COMMUNICATION

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

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The boron-centered water reactivity of the boraauride complex ([(Au(B₂P₂))][K(18-crown-6)]; (B₂P₂ 9,10-bis[2-(diisopropylphosphino)-phenyl]-9,10-dihydroboranthrene) and its corresponding two-electron oxidized complex, Au(B₂P₂)Cl₂, are presented. The tolerance of Au(B₂P₂)Cl towards H₂O was demonstrated and subsequent hydroxide/chloride exchange was achieved in the presence of H₂O and triethylamine to afford Au(B₂P₂)OH. 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 ³¹P NMR and low temperature ¹H and ¹³B NMR. The reaction of the reduced boraauride complex [Au(B₂P₂)]⁻ with 1 equivalent of H₂O produces a hydride/hydroxide product, [Au(B₂P₂)(H)(OH)]⁺; that, upon addition of a second equivalent of H₂O, rapidly evolves H₂ to yield the dihydroxide compound, [Au(B₂P₂)(OH)₂]⁺. [Au(B₂P₂)]Cl can be regenerated from [Au(B₂P₂)(OH)]⁻ 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 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 H₂ 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 H₂O to transition metal, heavy carbene analogues (E = Si, Ge), and a reduced diboron heterocycle.](image)

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 CO₂, O₂, C₆H₄, and H₂. Recently we developed a DBA based diphosphine 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.

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 CDCl₃: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 Cᵥ 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 (ZᵥCᵥ = 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 (J₁P₂ = 242 Hz) (Fig. 2). Additionally, the ¹H NMR at −45 °C of 2 was consistent with Cᵥ symmetry while the ¹¹B(H) 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.

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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 (ECC = 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-c)] (3) with H₂O (Scheme 1). Addition of excess H₂O (3 equiv.) to 3 resulted in immediate loss of color and effervescence to yield the dihydroxide complex [Au(B₂P₃)[OH]₂][K(18-c-c)] 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 ¹H(¹H) NMR. Single-crystal XRD studies on 4 (Fig. 3c) reveal tetrahedral B atoms in the DBA ring (ECC = 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 (Jₚ₋ₚ = 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 containing product being dominant. We formulate this new product as [Au(B₂P₃)[OH][OH]][K(18-c-c)] (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 (JₚH = 72.0 Hz). The ¹H-coupled ¹³B NMR displayed a corresponding doublet at ~9.73 ppm (JₚB = 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).

Fig. 3 Thermal ellipsoid plots (50%) of a) Au(B₂P₃)[OH] (2), b) 2-H₂O Au(B₂P₃)[OH][H₂O] c) the anionic component of [Au(B₂P₃)[OH]][K(18-c-c)] (4) and d) the anionic component of [Au(B₂P₃)[OH][OH]][K(18-c-c)] 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 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 [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 $H_2$, 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 nanoparticles25 and other boron-doped materials26 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$_2$P$_3$)] 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.

Notes and references


