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

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A new mechanism of H₂ activation is reported to occur on a carbene-ligated rhodatiaborane 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,¹ and it is well established that this is the result of synergistic electron transfer of the σ-bonding orbital of H₂ into a vacant orbital at the metal and from a filled d orbital to the antibonding orbital of H₂.² The perturbation brought about by this M–(η²-H₂) bond can lead to the homolytic cleavage with formation of M–(H₂) dihydride species, or, alternatively, the activated H₂ 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
A good number of metallaheteroboranes have been found to catalyze hydrogenation reactions; 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) 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 $[1,1-(\text{IMe})(\text{PPh}_3)\text{-3-(Py)-1,2-}\text{RhSB}_9\text{H}_8]$ (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. 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. 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 \(^{31}\)P-\(^{1}\)H 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 \(^1\)H-\(^{11}\)B 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 \(^{31}\)P-\(^{1}\)H spectra suggest strongly the presence of two \{Rh(IMe)(PPh₃)\}−{SB₉H₉(Py)} 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 \(^1\)H NMR spectrum (see ESI).
Diagnostic of the nido-structure of the new species (Scheme 3) are the proton resonances at $\delta_H$ -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 H$_2$ to a polyhedral boron-containing compound has been reported only once before.10 This reaction involves [1,1-(PPh$_3$)$_2$-3-(Py)-isonido-1,2-RhSB$_9$H$_8$] (6) that reacts slowly with H$_2$ to afford [8,8,8-(H)(PPh$_3$)$_2$-9-(Py)-nido-8,7-RhSB$_9$H$_9$] (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 H$_2$ most readily in a reversible manner.

Given this unusual reactivity by a metallasbicerborane, and with an interest in the H$_2$-activation mechanism, DFT was used to calculate intermediates, transition states and energies along the reaction pathway for H$_2$ 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 $\text{TS1}$ 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 $^{11}\text{B}$ spectrum should exhibit nine peaks. The fact that at room temperature the $^{11}\text{B}$ and $^1\text{H}-\{^{11}\text{B}\}$ NMR spectra show symmetric patterns indicates that the carbene-ligated rhodathiaborane, 4, is non-rigid. A rapid deformaional 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$\leftrightarrow$nido transformation (Scheme S5).

Following this isonido$\leftrightarrow$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 $\text{TS2}$ from the nido-cluster, 4', entails the perpendicular approach of H$_2$ to the rhodium centre and the subsequent rotation to form a side-on bonded intermediate, $\text{INT 1}$, and it has a free energy barrier of 19.4 kcal/mol (Scheme 4). This intermediate is comparable with well-characterized mononuclear dihydrogen complexes, 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, $\text{INT 1}$, is a good theoretical model of a H$_2$ molecule in the coordination environment furnished by a metallaheteroborane.
From this unstable $\eta^2$-(H$_2$)-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 CH$_2$Cl$_2$ 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 H$_2$. 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

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\begin{align*}
\text{Scheme 4} & \quad \text{Proposed reaction mechanism and relative free energies, } \Delta G_{298} \text{ (kcal/mol), for the activation of } H_2 \text{ by } [\text{(IMe)(PPh}_3\text{(Py)RhSB}_9\text{H}_8)] \ (4/4') \\
\text{structural change of the cluster, leading to vacant coordination sites at the metal centre. The subsequent binding of } H_2 \text{ results in the heterolytic splitting of the } H–H \text{ bond along the}
\end{align*}
\]
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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REFERENCES


