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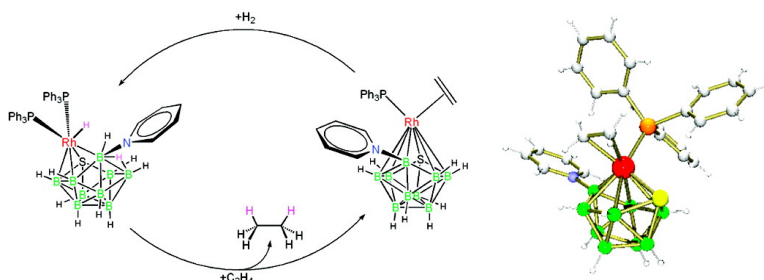
Reversible Ethylene Dihydrogen Mediated 11-Vertex *nido* ⇌ *closo* ⇌ *nido* Conversion in a Metallathiaborane Cluster

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Reversible Ethylene Dihydrogen Mediated 11-Vertex *nido* → *closo* → *nido* Conversion in a Metallathiaborane Cluster

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Recently, we have focused our work on the chemistry of the unsaturated 11-vertex *nido*-rhodathiaborane [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (**1**)[1] and the related N-heterocyclic-ligated species [8,8-$(\eta^2$-$L_2)$-*nido*-8,7-$RhSB_9H_{10}$] (L_2 = bpy, Me_2bpy, phen).[2] These compounds can add a Lewis base without change of the *nido* structure, and additionally, they can undergo ligand substitution reactions and *nido* to *closo* transformation, as well as exhibit other interesting reactivity.[3−6] With small ligands such as CO or CH_3-CN, the addition of the Lewis base takes place at the metal center;[7,8] in contrast, the reaction of **1** with $PPh_2(CH_2)_3PPh_2$ (dppp) affords [8,8,8-$(\eta^2$-dppp)(H)-9-$(\eta^1$-dppp)-*nido*-8,7-$RhSB_9H_9$] in which the Lewis base has attacked the boron cage leading to a B−L linkage and a hydride ligand.[6] Herein we report a novel reaction cycle with potential catalytic applications that is driven by oxidation/reduction chemistry of ethene and dihydrogen with rhodathiaboranes.

The reaction of **1** with a 4-fold excess of pyridine (py) leads to the clean formation of a new hydrido-ligated species of formulation [8,8,8-$(PPh_3)_2$(H)-9-(py)-*nido*-8,7-$RhSB_9H_9$] (**2**). This compound exhibits an 11-vertex *nido* structure, which is shown in Figure 1. The pair of electrons contributed by the boron-ligated pyridine increases the skeletal electron pairs (sep) to 13, consistent with the observed structure. This differs from the parent rhodathiaborane **1** that with 12 sep does not conform to the electron-counting rules.[9]

The ^{11}B NMR spectrum of **2** exhibits nine resonances, and the peak at the highest frequency corresponds to the pyridine-bound boron atom at the nine position that does not bear a terminal hydrogen atom. More informative is the ^{1}H NMR spectrum that shows the resonances of the eight boron-bound terminal hydrogen atoms, the BHB bridging hydrogen atom, and the hydride ligand. The latter appears at δ_H −12.46 as an apparent quartet that becomes a doublet upon ^{31}P decoupling. Interestingly, the ^{31}P NMR spectrum of **2** exhibits a temperature-dependent behavior that is consistent with a PPh_3 ligand that undergoes fast dissociation, whereas the second phosphine remains bound to the Rh atom. The labilization of metal-bound ligands by the presence of hydrides is documented in organometallic and metallacarborane chemistry;[10,11] however, we are not aware of examples in the chemistry of either metallaboranes or metallaheteroboranes; **2** is, therefore, a rare example of a labile *nido*-hydridorhodathiaborane.

Compound **1** does not react with olefins; in contrast, reaction of **2** with excess ethene in dichloromethane at room temperature affords ethane and the rhodathiaborane [1,1-$(PPh_3)(\eta^2$-$C_2H_4)$-3-(py)-*closo*-1,2-$RhSB_9H_8$] (**3**) (Figure 2). Compound **3** is novel. We are unaware of any previous crystallographic characterization of metallaheteroboranes (included metallacarboranes) containing metal-bound ethene ligands, although there are some olefin-ligated metallacarboranes such as [1,3-{μ-$(\eta^2$-3-CH_2=$CHCH_2CH_2)$}-3-(H)-3-(PPh_3)-3,1,2-$RhC_2B_9H_{10}$].[12] Compound **3** crystallizes in the orthorhombic system with eight molecules in the unit cell, arranged
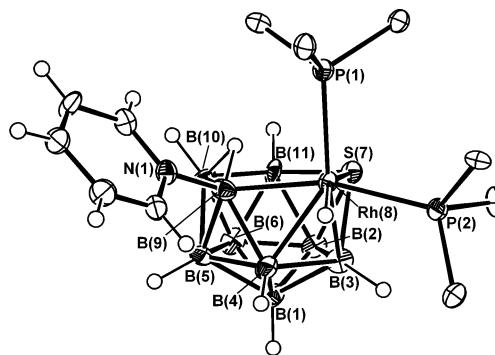

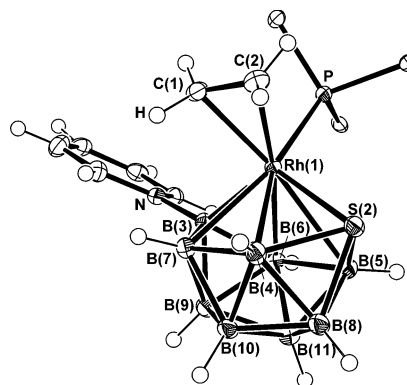**Figure 1.** Molecular structure of **2**.


Figure 2. Molecular structure of **3**.

as enantiomeric pairs that are related by an inversion center; the molecule exhibits the structure of an octadodecahedron as predicted for a 12 skeletal electron pair cluster. The ethene C=C distance of 1.383(5) Å in **3** falls within the reported range of 1.126−1.508 Å,[13] but it is slightly shorter than that found at 1.402(6) Å in the organometallic compound [Rh(η^5-Cp)$(PPh_3)(C_2H_4)$],[14] which exhibits an analogous ligand distribution with the η^5-Cp ring formally replacing the {SB_9H_8(py)} fragment. The shorter C=C distance in **3** may indicate that the ethene exhibits lower π-back-bonding in **3** than in the organometallic analogue, suggesting that the thiaborane-to-rhodium interaction leads to a lower electronic density at the rhodium center than the η^5-Cp-to-rhodium interaction.

The ^{11}B NMR data for **3** revealed seven peaks rather than the nine resonances that are expected for its unsymmetrical structure, indicating that some of the signals are accidentally coincident. The ^{1}H{^{11}B} NMR spectrum indirectly resolves the ^{11}B spectrum showing the presence of eight BH terminal hydrogen atoms. The ^{1}H signals of the ethene group show a temperature-dependent behavior that is consistent with full rotation of the ligand about the coordination bond [$\Delta G^{\ddagger}$(252 K) = 11.8 kcal mol^{-1}].[15]
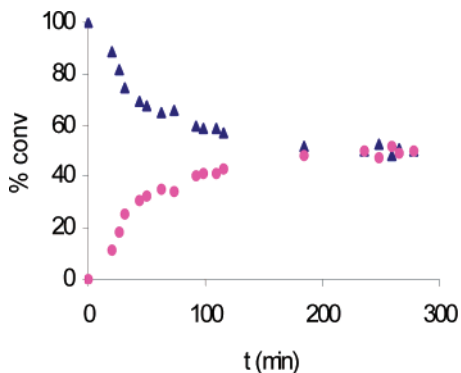
Figure 3. Plot of reaction time versus relative abundances of **3** and **2** based on ^1H NMR signal intensities (**3** dark blue triangles, **2** magenta circles).

**Scheme 1.** Reaction of **3** with H_2 in the Presence of One Equivalent of PPh_3
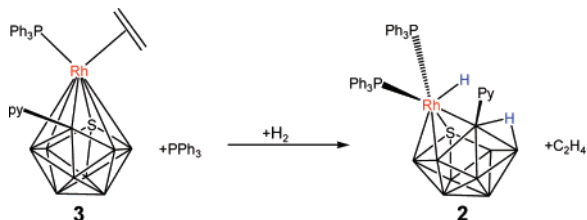
In CD_2Cl_2 at room temperature, the exposure of an equimolecular mixture of **3** and free PPh_3 to a hydrogen atmosphere regenerates the *nido*-rhodathiaborane **2**. After about 3 h, the *closo* → *nido* transformation has reached 50% (Figure 3); 2 days later, the *nido* compound **2** is at 80% of the reaction mixture. The reduction of *closo* clusters furnishing open structures usually requires strong reducing reagents, and the dihydrogen-promoted *closo*-to-*nido* transformation of **3** to give **2** is without precedent (Scheme 1).

A possible mechanism for the reaction of **2** with ethene is the substitution of the labile phosphine ligand in **2** to give an undetected η^2-alkene derivative $[8,8,8-(PPh_3)(\eta^2-C_2H_4)(H)-9-(py)-nido-8,7-RhSB_9H_9]$, which could undergo intramolecular ethene migratory insertion into the rhodium−hydride bond to give an alkyl inter-mediate. At this point, the second hydrogen atom necessary to complete the reductive elimination of the alkane would come from the boron cage (probably the BHB hydrogen atom). This second hydrogen could either transfer directly to the alkyl ligand or migrate first to the rhodium atom (Scheme 2). This mechanism resembles the generally accepted hydride route for alkene hydrogenation by organometallic compounds,[16] with the particularity that the reaction implies oxidation of a whole cluster rather than a single metal center.

Interestingly, the activation of dihydrogen by **3** regenerating the *nido*-hydridorhodathiaborane **2** opens a door for catalytic hydro-genation of olefins (Scheme 2). The easy preparation of the 11-vertex *nido* precursor **1**, the stability of these rhodathiaboranes, and the facile functionalization via new N-heterocyclic ligands, phos-phines, or heteroborane cages make this system attractive for potential catalytic applications. We are presently exploring the reactions of these compounds with other olefins and alkynes, and we are evaluating their catalytic activity.

Scheme 2
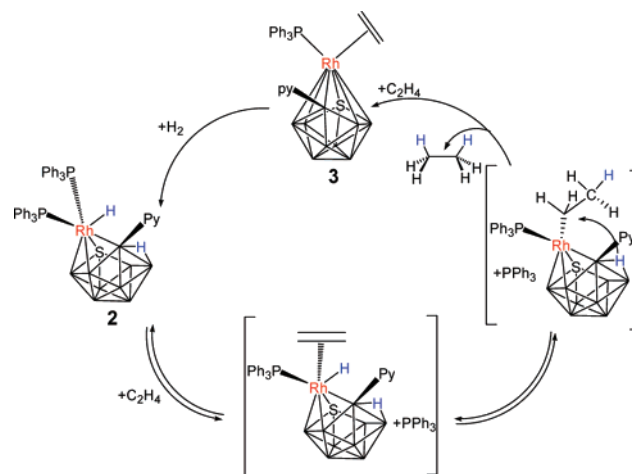
Supporting Information Available: Experimental procedures, spectroscopic data for all the compounds reported, including X-ray data for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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