

Heterolytic H₂ activation on a carbene-ligated rhodathiaborane promoted by *isonido-nido* cage opening

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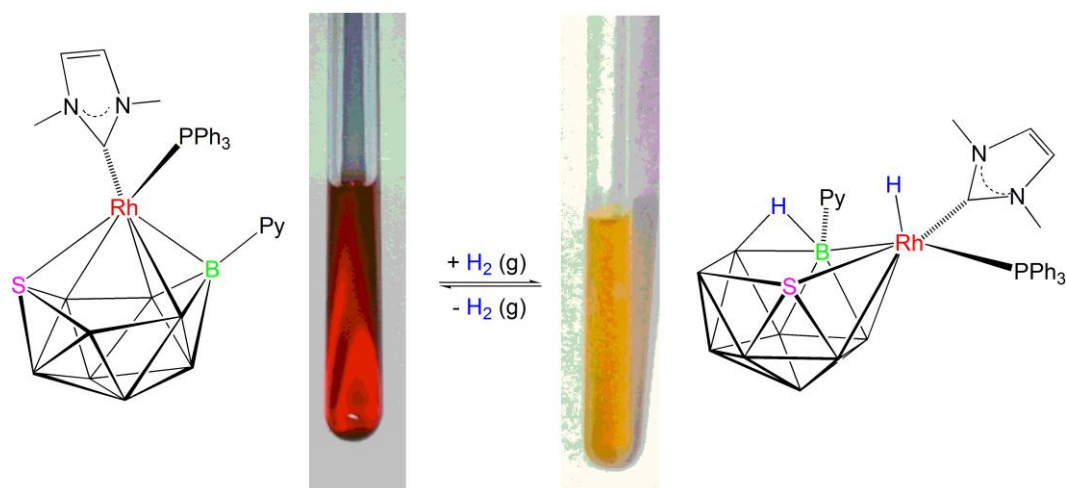
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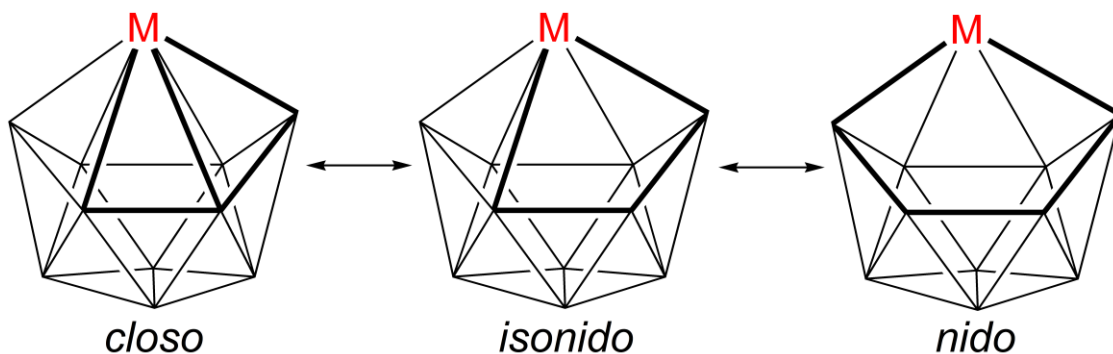
GRAPHICAL ABSTRACT



A new mechanism of H_2 activation is reported to occur on a carbene-ligated rhodathiaborane that features metal / thiaborane bifunctional synergistic effects. The key is the creation of vacant coordination sites by an *isonido-nido* structural transformation leading to the heterolytic H–H bond splitting.

MAIN TEXT

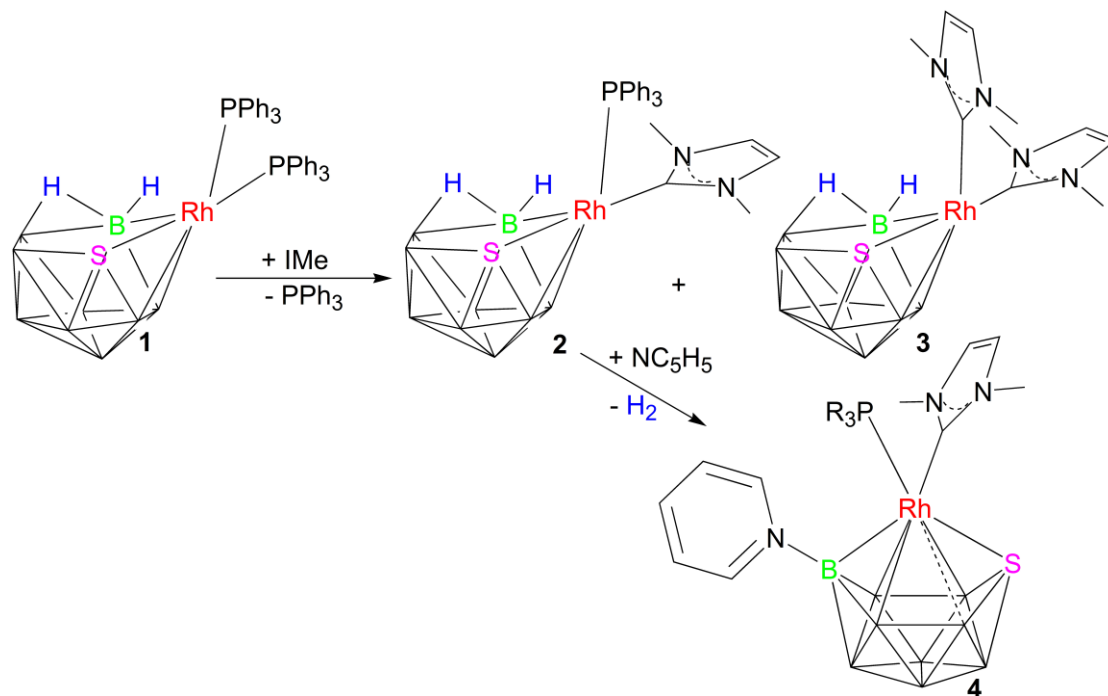
The activation of dihydrogen has attracted considerable interest over the years since it is a key step in many catalytic reactions.^{1a, 1b} and it is well established that this is the result of synergistic electron transfer of the σ -bonding orbital of H_2 into a vacant orbital at the metal and from a filled d orbital to the antibonding orbital of H_2 .² The perturbation brought about by this $\text{M}-(\eta^2\text{-H}_2)$ bond can lead to the homolytic cleavage with formation of $\text{M}-(\text{H})_2$ dihydride species, or, alternatively, the activated H_2 can transfer a proton to another metal-bound ligand.³ This latter process is referred to as heterolytic rupture and it is often found to occur in systems that combine the reactivity of the ligands and the metals.⁴ Thus, the proliferation of complexes that feature metal / ligand bifunctional synergistic effects has given rise to range of new mechanisms, showing that the pathways to the heterolytic splitting of dihydrogen are diverse.⁵



Scheme 1 11-vertex *closo-isonido-nido* structural continuum

A good number of metallaheteroboranes have been found to catalyze hydrogenation reactions;⁶ however, there are not mechanistic studies which can prove that a bifunctional metal-heteroborane synergistic effect driven by classical *closo-isonido-nido* structural transformations (Scheme 1) can result in the heterolytic splitting of dihydrogen.

We report here experimental and theoretical evidence of a new mechanism of dihydrogen activation on a carbene-ligated metallaheteroborane cluster. The key is the structural lability of an 11-vertex rhodathiaborane that opens vacant coordination sites by an *isonido-to-nido* structural change, allowing the heterolytic H–H bond cleavage by metal-thiaborane cooperation.



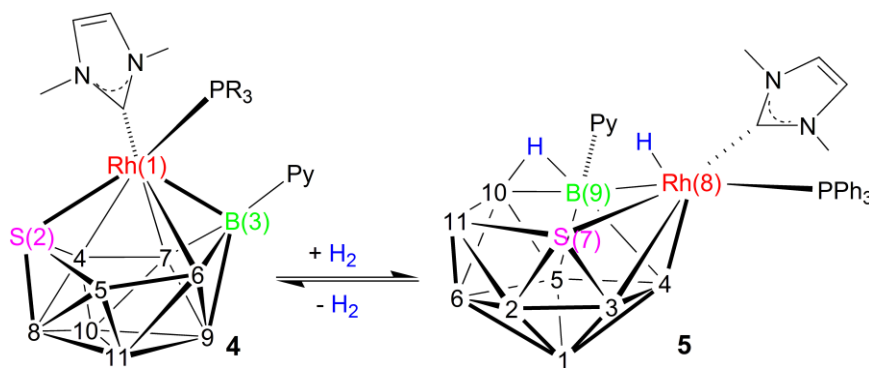
Scheme 2 Preparation of carbene-ligated rhodathiaboranes, **2-4**

Reaction of $[8,8-(\text{PPh}_3)_2\text{-nido-}8,7\text{-RhSB}_9\text{H}_{10}]$ (**1**)⁷ with the N-heterocyclic carbene (NHC), 1,3-dimethylimidazol-2-ylidene (IME) yields the rhodathiaboranes, $[8,8-(\text{IME})(\text{PPh}_3)\text{-nido-}8,7\text{-RhSB}_9\text{H}_{10}]$ (**2**) and $[8,8-(\text{IME})_2\text{-nido-}8,7\text{-RhSB}_9\text{H}_{10}]$ (**3**), which are formed by ligand substitution of Rh-bound PPh_3 ligands. The treatment of **2** with pyridine (Py) affords the pyridine adduct $[1,1-(\text{IME})(\text{PPh}_3)\text{-}3\text{-(Py)}\text{-}1,2\text{-RhSB}_9\text{H}_8]$ (**4**) (Scheme 2) with loss of H_2 . Compounds **2-4**, and **5** (*vide infra*) represent the first documented examples of carbene-ligated metallathiaboranes.

Carbene-ligated clusters, **2** and **3**, are isoelectronic with **1**, having 12 skeletal-electron pairs. This number suggests a *closo*-structure based on an octadecahedron.⁸ Therefore, these 11-vertex rhodathiaboranes are formally “unsaturated”, with the “unsaturation” arising from the tendencies of rhodium to adopt square-planar 16-electron metal configuration.⁹ And, *a priori*, these clusters are expected to exhibit reactivity with Lewis bases; thus, **2** reacts with pyridine (Py) to afford **4**, resulting from the linkage of the N-heterocyclic ligand and release

of dihydrogen (Scheme 2). In surprising contrast, the *bis*-IMe-ligated cluster, **3**, does not react with pyridine.

The exposure of **4** to a dihydrogen atmosphere results in the formation of an equilibrium between this cluster and a new labile hydridorhodathiaborane, [8,8,8-(H)(IMe)(PPh₃)-9-(Py)-*nido*-8,7-RhSB₉H₉] (**5**) (Scheme 3). Under an atmosphere of 6 bar of dihydrogen, the ³¹P-¹H NMR spectrum at room temperature shows a doublet at $\delta_P +35.6$ attributable to the *isonido*-rhodathiaborane, **4**, which disappears as the temperature decreases to give two doublets at $\delta_P +40.6$ and 31.7 with relative intensities in the ratio 1:8 (ESI, Figure S3). These variable temperature (VT) NMR changes are reflected in the corresponding ¹H-¹¹B NMR spectra (Figures S4, in ESI). Thus, at low temperatures the spectra show the development of two new hydride resonances at $\delta_H -12.26$ (t, minor) and -12.67 (dd, major). These data and the commented ³¹P-¹H spectra suggest strongly the presence of two {Rh(IMe)(PPh₃)}-¹¹B} conformers in solution, labelled as **5a** (major) and **5b** (minor) in Figure S3.



Scheme 3 Dihydrogen-assisted *nido*→*isonido* opening: a true reversible activation of H₂ by a rhodathiaborane system

The *exo*-polyhedral carbene ligand of the hydride-ligated cluster is characterized by the appearance of two methyl and two imidazolic peaks in the ¹H NMR spectrum (see ESI).

Diagnostic of the *nido*-structure of the new species (Scheme 3) are the proton resonances at δ_{H} -0.11 (**5a**) and -1.75 (**5b**) due to the B-H-B bridging hydrogen atoms along the B(9)-B(10) edge on the pentagonal face (Scheme 3, Figure S4).

The release of the dihydrogen atmosphere, by simple opening of the quick pressure valve NMR tube, regenerates the *isonido*-cluster **4** quantitatively, demonstrating the full reversibility of the system and the lability of the hydridorhodathiaborane **5** (mixture of conformers **5a** and **5b**) towards dehydrogenation.

The number of transition metal complexes capable of adding dihydrogen is certainly large.^{2b} In contrast, to our knowledge, reversible addition of H₂ to a polyhedral boron-containing compound has been reported only once before.¹⁰ This reaction involves [1,1-(PPh₃)₂-3-(Py)-*isonido*-1,2-RhSB₉H₈] (**6**) that reacts slowly with H₂ to afford [8,8,8-(H)(PPh₃)₂-9-(Py)-*nido*-8,7-RhSB₉H₉] (**7**). Compound **7** is stable at room temperature in solution, but it undergoes dehydrogenation at higher temperatures to give **6**.

In the context of this communication, it is important to stress that **6** and **7** do not form an equilibrium sustained by dihydrogen. Therefore, compound **4** may be regarded as the polyhedral boron-containing compound that splits H₂ most readily in a reversible manner.

Given this unusual reactivity by a metallaheteroborane, and with an interest in the H₂-activation mechanism, DFT was used to calculate intermediates, transition states and energies along the reaction pathway for H₂ addition to the carbene-ligated cluster **4**. Scheme 4 depicts the results of this theoretical analysis.

The key step to the addition of dihydrogen appears to be the opening of the cluster from a quadrilateral faceted *isonido*-structure, **4**, to a *nido*-cage, **4'**, featuring a pentagonal face (Scheme 4). Thus, the calculations show that a *nido*-structure lies only 1.0 kcal/mol above an *isonido*-isomer that exhibits the configuration found in the solid state for compound **4**. Both

isomers are available through a transition state **TS1** that has a DFT-calculated free energy barrier, $\Delta G_{253}^{\ddagger}$, of 8.0 kcal/mol (ESI, Scheme S5). This possible pathway is supported by VT $^1\text{H}\{-^{11}\text{B}\}$ experiments, which demonstrate that compound **4** exhibits a fluxional behaviour in solution. Thus, Figure S6 shows that B–H terminal proton resonances of intensity two split in pairs as the temperature decreases to give a proton NMR spectrum with eight B–H terminal resonances. For an asymmetric cluster such as **4**, the $^1\text{H}\{-^{11}\text{B}\}$ NMR spectrum is expected to exhibit eight cluster proton signals, which correspond to the eight different B–H chemical environments of the cluster; whereas the ^{11}B spectrum should exhibit nine peaks. The fact that at room temperature the ^{11}B and $^1\text{H}\{-^{11}\text{B}\}$ NMR spectra show symmetric patterns indicates that the carbene-ligated rhodathiaborane, **4**, is non-rigid. A rapid deformational rearrangement between a clearly asymmetric *nido*-cluster and a *pseudo-C_s closo/isonido*-structure, would explain the VT behaviour of this compound. The activation energy, $\Delta G_{253}^{\ddagger}$, involved in this fluxional behaviour is 10.5 kcal/mol, a value that approaches the DFT-calculated barrier for a *isonido*↔*nido* transformation (Scheme S5).

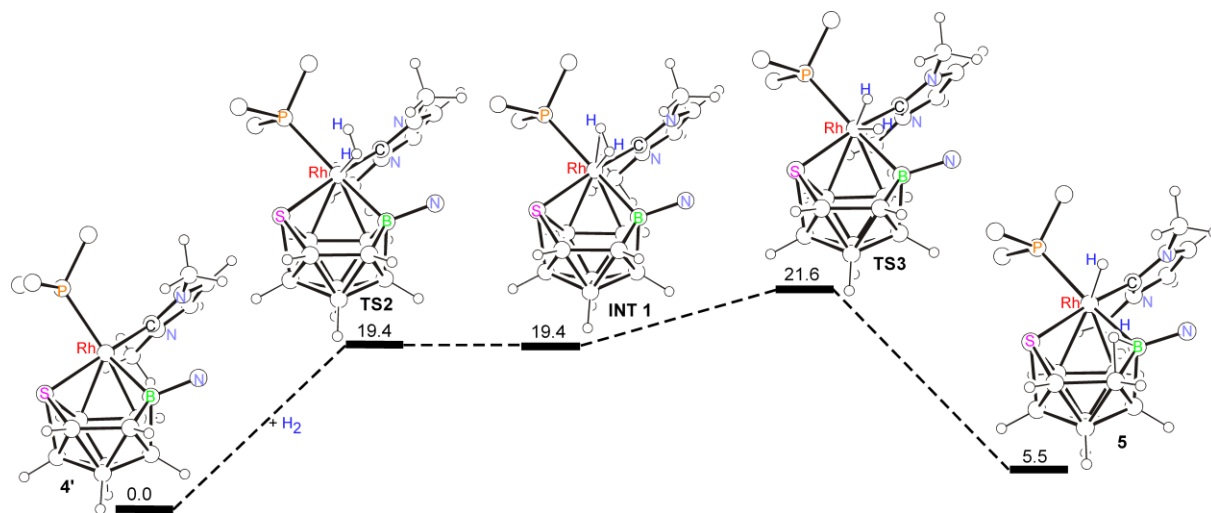
Following this *isonido*↔*nido* structural lability, the DFT-calculations predict that the *nido*-isomer is capable of forming a complex with an entering dihydrogen molecule. The transition state **TS2** from the *nido*-cluster, **4'**, entails the perpendicular approach of H₂ to the rhodium centre and the subsequent rotation to form a side-on bonded intermediate, **INT 1**, and it has a free energy barrier of 19.4 kcal/mol (Scheme 4). This intermediate is comparable with well-characterized mononuclear dihydrogen complexes,^{2b} and it exhibits an elongated H–H distance at 0.809 Å.

To our knowledge, there are no examples of dihydrogen-ligated polyhedral boron-containing compounds. Therefore, the DFT-calculated complex, **INT 1**, is a good theoretical model of a H₂ molecule in the coordination environment furnished by a metallaheteroborane.

From this unstable η^2 -(H₂)-ligated rhodathiaborane, the H–H bond is heterolytically cleaved by proton transfer to the adjacent B(9)–B(10) edge, passing over the transition state **TS3** to form a hydridorhodathiaborane, which should be one of the two conformers of compound **5** that have been identified *in situ* by NMR spectroscopy.

In a NMR tube at room temperature, the exposure of a CH₂Cl₂ solution of **4** and ethylene to a dihydrogen atmosphere affords ethane (Figure S7 in ESI). In catalytic conditions, the carbene-ligated rhodathiaborane exhibited activity in the hydrogenation and isomerisation of 1-hexene, reaching a conversion of 69 % in 5 hours (see Table S1 in ESI).

In summary, the carbene-ligated clusters **4** and **5** exhibit an unprecedented *isonido*↔*nido* equilibrium sustained by H₂. The response of **4** to the addition of dihydrogen can be regarded as a form of metal-ligand cooperation,⁴ which is triggered by a



Scheme 4 Proposed reaction mechanism and relative free energies, ΔG_{298} (kcal/mol), for the activation of H₂ by [(IMe)(PPh₃)(Py)RhSB₉H₈] (**4** / **4'**)

structural change of the cluster, leading to vacant coordination sites at the metal centre. The subsequent binding of H₂ results in the heterolytic splitting of the H–H bond along the

Rh(8)–B(9) edge to a hydride ligand and a proton that is transferred to the B(9)–B(10) edge. The system is active in the catalytic hydrogenation of ethylene and 1-hexene.

Given the tailorability of these 11-vertex clusters by alteration of their *exo*-polyhedral units, the use of strong *trans*-effect ligands such as carbenes may induce further examples of cage non-rigidity in metallaheteroboranes that can be reactive *versus* inactive bonds, resulting in abundant opportunities for research of new ways of bond activation.

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