The boron-centered water reactivity of the borauiride complex ([Au(B₂P₃)](K(18-c-c))₆; (B₂P₃)₂, 9,10-bis(2-(diisopropylphosphino)-phenyl)-9,10-dihydroboranthrene) and its corresponding two-electron oxidized complex, Au(B₂P₃)Cl, are presented. The tolerance of Au(B₂P₃)Cl towards H₂O was demonstrated and subsequent hydroxide/chloride exchange was achieved in the presence of H₂O and triethylamine to afford Au(B₂P₃)OH. Au(B₂P₃)Cl and [Au(B₂P₃)]OH are poor Lewis acids as judged by the Gutmann-Becket method, with [Au(B₂P₃)]OH displaying facile hydroxide exchange between B atoms of the DBA ring as evidenced by variable temperature ³¹P NMR and low temperature ¹H and ¹¹B NMR. The reaction of the reduced borauiride complex [Au(B₂P₃)]⁻ with 1 equivalent of H₂O produces a hydride/hydroxide product, [Au(B₂P₃)[H]/(OH)]⁺; that, upon addition of a second equivalent of H₂O, rapidly evolves H₂ to yield the dihydroxide compound, [Au(B₂P₃)[OH]₂]⁻. [Au(B₂P₃)]Cl can be regenerated from [Au(B₂P₃)[OH]₂]⁻ via HCl/Et₂O, providing a synthetic cycle for H₂ evolution from H₂O enabled by O–H oxidative addition at a diborauiride unit.

The chemistry of water is intimately tied energy production, notably in the steam reforming of methane. However, the quest for sustainable energy sources has focused attention on the efficient photo- or electrochemical splitting of water into hydrogen and oxygen. In the realm of molecular organometallic chemistry, transition metal species of both molecular and heterogeneous types have been a central focus of research in this area. 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), with most examples featuring heavier late metals.

Approaches to small molecule activation that forgo transition metals, such as frustrated Lewis-pairs (FLPs), main-group multiple bonds, 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. Coordinating redox-active ligands to main-group centers is another strategy to afford multi-electron reaction chemistry with these elements. The insertion of low-valent main group compounds (e.g. silylenes) into the O–H bond of water is fairly common, however, these reactions often require careful control of the water stoichiometry and resulting hydrides are generally insufficiently basic to undergo subsequent H₂ evolution in the absence of additional reagents. 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 H₂O 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. 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. The 9,10-dihydro-9,10-diborauiride (DBA) framework has garnered...
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 CO₂, O₂, C₂H₄ and H₂. Recently we developed a DBA based disphosphine ligand (B₃P₂) and reported its Ni, Cu, Ag and Au complexes. The reduced form of the Au complex exhibits diverse two-electron reductive chemistry with H₂, CO₂ and organic carbonyls. 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. Further, we demonstrate that the [Au(B₃P₂)] 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 H₂ mediated by the DBA core.

![Diagram](image)

**Scheme 1** Water stability and water reduction from the Au(B₃P₂) platform.

Steric protection of borane centers (e.g. with mesityl substituents) is an established method of stabilizing DBA molecules against borane hydrolysis, and we wondered if the rigid phenylene substituents presented by [Au(B₃P₂)] might offer similar protection. The water stability of [Au(B₃P₂)]Cl (1) was explored by allowing a 0.02 M solution in CD₃CN:D₂O (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 CDCl₃:D₂O suspensions, suggesting a negligible role for solvent donor ability on stability. However, addition of triethylamine (2 equiv.) to a suspension of 1 in toluene:H₂O (10:1) formed the hydroxide substituted compound, [Au(B₃P₂)]OH (2), in 89% yield as a pale-yellow solid (Scheme 1). Solution NMR spectroscopy of 2 in toluene-d₈ at 22 °C revealed a singlet at 48.5 ppm in the ³¹P NMR along with a ¹H NMR spectrum consistent with Cs 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 (ZbcC = 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(B₃P₂)Cl (dAu–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-d₈ was incrementally cooled to −45 °C during which time the singlet at 48.6 ppm in the ³¹P spectrum broadened and finally resolved to a set of doublets at 47.5 and 50.3 ppm (J₁PP = 242 Hz) (Fig. 2). Additionally, the ¹H NMR at −45 °C of 2 was consistent with Cs symmetry while the ¹¹B(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-³¹P 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⁻¹K⁻¹. The small, positive entropy of activation is inconsistent with a bimolecular mechanism, supporting instead an intramolecular process for hydroxide shuttling between boron sites. Given the solvent and temperature employed, an ionic dissociation/reassociation pathway is unlikely.

![Graph](image)

**Fig. 2** Variable temperature ³¹P NMR spectra of Au(B₃P₂)OH (2) in toluene-d₈ 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 along with [Au(B₃P₂)]Cl and the complex salt, [Au(B₃P₂)][BAR₄⁺]. Acceptor numbers (ANs) of 0, 0, and 69 were determined in THF (AN = 45.25) for the series 1, 2, and [Au(B₃P₂)][BAR₄⁺], respectively. These results are consistent with the observed H₂O 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 H₂O, affording [Au(B₂P₃)][OH](H₂O) (2-H₂O, Fig. 3b). Each B atom is puckered from the DBA ring to adopt a pseudo-tetrahedral geometry (ΔCBC = 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-d₈ 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 the formation of 2-H₂O is reversible.

Having gauged the stability of the zwitterionic Au(B₂P₃)X (X = Cl, OH) complexes towards H₂O, we turned to the reaction of the reduced species [Au(B₂P₃)][K(18-c-6)] (3) with H₂O (Scheme 1). Addition of excess H₂O (3 equiv.) to 3 resulted in immediate loss of color and effervescence to yield the dihydroxy complex [Au(B₂P₃)][OH]₂][K(18-c-6)] 4 in essentially quantitative yield. ¹H NMR spectroscopy confirmed the evolution of H₂O along with the appearance of a singlet at 45.5 ppm in the ³¹P NMR a broad singlet at –1.10 ppm by ¹¹B([H]) NMR. Single-crystal XRD studies on 4 (Fig. 3c) reveal tetrahedral B atoms in the DBA ring (ΔCBC = 333.8 and 336.0°) and B–OH bonds of 1.530(3) and 1.509(3) Å, significantly shorter than those in 2-H₂O. Having established the viability of protonation at B in previous studies of this system, we were interested if a B–H containing intermediate could be isolated from the reaction of 3 with H₂O. Slow addition of 1 equiv. of H₂O to a solution of 3 at 0°C rapidly gave a colorless solution. ³¹P NMR of this solution revealed a new set of coupled doublets at 46.0 and 50.6 ppm (Jₚₚ = 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 dihydroxide species being dominant. We formulate this new product as [Au(B₂P₃)OH][OH][K(18-c-6)] (5) on the basis of the following data. ¹H NMR analysis of the major product was consistent with C₂ 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 (JᵥH = 72.0 Hz). The ¹H-coupled ¹³B NMR displayed a corresponding doublet at –9.73 ppm (JᵥH = 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 hydrate 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 H₂O 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 bBuCC–H₅ and H₂B₃–H₂ additions to DBA dianions reported by Wagner and the H₂N–H and H₂ additions to diazaborinines reported by Kinjo. However, the chemistry reported here is the first example of such a reaction with water.

To probe the possibility of formally closing a synthetic cycle for H₂ evolution from H₂O mediated by this system, we investigated reaction conditions to regenerate 1 from 5. Following an acid screening, HCl·Et₂O (3 equiv.) was identified to cleanly induce this reaction, with no other products observed by ¹H and ³¹P NMR. This reaction highlights the unique stability of the [Au(B₂P₃)] system to both water and acid and provides an outline for the potential catalysis of H₂ evolution from H₂O with this and related systems.

The [Au(B₂P₃)] system has displayed many desirable properties for water oxidation catalysts, including reversible H₂O activation, hydroxide lability across the DBA unit, reduction of H₂O to H₂ 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 H₂, 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 nanoparticles²⁵ and other boron-doped materials²⁶ continue to attract interest as metal-free alternatives to H₂ production from H₂O, 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(BₓPᵧ)] system directed at performing electrocatalytic H₂O reduction are currently being explored.

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Conflicts of interest
There are no conflicts to declare.

Notes and references


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