo*-cluster, [1,1-(PMePh₂)₂-3-(Py)-*closo*-1,2-RhSB₉H₈], by loss of H₂ is significantly higher. In any event, it is evident that the nature of the phosphine ligands plays a crucial role in tuning the reactivity of the *closo*-clusters towards the activation of dihydrogen; therefore, the right choice of ligands should improve the reactivity of the system towards small molecules.

Reactions with CO and C₂H₄.

Both reagents, CO and C₂H₄, react with **2** to give CO- and C₂H₄-ligated *closo*-rhodathiaboranes, [1,1-(PPh₃)(L)-3-(Py)-*closo*-1,2-RhSB₉H₈], where L = C₂H₄ (**13**, Scheme 1 above) or CO (**14**, Schematics II below);^{2a,b} in the reaction with ethylene, there is also formation of ethane (detected *in situ* by ¹H NMR spectroscopy), demonstrating that the alkene is hydrogenated. In the current study, it has been found that the reaction of **5** (mixture of isomers) and **6** with ethylene, promotes the *nido*-to-*closo* transformation, yielding **10** and **11**, respectively at room temperature, also formed thermally in longer reaction times as discussed-above. Under a higher pressure of ethylene (see experimental section), the reaction of **6** has been found to afford, in addition to the major component **10**, small amounts of the ethylene-ligated rhodathiaborane, **13**, and the PMe₃-ligated counterpart, [1,1-(PMe₃)(η²-C₂H₄)-3-(Py)-*closo*-1,2-RhSB₉H₈] (**15**). This new compound has been characterized *in situ* by NMR spectroscopy, and the chemical non-rigidity of the Rh-C₂H₄ linkage studied by variable temperature ¹H NMR experiments (Figure S17). The activation energy of this rotational fluxional process is 4 kJ/mol higher for **15** than for **13**, suggesting a stronger Rh-(η²-C₂H₄) bond as the result of an increase in the π-back donation from the metal center to the olefin ligand in the former compound, which is expected from the presence of the better σ-donor ligand, PMe₃ in **15**. In the same conditions, in contrast, the mixture of isomers **5** leads only **13** in small amounts. Both reactions afford ethane (**10**-to- and **11**-to-C₂H₆ ratio 1:0.2), indicating that although the major reaction appears to be H₂ loss, the transfer of the two hydrogen atoms to the C=C bond of the olefin also occurs for the new PR₃-ligated hydrido-ligated clusters (Scheme 5).

Scheme 5

With carbon monoxide, the mixture of isomers **5** reacts to give the CO-ligated *closo*-cluster **14** (Schematics II) and the new derivative, [1,1-(PMe₂Ph)(CO)-3-(Py)-*closo*-1,2-RhSB₉H₈] (**16**) in a 1:4 ratio. Similarly, compound **6** reacts to give a mixture of **14** and [1,1-(PMe₃)(CO)-3-(Py)-*closo*-1,2-RhSB₉H₈] (**17**), this time in a 1:5 ratio. Therefore, carbon monoxide substitutes one phosphine ligand in the hydridorhodathiaboranes, causing the *nido*-to-*closo* transformation of the cluster by hydrogen loss. The PPh₃ ligand is preferably substituted by the entering CO molecule, reflecting the fact that PMe₂Ph in **5** and PMe₃ in **6**, are worse leaving groups than PPh₃.

Conclusions

The parent hydrido-Rh cluster **2** reacts readily with monodentate phosphines, affording new 11-vertex derivatives with compositions and configurations that depend on the entering phosphine. Thus the treatment of **2** with PMePh₂ forms exclusively the *bis*-substituted cluster **4**. In contrast, the less bulky and more basic phosphines, PMe₃ and PMe₂Ph, afford mono-substituted species **5** (mixture of isomers) and **6**; with PMe₂Ph, it is also possible to prepare the *bis*-substituted derivative **7**. Kinetic studies demonstrate that the substitution of the PPh₃ ligand in **2** follows a dissociative mechanism that most

likely involves the phosphine ligand *trans* to the B(9) position. These results support previous conclusions dealing with the reactivity of **2** with olefins in which dissociative mechanisms were invoked.^{2a,b}

The new 11-vertex *nido*-hydridorhodathiaboranes, **5-7**, undergo faster thermal dehydrogenation than the parent compound **2** to give the corresponding *closo*-clusters, **9-11**, which do not react with H₂ in the same reaction conditions used for the *bis*-PPh₃-ligated derivative **3**. Therefore, the dehydrogenation / hydrogenation cycle found for the *bis*-PPh₃-ligated **2** / **3** pair is not completed (in the conditions of pressure and temperature studied) with the new rhodathiaboranes reported in this work. Ethylene promotes hydrogen loss and consequent *nido*-to-*closo* transformation, but compared with **2**, the new species **5** and **6** do not exhibit an enhanced reactivity with the olefin; perhaps reflecting the fact that the dissociation of the Rh-PMe₂Ph and Rh-PMe₃ bonds in **5** and **6** is more difficult than the dissociation of Rh-PPh₃ in **2**. This fact together with the lack of reactivity of the new *closo*-clusters with dihydrogen, essential for subsequent hydrogenation of unsaturated organic molecules, indicates that the change of PPh₃ in **2** with the phosphines studied in this work would not lead to an improvement in the catalytic activity of the system. Likewise, the new CO-ligated *closo*-clusters, **16** and **17**, are inert in the presence of molecular hydrogen, matching this time the reactivity of the PPh₃-ligated counterpart **14**.

Although the objective of improving the reactivity the **2** / **3** pair *versus* dihydrogen and olefins is not accomplished by substitution of PPh₃ with the studied phosphines, the treatment of **2** with PR₃, where R₃ = Me₃, Me₂Ph and MePh₂, is a convenient synthetic route for the alteration of the *exo*-polyhedral ligand sphere, confirming the tailorability of this eleven-vertex rhodathiborane system. The lack of reactivity of the *bis*-PMePh₂-ligated cluster **4** is an interesting contrast, which suggests that other *exo*-polyhedral metal ligands may tune the clusters towards the opposite behavior: an enhancement of the catalytic activity with respect to **2**.

Experimental

General Procedures

Reactions were carried out under an argon atmosphere using standard Schlenk-line techniques. Solvents were obtained dried from a Solvent Purification System of Innovative Technology Inc. The commercially available phosphines, PMe_3 , PMe_2Ph and PMePh_2 were used as received without further purification. The 11-vertex rhodathiaborane **2**, was prepared according to the literature methods.^{2a,b} Preparative thin-layer chromatography (TLC) was carried out using 1 mm layers of silica gel G (Fluka, type GF254) made from water slurries on glass plates of dimensions 20 × 20 cm and dried in air at 25 °C. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer, using an Universal ATR Sampling Accessory. NMR spectra were recorded on Bruker Avance 300-MHz and AV 400-MHz spectrometers, using ^{11}B , $^{11}\text{B}\{-^1\text{H}\}$, ^1H , $^1\text{H}\{-^{11}\text{B}\}$ and $^1\text{H}\{-^{11}\text{B}(\text{selective})\}$ techniques. ^1H NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative to tetramethylsilane. ^{11}B chemical shifts are quoted relative to $[\text{BF}_3(\text{OEt})_2]$ and ^{31}P chemical shifts are quoted relative to 85% aqueous H_3PO_4 . Mass spectrometric data were recorded on a MICROFLEX instrument operating in either positive or negative modes, using matrix-assisted laser desorption/ionization (MALDI). A nitrogen laser of 337 nm (photon energy of 3.68 eV) was used for the ionization processes, and the molecules under study were protected with a matrix of *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB).

X-ray crystallography

Crystals of compounds **4**, **10** and **11** suitable for X-ray diffraction analysis were grown by slow diffusion of hexane into a concentrated solution of each rhodathiaborane in dichloromethane. X-ray diffraction data were collected at low temperature (100(2) K) on the BM16 CRG beamline at the ESRF in the case of **4**, and for **10** and **11** using an automatic Bruker Kappa APEX DUO CCD area detector diffractometer equipped with graphite-monochromatic Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$) using narrow frames (0.3° in ω). In all cases, single crystals were mounted on micro-mount supports and were covered with a protective perfluoropolyether. In the case of **4**, data were measured in a single axis HUBER

diffractometer, equipped with Oxford 600 Cryosystem open-flow nitrogen cryostat (100(1) K), using monochromatic Silicon(111) synchrotron radiation ($\lambda = 0.73780 \text{ \AA}$). Intensities were integrated including Lorentz and polarization effect with HKL2000 suite (**4**) or SAINT-Plus program⁹ (**10** and **11**) and corrected for absorption using multi-scan methods applied with SORTAV (**4**) or SADABS (**10** and **11**) programs.¹⁰ The structures were solved using the SHELXS-86 program.¹¹ Refinements were carried out by full-matrix least-squares on F^2 with SHELXL-97,¹² including isotropic and subsequent anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms for compounds **4** and **10** were included from observed positions and refined isotropically. For **11**, most of the hydrogen atoms were observed but some others were included in calculated positions and refined with a riding model. The programs ORTEP-3¹³ and PLATON¹⁴ were used to prepare the figures and the crystallographic data.

Crystal data for compound 4: $\text{C}_{31}\text{H}_{41}\text{B}_9\text{NP}_2\text{RhS} \cdot 2(\text{CH}_2\text{Cl}_2)$, $M = 891.74$; yellow block, $0.078 \times 0.065 \times 0.052 \text{ mm}^3$; monoclinic, $P2_1/n$; $a = 10.1578(3)$, $b = 25.6316(2)$, $c = 16.3428(3) \text{ \AA}$; $\beta = 100.3430(10)^\circ$; $Z = 4$; $V = 4185.88(15) \text{ \AA}^3$; $D_c = 1.415 \text{ g/cm}^3$; $\mu = 0.812 \text{ mm}^{-1}$, min. and max. correction factors 0.80 and 1.24; $2\theta_{\text{max}} = 56.24^\circ$; 42060 reflections collected, 8895 unique [$R_{\text{int}} = 0.0731$]; number of data/restraints/parameters 8895/0/624; final GoF 1.058, $R_1 = 0.0420$ [8707 reflections, $I > 2\sigma(I)$], $wR_2 = 0.1117$ for all data.

Crystal data for compound 10: $\text{C}_{26}\text{H}_{37}\text{B}_9\text{NP}_2\text{RhS} \cdot \text{CH}_2\text{Cl}_2$, $M = 742.69$; red plate, $0.195 \times 0.094 \times 0.037 \text{ mm}^3$; triclinic, $P-1$; $a = 10.8930(11)$, $b = 12.0718(12)$, $c = 14.3942(14) \text{ \AA}$; $\alpha = 87.299(2)$, $\beta = 69.5940(10)$, $\gamma = 81.4180(10)^\circ$; $Z = 2$; $V = 1754.1(3) \text{ \AA}^3$; $D_c = 1.406 \text{ g/cm}^3$; $\mu = 0.811 \text{ mm}^{-1}$, min. and max. transmission factors 0.798 and 0.943; $2\theta_{\text{max}} = 59.08^\circ$; 19013 reflections collected, 8827 unique [$R_{\text{int}} = 0.0474$]; number of data/restraints/parameters 8827/0/544; final GoF 1.010, $R_1 = 0.0481$ [6398 reflections, $I > 2\sigma(I)$], $wR_2 = 0.1154$ for all data.

Crystal data for compound 11: $C_{21}H_{35}B_9NP_2RhS \cdot CH_2Cl_2$, $M = 680.67$; red prism, $0.203 \times 0.149 \times 0.117 \text{ mm}^3$; monoclinic, $P2_1/c$; $a = 9.1278(13)$, $b = 24.263(4)$, $c = 14.915(2) \text{ \AA}$; $\beta = 103.397(2)^\circ$; $Z = 4$; $V = 3213.2(8) \text{ \AA}^3$; $D_c = 1.407 \text{ g/cm}^3$; $\mu = 0.878 \text{ mm}^{-1}$, min. and max. transmission factors 0.798 and 0.902; $2\theta_{\text{max}} = 58.82^\circ$; 34469 reflections collected, 8363 unique [$R_{\text{int}} = 0.0270$]; number of data/restraints/parameters 8363/0/470; final GoF 1.170, $R_1 = 0.0591$ [8707 reflections, $I > 2\sigma(I)$], $wR_2 = 0.1487$ for all data.

Calculations

All calculations were performed using the Gaussian 03 package.¹⁵ Structures were initially optimized using standard methods with the STO-3G* basis-sets for C, B, P, S, and H with the LANL2DZ basis-set for the rhodium atom. The final optimizations, including frequency analyses to confirm the true minima, together with GIAO nuclear-shielding calculations, were performed using B3LYP methodology, with the 6-31G* and LANL2DZ basis-sets. The GIAO nuclear shielding calculations were performed on the final optimized geometries, and computed ^{11}B shielding values were related to chemical shifts by comparison with the computed value for B_2H_6 , which was taken to be $\delta(^{11}\text{B}) + 16.6 \text{ ppm}$ relative to the $BF_3(OEt_2) = 0.0 \text{ ppm}$ standard.

Kinetic analysis

The kinetics of the substitution reaction between **2** and PMe_2Ph were measured in 0.02 M solutions of the hydridorhodathiaborane in CD_2Cl_2 . The decay of the hydride complex resonance was monitored by ^1H NMR spectroscopy (tables S4 and S5). The integrals were normalized relative to the solvent peak that was used as an internal standard.

The activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, were obtained from a linear least-square fit of $\ln(k/T)$ vs $1/T$ (Eyring equation). Errors were computed by published methods.¹⁶ The error in temperature was assumed to be 1 K; error in k_{obs} was estimated as 10%.

Synthesis of [8,8,8-(PMePh₂)₂(H)-9-(Py)-nido-8,7-RhSB₉H₉] (4): 82.7 mg (0.083 mmol) of **2**, placed in a Schlenk tube, was dissolved in 15 mL of CH_2Cl_2 under an atmosphere of argon. Three

equivalents of PMePh₂ (58.06 mL, 0.29 mmol) were added and the resulting solution was stirred for 4 h. Solvent was reduced in volume and hexane added to form a yellow precipitate that was separated by decantation, washed with hexane and dried under vacuum. The resulting yellow product was characterized as **4** (39.2 mg, 0.054 mmol, 56 %). IR(ATR): ν_{max} /cm⁻¹ 2512m (BH), 2011m (RhH). ¹¹B-¹H NMR (160 MHz; CDCl₃; 298K): δ 12.2 (1B, br, BH), 6.0 (1B, d, ¹J_{B-H} = 112 Hz, BH), 1.9 (1B, br, BH), -0.5 (1B, br, BH), -4.5 (1B, br, BH), -10.1 (1B, d, ¹J_{B-H} = 142 Hz, BH), -19.7 (1B, br, BH), -27.1 (2B, d, ¹J_{B-H} = 142 Hz, BH); ¹H-¹¹B NMR (300 MHz; CD₂Cl₂; 298K): δ 8.17 (2H, m, Py), 7.85 (1H, m, Py), 7.54 (1H, m, Py), 7.45 (1H, m, Py), 7.32-6.85 (20H, aromatic, 2PMePh₂), 3.86 (1H, br, BH), 3.46 (1H, br, BH), 2.86 (1H, br, BH), 2.39 (1H, br, BH), 1.84 (1H, br, BH), 1.83 (3H, d, ²J_{P-H} = 7.1 Hz, PMePh₂), 1.64 (3H, d, ²J_{P-H} = 7.0 Hz, PMePh₂), 1.39 (1H, s, BH), 1.32 (1H, s, BH), 0.92 (1H, s, BH), -1.34 (1H, s, BHB), -12.54 (1H, q, ¹J_{Rh-H} $\approx$ ²J_{P-H} = 13 Hz, Rh-H). ³¹P-¹H NMR (161 MHz; CDCl₃; 223 K): δ 17.4 (1P, dd, ¹J_{Rh-P} = 104 Hz, ²J_{PP} too broad to be resolved), 12.6 (1P, dd, ¹J_{Rh-P} = 128 Hz, ²J_{P-P} = 18 Hz); *m/z* (MALDI) 520 [M⁺ - (PPh₂Me + 2H), isotope envelope. PC₁₈H₂₆RhSB₉N requires 520; C₁₁H₃₃B₉NP₂RhS requires 722].

[8,8,8-(L)(PPh₃)(H)-9-(Py)-nido-8,7-RhSB₉H₉] where L = PMe₂Ph (5**), PMe₃ (**6**)**

Compound 5: The procedure was the same than for **4**, using 38.5 mg (0.045 mmol) of **2** and two equivalents of PMe₂Ph (19.4 μ L, 0.14 mmol), and stirring the resulting solution for 15 minutes. The resulting orange product was characterized as **5** (30.5 mg, 0.042 mmol, 93 %), which is a mixture of two isomers, **5a** and **5b**. Both isomers appear to exhibit the same ¹¹B-¹H NMR (160 MHz; CDCl₃; 298K): δ 12.1 (1B, s, BN), 4.3 (1B, br BH), -0.9 (2B, d, ¹J_{B-H} = 102 Hz, BH), -4.9 (1B, br, BH), -9.6 (1B, d, BH), -21.4 (1B, br, BH), -25.9 (1B, d, ¹J_{B-H} = 159 Hz, BH), -27.6 (1B, d, ¹J_{B-H} = 142 Hz, BH); similarly, the directly boron-bound proton resonances were indistinguishable for the isomers: ¹H-¹¹B NMR (300 MHz; CD₂Cl₂; 298K): δ 3.86 (1H, s, BH), 3.48 (1H, s, BH), 3.27 (1H, s, BH), 2.68 (1H, s, BH), 1.73 (1H, s, BH), 1.43 (1H, s, BH), 1.29 (1H, s, BH), 0.83 (1H, s, BH), -1.27 (1H, s, BHB). *m/z* (MALDI) 721 [(M⁺ - H), isotope envelope. P₂C₃₁H₄₁RhSB₉N requires 722], 582 [(M⁺ - PMe₂Ph - 2H), isotope envelope].

Additional NMR data for **5a**: ^1H - $\{^{11}\text{B}\}$ NMR (400 MHz, CD_2Cl_2): δ +1.53 (3H, doublet, $^2J_{\text{H-P}} = 7.5$ Hz, PMe_2Ph), +1.36 (3H, doublet, $^2J_{\text{H-P}} = 7.5$ Hz, PMe_2Ph) -13.02 (1H, q, $^1J_{\text{H-Rh}} \approx ^2J_{\text{H-P}} = 20$ Hz, Rh-H). ^{31}P - $\{^1\text{H}\}$ NMR (162 MHz; CD_2Cl_2 ; 223 K): δ +35.2 (1P, dd, $^1J_{\text{P-Rh}} = 128$ Hz, $^2J_{\text{P-P}} = 28$ Hz, PPh_3), -2.9 (1P, dd, $^1J_{\text{P-Rh}} = 105$ Hz, $^2J_{\text{P-P}} = 27$ Hz, PMe_2Ph).

Additional NMR data for **5b**: ^1H - $\{^{11}\text{B}\}$ NMR (300 MHz, CDCl_3): δ +1.44 (3H, d, $^2J_{\text{H-P}} = 7.4$ Hz, PMe_2Ph); +1.01 [3H, d, $^2J_{\text{H-P}} = 7.7$ Hz, PMe_2Ph], -12.78 (1H, q, $^1J_{\text{H-Rh}} \approx ^2J_{\text{H-P}} = 22$ Hz, Rh-H). ^{31}P - $\{^1\text{H}\}$ NMR (162 MHz; CD_2Cl_2 ; 223 K): δ +39.2 (1P, dd, $^1J_{\text{P-Rh}} = 108$ Hz, $^2J_{\text{P-P}} = 19$ Hz, PPh_3), -2.1 (1P, dd, $^1J_{\text{P-Rh}} = 128$ Hz, $^2J_{\text{P-P}} = 19$ Hz, PMe_2Ph).

Compound 6: Following the same synthetic steps described for compounds **4** and **5**, 76.1 mg (0.069 mmol) of **2** were treated with two equivalents of PMe_3 (18.5 mL, 0.18 mmol). Yield: yellow product, 0.023 g (0.048 mmol, 54 %). Anal. Calcd. for $\text{C}_{26}\text{H}_{39}\text{B}_9\text{NP}_2\text{RhS}$: C, 47.33; H, 5.96; N, 2.12; S 4.86. Found: C, 47.07; H, 5.88; N, 1.45; S 3.95. IR(ATR): ν_{max} / cm^{-1} 2910m (BH), 2112m (RhH). ^{31}P - $\{^1\text{H}\}$ NMR (161 MHz; CD_2Cl_2 ; 223 K): δ 36.9 [dd, $^1J_{\text{Rh-P}} = 129$ Hz, $^2J_{\text{P-P}} = 30$ Hz, PPh_3], -12.9 (broad d, $^1J_{\text{P-Rh}} = 103$ Hz, PMe_3). m/z (MALDI) 409 [M^+ - ($\text{PPh}_3 + 1\text{H}$), isotope envelope. $\text{PC}_8\text{H}_{33}\text{RhSB}_9\text{N}$].

Synthesis of [8,8,8-(PMe_2Ph)₂H-9-(Py)-*nido*-8,7-RhSB₉H₉] (**7**)

2 (12 mg, 0.014 mmol) was treated with PMe_2Ph (7.8 mg, 8 mL, 0.057 mmol) in 10 mL of CH_2Cl_2 . The resulting solution was stirred under an atmosphere of argon for 2.5 h. Solvent was evaporated, and the solid subjected to NMR studies in CD_2Cl_2 . The NMR spectra showed that the product of the reaction contained the isomers **5a** and **5b** together with the *bis*- PMe_2Ph substituted cluster, **7** in a 1:1:2 ratio. Isolation of compound **7** was not possible due to its instability towards dehydrogenation; therefore, the characterization of **7** was carried out in situ by NMR spectroscopy. ^{31}P - $\{^1\text{H}\}$ NMR (161 MHz; CD_2Cl_2 ; 298 K): δ 3.2 [d, $^1J_{\text{Rh-P}} = 77$ Hz, P_B *trans* to B(9)], -1.8 [dd, $^1J_{\text{Rh-P}} = 124$ Hz, $^2J_{\text{P-P}} = 24$ Hz, P_A *trans* to B(3)-B(4) edge].

Synthesis of [1,1-(PPh_3)(PMe_2Ph)-3-(Py)-*closo*-1,2-RhSB₉H₈] (**9**)

5.9 mg (0.0082 mmol) of a mixture of isomers **5a** and **5b** was dissolved in CD_2Cl_2 in an NMR tube and heated at 70 °C for 3 h. Solvent was reduced in volume and hexane added to form a yellow

precipitate that was separated by decantation, washed with hexane and dried under vacuum. The resulting red product was characterized as **9** (4.2 mg, 0.059 mmol, 72 %). $^{31}\text{P}\{-^1\text{H}\}$ NMR (161 MHz; CDCl_3 ; 223 K): δ 50.7 (dd, $^1J_{\text{RhP}} = 155$ Hz, $^2J_{\text{PP}} = 30$ Hz, PPh_3), -6.2 (dd, $^1J_{\text{RhP}} = 138$ Hz, $^2J_{\text{PP}} = 32$ Hz, PMe_2Ph).

Synthesis of [1,1-(PPh_3)(PMe_3)-3-(Py)-*closo*-1,2-RhSB $_9$ H $_8$] (**10**)

10 mg (0.021 mmol) of **6**, placed in a Schlenk tube, were dissolved in CH_2Cl_2 and heated to the reflux temperature under an atmosphere of argon for 3 h. Solvent was reduced in volume and hexane added to form a yellow precipitate that was separated by decantation, washed with hexane and dried under vacuum. The resulting yellow product was characterized as **10** (6.9 mg, 0.015 mmol, 69 %). $^{31}\text{P}\{-^1\text{H}\}$ NMR (161 MHz; CDCl_3 ; 300 K) ordered as δ_{P} [DFT-cald. δ_{P}]: 49.2 [67.7] (dd, $^1J_{\text{Rh-P}} = 157$ Hz, $^2J_{\text{P-P}} = 29$ Hz, PPh_3), -15.4 [-3.2] (1P, dd, $^1J_{\text{Rh-P}} = 146$ Hz, PMe_3). Anal. Calcd. for $\text{C}_{26}\text{H}_{37}\text{B}_9\text{NP}_2\text{RhS}$: C, 47.47; H, 5.67; N, 2.13; S 4.87. Found: C, 47.07; H, 5.88; N, 2.39; S 3.77.

Synthesis of [1,1-(PMe_2Ph) $_2$ -3-(Py)-*closo*-1,2-RhSB $_9$ H $_8$] (**11**)

A Schlenk tube was charged with the mixture of isomers **5** (10.1 mg, 0.012 mmol). The mixture of hydridorhodatiaboranes was dissolved in 10 mL of CH_2Cl_2 , and then PMe_2Ph (2.5 μL , 0.024 mmol) was added under an argon atmosphere. The resulting solution was heated at reflux in an argon atmosphere for 12 h. Solvent was evaporated and the red residue crystallized in CH_2Cl_2 / hexane to give 6.0 mg of compound **11** (0.010 mmol, 84 %). $^{31}\text{P}\{-^1\text{H}\}$ NMR (161 MHz; CD_2Cl_2 ; 300 K): δ 2.9 (d, $^1J_{\text{Rh-P}} = 140$ Hz). Anal. Calcd. for $\text{C}_{21}\text{H}_{35}\text{B}_9\text{NP}_2\text{RhS}$: C, 42.34; H, 5.92; N, 2.35; S 5.38. Found: C, 41.88; H, 5.87; N, 2.18; S 4.70. m/z (MALDI) 596 (M^+ , isotope envelope. $\text{C}_{21}\text{H}_{35}\text{B}_9\text{NP}_2\text{RhS}$ requires 596).

Synthesis of [1,1-(PMe_3) $_2$ -3-(Py)-*closo*-1,2-RhSB $_9$ H $_8$] (**12**)

A Schlenk tube was charged with **2** (112.8 mg, 0.1333 mmol). The rhodatiaborane was dissolved in 10 mL of CH_2Cl_2 , and then three equivalents of PMe_3 (399.9 μL , 0.399 mmol) were added under an argon atmosphere. The resulting solution was heated at 70 °C in an argon atmosphere for 12 h. Then, solvent was evaporated and the resulting solid crystallized in CH_2Cl_2 / hexane affording **12**. Yield: 56.1 mg,

0.1189 mmol, 89.2 %. $^{31}\text{P}\{-^1\text{H}\}$ NMR (121 MHz; CDCl_3 ; 300 K): δ -9.3 (2P, d, $^1J_{\text{Rh-P}} = 147$ Hz). Anal. Calcd. for $\text{C}_{11}\text{H}_{31}\text{B}_9\text{NP}_2\text{RhS}$: C, 28.02; H, 6.62; N, 2.97; S 6.80. Found: C, 27.86; H, 6.59; N, 2.86; S 6.48.

Synthesis of [1,1-(PMe₂Ph)(CO)-3-(Py)-*closo*-1,2-RhSB₉H₈] (16)

51.02 mg of the isomers mixture **5** (0.0707 mmol) was loaded in an Schlenk tube and dissolved in 10 mL of CH_2Cl_2 . A balloon filled with CO(g) was attached to the Schlenk tube, the system was, then, cooled in liquid nitrogen and evacuated under vacuum. The system was exposed to the carbon monoxide atmosphere created upon the opening of the balloon, and the reaction was stirred overnight at room temperature. The solvent was evaporated under vacuum, and the red solid studied by NMR. The data demonstrated formation of the PPh_3 -ligated *closo*-rhodathiaborane **14** and the CO-ligated analogue **15** in a 1 to 4 ratio, which results in a yield of 53 % for **16** (non-isolated, calculated from the NMR data). NMR data of **15**: IR(ATR): $\nu_{\text{max}}/\text{cm}^{-1}$ 2507 vs (BH), 1969 vs (CO), 1620 m, 1482 m, 1458 m, 1434 m, 1259 m, 1093 m, 1006 s, 905 s, 799 m, 682 s, 524 m, 488 m. $^{31}\text{P}\{-^1\text{H}\}$ NMR (202 MHz; CDCl_3 ; 300K) δ 1.9 (d, $^1J_{\text{Rh-P}} = 129$ Hz, PMe_2Ph).

Synthesis of [1,1-(PMe₃)(CO)-3-(Py)-*closo*-1,2-RhSB₉H₈] (17)

An orange solution of **6** (10 mg, 0.015mmol) in 2 mL of CD_2Cl_2 was stirred under an atmosphere of CO(g) at room temperature for 15 minutes during which time the initial bright-orange solution becomes yellow. The final mixture was washed repeatedly with hexane to give 5.9 mg of **17** (0.014mmol, 92 %). IR(ATR): $\nu_{\text{max}}/\text{cm}^{-1}$ 2521 s (BH), 2475 s (BH), 1979 vs (CO), 1620 m, 1480m, 1457 m, 1434 m, 1156 m, 1091 m, 1006 m, 933 m, 799 m, 681 m. $^{11}\text{B}\{-^1\text{H}\}$ NMR (160 MHz; CD_2Cl_2 ; 298K): δ 55.0 (1B, s, B-py), 27.4 (1B, d, $^1J_{\text{B-H}} = 129$ Hz, BH), 0.7 (1B, br, BH), -1.8 (1B, d, $^1J_{\text{B-H}} = 120$ Hz, BH), -14.1 (1B, br, BH), -25.8 (1B, br, BH), -32.3 (1B, d, $^1J_{\text{B-H}} = 149$ Hz, BH), -33.8 (1B, d, $^1J_{\text{B-H}} = 146$ Hz, BH). ^1H NMR (300 MHz; CD_2Cl_2 ; 300K) δ 9.41 (2H, d, $J = 5.6$ Hz, Py), 8.26 (1H, m, Py), 7.82 (2H, m, Py), 4.40 (1H, s, BH), 2.51 (1H, s, BH), 2.17 (1H, s, BH), 1.83 (1H, s, BH), +1.35 (3H, d, $^2J_{\text{P-H}} = 10.3$ Hz, PMe_3), 0.38 (1H, s, BH), 0.32 (1H, s, BH), 0.05 (1H, s, BH), 0.02 (1H, s, BH). $^{31}\text{P}\{-^1\text{H}\}$ NMR (202 MHz; CD_2Cl_2 ;

300K) δ -6.1 (d, $^1J_{\text{Rh-P}} = 137$ Hz, PMe_3); m/z (MALDI) 421 (M-4H; isotope envelop; $\text{PC}_9\text{H}_{22}\text{ORhSB}_9\text{N}$ requires 425).

Reactions of 9-12 and 16-17 with $\text{H}_2(\text{g})$

In a typical reaction, around 10 mg (0.016 mmol) of the *closo*-rhodathiaboranes was placed in a screw-capped NMR tube and dissolved in 0.6 mL of CD_2Cl_2 . The NMR tube was cooled in liquid nitrogen, evacuated, and then filled with H_2 . The samples were monitored at different intervals overnight by ^1H NMR spectroscopy, without evidence of changes in the spectra.

Reactions of 4-6 with C_2H_4

In a Schlenk tube, around 10 mg of the hydridorhodathiaboranes **4-6** was dissolved in CH_2Cl_2 (≈ 8 mL). A balloon filled with C_2H_4 was attached to the Schlenk tube, the system was, then, cooled in liquid nitrogen and evacuated under vacuum. The hydridorhodathiaborane solutions were exposed to the ethylene atmosphere created upon the opening of the balloon, and the reaction was stirred overnight at room temperature. In the case of compound **4**, the NMR data demonstrated that there was not reaction with the olefin. In the case of **6**, however, there was formation of the *closo*-derivative **10**. In the same conditions, a mixture of the isomers **5a** and **5b** leads to the formation of the *bis*- PMe_2Ph derivative **11**.

Compound 6 with ethylene: Alternatively, the reaction with compound **6** (5.5 mg, 0.0083 mmol, in 0.4 mL of CD_2Cl_2) was carried out in a screw-capped NMR tube, which was exposed to 1.5 bars of ethylene. After 3 days, the ^1H NMR spectrum at room temperature exhibits two broad multiplets at +2.27 and +2.05 ppm that correspond to the previously reported ethylene-ligated rhodathiaborane, **13**, in addition, there are two broad multiplets of higher intensity at +2.38 and +2.16 ppm, that can be assigned to the rhodium-bound ethylene ligand of the PMe_3 -ligated analogue, $[1,1-(\text{PMe}_3)(\eta^2\text{-C}_2\text{H}_4)\text{-3-(Py)-closo-1,2-RhSB}_9\text{H}_8]$ (**15**). At lower temperatures, the two signals of the ethylene ligand in **15** split into four peaks, which coalesce in pairs over the range 196-300 K to give a free energy for the rotation of the ethylene ligand of $\Delta G_{273} = 53$ kJ/mol (vs. $\Delta G_{252} = 49$ kJ/mol for **13**;^{2b} see supplementary material, Figure S17).

[1,1-(PMe₃)(η^2 -C₂H₄)-3-(Py)-*closo*-1,2-RhSB₉H₈] (**15**): NMR data assigned from a mixture that contains **10** (major), **13** (minor) and **15** (medium). ¹¹B-{¹H} NMR (160 MHz; CD₂Cl₂; 298K): δ 54.5 (1B, s, B-py), 24.9 (1B, b, BH), 0.9 (1B, b, BH), -1.1 (1B, b, BH), -20.5 (1B, b, BH), -27.6 (1B, b, BH), 30.5 (1B, b, BH), -31.7 (1B, b, BH). ¹H-{¹¹B} NMR (300 MHz; CD₂Cl₂; 298K): δ 4.37 (1H, s, BH), +1.18 (3H, d, ²J_{H-P} = 10.2 Hz, P-CH₃), 0.46 (1H, s, BH), 0.01 (1B, s, BH), -0.57 (1B, s, BH). ³¹P-{¹H} NMR (161 MHz; CD₂Cl₂; 300 K): δ -5.1 (1P, d, ¹J_{P-Rh} = 134 Hz, PMe₃).

Regarding the ¹¹B and ¹H NMR data, the assignments are tentative since there is overlapping of signals with the other two rhodathiaboranes, **10** and **13**. The ³¹P-{¹H} data, however, can be unambiguously assigned.

In a higher scale, 50.2 mg (0.059 mmol) of **6** were placed in a screw-capped Schlenk tube and dissolved in 25 mL of CH₂Cl₂. The resulting solution was frozen at the liquid nitrogen temperature, the system evacuated under vacuum, and, then, exposed to 1.5 bars of ethylene. After 7 days of stirring at room temperature, the solvent was evaporated to dryness and applied to preparative TLC plates. The chromatogram was developed using CH₂Cl₂/hexane (3:1) as mobile phase to give broad yellow (R_f = 0.33) and red (R_f = 0.13) bands. The former was a mixture of compounds **13** (1.71 mg, 0.0028 mmol, 5 %) and **15** (4.28 mg, 0.010 mmol, 17 %) in a 1:4 ratio; whereas the second was compound **10** (12 mg, 0.018 mmol, 31 %). It was found that compound **13** and **15** decompose largely on the plates; thus, a second preparative TLC plate resulted in the loss of both species.

In the same conditions, using screw-capped NMR and Schlenk tubes and 1.5 bars of ethylene, the mixture of isomers **5** afforded compound **11** as the major component and small amounts of the ethylene-ligated cluster, **13**. However, we did not detect the ethylene-ligated PMe₂Ph counterpart.

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SUPPORTING INFORMATION PARAGRAPH. $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra at different temperatures of compounds **2** and **6**; NMR spectra of the reactions of **2** with PMe_3 , PMe_2Ph and PMePh_2 at different temperatures; series of $^1\text{H}\text{-}^{31}\text{P}$ HSQC, $^{31}\text{P}\{-^1\text{H}\}$ and ^1H NMR spectra of samples that contain mixtures of **5a**, **5b** and **7**; tables of the kinetics studies; the Eyring plot; ORTEP-type of picture for compound **11**; experimental and DFT-calculated coordinates and energy for **6** and **10**; CIF files for **4**, **10** and **11**.

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