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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 boron-centered water reactivity of the boroauride complex ($[Au(B_2P_2)][K(18\text{-}c\text{-}6)]$; ($B_2P_2$, 9,10-bis(2-(diisopropylphosphino)-phenyl)-9,10-dihydroboranthrene) and its corresponding two-electron oxidized complex, $Au(B_2P_2)Cl$, are presented. The tolerance of $Au(B_2P_2)Cl$ towards H_2O was demonstrated and subsequent hydroxide/chloride exchange was acheived in the presence of H_2O and triethylamine to afford $Au(B_2P_2)OH$. $Au(B_2P_2)]Cl$ 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 ^{31}P NMR and low temperature ^{1}H and ^{11}B NMR. The reaction of the reduced boroauride complex $[Au(B_2P_2)]^-$ with 1 equivalent of H_2O produces a hydride/hydroxide product, $[Au(B_2P_2)(H)(OH)]^-$, that, upon addition of a second equivalent of H_2O, rapidly evolves H_2 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 $HCl{\cdot}Et_2O$, providing a synthetic cycle for H_2 evolution from H_2O enabled by O–H oxidative addition at a diboraanthracene unit.

The chemistry of water is intimately tied 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 (Figure 1),[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, have garnered considerable attention as these systems are capable of activating a range of small molecules, including via oxidative addition.[9] Coordinating redox-active ligands to main-group centers is another strategy to afford multi-electron reaction chemistry with these elements.[10] The insertion of low-valent main group compounds (e.g. silylenes) into the O–H bond of water is fairly common,[11] however, these reactions often require careful control of the water stoichiometry and resulting hydrides are generally insufficiently basic to undergo subsequent H_2 evolution in the absence of additional reagents.[12] Furthermore, the oxophilicity of many p-block elements (e.g. Si and B) poses the risk of irreversible E–O bond formation that would preclude catalysis.

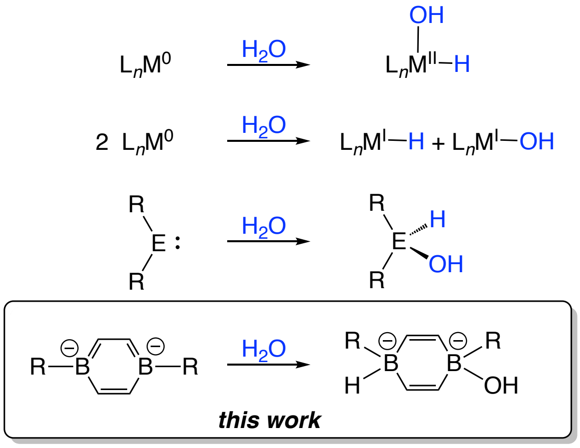

Fig. 1 Some conceptual mechanisms for the oxidative addition of H_2O to transition metal, heavy carbene analogues (E = Si, Ge), and a reduced diboron heterocycle.

Boron-containing heterocycles are another class of emerging main-group species for the activation of small molecules.[13] Reports of HO–H cleavage with these platforms are limited, however, and have largely involved irreversible B–C or B–H hydrolysis of the heterocycle or its substituents.[14] The 9,10-dihydro-9,10-diboraanthracene (DBA) framework has garnered

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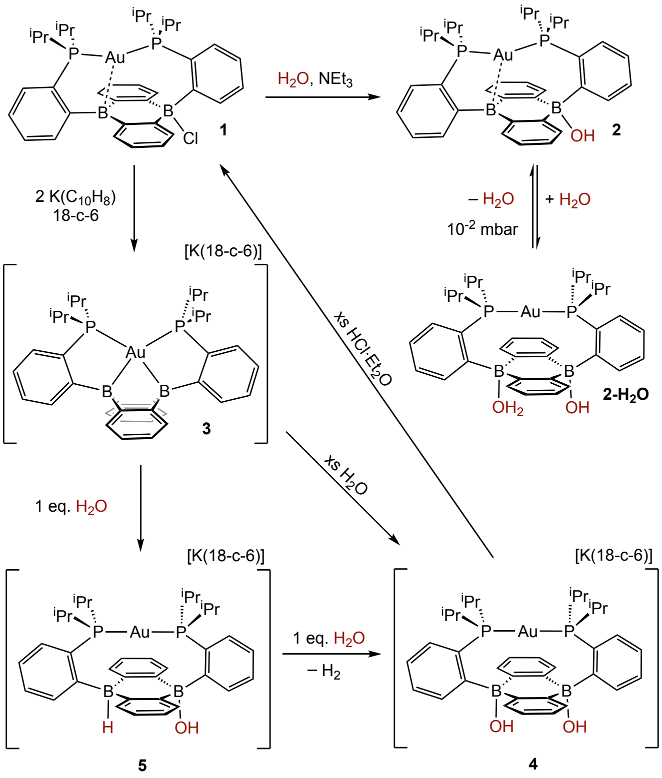
significant interest as a particularly robust reaction platform that is capable of accommodating multiple electron equivalents and subsequently performing multi-electron bond activations with a rapidly growing host of molecules such as CO_2, O_2, C_2H_4 and H_2.[15] Recently we developed a DBA based disphosphine ligand (B_2P_2) and reported its Ni,[16] Cu, Ag[17] and Au complexes.[18] The reduced form of the Au complex exhibits diverse two-electron reductive chemistry with H^+, CO_2[19] and organic carbonyls.[20] 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. Further, we demonstrate that the [Au(B_2P_2)] scaffold is generally stable in a large excess of water, and that the hydroxide byproducts can be liberated 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,[21] 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, with no reaction observed by NMR spectroscopy. (Compound **1** is insoluble in pure water.) Analogous results were obtained in $CDCl_3$:D_2O suspensions, suggesting a negligible role for solvent donor ability on stability. However, 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). Solution NMR spectroscopy of **2** in toluene-d_8 at 22 °C revealed a singlet at 48.5 ppm in the ^{31}P NMR along with a ^1H NMR spectrum consistent with C_{2v} symmetry in solution. Single-crystal X-ray diffraction (XRD) studies of **2** (Fig. 3a) revealed a hydroxide ion bound to one pseudo tetrahedral B atom ($\Sigma_{CBC}\angle$ = 336.9 °) with a distance of 1.529(2) Å. A Au–B contact of 2.615(1) Å occupies the other 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 investigate a potential hydroxide exchange pathway existing between the two boron atoms of the DBA unit by variable-temperature (VT) NMR spectroscopy. Accordingly, a solution of **2** in toluene-d_8 was incrementally cooled to –45 °C during which time the singlet at 48.6 ppm in the ^{31}P spectrum broadened and finally resolved to a set of doublets at 47.5 and 50.3 ppm (J_{PP} = 242 Hz) (Fig. 2). Additionally, the ^1H NMR at –45 °C of **2** was consistent with C_s symmetry while the $^{11}B\{^1H\}$ NMR had two signals (see SI); 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. From the VT-^{31}P NMR data, an Eyring plot was constructed (see SI) and activation parameters were extracted. A coalescence temperature of –18 °C was determined, corresponding to an enthalpy of activation of ΔH = 12(1) kcalmol^{-1} and an entropy of activation of ΔS = 4.3(2) calmol^{-1}K^{-1}. The small, positive entropy of activation is inconsistent with a bimolecular mechanism, supporting instead an intramolecular process for hydroxide shuttling between boron sites.[22] Given the solvent and temperature employed, an ionic dissociation/reassociation pathway is unlikely.

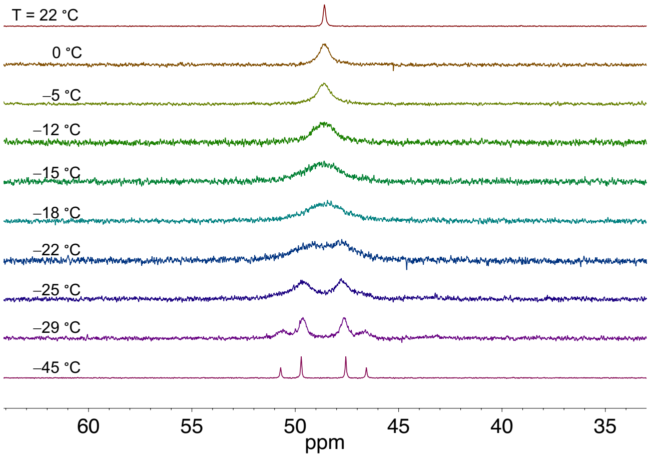


Fig. 2 Variable temperature ^{31}P NMR spectra of Au(B_2P_2)OH (**2**) in toluene-d_8 from 22 °C to –45 °C. See SI for further details.

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,[23] along with [Au(B_2P_2)]Cl and the complex salt, [Au(B_2P_2)][BAr^F_4]. 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], 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

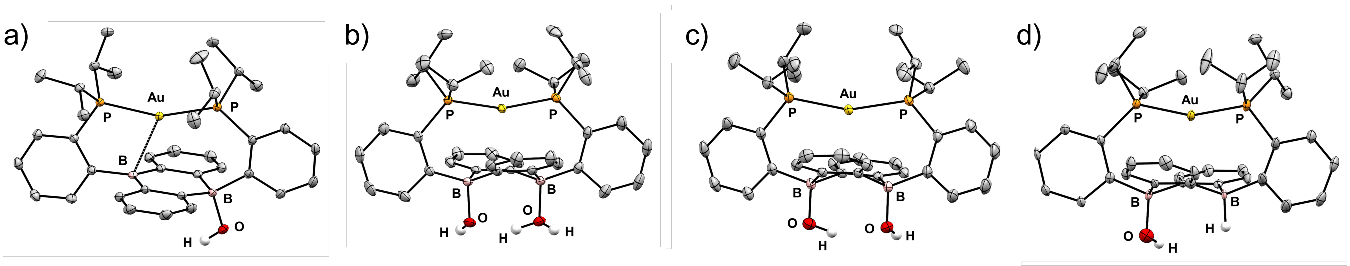


Fig. 3 Thermal ellipsoid plots (50%) of a) $Au(B_2P_2)OH$ (**2**), b) **2-H_2O** $Au(B_2P_2)(OH)(H_2O)$ c) the anionic component of $[Au(B_2P_2)(OH)_2][K(18\text{-}c\text{-}6)]$ (**4**) and d) the anionic component of $[Au(B_2P_2)(OH)(H)][K(18\text{-}c\text{-}6)]$ **5**. Unlabelled ellipsoids correspond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

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 the formation of **2-H_2O** is reversible.

Having gauged the stability of the zwitterionic $Au(B_2P_2)]X$ (X = Cl, OH) complexes towards H_2O, we turned to the reaction of the reduced species $[Au(B_2P_2)][K(18\text{-}c\text{-}6)]$ (**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 $[Au(B_2P_2)(OH)_2][K(18\text{-}c\text{-}6)]$ **4** in essentially quantitative yield. ^1H NMR spectroscopy confirmed the evolution of H_2 along with the appearance of a singlet at 45.5 ppm in the ^{31}P NMR a broad singlet at –1.10 ppm by $^{11}B\{^1H\}$ NMR. Single-crystal XRD studies on **4** (Fig. 3c) reveal tetrahedral B atoms in the DBA ring ($\Sigma_{CBC}\angle$ = 333.8 and 336.0 °) and B–OH bonds of 1.530(3) and 1.509(3) Å, significantly shorter than those in **2-H_2O**. Having established the viability of protonation at B in previous studies of this sytem, we were interested if a B–H containing intermediate could be isolated from the reaction of **3** with H_2O. Slow addition of 1 equiv. of H_2O to a solution of **3** at 0° C rapidly gave a colorless solution. ^{31}P NMR of this solution 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**. The relative ratio of the two products was ~ 4:1 with the doublet containing product being dominant. We formulate this new product as $[Au(B_2P_2)(OH)(H)][K(18\text{-}c\text{-}6)]$ (**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. S34). 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 supporting 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. The 1,4-addition of HO–H to the DBA core in **5** resembles other 1,4 additions of E–H bonds previously reported for diboron heterocycles, especially the tBuCC–H[15a] and H_2[15b] additions to DBA dianions reported by Wagner and the H_2N–H and H_2 additions to diazaborinines reported by Kinjo.[15h] However, the chemistry reported here is the first example of such a reaction with water.

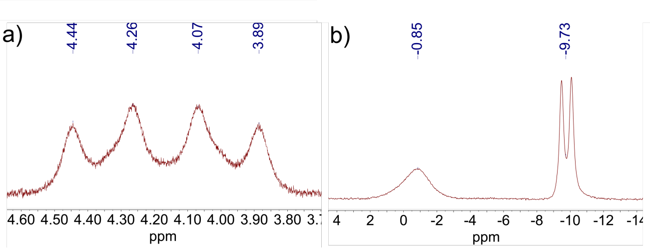


Fig. 4 ^1H (a) and ^{11}B (b) NMR of $[Au(B_2P_2)(H)(OH)][K(18\text{-}c\text{-}6)]$ (**4**) highlighting the B-H moeity.

To probe the possibility of formally closing a synthetic cycle for H_2 evolution from H_2O mediated by this system, we investigated reaction conditions to regenerate **1** from **5**. Following an acid screening, $HCl\cdot Et_2O$ (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.

The $[Au(B_2P_2)]$ system has displayed many desirable properties for water oxidation catalysts, including reversible H_2O activation, hydroxide lability across the DBA unit, reduction of H_2O to H_2 and the ability to regenerate hypothetical catalytic cycle intermediates via protonolysis of B-O bonds. In particular, the sequential, stochiometric splitting of water to hydride/hydroxide units, followed by reaction with a second equivalent of water to liberate H_2, provides rare insights into the mechanism of boron-based reaction systems for water reduction. As boron-based materials such as boron-doped graphene,[24] boron nanoparticles[25] and other boron-doped materials[26] 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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