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COMMUNICATION

Rhodathiaborane reaction cycles driven by C₂H₄ and H₂: synthesis and characterization of [(H)₂(PPh₃)RhSB₈H₇(PPh₃)] and [(η²-C₂H₄)(PPh₃)RhSB₈H₇(PPh₃)]

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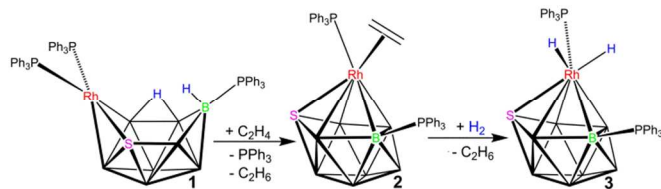
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New 10-vertex rhodathiaboranes are reported to exhibit reversible reaction chemistry leading to the formation of stoichiometric cycles driven by the hydrogenation of the alkene ligand.

Reversible reactions are common in environmental chemistry, the metabolic processes of living organisms and in industrial activities. The interest in new catalytic and stoichiometric cycles is therefore high, providing much of the impetus for research in the organometallic chemistry of transition element complexes.¹ By comparison, the reactivity of polyhedral boron-containing compounds is poorly explored with a relatively small number of reaction cycles either catalytic or stoichiometric.² Here we report on the reversible reaction chemistry of ten-vertex rhodathiaboranes which afford new stoichiometric cycles. This reversibility is essentially driven by the reduction of ethylene to ethane that is performed by the polyhedral clusters through H₂ splitting and ligand substitution reactions. These studies have resulted in the synthesis of a dihydridorhodathiaborane with a synergic metal-to-thiaborane redox reactivity that results in a unique capability of acting as a 'hydride store'.³ This attribute could have a number of potential catalytic applications.



Scheme 1

Recently we have described the synthesis and characterization of the 10-vertex hydridorhodathiaborane, [2,2,2-(H)(PPh₃)₂-*closo*-2,1-RhSB₈H₈], which reacts with PPh₃ to afford the adduct, [6,6,9-(PPh₃)₃-*arachno*-6,5-RhSB₈H₉] (**1**), as a result of a *closo*-to-*arachno* structural and electronic response.⁴ The reaction of **1** with an excess of ethylene in dichloromethane at room temperature yields [2,2-(η²-C₂H₄)(PPh₃)₆-(PPh₃)₂-*closo*-2,1-RhSB₈H₇] (**2**) (Scheme 1). This ethylene-ligated rhodathiaborane is the result of the substitution at

the metal centre of a PPh₃ ligand by ethylene, the loss of two hydrogen atoms from the cage and a consequent *arachno*-to-*closo* structural transformation. The formation of ethane in this reaction suggests that the H₂ loss occurs *via* hydrogenation of the double bond of the entering olefin. This reactivity resembles that found previously between 11-vertex hydridorhodathiaborane, [8,8,8-(H)(PPh₃)₂-9-(L)-*nido*-8,7-RhSB₉H₉] and ethylene to give the corresponding ethylene-ligated clusters, [1,1-(η²-C₂H₄)(PPh₃)₃-3-(L)-*closo*-1,2-RhSB₉H₈], where L = NC₅H₅, 2-Me-NC₅H₄, 3-Me-NC₅H₄ and 4-Me-NC₅H₄.⁵ These results demonstrate that the reaction of hydridorhodathiaboranes (*i.e.*, featuring M–H bonds) with C₂H₄ is a convenient approach for the development of new organometallic chemistry based on polyhedral boron-containing compounds.

Compound **2** is, to our knowledge, the second ethylene-ligated metallaheteroborane (including metallacarboranes) that has been crystallographically characterized [CSD search using the M-(η²-C₂H₄) fragment,⁶ where M is any metal, as query found 658 hits, of which only one corresponded to a metallaheteroborane^{5a}]. The rhodathiaborane exhibits the structure of a bicapped square antiprism as predicted for an eleven skeletal electron pair cluster (Figure 1).⁷ It is noteworthy that the Rh(2)–B(3) distance at 2.510(5) Å lies slightly outside the 2.4–2.5 Å interval that is normally regarded as bonding in polyhedral boron-based clusters. This elongation results in a *pseudo*-square {S(1)Rh(2)B(3)B(6)} face that confers to the structure an *isonido* character.⁸ The ethylene C=C distance of 1.390(7) Å in **2** is close to the reported mean value of 1.388(46) Å (CSD search as above), and it is similar to the length of 1.383(5) Å, found in the 11-vertex rhodathiaborane, [1,1-(η²-C₂H₄)(PPh₃)₃-3-(NC₅H₅)-*closo*-2,1-RhSB₉H₈].^{5a}

The ¹¹B NMR spectrum of **2** exhibits six broad resonances between δ(¹¹B) +43.5 and –23.4 ppm in a 1:2:1:2:1:1 relative intensity ratio. Based on ¹H–{¹¹B(sel)} experiments, the peak at δ(¹¹B) –8.3 ppm can be assigned to the Ph₃P-substituted boron atom, B(6). More informative is the ¹H–{¹¹B} NMR spectrum that shows the seven resonances of the B–H terminal hydrogen atoms. The peak at δ(¹H) +6.89 is significantly deshielded from the rest, and it corresponds to the apical B(10)–H unit. This shift to high frequencies can be ascribed to the antipodal effect of the heteroatom,

S(1).⁹ The ³¹P-¹H} NMR spectrum shows a doublet at $\delta(^{31}\text{P}) +30.8$ ppm and very broad peak at $\delta(^{31}\text{P}) +11.2$ ppm that can be safely assigned to the two *exo*-polyhedral PPh₃ ligands that are bound to the rhodium centre and to the B(6) vertex, respectively.

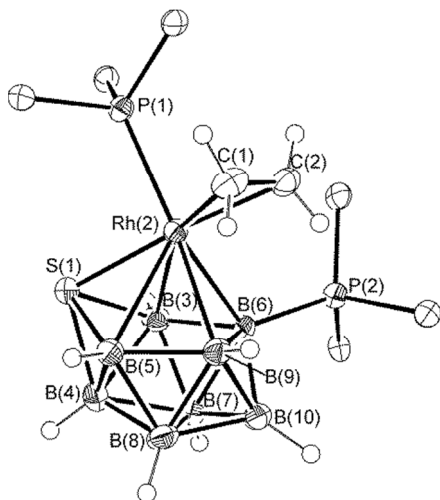


Figure 1 Molecular structure of [2,2-(η^2 -C₂H₄)(PPh₃)₆-(PPh₃)-closo-2,1-RhSB₈H₇] (**2**). Only the *ipso*-carbon atoms on the phenyl groups are included to aid clarity. Ellipsoids are shown at 50 % probability levels. Selected distances [Å] and angles [°]: Rh(2)-P(1) 2.3216(11), Rh(2)-C(1) 2.135(5), Rh(2)-C(2) 2.156(5), Rh(2)-S(1) 2.2755(12), Rh(2)-B(3) 2.510(5), Rh(2)-B(5) 2.411(5), Rh(2)-B(6) 2.309(5), Rh(2)-B(9) 2.268(5), C(1)-C(2) 1.390(7), P(2)-B(6) 1.924(5), C(1)-Rh(2)-C(2) 37.80(18), P(1)-Rh(2)-C(1) 87.36(14), P(1)-Rh(2)-C(2) 87.36(14), S(1)-Rh(2)-P(1) 91.38(4), S(1)-Rh(2)-C(1) 143.51(15), S(1)-Rh(2)-C(2) 175.90(14), P(2)-B(6)-Rh(2) 116.3(2), P(2)-B(6)-B(3) 118.3(3), P(2)-B(6)-B(9) 135.3(3), P(2)-B(6)-B(10) 110.5(3).

The reaction of **2** with dihydrogen affords [2,2,2-(H)₂(PPh₃)₆-(PPh₃)-closo-2,1-RhSB₈H₇] (**3**). This compound has been characterized by multielement NMR spectroscopy and X-ray diffraction. And, although some dihydrido metallaboranes and metallacarboranes have been reported,¹⁰ **3** represents the first dihydridorhodathiaborane to be characterized crystallographically. Its structure is based on an Archimedean antiprism, resembling, therefore, compound **2**. In fact, **3** can notionally be formed from **2** by replacing the η^2 -ethylene ligand with two hydride ligands. In the solid state, one Rh–H hydrogen atom lies *trans* to the sulphur atom, S(1), and the other is *trans* to the B(5)–B(9) edge. The Rh(2)–B(5) distance at 2.439(5) is elongated compared with the other Rh–B distances in **3**, but it is significantly shorter than the Rh(2)–B(3) in compound **2**, described above. This structural attribute, in the context of a *closo-isonido-nido* structural continuum,⁸ confers to **3** a higher *closo* character than **2**.

The NMR data for **3** are in accord with the solid state molecular structure. The ¹¹B NMR spectrum shows a pattern that resembles that of compound **2**, the main difference is that the resonance corresponding to the B(10) atom shifts 11 ppm to high frequencies in **3**. In the ³¹P-¹H} spectrum of **3**, we can also see that the resonance due to the Rh–PPh₃ ligand shifts 20 ppm towards high frequency with respect that of compound **2**. It is interesting to note the lower value of the ¹J_{RhP} coupling constant in **3** (120 Hz) compared with that of **2** (140 Hz), which demonstrates a different oxidation state of the metal centre: tentatively assigned as Rh(III) in the dihydride cluster vs. Rh(I) in the ethylene-ligated compound.

The ¹H NMR spectrum of **3** exhibits a *pseudo*-triplet at $\delta(^1\text{H}) - 9.77$ that at low temperatures splits to give two multiplets at $\delta(^1\text{H}) - 8.42$ and -11.13 , indicating that the two hydride ligands undergo fast intra-molecular exchange at the rhodium centre at room temperature. The free energy of this fluxional process (measured by ¹H NMR (300 MHz) at the coalescence temperature of 237 K) is 10 kcalmol⁻¹.

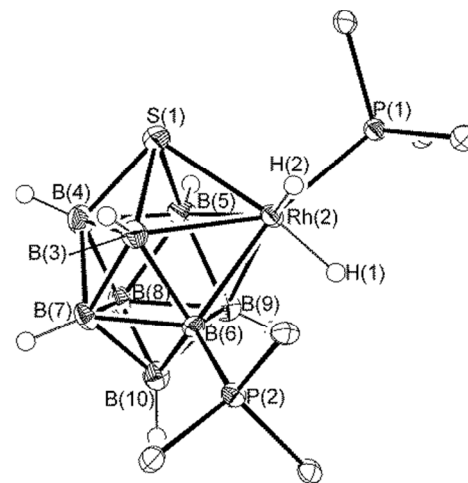
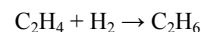


Figure 2 [2,2,2-(H)₂(PPh₃)₆-(PPh₃)-closo-2,1-RhSB₈H₇] (**3**). Only the *ipso*-carbon atoms on the phenyl groups are included to aid clarity. Ellipsoids are shown at 50 % probability levels. Selected distances [Å] and angles [°]: Rh(2)-P(1) 2.2561(13), Rh(2)-H(1) 1.41(5), Rh(2)-H(2) 1.44(4), Rh(2)-S(1) 2.3473(13), Rh(2)-B(3) 2.384(6), Rh(2)-B(5) 2.439(5), Rh(2)-B(6) 2.252(5), Rh(2)-B(9) 2.284(6), P(2)-B(6) 1.950(5), P(1)-Rh(2)-H(1) 82.3(19), P(1)-Rh(2)-H(2) 74.1(18), H(1)-Rh(2)-H(2) 90(3), S(1)-Rh(2)-P(1) 104.03(5), S(1)-Rh(2)-H(1) 170(2), S(1)-Rh(2)-H(2) 99.7(17), P(2)-B(6)-Rh(2) 111.0(2), P(2)-B(6)-B(3) 117.7(3), P(2)-B(6)-B(9) 135.4(3), P(2)-B(6)-B(10) 121.2(3).

The intramolecular hydride exchange in compound **3** could take place through the formation of an Rh-(η^2 -H₂) dihydrogen interaction and subsequent rotation about this bond. This would be comparable to the scenario found in the side-on bonded dihydrogen complex, [8,8,8-(η^2 -H₂)(IMe)(PPh₃)₉-(NC₅H₅)-*nido*-8,7-RhSB₉H₈], calculated by DFT as intermediate in the heterolytic splitting of H–H on the carbene-ligated cluster, [1,1-(IMe)(PPh₃)₃-(NC₅H₅)-*isocloso*-1,2-RhSB₉H₈], where IMe = 1,3-dimethylimidazol-2-ylidene.¹¹

In dichloromethane at room temperature, the exposure of an equimolar mixture of **2** and free PPh₃ to a dihydrogen atmosphere regenerates the 10-vertex *arachno*-rhodathiaborane **1**. The reaction of the dihydridorhodathiaborane, **3**, with ethylene yields the ethylene-ligated cluster, **2**. Finally, the treatment of **3** with PPh₃ also affords the starting reagent, **1**. As summarized in Scheme 2, these reactions permit a cycle to be constructed. For **1** and **3**, the reactions with ethylene, leading to formation of **2**, constitute reversible steps. These two reversible reactions are connected by PPh₃ addition to **1**, thereby, generating a three-step reaction cycle (Scheme 2). If we consider species that enter the cycle minus the species that exit the cycle the net reaction is



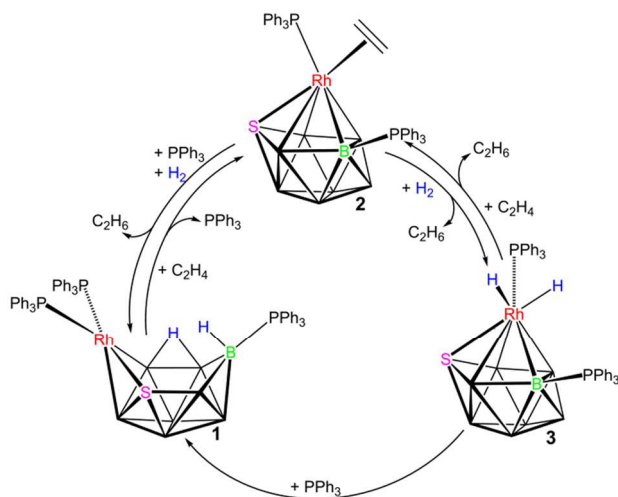
The chemistry that drives this cycle is, therefore, the hydrogenation of ethylene to ethane.

The reversible reaction step between **1** and **2** is reminiscent of the reaction cycle between the pyridine-ligated 11-vertex clusters, [8,8,8-(PPh₃)₂(H)-9-(NC₅H₅)-*nido*-8,7-RhSB₉H₉] (**4**) and [1,1-(η^2 -C₂H₄)(PPh₃)₃-(NC₅H₅)-*closo*-1,2-RhSB₉H₈] (**5**), which is also

driven by oxidation / reduction chemistry of ethylene and dihydrogen.^{5a}

The reaction of **3** with free PPh₃ merits some further comments. It demonstrates that this dihydridorhodathiaborane exhibits a remarkable Lewis acid character, binding a relatively weak two electron donor ligand such as PPh₃ through the metal centre in a reaction that, from a cluster approach, can be regarded as a reduction process: two additional skeletal electrons are added to the cage. The consequent response of the hydride is spectacular, modifying its structure from a 10-vertex *closo*-rhodathiaborane to a 10-vertex *arachno*-cluster.

Given the isolation of **3**, it is clear that the reaction of **2** (in the presence of free PPh₃) to give **1** should follow the formation of the dihydridorhodathiaborane, **3**, as intermediate. If the addition of H₂ to **2** to give **3** can be described as a single-site homolytic H–H splitting, the incorporation of H₂ into the cluster **2** to give **1** has the attributes of a heterolytic H₂ activation on a cluster; and these results provide new mechanistic insights regarding the reaction of **5** with H₂ to give **4**.^{5a} Thus, the addition of dihydrogen to the ethylene-ligated cluster, **5**, is quite likely to also occur *via* a dihydridorhodathiaborane, [1,1,1-(H)₂(PPh₃)-3-(NC₅H₅)-*closo*-1,2-RhSB₉H₈] intermediate.



Scheme 2 Ethylene / H₂-driven cycle

The stoichiometric cycle reported here, involving the new dihydridorhodathiaborane, **3**, has no precedent in polyhedral boron chemistry, demonstrating that this series of ten-vertex rhodathiaboranes exhibits a remarkable structural flexibility through metal-to-thiaborane *hapticity* changes in which the { η^n -SB₈H₇(PPh₃)} fragment, where *n* = 3, 4 or 5, acts as a non-innocent ligand.

The easy preparation of these 10-vertex rhodathiaboranes and their facile functionalization via Lewis acid / base chemistry with new ligands that can bind either the metal center or the boron vertices of the thiaborane fragment, make these compounds attractive for potential catalytic applications. In fact, the results reported here demonstrate that the system is active in the hydrogenation of ethylene to ethane (see Figure S2 in the ESI of this communication). We are currently exploring the reactions of these compounds with other olefins and alkynes, and we are evaluating their catalytic activity.

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Notes and references

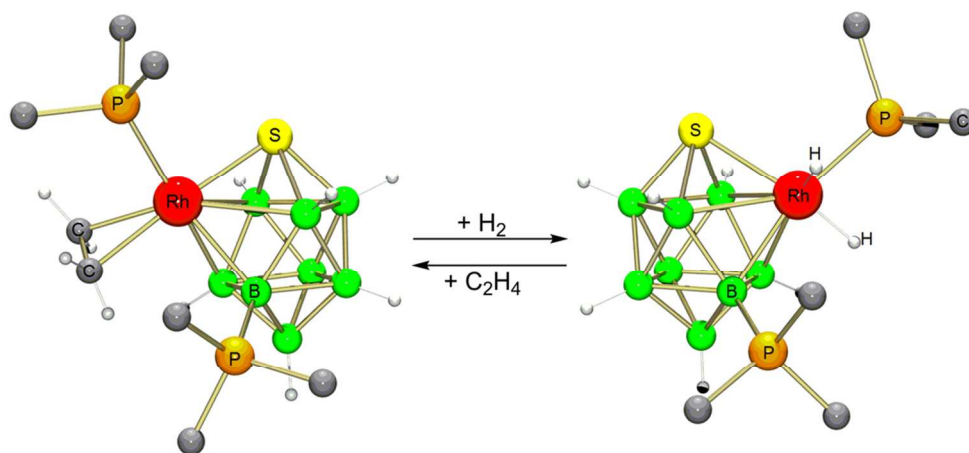
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