

COMMUNICATION

H₂ evolution from H₂O via O–H oxidative addition across a 9,10-diboraanthracene

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The water reactivity of the boroauride complex ([Au(B₂P₂)] [K(18-c-6)]; (B₂P₂, 9,10-bis(2-(diisopropylphosphino)-phenyl)-9,10-dihydroboranthrene) and its corresponding two-electron oxidized complex, Au(B₂P₂)Cl, are presented. Au(B₂P₂)Cl is tolerant to H₂O and forms the hydroxide complex Au(B₂P₂)OH in the presence of H₂O and triethylamine. Au(B₂P₂)Cl and [Au(B₂P₂)]OH are poor Lewis acids as judged by the Gutmann-Becket method, with [Au(B₂P₂)]OH displaying facile hydroxide exchange between B atoms of the DBA ring as evidenced by variable temperature NMR spectroscopy. The reduced boroauride complex [Au(B₂P₂)][−] reacts with 1 equivalent of H₂O produces a hydride/hydroxide product, [Au(B₂P₂)(H)(OH)][−], that rapidly evolves H₂ upon further H₂O reaction to yield the dihydroxide compound, [Au(B₂P₂)(OH)₂][−]. [Au(B₂P₂)Cl] can be regenerated from [Au(B₂P₂)(OH)₂][−] via HCl–Et₂O, providing a synthetic cycle for H₂ evolution from H₂O enabled by O–H oxidative addition at a diboraanthracene unit.

The chemistry of water is intimately tied to energy production, notably in the steam reforming of methane.¹ However, the quest for sustainable energy sources has focused attention on the efficient photo- or electrochemical splitting of water into hydrogen and oxygen.² Owing to their intrinsic redox activity and rich hydride and oxygen-derived ligand chemistry, transition metal species of both molecular and heterogeneous types have been a central focus of research in this area.³ In the realm of molecular organometallic chemistry, O–H bond oxidative addition to give M–H and M–OH fragments has been considered as a potential strategy for activating water towards redox transformations,⁴ with most examples featuring heavier late metals.⁵

Approaches to small molecule activation that forgo transition metals,⁶ such as frustrated Lewis-pairs (FLPs),⁷ main-group multiple bonds,⁸ and low-valent p-block elements,⁹ have

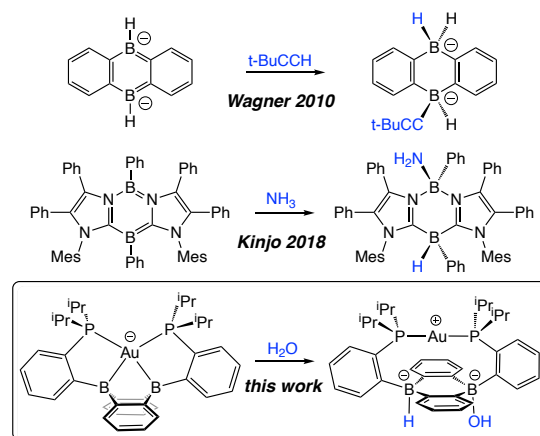


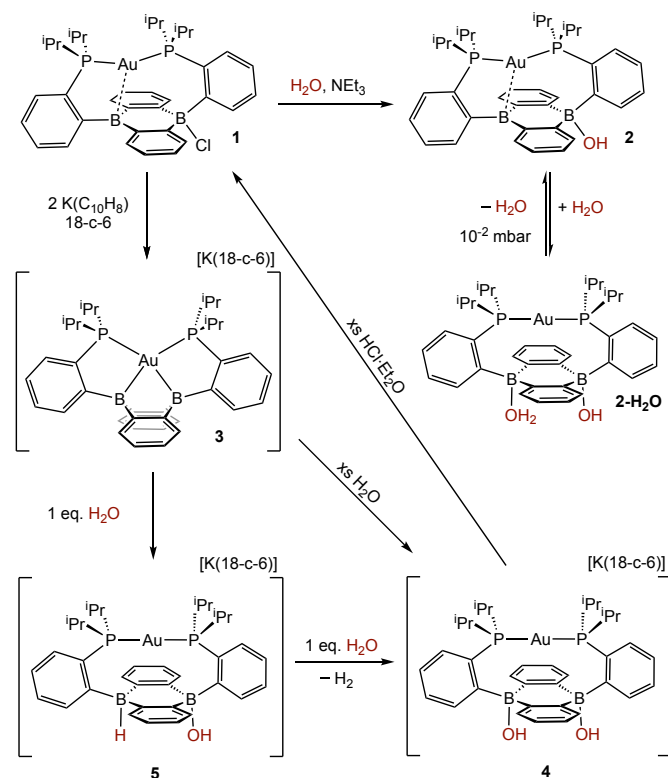
Fig. 1 Examples of E–H bond activation processes at 1,4 diboron heterocycles.

garnered considerable attention as these systems are capable of activating a range of small molecules, including via oxidative addition.¹⁰ Boron-containing heterocycles have demonstrated promise in this regard, as they have been shown to activate a wide range of single bonds as well as binding unsaturated molecules via [4+2] or [4+1] cycloaddition chemistry.¹¹ In 2010, Wagner demonstrated the C–H activation of alkynes at a reduced 9,10-diboraanthracene (DBA)¹² (Figure 1, top) and has since extended this reactivity to H–H cleavage.¹³ Kinjo has developed a range of diazadiborinines capable of activating C–O, P–H, Si–H, and B–H bonds¹⁴ as well as H₂ and NH₃ (Figure 1, middle).¹⁵ Reports of HO–H cleavage with boron heterocycles are limited, however, and have largely involved irreversible B–C or B–H hydrolysis of the heterocycle or its substituents.¹⁶ Recently we developed a DBA based disphosphine ligand (B₂P₂) and reported its Ni,¹⁷ Cu, Ag¹⁸ and Au complexes.¹⁹ The auride complex of B₂P₂, [Au(B₂P₂)][−] (Figure 1, bottom), exhibits diverse two-electron reductive chemistry with H⁺, CO₂,²⁰ and organic carbonyls.²¹ Herein we report that this species also can react directly with two equivalents of water to yield H₂ via a pathway involving the oxidative addition of an O–H bond of water across the two boron atoms. The [Au(B₂P₂)] scaffold is generally stable in excess H₂O and the hydroxide byproducts can be liberated

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from the boron centers with acid, formally closing a synthetic cycle for water reduction to H_2 mediated by the DBA core.



Scheme 1 Water stability and water reduction from the $\text{Au}(\text{B}_2\text{P}_2)$ platform.

Steric protection of borane centers (e.g. with mesityl substituents) is an established method of stabilizing DBA molecules against borane hydrolysis,²² and we wondered if the rigid phenylene substituents presented by $[\text{Au}(\text{B}_2\text{P}_2)]$ might offer similar protection. The water stability of $[\text{Au}(\text{B}_2\text{P}_2)]\text{Cl}$ (**1**) was explored by allowing a 0.02 M solution in $\text{CD}_3\text{CN}:\text{D}_2\text{O}$ (2:1) to stand at 22 °C for two weeks. (Compound **1** is insoluble in pure water.) Although we cannot rule out reversible chloride ionization under these conditions, the ^1H and ^{31}P NMR spectra are indistinguishable from the same in pure CD_3CN (Figs. S1–S2), and pure **1** is recovered upon solvent removal. Analogous results were obtained in $\text{CDCl}_3:\text{D}_2\text{O}$ suspensions, suggesting a negligible role for solvent donor ability on stability. Addition of triethylamine (2 equiv.) to a suspension of **1** in toluene: H_2O (10:1) formed the hydroxide substituted compound, $\text{Au}(\text{B}_2\text{P}_2)\text{OH}$ (**2**), in 89% yield as a pale-yellow solid (Scheme 1). The ^{31}P NMR spectrum of **2** in toluene- d_8 at 22 °C contained a singlet at 48.5 ppm. However, single-crystal X-ray diffraction (XRD) studies of **2** (Fig. 3a) revealed distinct boron atoms, with hydroxide bound to one ($\Sigma_{\text{CBC}} = 336.9^\circ$) with a distance of 1.529(2) Å. A Au–B contact of 2.615(1) Å occupies the essentially planar B atom on the opposite face of the DBA ring and is slightly longer than the analogous distance in $\text{Au}(\text{B}_2\text{P}_2)\text{Cl}$ ($d_{\text{Au-B}} = 2.575(2)$ Å).

The discrepancy between the solid-state and apparent solution symmetries of **2** led us to consider a rapid hydroxide exchange mechanism that would symmetrize the molecule on the NMR timescale. A solution of **2** in toluene- d_8 was cooled to

–45 °C causing ^{31}P NMR singlet at 48.6 ppm to broaden and resolve to a set of doublets at 47.5 and 50.3 ppm ($J_{\text{PP}} = 242$ Hz) (Fig. 2). The ^1H NMR at –45 °C of **2** was consistent with C_s symmetry, and the $^{11}\text{B}\{^1\text{H}\}$ NMR contained a broad peak at 36.36 ppm and a sharp signal at –5.57 ppm corresponding to distinct, three- and four-coordinate B atoms, respectively. Eyring analysis of these data gave activation parameters of $\Delta H = 12(1)$ kcalmol $^{-1}$ and $\Delta S = 4.3(2)$ calmol $^{-1}\text{K}^{-1}$ (Fig. S31). The small, positive entropy of activation is inconsistent with a bimolecular mechanism, supporting instead an intramolecular process for hydroxide shuttling between boron sites.²³ Given the solvent and temperature employed, an ionic dissociation/reassociation pathway is unlikely.

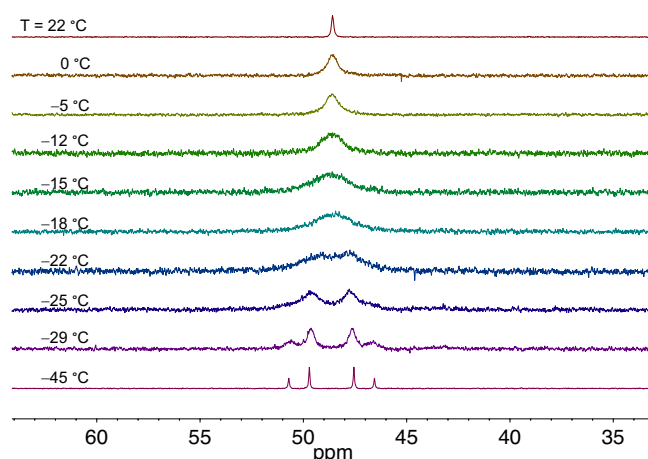


Fig. 2 Variable temperature ^{31}P NMR spectra of $\text{Au}(\text{B}_2\text{P}_2)\text{OH}$ (**2**) in toluene- d_8 from 22 °C to –45 °C. See SI for further details.

To better understand the reactivity of these complexes with water, we measured the relative Lewis acidity of **1** and **2** by the Gutmann-Becket method,²⁴ along with $[\text{Au}(\text{B}_2\text{P}_2)]\text{Cl}$ and the complex salt, $[\text{Au}(\text{B}_2\text{P}_2)][\text{BARF}_4]$ (Fig. S10). Acceptor numbers (ANs) of 0, 0, and 69 were determined in THF ($\text{AN} = 45.25$) for the series **1**, **2**, and $[\text{Au}(\text{B}_2\text{P}_2)][\text{BARF}_4]$ when exposed to 1.05 eq. of triethylphosphine oxide, respectively. These results are consistent with the observed H_2O stability of **1** and **2**. However, in contrast with **1**, when allowing a 0.02 M benzene solution of **2** to stand in the presence water (10 equiv.), colorless crystals formed over the course of 3 days. Single-crystal XRD revealed a water addition product in which the previously three-coordinate B atom in **2** binds an equivalent of H_2O , affording $\text{Au}(\text{B}_2\text{P}_2)(\text{OH})(\text{H}_2\text{O})$ (**2-H₂O**, Fig. 3b). Each B atom is puckered from the DBA ring to adopt a pseudo-tetrahedral geometry ($\Sigma_{\text{CBC}} = 338.4$ and 339.7°) with B–O bond lengths of 1.596(2) and 1.587(2) Å. Disordered H atoms were located in the electron difference map between the two O atoms, suggesting some degree of H-bonding between each B–OH unit in the solid

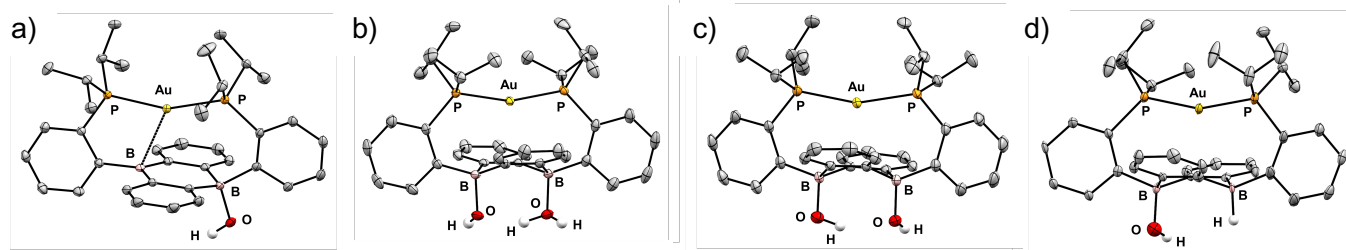


Fig. 3 Thermal ellipsoid plots (50%) of a) $\text{Au}(\text{B}_2\text{P}_2)\text{OH}$ (**2**), b) $2\text{-H}_2\text{O Au}(\text{B}_2\text{P}_2)(\text{OH})(\text{H}_2\text{O})$ c) the anionic component of $[\text{Au}(\text{B}_2\text{P}_2)(\text{OH})_2][\text{K}(18\text{-c-}6)]$ (**4**) and d) the anionic component of $[\text{Au}(\text{B}_2\text{P}_2)(\text{OH})(\text{H})][\text{K}(18\text{-c-}6)]$ (**5**). Unlabelled ellipsoids correspond to carbon. Most hydrogen atoms and all cocrystallized solvent molecules have been omitted for clarity. Only a single disorder component is shown for b) and c). See text for details.

state. NMR spectra collected in toluene- d_8 after exposure of solid **2-H₂O** to 10^{-2} mbar vacuum for 15 minutes were consistent with pure **2**, and a crystal grown from this material was identified by preliminary XRD to be **2**, confirming that the formation of **2-H₂O** is reversible.

We next turned to the reaction of the reduced species $[\text{Au}(\text{B}_2\text{P}_2)][\text{K}(18\text{-c-}6)]$ (**3**) with H_2O (Scheme 1). Addition of excess H_2O (3 equiv.) to **3** resulted in immediate loss of color and effervescence to yield the dihydroxide complex $[\text{Au}(\text{B}_2\text{P}_2)(\text{OH})_2][\text{K}(18\text{-c-}6)]$ (**4**) in essentially quantitative yield. ^1H NMR spectroscopy confirmed the evolution of H_2 and single-crystal XRD studies on **4** (Fig. 3c) revealed B–OH bonds of 1.530(3) and 1.509(3) Å, significantly shorter than those in **2-H₂O**. When 1 equiv. of H_2O is added slowly to a solution of **3** at 0°C , ^{31}P NMR spectroscopy revealed a new set of coupled doublets at 46.0 and 50.6 ppm ($J_{\text{PP}} = 276.9$ Hz) along with a singlet at 45.5 ppm corresponding to the dihydroxide **4**, in a 4:1 ratio, respectively. We formulate this new product as $[\text{Au}(\text{B}_2\text{P}_2)(\text{OH})(\text{H})][\text{K}(18\text{-c-}6)]$ (**5**) on the basis of the following data. ^1H NMR analysis of the major product was consistent with C_s symmetry due to different substituents at the two B atoms, with a distinct four-line signal arising from one-bond B–H coupling at 4.19 ppm ($J_{\text{B-H}} = 72.0$ Hz). The ^1H -coupled ^{11}B NMR displayed a corresponding doublet at -9.73 ppm ($J_{\text{B-H}} = 75.7$ Hz) and a broader singlet at -0.85 ppm (Fig. 4), strongly suggestive of a B–H unit. Although crystals could be obtained from this mixture, they invariably consisted of cocrystallization of **5** with roughly equimolar amounts of **4**, resulting in significant disorder (Fig. S37). Despite this, a satisfactory crystallographic model could be constructed consistent with an approximately equimolar cocrystallization, which can be thought of as a 50% OH occupancy in the hydride site of **5** (Fig. 3d). There are no other compelling hypotheses for the lack of electron density in this position given the clear pyramidalization of the B atom. Although these crystallographic data are consistent with this structure yet not definitive, the solution spectroscopic characterization of **5**, including the incontrovertible signature of a B–H moiety, provides strong evidence for this formulation. As implied by the difficulty of isolating **5** in pure form, it is extraordinarily water sensitive, rapidly converting to **4** upon

addition of H_2O or by scavenging adventitious water from the glovebox atmosphere.

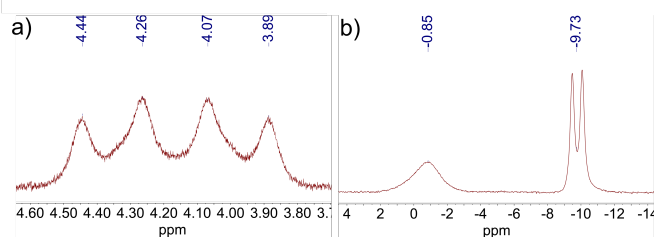


Fig. 4 ^1H (a) and ^{11}B (b) NMR of $[\text{Au}(\text{B}_2\text{P}_2)(\text{H})(\text{OH})][\text{K}(18\text{-c-}6)]$ (**4**) highlighting the B–H moiety.

To close a synthetic cycle for H_2 evolution from H_2O , we investigated reaction conditions to regenerate **1** from **5**. $\text{HCl}\cdot\text{Et}_2\text{O}$ (3 equiv.) was identified to cleanly induce this reaction, with no other products observed by ^1H and ^{31}P NMR. This reaction highlights the unique stability of the $[\text{Au}(\text{B}_2\text{P}_2)]$ system to both water and acid and provides an outline for the potential catalysis of H_2 evolution from H_2O with this and related systems.

In conclusion, we have demonstrated the reduction of H_2O to H_2 mediated by a redox-active borane. As boron-containing materials such as boron-doped graphene,²⁵ boron nanoparticles²⁶ and other boron-doped materials²⁷ continue to attract interest as metal-free alternatives to H_2 production from H_2O , molecular platforms like the ones discussed here can play a key role in informing underlying mechanistic discussion and aiding in rational design. Modifications to the $[\text{Au}(\text{B}_2\text{P}_2)]$ system directed at performing electrocatalytic H_2O reduction are currently being explored.

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Conflicts of interest

There are no conflicts to declare.

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