

Brønsted acid/base driven chemistry with rhodathiaboranes: a labile {SB₉H₉}-thiodecaborane fragment system

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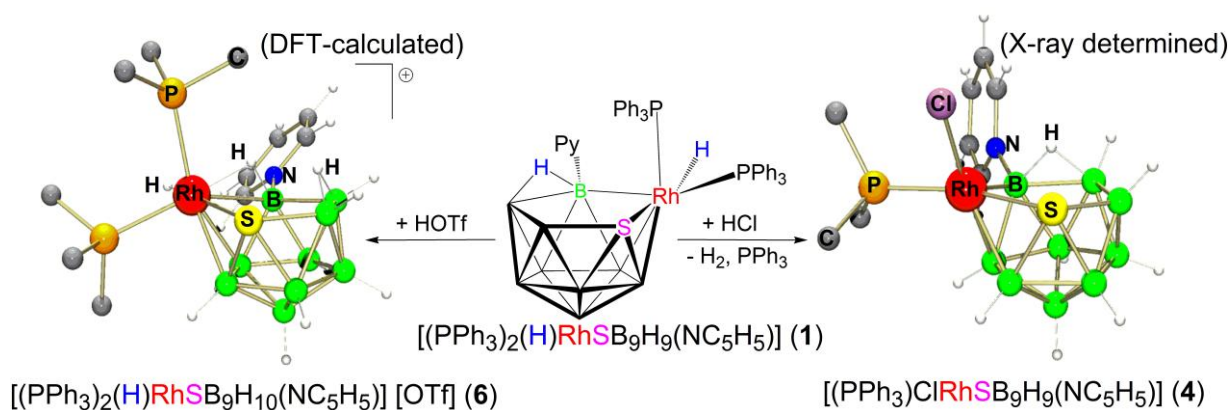
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Dedicated to the memory of an outstanding and creative scientist, Prof. F. Gordon A. Stone, Doctor Honoris Causa by the University of Zaragoza. He has been a superb mentor of a number of Spanish scientists working on organometallic chemistry.

ABSTRACT



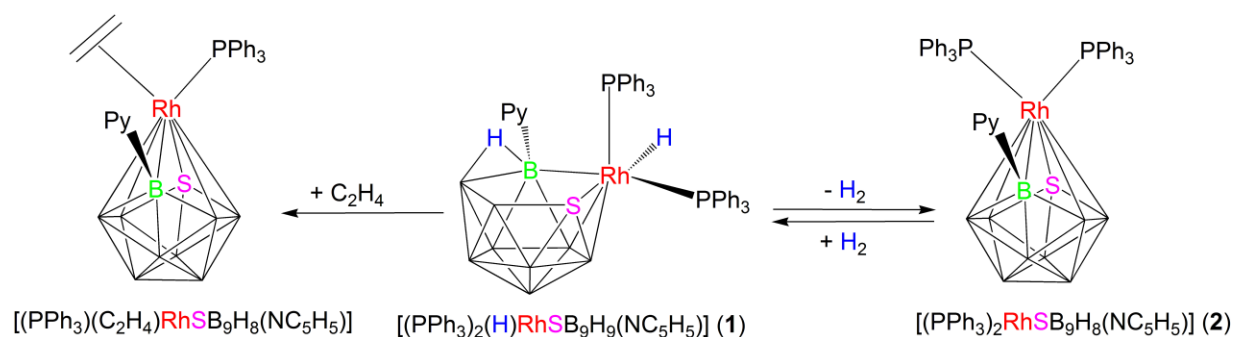
Reversible H_2 cleave promoted by *closo*-to-*nido* transformations of [1,1-(PPh_3)₂-3-(NC_5H_5)-*closo*-1,2-RhSB₉H₈] (**2**) / [8,8,8-(PPh_3)₂(H)-9-(NC_5H_5)-*nido*-8,7-RhSB₉H₉] (**1**) is a cooperative action with application in catalysis; the treatment of **2** and [1,1-(PPh_3)(CO)-3-(NC_5H_5)-*closo*-RhSB₉H₈] (**3**) with either HCl or HOTf in CH_2Cl_2 affords the 11-vertex *nido*-rhodathiaboranes [8,8-(PPh_3)(Cl)-9-(NC_5H_5)-*nido*-8,7-RhSB₉H₉] (**4**) and [8,8,8-(PPh_3)(CO)(Cl)-9-(NC_5H_5)-*nido*-8,7-RhSB₉H₉] (**5**), respectively; in contrast the reaction of **1** with triflic acid yields the salt [8,8-(PPh_3)₂(H)-9-(NC_5H_5)-*nido*-RhSB₉H₁₀][**OTf**] (**6**). These results illustrate the bifunctional nature of the clusters and their *nido*-to-*closo* redox flexibility, which open new routes for the tuning of the reactivity of these polyhedral compounds and widen their potential applications.

MAIN TEXT

Complexes in which both the metal center and the ligands are involved in chemical transformations are attracting an increasing attention as new catalyst promoters. In this regard, ligand-assisted reactivity plays an important role in reactions that involve heterolytic dihydrogen activation and/or hydrogen transfer from alcohols. The most active complexes combine a transition metal center with reversible alcohol-ketone,¹⁻³ reversible amine-amide functionalities,⁴⁻⁶ or with ligands that undergo facile reversible dearomatization.^{7,8}

Cluster cooperation in polyhedral boron-containing compounds via reversible *nido-to-closo* transformations can play a role in homogeneous catalysis. In this regard, the 11-vertex rhodathiaborane system, [8,8,8-(PPh₃)₂(H)-9-(NC₅H₅)-*nido*-8,7-RhSB₉H₉] (**1**) / [1,1-(PPh₃)₂-3-(NC₅H₅)-*closo*-1,2-RhSB₉H₈] (**2**) has been shown to undergo reversible dehydrogenation.⁹ In conjunction with the reactivity of **1** toward C₂H₄ (Scheme 1), the hydrogen activation step defines a catalytic cycle, which has been proved to operate in the hydrogenations of alkenes.¹⁰ Furthermore, this 11-vertex hydridorhodathiaborane promotes the oxidative addition of sp C–H bonds, driven by dihydrogen release from the cluster.¹¹

Scheme 1

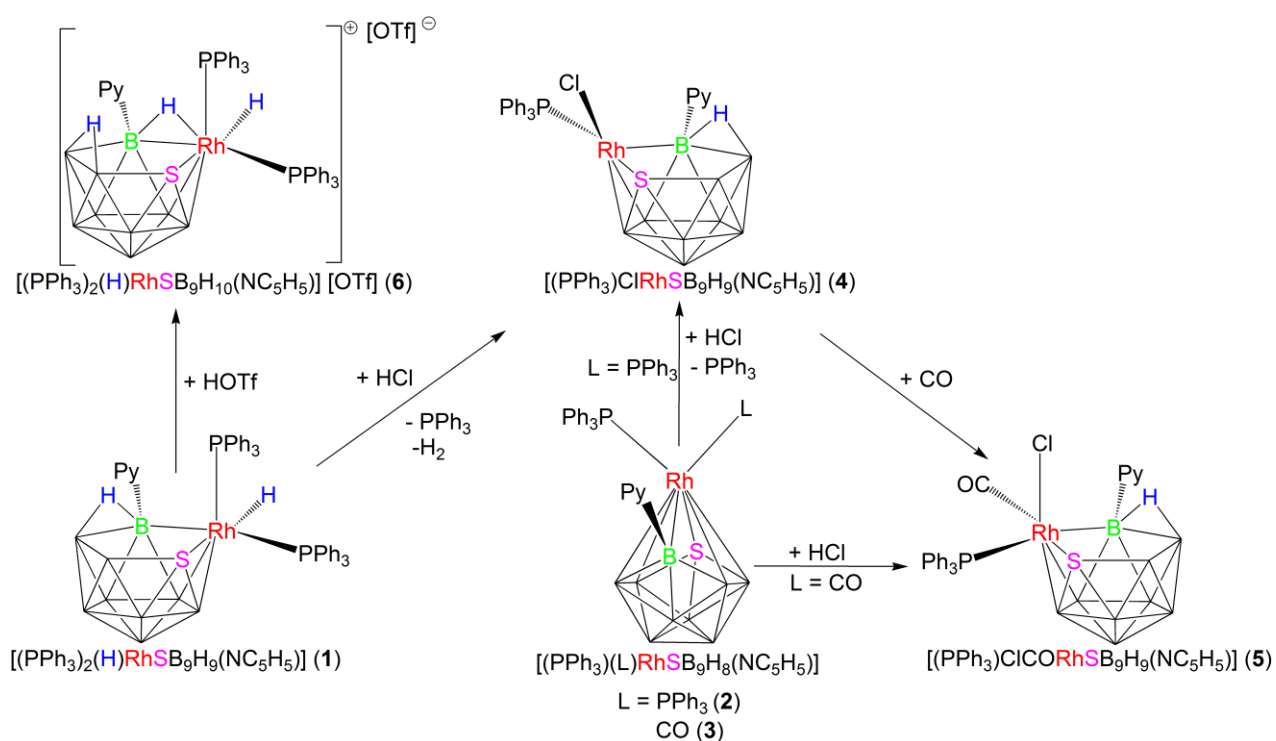


Although the mode of action on these rhodathiaboranes differs from that of the non-innocent-ligand containing complexes commented above, the {SB₉H₈(NC₅H₅)} fragment in compounds **1** and **2** can be regarded as a ligand that participates actively in the reactions, behaving as a “hydride store”¹² and a flexible polydentate fragment. Alternatively, the bifunctional nature of the clusters, supported by the heterolytic cleave of H₂, makes these rhodathiaboranes evocative of a “frustrated Lewis pair”,¹³ implying that the clusters combine Lewis basic and acid centers. Here we describe reactions of compound **1** and its *closo* derivatives [1,1-(PPh₃)(L)-3-(NC₅H₅)-1,2-RhSB₉H₈], where L = PPh₃ (**2**) or CO (**3**),¹⁰ with HCl and HOTf that further support the mentioned bifunctional nature of the system and illustrate the remarkable flexibility of these 11-vertex rhodathiaboranes.

Reaction of **2** with HCl in CD₂Cl₂ at room temperature afforded the chloro-ligated 11-vertex rhodathiaborane, [8,8-(PPh₃)(Cl)-9-(NC₅H₅)-*nido*-8,7-RhSB₉H₉] (**4**). This cluster can be also

synthesized from the reaction of the hydridorhodathiaborane **1** with HCl in dichloromethane at ambient temperature. In both cases, hydrochloric acid can be used either as gas or in a water solution (see supporting information), yielding **4** in high yields as an air stable yellow solid. Starting from **2**, the reaction involves a *closo*-to-*nido* transformation, release of one of the PPh₃ ligands and the splitting and consequent accommodation of the HCl molecule on the cluster. From **1**, the reaction involves phosphine substitution by a chlorine ligand and release of the hydride ligand (most probably as H₂; Scheme 2).

Scheme 2



Compound **4** was characterized by X-ray diffraction analysis (Figure 1), and the molecular structure shows it to be a rhodathiaborane consisting of an 11-vertex *nido*-cage, derived from an icosahedron by the removal of one vertex. Simple application of the Wade's rules,^{14,15} however, predicts a cluster structure based on an octadodecahedron; thus, compound **4** is another example of an 11-vertex, 12 skeletal electron pairs (sep's) cluster that adopts a *nido*-structure instead of *closo*. This discrepancy between the electron-counting rules and the structure has become common among 11-vertex metallathiaboranes that incorporated a formally square-planar M(I) transition-metal centers.¹⁶⁻¹⁸ In

compound **4**, the rhodium centre could be tentatively described as having a distorted square-planar environment, with bonding vectors directed toward the two *exo*-polyhedral ligands, and to the two midpoints of the S(7)-B(3) and B(4)-B(9) bonds of the {SB₉H₉(NC₅H₅)}-fragment, which appear to be *trans* situated to the PPh₃ and Cl ligands, respectively. Based on this stereochemistry, the 10-vertex thiaborane fragment could be regarded as a neutral bidentate ligand that acts in a tetrahapto fashion.

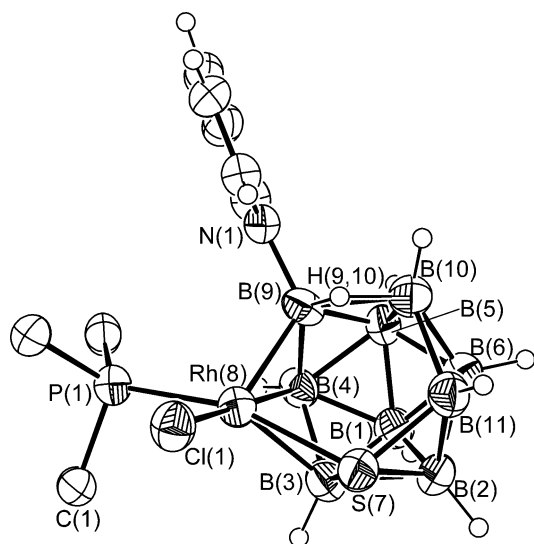


Fig. 1 ORTEP representation of the structure of **4**; only the ipso-carbon atoms of the Ph rings are showed for clarity. Selected distances [Å] and angles [°]: Rh(8)–S(7) 2.361(2), Rh(8)–P(1) 2.294(2), Rh(8)–Cl(1) 2.354(2), Rh(8)–B(9) 2.100(8), Rh(8)–B(3) 2.202(10), Rh(8)–B(4) 2.198(9), B(9)–N(1) 1.548(11); P(1)–Rh(8)–Cl(1) 90.61(8), P(1)–Rh(8)–S(7) 163.82(7), P(1)–Rh(8)–B(4) 92.9(3), P(1)–Rh(8)–B(9) 102.0(3), Cl(1)–Rh(8)–S(7) 86.73(8), Cl(1)–Rh(8)–B(4) 176.0(2), Cl(1)–Rh(8)–B(9) 128.2(2), B(9)–Rh(8)–S(7) 92.2(3), Rh(8)–B(9)–N(1) 120.6(6).

The NMR data of this new chloro-ligated 11-vertex *nido*-rhodathiaborane are in accord with the commented solid-state structure (see supplementary material). The ¹¹B-¹H} NMR spectrum consists of nine signals of relative intensity 1, indicating that the C_s symmetry of the cluster is maintained in solution. This is confirmed by the ¹H-¹¹B} spectrum that exhibits nine proton resonances of hydrogen atoms bound to boron atoms; it is interesting to comment the fact that the resonance of the B(9)-H-B(10) bridging hydrogen atom appears at δ(¹H) +1.62 ppm, significantly shifted towards low-field with

respect the *bis*-PPh₃-ligated **1** and related 11-vertex {SB₉H₉}-containing *nido*-rhodathiaboranes,^{19,20} in which the resonance of the hydrogen atom on the pentagonal open face occurs in the negative region of the ¹H NMR spectra. The ³¹P-¹H NMR resonance of the PPh₃ ligand occurs at +32.2 ppm as a sharp doublet; the high Rh-P coupling constant indicates that **4** is formally a Rh^I complex [¹J(¹⁰³Rh-³¹P) = 153 Hz].⁷

In contrast to compound **2**, the treatment of the CO-ligated analogue **3**¹⁰ with hydrochloric acid affords orange 11-vertex [8,8,8-(PPh₃)(CO)(Cl)-9-(NC₅H₅)-*nido*-8,7-RhSB₉H₉] (**5**), in a reaction that formally implies the addition of HCl to the cluster and the consequent *closo*-to-*nido* transformation. The molecular structure of this new Cl-ligated compound has been determined by X-ray diffraction analysis (Figure 2), and it maintains an 11-vertex *nido*-structure that resembles that of **4**. Compound **5**, however, exhibits the structure predicted by the number of sep's (11+2): one more than **4**. The formal unsaturation of **4** with respect **5** is supported by the fact that the CO-ligated counterpart can be prepared in high yield from the reaction of **4** with carbon monoxide (scheme 2). In **5**, the CO ligand is *trans* to the sulfur vertex, the chlorine to the B(3)-B(4) edge and the PPh₃ ligand to the B(9) vertex. The NMR data agree with this structural determination (supplementary material). Similarly to **4**, the resonance of the BHB hydrogen atom appears in the positive region of the ¹H-¹¹B NMR spectrum at δ(¹H) +0.81 ppm. The ³¹P-¹H NMR spectrum of **5** exhibits a signal with a shape that resembles a broad triplet (see Figure S1); at low temperatures, this broad resonance becomes a simple doublet, which is the pattern expected according to the X-ray structure. This variable temperature behavior is due to ³¹P-¹¹B coupling between the phosphorous nucleus of the PPh₃ ligand and boron nuclei, which at lower temperatures relax faster leading to the so call “thermal decoupling” effect that results in a sharpening of the ³¹P signals.²¹

Interestingly, the treatment of **2** with triflic acid, in dichloromethane solvent, affords also the chloro-ligated cluster, **4**. This suggests that the *closo*-rhodathiaborane **2** might be protonated, affording cationic intermediates with enhanced Lewis acidity that could promote reactions with the solvent CH₂Cl₂.

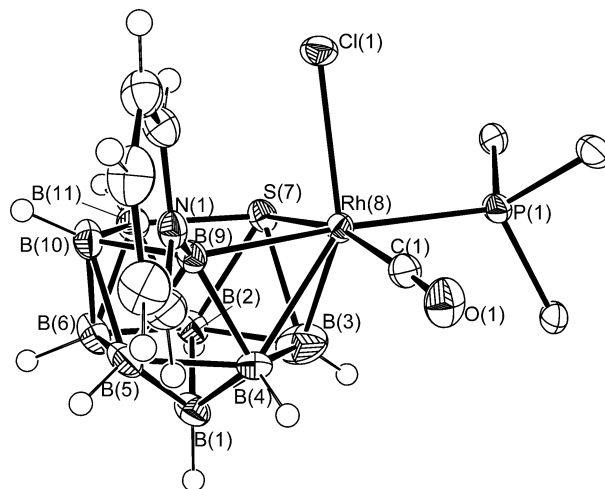


Fig. 2 ORTEP representation of the structure of **5**; only the ipso-carbon atoms of the Ph rings are showed for clarity. Selected distances [\AA] and angles [$^\circ$] (data is stated for the most abundant disordered molecule): Rh(8)–S(7) 2.4060(15), Rh(8)–P(1) 2.4090(6), Rh(8)–Cl(1) 2.4295(8), Rh(8)–C(1), 1.832(4), Rh(8)–B(9) 2.212(2), Rh(8)–B(3), 2.208(18), C(1)–O(1) 1.130(4), B(9)–N(1) 1.546(3); P(1)–Rh(8)–Cl(1) 92.08(2), P(1)–Rh(8)–S(7) 93.95(4), P(1)–Rh(8)–B(4) 128.67(9), P(1)–Rh(8)–B(9) 175.98(7), Cl(1)–Rh(8)–B(4) 139.16(9), Cl(1)–Rh(8)–S(7) 88.09(4), Cl(1)–Rh(8)–B(9) 91.30(7), Rh(8)–B(9)–N(1) 117.19(15), B(9)–Rh(8)–S(7) 88.35(7).

Giving a new flavor to this Brønsted acid/base driven reaction chemistry, the treatment of the hydridorhodathiaborane **1** with triflic acid in dichloromethane affords the brown salt [8,8,8-(PPh₃)₂(H)-9-(NC₅H₅)-nido-8,7-RhSB₉H₁₀][OTf] (**6**). The ¹¹B-¹H} NMR spectrum of **6** in CD₂Cl₂ consist of 8 peaks from $\delta(^{11}\text{B})$ +15.7 to -22.5 that exhibit a 1:2:1:1:1:1:1:1 relative intensity ratio. The eight terminal hydrogen atoms of the cluster are clearly found in the ¹H-¹¹B} spectrum, and they are correlated to their directly bound-boron atoms by means of ¹H-¹¹B(selective)} experiments (see Table S1). In the negative region of the ¹H-¹¹B} spectrum, there are three peaks at $\delta(^1\text{H})$ -4.32 (singlet), -7.85 (doublet) and -9.84 (quartet) ppm, which can be safely assigned to resonances of BHB and Rh-H-B bridging hydrogen atoms, and a Rh-H hydride ligand, respectively. This ¹H pattern is diagnostic of cationic {RhSB₉H₁₀(NC₅H₅)}⁺ vs neutral {RhSB₉H₉(NC₅H₅)}-cage. The ¹⁹F-¹H} spectrum of **6** exhibits a signal at $\delta(^{19}\text{F})$ -79.8 ppm typical of no-coordinated OTf⁻ anion, supporting the existence of

the polyhedral triflate salt in solution. The $^{31}\text{P}\{-^1\text{H}\}$ reveals two doublets of doublets in agreement with the asymmetric proposed structure of the polyhedral cation in **6**. The growth of monocrystals of the salt **6** has been elusive in our hands, prompting us to calculate the structure and the nuclear magnetic chemical shielding properties. The ^{11}B chemical shifts calculated for the cation in **6** reproduce the experimental trend, and show a reasonable agreement (Table S1). Boron nuclear shielding properties calculated *via* the GIAO approach are a reasonable measure of the validity of the calculated structures of polyhedral boron-containing compounds; therefore, the DFT-calculated structure of the rhodathiaborane cation in **6** can be regarded as a good model.

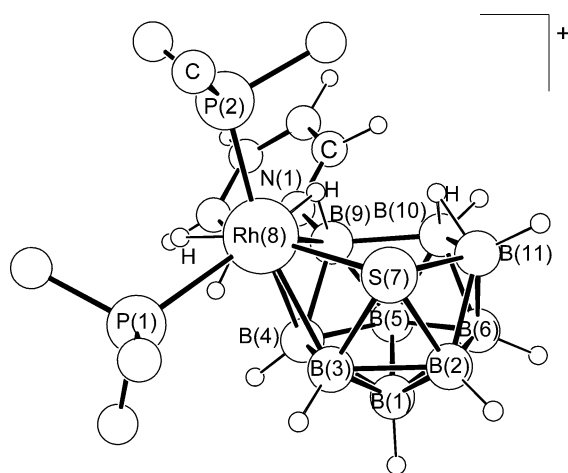


Fig. 3 DFT-calculated structure of **6**; only the ipso-carbon atoms of the Ph rings are showed for clarity. Selected distances [\AA] and angles [$^\circ$]: Rh(8)–S(7) 2.569, Rh(8)–P(1) 2.413, Rh(8)–P(2) 2.474, Rh(8)–B(9) 2.424, Rh(8)–B(3) 2.351, Rh(8)–B(4) 2.298, Rh(8)–H(1) 1.545, B(9)–N(1) 1.579, P(1)–Rh(8)–P(2) 101.3, P(1)–Rh(8)–S(7) 106.8, P(1)–Rh(8)–B(9) 144.6, P(2)–Rh(8)–S(7) 97.0, P(2)–Rh(8)–B(3) 145.0, P(2)–Rh(8)–B(4) 154.1, Rh(8)–B(9)–N(1) 120.7, B(9)–Rh(8)–S(7) 87.3.

In summary, the 11-vertex rhodathiaboranes, **1-3**, react cleanly with Brønsted acids. The reactivity of the clusters varies with the rhodium-bound *exo*-polyhedral ligands and the nature of the acid. With HCl, the 11-vertex *closo*-derivatives **2** and **3** undergo structural transformation to *nido* and concomitant heterolytic addition of the acid to the cluster, yielding the (11+1)-sep unsaturated cluster **4**, and the (11+2)-sep saturated cluster **5**, respectively. The reactivity of the *nido*-hydridorhodathiaborane **1** depends on the acid, affording the chloro-ligated cluster **4** with HCl or the salt **6**, formed by simply

protonation of **1**, with triflic acid. The results delineate further the bifunctional acid / base nature of these 11-vertex rhodathiaboranes, which can also promote the heterolytic cleave of H₂.⁹ Given their distinctive electronic structure and their dramatic structural and electronic responses to Brønsted acids, these clusters represent a unique system with *nido-to-closo* redox flexibility that enable the activation of small molecules. Their easy preparation, stability and potential facile functionalization via, for example, chlorine abstraction or ligand substitutional chemistry, make this new series of compounds attractive for potential catalytic applications. We are presently exploring the reactions of these complexes with different unsaturated organic molecules, and evaluating their catalytic activity.

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SUPPORTING INFORMATION PARAGRAPH. Experimental and DFT-calculated NMR data for **4**, **5** and **6**; DFT-calculated coordinates for **6**.

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