3-Pyridylacetonitrile-ligated 11-Vertex Rhodathiaboranes: Synthesis, Characterization and X-ray Crystal Structure

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Dedicated to Prof. Juan Costamagna, a superb mentor of a large number of Latin American scientists working on coordination chemistry.

Received xxx; accepted xxx

Abstract: The reaction between the 11-vertex rhodathiaborane [8,8-(PPh₃)₂-nido-8,7-RhSB₉H₁₀] (**1**) and 3-pyridylacetonitrile affords the hydridorhodathiaborane [8,8,8-(PPh₃)₂H-9-(3-Py-CH₂CN)-nido-8,7-RhSB₉H₉] (**2**) in good yield. Treatment of this cluster with ethylene leads to the formation of red, [1,1-(PPh₃)(η²-C₂H₄)-3-(3-Py-CH₂CN)-closo-1,2-RhSB₉H₈] (**3**). Both 11-vertex polyhedral boron-based clusters have been characterized by multielement NMR spectroscopy. In addition, compound **3** has been analyzed by single-crystal X-ray diffraction analysis, and is only the second ethylene ligated metallaheteroborane to be characterized in the solid state. The molecular structure of this cluster is based on an octadecahedron. In the crystal lattice, the individual clusters form layers supported by short edge-to-face π -interactions between the phenyl rings of neighboring molecules.

Keywords: polyhedral clusters, rhodathiaboranes, ethylene, boron, rhodium

1. Introduction

Metallaheteroboranes are polyhedral boron-based clusters that feature M–B, E–B and B–B bonds, where M and E are metallic and *p*-block elements, respectively. Metallacarboranes, where E = C, form the largest group of metallaheteroboranes for which a systematic study of their reaction chemistry has been carried out [1-13]. In contrast, the reaction chemistry of other metallaheteroboranes is poorly developed [14-20].

The high-yield synthesis of the 11-vertex [8,8-(PPh₃)₂-*nido*-8,7-RhSB₉H₁₀] (**1**) [21] from the reaction of the Wilkinson's compound with CsSB₉H₁₂ has allowed the development of a systematic chemistry based on this cluster. During our research dealing with **1**, we have discovered that the reaction with pyridine affords the hydridorhodathiaborane, [8,8,8-(PPh₃)₂H-9-(NC₅H₅)-*nido*-8,7-RhSB₉H₉]. This 11-vertex cluster exhibits a remarkable structural *nido*-to-*closo* flexibility that has led to a rich reaction chemistry that embraces: (i) *nido*-to-*closo* dehydrogenations [22], (ii) dihydrogen promoted *closo*-to-*nido* transformations [23, 24], (iii) oxidative addition of *sp* C–H bonds, [25] (iv) proton-assisted H₂ activation [26] and (v) catalysis of hydrogenation and isomerization of olefins [23].

Scheme 2 Formation of [8,8,8-(H)(PPh₃)₂-9-(3-Py-CH₂CN)-nido-8,7-RhSB₉H₉] (**2**) and its reaction with ethylene to give [1,1-(η²-C₂H₄)(PPh₃)₂-3-(3-Py-CH₂CN)-closo-1,2-RhSB₉H₈] (**3**).

In this reaction, the terminal hydrogen atom at the B(9) vertex adjacent to the metal centre at position 8, is formally substituted by the N-heterocyclic reagent, 3-Py-CH₂CN (see Scheme 2 for the cluster numbering). The detailed mechanism of this reaction is unknown at this time, although two possible reaction pathways may be envisioned: (a) the Lewis base directly attacks boron atom B(9), leading to the migration of the terminal hydrogen atom to the metal centre, (b) the incoming ligand coordinates the metal centre and subsequently migrates to the B(9) vertex in a process that involves the concerted movement of the terminal hydrogen atom to the rhodium centre (Scheme 2). Alternatively, the B(9)-H-B(10) bridging hydrogen atom may be involved in both proposed concerted migrations instead of the terminal hydrogen atom, B(9)-H. Recently, we have demonstrated that the substitution reactions of **1** with monodentate phosphines follow an associative mechanism and, based on these results, it is therefore

more probable that the formation of the hydridorhodathiaborane occurs *via* coordination of the incoming Lewis base to the metal centre.

Scheme 3. Proposed pathways for the reaction of **1** with 3-Py-CH₂CN (L): (a) direct attack at the B(9) vertex, (b) attack mediated by the metal centre.

The 3-pyridylacetonitrile-ligated hydridorhodathiaborane, **2**, has been characterized by multielement NMR spectroscopy and mass spectrometry. This compound is sparingly soluble in dichloromethane, suggesting that the cluster may exhibit intermolecular interactions leading to an extended association in the solid state. Unfortunately, we have not yet been able to grow a crystal suitable for single-crystal X-ray diffraction analysis. The ¹¹B-{¹H} NMR spectrum exhibits nine resonances ranging between δ_B +12.1 and -26.9 ppm, which is within the range found for the pyridine and picoline-ligated analogues, [8,8,8-(H)(PPh₃)₂-9-(L)-*nido*-8,7-RhSB₉H₉], where L = Py, 2-Me-Py, 3-Me-Py and 4-Me-Py.[22] The highest frequency peak corresponds to the 3-pyridylacetonitrile substituted boron atom as is found the pyridine and picoline analogues.

The ¹H-{¹¹B} NMR spectrum of **2** shows a broad singlet and an apparent quartet in the high-field region, which may be assigned to the B(9)–B(10) bridging hydrogen atom and to the Rh–H hydride ligand, respectively. These spectroscopic data are diagnostic for this class of 11-vertex *nido*-hydridorhodathiaboranes.

The low temperature $^{31}\text{P}\{-^1\text{H}\}$ spectrum of **2** exhibits two doublets-of-doublets with the resonance at highest frequency being much broader. This latter resonance increasingly broadens and shifts to lower frequency as the temperature is increased. The low-frequency signal moves to a slightly higher frequency. This variable temperature NMR behaviour is similar to that found for the $[8,8,8\text{-}(\text{H})(\text{PPh}_3)_2\text{-}9\text{-}(\text{L})\text{-}nido\text{-}8,7\text{-RhSB}_9\text{H}_9]$ analogues (where L = Py, 2-Me-Py, 3-Me-Py and 4-Me-Py) [27].

It has been proposed that the temperature dependent broadening in the $^{31}\text{P}\{-^1\text{H}\}$ spectra of N-heterocyclic-ligated hydridorhodathiaboranes may arise mainly from the effects of “thermal decoupling” of the boron nuclei [28] together with the dissociation of the phosphine ligand *trans* to B(9) [22, 23]. Using this rationale, the broader peak at high frequency, in this new family of 11-vertex hydrido-ligated clusters, may be assigned to the phosphine ligand that is *trans* to the Lewis base-substituted boron vertex at the 9-position.

Compound **2** reacts with ethylene to afford $[1,1\text{-}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)\text{-}3\text{-}(3\text{-Py-CH}_2\text{CN})\text{-}1,2\text{-RhSB}_9\text{H}_8]$ (**3**) in 74% isolated yield, through 3-pyridylacetonitrile cage substitution and dihydrogen loss (*vide infra*), resulting in a cluster with a *closo* / *isonido*-electron count. This ethylene-ligated cluster has been characterized by multielement NMR spectroscopy and X-ray diffraction analysis. The ^{11}B NMR spectrum shows seven signals a 1:1:2:1:1:1:2 relative intensity ratio in accord with an asymmetric cluster. The resonance at δ_{B} +55.4 ppm corresponds to the B(3) substituted 3-pyridylacetonitrile vertex. At room temperature in the ^1H NMR spectrum, the ethylene ligand shows two signals that split into four peaks at low temperature. This variable temperature behaviour demonstrates that the $\text{Rh}\text{-}(\eta^2\text{-C}_2\text{H}_4)$ interaction is fluxional, undergoing a hindered rotation that renders the two C–H pairs equivalent. The free energy barrier, calculated at the coalesce temperature, for this rotational process is 11.7 kJ/mol (see supplementary material). This is also the activation energy $\Delta G^\ddagger$ found for the full rotation of the ethylene ligand about the coordination bond in the pyridine-ligated analogue, $[1,1\text{-}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)\text{-}3\text{-}(\text{Py})\text{-}1,2\text{-RhSB}_9\text{H}_8]$ (**4**) [22].

Figure 1 Crystallographically determined molecular structure of $[1,1-(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)\text{-3-(3-Py-CH}_2\text{CN)-closo-1,2-RhSB}_9\text{H}_8]$ (compound **3**).

Figure 1 depicts the molecular structure of **3** determined by X-ray diffraction and Table 1 lists selected distances and angles together with comparison values for the pyridine-ligated analogue, $[1,1-(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)\text{-3-(Py)-1,2-RhSB}_9\text{H}_8]$ (**4**) [22]. At first sight, the structure of the cluster is based on an octadecahedron. It should be noted that both, the 3-pyridyl-acetonitrile and the pyridine derivatives, feature long Rh(1)–B(5) distances close to 2.5 Å, which is the upper limit normally considered as bonding. This relatively long Rh(1)–B(5) linkage is *trans* to the η^2 -ethylene ligand in both rhodathiaboranes, **3** and **4**. This type of elongation has been found in others 11-vertex metallaheteroboranes that exhibit a *pseudo*-square open face [29], which represent intermediates along the structural continuum from *closo* to *nido* [30–33].

Figure 2 Section of the crystal structure of $[1,1-(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)\text{-3-(3-Py-CH}_2\text{CN)-closo-1,2-RhSB}_9\text{H}_8]$ (compound **3**), showing the short contacts between the clusters. There are edge-to-face π -interactions between the phenyl rings ranging from 2.70–2.85 Å, and $\text{B}\cdots\text{H-C}$ distances at 2.97 and 3.13 Å between the C–H units of one phenyl rings and the B(7) and B(10) vertices, and between a C–H unit of the acetonitrile group and the B(10) vertex at 3.12 Å.

In the crystal lattice, the clusters show intermolecular edge-to-face π -interactions. The observed $\text{C-H}\cdots\text{C}$ contacts are in the range 2.70–2.85 Å, being shorter than the Van der Waals radii. Each cluster shows three of these interactions with two adjacent neighbors (Figure 2). It is noteworthy that these attractive π -forces lead to the approach of the B(7) and B(10) vertices and C–H unit of phenyl rings and the $-\text{CH}_2\text{CN}$ dangling groups between adjacent clusters. The result is the formation of chains that grow along the crystallographic c -axis. These chains pack on the ac -plane to form a layer, which self-assemble, *via* the commented π -interactions, with an adjacent parallel layer, forming an

AB-type of a double layer. The repetition of this close-packed double layer in the unit cell forms the solid structure of compound **3** (Figure 3).

Figure 3 Packing of the crystal structure of $[1,1-(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)\text{-}3\text{-(}3\text{-Py-CH}_2\text{CN)-closo-1,2-RhSB}_9\text{H}_8]$ (compound **3**). View along the *c*-axis: the layers grow on the *ac*-plane.

It is interesting to note that the low resolution mass spectra of compounds **2** and **3** give an ion centred at m/z 979 with an isotopic pattern that matches well a molecular ion with the formula, $[\{(\text{PPh}_3)(\text{RhSB}_9\text{H}_8)\}(3\text{-Py-CH}_2\text{CN})\{3\text{-Py-CH}_2\text{CN}(\text{RhSB}_9\text{H}_8)\}]^+$ (see Figures S1 and S2). A reasonable interpretation is that this ion contains a $\{(\text{PPh}_3)(\text{RhSB}_9\text{H}_8)\}$ fragment and a $\{(3\text{-Py-CH}_2\text{CN})(\text{RhSB}_9\text{H}_8)\}$ unit bridged by a 3-pyridyl ligand. In addition, the spectra show the fragmented ion $[(\text{PPh}_3)\text{RhSB}_9\text{H}_8(3\text{-Py-CH}_2\text{CN})]^+$ at m/z 621 (Figure 4). These results suggest that the dangling nitrile group in compounds **2** and **3** can coordinate other metal centers leading to the formation of dimeric species:

The observed fragmentation processes involve the loss of dihydrogen and one PPh₃ ligand from the hydridorhodathiaborane **2**, and the ethylene ligand from **3**:

It should be noted that identical results were obtained using the matrices DCTB, terthiophene and dithranol, suggesting that the formation of the dimeric ion is a fundamental property of these 3-pyridyl-ligated clusters.

Figure 4 Positive ion LSMS spectrum of [1,1-(η^2 -C₂H₄)(PPh₃)-3-(3-Py-CH₂CN)-*closo*-1,2-RhSB₉H₈] (compound **3**).

3. Conclusion

Reaction of the 11-vertex rhodathiaborane **1** with 3-pyridylacetonitrile is a convenient method for the modification of the boron-bound *exo*-polyhedral ligands in 11-vertex rhodathiaboranes. The resulting labile hydridorhodathiaborane **2** reacts with ethylene to

give an ethylene-ligated cluster, which has been characterized by X-ray diffraction analysis. This is only the second crystallographically-determined ethylene-ligated polyhedral boron-based cluster reported in the literature.

The dangling nitrile group in compounds **2** and **3** is open for coordination to other metal centres: thus, both clusters are appropriate reagents for the potential synthesis of bimetallic systems. In addition, the reaction of **3** with dihydrogen may afford unsaturated species, formed by release of ethane, which could lead to intercluster coordination via the nitrile groups.

The incorporation of 3-pyridylacetonitrile on the 11-vertex *nido*- and *closo*-clusters is straight-forward method for the modification of the *exo*-polyhedral surface of the clusters, thereby opening new possibilities for coordination of different metals and leading to the development of their reaction chemistry.

Table 1. Selected interatomic distances (Å) and angles (°) with Estimated Standard Uncertainties (s.u.) in parentheses for [1,1-(η^2 -C₂H₄)(PPh₃)-3-(3-NCCH₂Py)-*closo*-1,3-RhSB₉H₈] **3** and [1,1-(η^2 -C₂H₄)(PPh₃)-3-(Py)-*closo*-1,3-RhSB₉H₈] **4**.

	3	4 ^[22]
Rh(1)–S(2)	2.3615(7)	2.3721(9)
Rh(1)–P(1)	2.3000(7)	2.2981(9)
Rh(1)–C(1)	2.164(3)	2.165(3)
Rh(1)–C(2)	2.172(3)	2.171(4)
Rh(1)–B(3)	2.087(3)	2.079(4)
Rh(1)–B(4)	2.445(3)	2.427(4)
Rh(1)–B(5)	2.490(3)	2.503(4)
Rh(1)–B(6)	2.411(3)	2.365(4)
Rh(1)–B(7)	2.330(3)	2.376(4)
S(2)–B(4)	1.938(3)	1.948(4)
S(2)–B(5)	1.935(3)	1.929(4)
S(2)–B(8)	1.990(3)	1.985(4)
C(1)–C(2)	1.383(4)	1.383(5)
N(1)–B(3)	1.544(3)	1.539(5)
P(1)–Rh(1)–S(2)	103.81(2)	112.86(3)
P(1)–Rh(1)–B(3)	116.85(8)	109.13(11)
S(2)–Rh(1)–B(3)	119.34(8)	119.58(11)
Rh(1)–B(3)–N(1)	130.72(19)	127.7(2)
C(1)–Rh(1)–P(1)	95.84(8)	89.32(11)
C(2)–Rh(1)–P(1)	89.08(8)	93.39(10)

Table 2 Crystallographic Data and Structure Refinement Information for [1,1-(η^2 -C₂H₄)(PPh₃)-3-(3-Py-CH₂CN)-*closo*-1,2-RhSB₉H₈] (compound **3**).

Chemical formula	C ₂₇ H ₃₃ B ₉ N ₂ PRhS
Formula Mass	648.82
Crystal system	Monoclinic
<i>a</i> /Å	11.1218(8)
<i>b</i> /Å	21.6719(15)
<i>c</i> /Å	13.8727(10)
α /°	90.00
β /°	113.3086(10)
γ /°	90.00
Unit cell volume/Å ³	3070.9(4)
Temperature/K	100(2)
Space group	<i>P</i> 21/ <i>n</i>
No. of formula units per unit cell, <i>Z</i>	4
Radiation type	MoK α
Absorption coefficient, μ /mm ⁻¹	0.698
No. of reflections measured	33287
No. of independent reflections	8019
<i>R</i> _{int}	0.0612
Final <i>R</i> _I values (<i>I</i> > 2 σ (<i>I</i>))	0.0371
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2 σ (<i>I</i>))	0.0711
Final <i>R</i> _I values (all data)	0.0687
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.0805
Goodness of fit on <i>F</i> ²	1.010

4. Experimental

4.1. General Procedures

Reactions were carried out under an argon atmosphere using standard Schlenk-line techniques. Solvents were obtained dried from a Solvent Purification System of Innovative Technology Inc. The 11-vertex rhodathiaborane **1** was prepared according to the literature methods [21]. NMR spectra were recorded on Bruker Avance 300-MHz and AV 400-MHz spectrometers, using ^{31}P - $\{^1\text{H}\}$, ^{11}B , ^{11}B - $\{^1\text{H}\}$, ^1H , ^1H - $\{^{11}\text{B}\}$ and ^1H - $\{^{11}\text{B}(\text{selective})\}$ techniques. Residual solvent protons were used as reference (δ , ppm, CDCl_3 , 7.26; CD_2Cl_2 , 5.33; CD_3CN , 1.96). ^{11}B chemical shifts are quoted relative to $[\text{BF}_3(\text{OEt})_2]$ and ^{31}P chemical shifts are quoted relative to 85% aqueous H_3PO_4 . Mass spectrometric data were recorded on a MICROFLEX instrument operating in the positive mode, 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 three matrices: *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), dithramol and terthiophene.

4.2. X-ray crystallography

Crystals of compound **3** suitable for X-ray diffraction analysis were grown by slow diffusion of hexane into a concentrated solution of the rhodathiaborane in dichloromethane. X-ray diffraction data were collected at low temperature (100(2) K) on an automatic Bruker Kappa APEX DUO CCD area detector diffractometer equipped with graphite-monochromatic Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$) using narrow frames (0.3° in ω). In all cases, single crystals were mounted on a fiber and were covered with a protective perfluoropolyether. Intensities were integrated including Lorentz and polarization effect with SAINT-Plus program [34] and corrected for absorption using multi-scan methods applied with SADABS program [35]. The structures were solved using the SHELXS-97 program [36]. Refinements were carried out by full-matrix least-squares on F^2 with SHELXL-97 [37], including isotropic and subsequent anisotropic displacement parameters for all non-hydrogen atoms. Experimental diffraction parameters and crystal data are gathered in Table 3.

4.3. Synthesis and NMR data

4.3.1. [8,8,8-(H)(PPh₃)-9-(3-Py-CH₂-CN)-*nido*-8,7-RhSB₉H₉] (2). In a Schlenk tube, 116 mg (0.151 mmol) of **1** was dissolved in 10 mL of CH₂Cl₂, resulting in a bright-red solution. 160 μ l (179 mg, 1.51 mmol) of 3-pyridylacetonitrile (3-Py-CH₂CN) was syringed into the solution, and the reaction mixture was stirred at room temperature for 7 hours. After this time the solvent was evaporated to dryness and the solid residue washed three times with hexane. The final product was characterized as compound **2**. Yield: 100.8 mg, 0.139 mmol, 92%. IR (ATR): ν 2535 vs (BH), 2511 vs (BH), 2460 vs (BH), 2255 w (CN), 2060 m (RhH). ¹¹B-¹H NMR (128 MHz; CD₂Cl₂; 298K): δ +12.1, +7.8, +3.5, +0.3, -3.8, -9.9, -18.5, -25.6, -29.6. ¹H NMR (500 MHz; CD₂Cl₂; 298K): δ +7.91 (1H, br, 3-PyCH₂CN), +7.82 (1H, br, 3-PyCH₂CN), +7.35 – +7.05 (aromatics, PPh₃), +4.04 (v br, BH), +3.67 (ABq, 1H, $\Delta\nu_{AB}$ = 30.8 Hz, J_{AB} = 19.2 Hz, CH₂CN), +3.55 (ABq, CH₂CN), +2.85 (v br, BH), +1.84 (v br, BH), -1.37 (br s, BHB), -12.51 (apparent q, J = 18.9 Hz, RhH); due to the insolubility of the compound, the terminal B-H peaks could not be observed. ³¹P-¹H NMR (121 MHz; CD₂Cl₂; 298 K): δ +33.7 (v br), +32.3 (br d, J_{RhP} = 97 Hz), 37.4 (d, J_{RhP} = 144 Hz), +28.3 (s, O=PPh₃). ³¹P-¹H NMR (121 MHz; CD₂Cl₂; 213 K): δ +36.3 (dd, J_{RhP} = 104.1 Hz), +30.4 (dd, J_{RhP} = 127.1 Hz, $^2J_{PP}$ = 19 Hz). LRMS (MALDI⁺/DCTB): m/z [2M - 3(PPh₃) - 4H]⁺ obsvd 979, calcd for P₁C₃₂H₄₃Rh₂S₂B₁₈N₄: 979; [M - PPh₃ - 2H]⁺ obsvd 621, calcd for P₁C₂₅H₂₉Rh₁S₁B₉N₂: 621. The obsvd isotope envelope matches that calculated from the known isotopic abundances of the constituent elements.

4.3.2. [1,1-(PPh₃)(η^2 -C₂H₄)-3-(3-Py-CH₂CN)-*closo*-1,2-RhSB₉H₈] (3): 50 mg (0.056 mmol) of [8,8,8-(H)(PPh₃)₂-9-(3-Py-CH₂-CN)-*nido*-8,7-RhSB₉H₉] (**2**) was dissolved in 10 ml of CH₂Cl₂ in a Schlenk tube. After three freeze-thaw cycles, a balloon containing ethylene was attached to the Schlenk tube, and the rhodathiaborane solution exposed to the gas. The system was stirred at room temperature for 24 h and then concentrated by solvent evaporation under vacuum, after which hexane was added to produce an orange-red precipitate, which was then washed several times with hexane. The solid was crystallized from CH₂Cl₂/hexane to isolate the respective ethylene-ligated cluster, [1,1-(η^2 -C₂H₄)(PPh₃)-3-(3-Py-CH₂CN)-*closo*-1,2-RhSB₉H₈]. Yield: 27 mg, 0.042 mmol, 74%. IR (ATR): ν 2529 vs (BH), 2509 vs (BH). ¹¹B-¹H NMR (96 MHz, CDCl₃, 298 K): δ +55.4 (s, B-N), +26.2 (s, BH, $^1J(^{11}\text{B}-^1\text{H})$ = 122 Hz), +1.1 (s, 2B-H), -14.2 (s, B-H), -21.9 (s, B-H, $^1J(^{11}\text{B}-^1\text{H})$ = 128 Hz), -24.5 (s, B-H, $^1J(^{11}\text{B}-^1\text{H})$ = 126 Hz), -29.8 (s,

2B-H). $^1\text{H}\{-^{11}\text{B}\}$ NMR (300 MHz, CDCl_3 , 298 K): δ +9.30 (1H, br, 3-PyCH₂CN), +9.19 (1H, br, 3-PyCH₂CN), +8.35 (1H, br, 3-PyCH₂CN), +7.84 (1H, br, 3-PyCH₂CN), +4.22 (s, B-H), +3.94 (ABq, 1H, $\Delta\nu_{\text{AB}} = 27.5$ Hz, $J_{\text{AB}} = 18.5$ Hz, CH₂CN), +3.81 (ABq, CH₂CN), +2.27 (s, B-H), +2.28 (C₂H₄), +2.09 (C₂H₄), +1.96 (s, B-H), +1.60 (s, B-H), +0.43 (s, B-H), +0.22 (s, B-H), -0.19 (s, B-H), -0.23 (s, B-H). $^{31}\text{P}\{-^1\text{H}\}$ NMR (121 MHz, CDCl_3 , 298 K): δ +39.0 (d, PPh₃, $J_{\text{RhP}} = 141$ Hz). LRMS (MALDI⁺/DCTB): m/z [2M - (PPh₃) - 2(C₂H₄)]⁺ obsvd 979, calcd for P₁C₃₂H₄₃Rh₂S₂B₁₈N₄: 979; [M - (C₂H₄)]⁺ obsvd 621, calcd for P₁C₂₅H₂₉Rh₁S₁B₉N₂: 621. The obsvd isotope envelope matches that calculated from the known isotopic abundances of the constituent elements.

Supplementary material

CSD-CCDC 1006809 contains the supplementary crystallographic data for this article. Measured and calculated isotopic patterns for compounds **2** and **3**.

Acknowledgments

We acknowledge the Spanish Ministry of Science and Innovation (CTQ2012-32095, CONSOLIDER INGENIO, CSD2009-00050, MULTICAT and CSD2006-0015, Crystallization Factory) for support of this work and the KFUPM-University of Zaragoza research agreement. B.C. thanks the “Diputación General de Aragón” for a pre-doctoral scholarship.

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