# ORGANOMETALLICS

## Brønsted Acid/Base Driven Chemistry with Rhodathiaboranes: A Labile {SB<sub>9</sub>H<sub>9</sub>}-Thiadecaborane Fragment System

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Supporting Information



Reversible H<sub>2</sub> cleavage promoted by closo to nido transformations of  $[1,1-(PPh_3)_2-3-(NC_5H_5)-closo-1,2-RhSB_9H_8]$  (2)/[8,8,8-(PPh\_3)<sub>2</sub> (H)-9-(NC\_5H\_5)-*nido*-8,7-RhSB\_9H\_9] (1) is a cooperative action with application in catalysis; the treatment of 2 and  $[1,1-(PPh_3)(CO)-3-(NC_5H_5)-closo-RhSB_9H_8]$  (3) with either HCl or HOTf in CH<sub>2</sub>Cl<sub>2</sub> affords the 11-vertex *nido*-rhodathiaboranes [8,8-(PPh\_3)(Cl)-9-(NC\_5H\_5)-*nido*-8,7-RhSB\_9H\_9] (4) and [8,8,8-(PPh\_3)(CO)(Cl)-9-(NC\_5H\_5)-*nido*-8,7-RhSB\_9H\_9] (5), respectively. In contrast, the reaction of 1 with triflic acid yields the salt [8,8-(PPh\_3)<sub>2</sub>(H)-9-(NC<sub>5</sub>H<sub>5</sub>)-*nido*-RhSB<sub>9</sub>H<sub>10</sub>][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.

Complexes in which both the metal center and the ligands are involved in chemical transformations have been attracting 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,<sup>1-3</sup> with reversible amine—amide functionalities,<sup>4-6</sup> or with ligands that undergo facile reversible dearomatization.<sup>7,8</sup>

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  $[8,8,8-(PPh_3)_2(H)-9-(NC_5H_5)-nido-8,7-$ RhSB<sub>9</sub>H<sub>9</sub>] (1)/[1,1-(PPh\_3)\_2-3-(NC\_5H\_5)-closo-1,2-RhSB<sub>9</sub>H<sub>8</sub>] (2) has been shown to undergo reversible dehydrogenation.<sup>9</sup> In conjunction with the reactivity of 1 toward  $C_2H_4$  (Scheme 1), the hydrogen activation step defines a catalytic cycle, which has been proven to operate in the hydrogenations of alkenes.<sup>10</sup> Furthermore, this 11-vertex hydridorhodathiaborane promotes the oxidative addition of sp C–H bonds, driven by dihydrogen release from the cluster.<sup>11</sup> Although the mode of action on these rhodathiaboranes differs from that of the noninnocent-ligand-containing complexes noted above, the  $\{SB_9H_8(NC_5H_5)\}$  fragment in compounds 1 and 2 can be regarded as a ligand that participates actively in the reactions, behaving as a "hydride store"<sup>12</sup> and a flexible polydentate fragment. Alternatively, the bifunctional nature of the clusters, supported by the heterolitic cleavage of H<sub>2</sub>, makes these rhodathiaboranes evocative of a "frustrated Lewis pair",<sup>13</sup> implying that the clusters combine Lewis base and acid centers. Here we describe the reactions of compound 1 and its closo derivatives  $[1,1-(PPh_3)(L)-3-(NC_5H_5)-1,2-RhSB_9H_8]$ , where L = PPh<sub>3</sub> (2), CO (3),<sup>10</sup> 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  $CD_2Cl_2$  at room temperature afforded the chloro-ligated 11-vertex rhodathiaborane [8,8-(PPh<sub>3</sub>)-

Special Issue: F. Gordon A. Stone Commemorative Issue

Received: August 8, 2011 Published: October 07, 2011

#### Scheme 1



Scheme 2



(Cl)-9-(NC<sub>5</sub>H<sub>5</sub>)-*nido*-8,7-RhSB<sub>9</sub>H<sub>9</sub>] (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 a gas or in a water solution (see the Supporting Information), giving 4 in high yield as an air-stable yellow solid. Starting from 2, the reaction involves a closo to nido transformation, release of one of the PPh<sub>3</sub> 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 H<sub>2</sub>; 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 1 vertex. Simple application of Wade's rules,<sup>14,15</sup> however, predicts a cluster structure based on an octadodecahedron; thus, compound 4 is another example of an 11-vertex, 12 skeletal electron pair (SEP) cluster that adopts a nido instead of closo structure. This discrepancy between the electron-counting rules and the structure has become common among 11-vertex metallathiaboranes that incorporate formally square-planar M(I) transition-metal centers.<sup>16–18</sup> In compound 4, the rhodium center 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 {SB<sub>9</sub>H<sub>9</sub>(NC<sub>5</sub>H<sub>5</sub>)} fragment, which appear to be situated trans to the PPh<sub>3</sub> and Cl ligands, respectively. On the basis of this stereochemistry, the 10vertex thiaborane fragment could be regarded as a neutral bidentate ligand that acts in a  $\eta^4$  fashion.

The NMR data of this new chloro-ligated 11-vertex nidorhodathiaborane are in accord with the solid-state structure (see the Supporting Information). The <sup>11</sup>B{<sup>1</sup>H} NMR spectrum consists of 9 signals of relative intensity 1, indicating that the  $C_s$  symmetry of the cluster is maintained in solution. This is confirmed by the  ${}^{1}H{{}^{11}B}$  spectrum, which exhibits 9 proton resonances of hydrogen atoms bound to boron atoms; it is interesting to note the fact that the resonance of the B-(9)-H-B(10) bridging hydrogen atom appears at  $\delta({}^{1}\text{H})$ +1.62 ppm, significantly shifted toward low field with respect to the bis-PPh3-ligated 1 and related 11-vertex {SB9H9}-containing nido-rhodathiaboranes,<sup>19,20</sup> in which the resonance of the hydrogen atom on the pentagonal open face occurs in the negative region of the <sup>1</sup>H NMR spectra. The  ${}^{31}P{}^{1}H{}$  NMR resonance of the PPh<sub>3</sub> ligand occurs at +32.2 ppm as a sharp doublet; the high Rh-P coupling constant indicates that 4 is formally a Rh<sup>I</sup> complex  $({}^{1}J({}^{103}\text{Rh}{-}^{31}\text{P}) = 153 \text{ Hz}).^{7}$ 



Figure 1. ORTEP representation of the structure of 4. Only the ipso carbon atoms of the Ph rings are shown for clarity. Selected distances (Å) and angles (deg): 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).



Figure 2. ORTEP representation of the structure of 5. Only the ipso carbon atoms of the Ph rings are shown for clarity. Selected distances (Å) and angles (deg) (data are 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).

In contrast to the case for compound **2**, the treatment of the CO-ligated analogue  $3^{10}$  with hydrochloric acid affords orange 11-vertex [8,8,8-(PPh<sub>3</sub>)(CO)(Cl)-9-(NC<sub>5</sub>H<sub>5</sub>)-*nido*-8,7-RhSB<sub>9</sub>H<sub>9</sub>] (**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



**Figure 3.** DFT-calculated structure of 6. Only the ipso carbon atoms of the Ph rings are shown for clarity. Selected distances (Å) and angles (deg): 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.

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 for 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 is trans to the B(3)-B(4) edge, and the PPh<sub>3</sub> ligand is trans to the B(9)vertex. The NMR data agree with this structural determination (Supporting Information). Similarly to 4, the resonance of the BHB hydrogen atom appears in the positive region of the  ${}^{1}H{}^{11}B{}$ NMR spectrum at  $\delta({}^{1}\text{H})$  +0.81 ppm. The  ${}^{31}\text{P}\{{}^{1}\text{H}\}$  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 <sup>31</sup>P-<sup>11</sup>B coupling between the phosphorus nucleus of the PPh<sub>3</sub> ligand and boron nuclei, which at lower temperatures relax faster, leading to the so-called "thermal decoupling" effect that results in a sharpening of the <sup>31</sup>P signals.<sup>21</sup>

Interestingly, the treatment of **2** with triflic acid, in dichloromethane solvent, also affords 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  $CH_2Cl_2$ .

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-(PPh<sub>3</sub>)<sub>2</sub>(H)-9-(NC<sub>5</sub>H<sub>5</sub>)-*nido*-8,7-RhSB<sub>9</sub>H<sub>10</sub>][OTf] (**6**). The <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of **6** in CD<sub>2</sub>Cl<sub>2</sub> consist of eight peaks from  $\delta$ (<sup>11</sup>B) +15.7 to -22.5 ppm 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 <sup>1</sup>H{<sup>11</sup>B} spectrum, and they are correlated to their directly bound boron atoms by means of <sup>1</sup>H{<sup>11</sup>B(selective)} experiments (see Table S1). In the negative region of the <sup>1</sup>H{<sup>11</sup>B} spectrum, there are three peaks at  $\delta$ (<sup>1</sup>H) -4.32 (singlet), -7.85 (doublet), and -9.84 (quartet) ppm, which can be safely assigned to resonances of B-H-B and Rh-H-B bridging hydrogen atoms and a Rh-H hydride ligand, respectively. This <sup>1</sup>H pattern is diagnostic of cationic  $\{RhSB_{0}H_{10}(NC_{5}H_{5})\}^{+}$  vs a neutral {RhSB<sub>9</sub>H<sub>9</sub>(NC<sub>5</sub>H<sub>5</sub>)} cage. The  ${}^{19}F{}^{1}H$ } spectrum of 6 exhibits a signal at  $\delta(^{19}\text{F})$  –79.8 ppm typical of a noncoordinated OTf<sup>-</sup> anion, supporting the existence of the polyhedral triflate salt in solution. The  ${}^{31}P{}^{1}H{}$  spectrum reveals two doublets of doublets, in agreement with the proposed asymmetric 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 <sup>11</sup>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 (Figure 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 the nido form 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 nidohydridorhodathiaborane 1 depends on the acid, affording the chloro-ligated cluster 4 with HCl or the salt 6, formed by simple 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 cleavage of H<sub>2</sub>.<sup>9</sup> 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 enables 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.

### ASSOCIATED CONTENT

**Supporting Information.** CIF files giving crystallographic data for 4 and 5 and text, tables, and figures giving experimental and DFT-calculated NMR data for 4-6 and DFT-calculated coordinates for 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### ACKNOWLEDGMENT

We acknowledge the Spanish Ministry of Science and Innovation (CTQ2009-10132, CONSOLIDER INGENIO, CSD2009-00050, MULTICAT and CSD2006-0015, Crystallization Factory) for support of this work. B.C. thanks the "Diputación General de Aragón" for a predoctoral scholarship and ESRF BM16 beamline staff for their support on data acquisition of **5**.

#### DEDICATION

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.

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