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H_2 evolution from H_2O via O–H oxidative addition across a 9,10-diboraanthracene

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The water reactivity of the boroauride complex ([Au(B_2P_2)][K(18-c-6)]; (B_2P_2, 9,10-bis(2-(diisopropylphosphino)-phenyl)-9,10-dihydroboranthrene) and its corresponding two-electron oxidized complex, Au(B_2P_2)Cl, are presented. Au(B_2P_2)Cl is tolerante to H_2O and forms the hydroxide complex Au(B_2P_2)OH in the presence of H_2O and triethylamine. Au(B_2P_2)]Cl and [Au(B_2P_2)]OH are poor Lewis acids as judged by the Gutmann-Becket method, with [Au(B_2P_2)]OH displaying facile hydroxide exchange between B atoms of the DBA ring as evidenced by variable temperature NMR spectroscopy. The reduced boroauride complex [Au(B_2P_2)]$^-$ reacts with 1 equivalent of H_2O produces a hydride/hydroxide product, [Au(B_2P_2)(H)(OH)]$^-$, that rapidly evolves H_2 upon further H_2O reaction to yield the dihydroxide compound, [Au(B_2P_2)(OH)$_2$]$^-$. [Au(B_2P_2)]Cl can be regenerated from [Au(B_2P_2)(OH)$_2$]$^-$ via HCl·Et_2O, providing a synthetic cycle for H_2 evolution from H_2O enabled by O–H oxidative addition at a diboraanthracene unit.

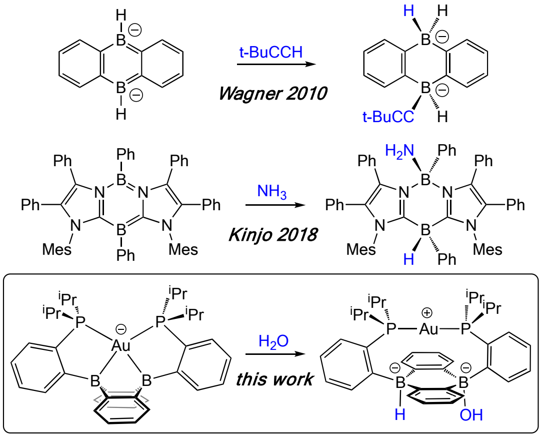

Fig. 1 Examples of E–H bond activation processes at 1,4 diboron heterocycles.

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 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 bonds[14] as well as H_2 and NH_3 (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 (B_2P_2) and reported its Ni,[17] Cu, Ag[18] and Au complexes.[19] The auride complex of B_2P_2, [Au(B_2P_2)]$^-$ (Figure 1, bottom), exhibits diverse two-electron reductive chemistry with H^+, CO_2,[20] and organic carbonyls.[21] Herein we report that this species also can react directly with two equivalents of water to yield H_2 via a pathway involving the oxidative addition of an O–H bond of water across the two boron atoms. The [Au(B_2P_2)] scaffold is generally stable in excess H_2O and the hydroxide byproducts can be liberated

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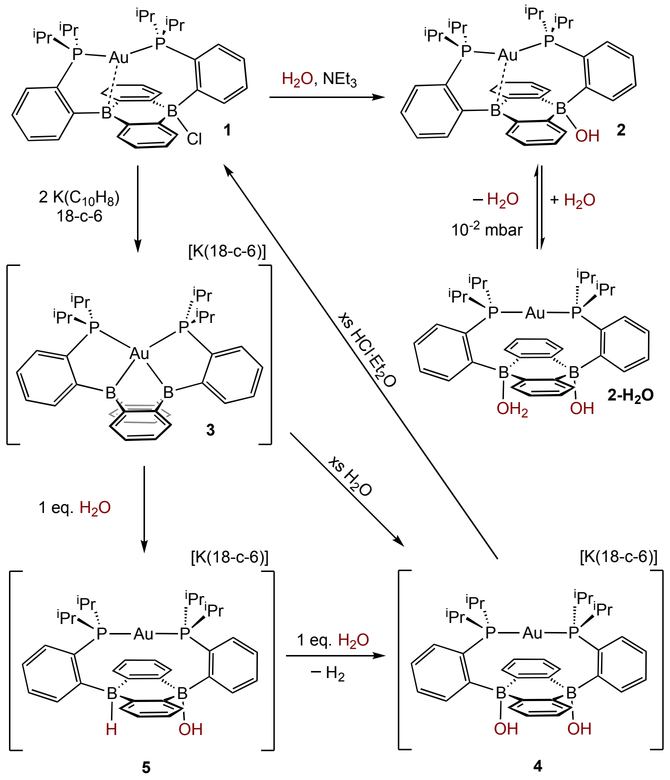
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x from the boron centers with acid, formally closing a synthetic cycle for water reduction to H_2 mediated by the DBA core.



Scheme 1 Water stability and water reduction from the $Au(B_2P_2)$ 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 $[Au(B_2P_2)]$ might offer similar protection. The water stability of $[Au(B_2P_2)]Cl$ (**1**) was explored by allowing a 0.02 M solution in CD_3CN:D_2O (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 $CDCl_3$:D_2O 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, $Au(B_2P_2)OH$ (**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 ($\Sigma_{CBC}\angle$ = 336.9 °) 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 $Au(B_2P_2)Cl$ ($d_{Au\text{-}B}$ = 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_{PP} = 242 Hz) (Fig. 2). The ^1H NMR at –45 °C of **2** was consistent with C_s symmetry, and the $^{11}B\{^1H\}$ 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 ΔH = 12(1) kcalmol^{-1} and ΔS = 4.3(2) calmol^{-1}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.

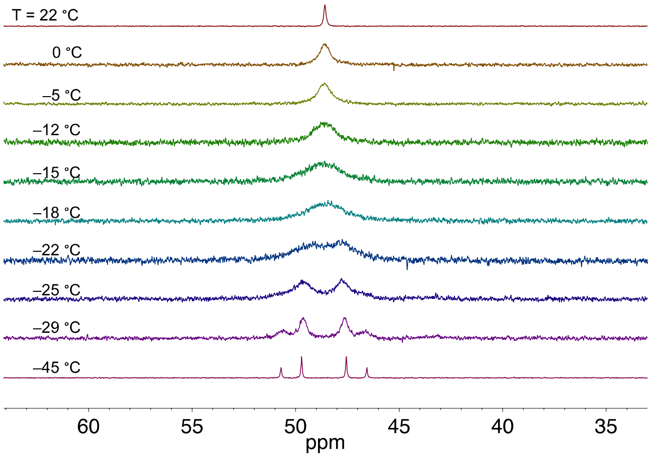


Fig. 2 Variable temperature ^{31}P NMR spectra of $Au(B_2P_2)OH$ (**2**) in toluene-d_8 from 22 °C to –45 °C. See SI for further details.

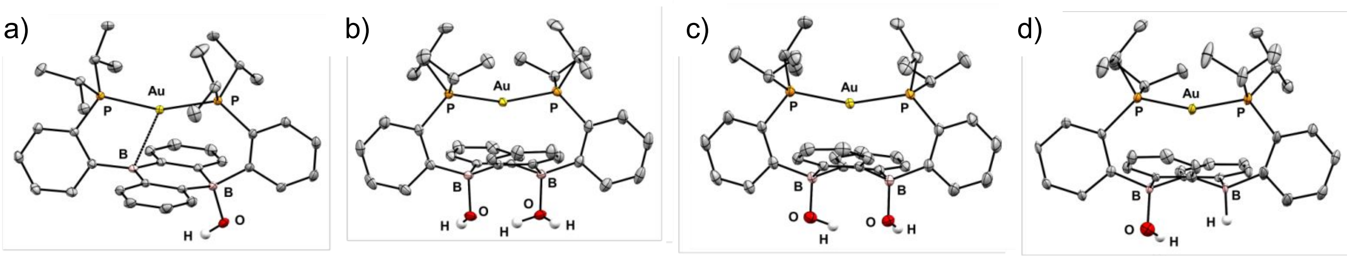


Fig. 3 Thermal ellipsoid plots (50%) of a) Au(B_2P_2)OH (**2**), b) **2-H_2O** Au(B_2P_2)(OH)(H_2O) c) the anionic component of [Au(B_2P_2)$(OH)_2$][K(18-c-6)] (**4**) and d) the anionic component of [Au(B_2P_2)(OH)(H)][K(18-c-6)] **5**. Unlabelled ellipsoids correspond to carbon. Most hydrogen atoms 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.

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 [Au(B_2P_2)]Cl and the complex salt, [Au(B_2P_2)][BAr^F_4] (Fig. S10). Acceptor numbers (ANs) of 0, 0, and 69 were determined in THF (AN = 45.25) for the series **1**, **2**, and [Au(B_2P_2)][BAr^F_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 Au(B_2P_2)(OH)(H_2O) (**2-H_2O**, Fig. 3b). Each B atom is puckered from the DBA ring to adopt a pseudo-tetrahedral geometry ($\Sigma_{CBC}\angle$ = 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 state. NMR spectra collected in toluene-d_8 after exposure of solid **2-H_2O** 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-H_2O** is reversible.

We next turned to the reaction of the reduced species [Au(B_2P_2)][K(18-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 [Au(B_2P_2)$(OH)_2$][K(18-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-H_2O**. 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_{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 [Au(B_2P_2)(OH)(H)][K(18-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 ($J_{B\text{-}H}$ = 72.0 Hz). The ^1H-coupled ^{11}B NMR displayed a corresponding doublet at –9.73 ppm ($J_{B\text{-}H}$ = 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.

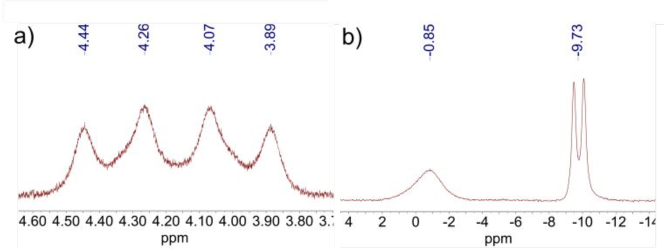


Fig. 4 ^1H (a) and ^{11}B (b) NMR of [Au(B_2P_2)(H)(OH)][K(18-c-6)] (**4**) highlighting the B-H moeity.

To close a synthetic cycle for H_2 evolution from H_2O, we investigated reaction conditions to regenerate **1** from **5**. HCl·Et_2O (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 [Au(B_2P_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 nanoparticles[26] and other boron-doped materials[27] 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 [Au(B_2P_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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