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Proton to hydride umpolung at a phosphonium center *via* electron relay: a new strategy for main-group based water reduction†

Takumi Oishi,[a] Leonardo I. Lugo-Fuentes,[b] Yichuan Jing,[a] J. Oscar C. Jimenez-Halla,[b] Joaquín Barroso-Flores,[cd] Masaaki Nakamoto,[a] Yohsuke Yamamoto,[a] Nao Tsunoji[e] and Rong Shang*[a]

Generation of dihydrogen from water splitting, also known as water reduction, is a key process to access a sustainable hydrogen economy for energy production and usage. The key step is the selective reduction of a protic hydrogen to an accessible and reactive hydride, which has proven difficult at a p-block element. Although frustrated Lewis pair (FLP) chemistry is well known for water activation by heterolytic H–OH bond cleavage, to the best of our knowledge, there has been only one case showing water reduction by metal-free FLP systems to date, in which silylene (Si^{II}) was used as the Lewis base. This work reports the molecular design and synthesis of an *ortho*-phenylene linked bisborane-functionalized phosphine, which reacts with water stoichiometrically to generate H_2 and phosphine oxide quantitatively under ambient conditions. Computational investigations revealed an unprecedented multi-centered electron relay mechanism offered by the molecular framework, shuttling a pair of electrons from hydroxide (OH^-) in water to the separated proton through a borane-phosphonium-borane path. This simple molecular design and its water reduction mechanism opens new avenues for this main-group chemistry in their growing roles in chemical transformations.

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Introduction

Main group compounds have shown growing potential for transition metal-like reactivities, and thus offer an economical alternative to metal-based chemical transformations.[1–8] One fundamentally important process related to sustainable energy production is the direct generation of high-energy dihydrogen molecules by water splitting (water reduction).[9,10] Currently, besides direct electrolysis,[9–15] artificial water reduction strategies usually require a reduced form of (s- or d-block) metal as a reactant or catalyst, where heterolytic O–H bond cleavage during water splitting occurs through oxidative addition over one or two metal centres (Chart 1A).[16–18] The electron-rich metal centre accepts electrons from the electronegative oxygen and transfers it to a proton (in H_2O) to form a hydride, which then recombines with the second proton on oxygen to generate dihydrogen.

This general heterolytic mechanism of water cleavage (Chart 1A) has proven difficult to replicate by main-group elements. Although water HO–H bond cleavage, to generate element–hydride (E–H) bonds, has been achieved by oxidative addition at low valent elements (*e.g.* Al/Ga(I)[19–23] and Si/Ge(II)[24] species) and 1,2-addition across main-group multiple bonds (*e.g.* disilenes),[25–34] a p-block E–H bond is usually less reactive than an s-/d-block M–H bond. Their reduced reactivity and large steric bulk (usually employed for their isolation) tend to favor the activation product instead of liberation of dihydrogen. A remarkable p-block example of water reduction was reported by Nielsen and Skrydstrup, which took advantage of the reducing power of the B–B bond in an sp^3–sp^3 diboron(4) system,[35] resembling a binuclear metal system.

Another main-group strategy for facile H_2O activation involves a bulky Lewis acid and base pair (frustrated Lewis pair, FLP, Chart 1B). In this case, group 15 functionalities, such as phosphines with electron-donating substituents, are usually employed as a Lewis base to deprotonate the Lewis acid-coordinated water molecule. However, the conversion of a proton, in a water molecule, into hydride cannot be achieved and thus the

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[a] *Department of Chemistry, Graduate School of Advanced Science and Engineering, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8526, Japan. E-mail: rshang@hiroshima-u.ac.jp*

[b] *Department of Chemistry, Division of Natural and Exact Sciences, University of Guanajuato, Campus Gto, Noria Alta s/n, 36050 Guanajuato, Mexico*

[c] *Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Unidad San Cayetano, 50200 Toluca de lerdo, México*

[d] *Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior S/N, Ciudad Universitaria, alcaldía de Coyoacán, CP 04510, Ciudad de México, México*

[e] *Department of Chemistry, Graduate School of Advanced Science and Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, 739-8527, Japan*

† Electronic supplementary information (ESI) available: Synthetic and computational details, structural and spectroscopic data of **1a–b**, **1-int**, **2** and **3**. Computational details. CCDC 2096462–2096465 and 2109052. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1sc05135k

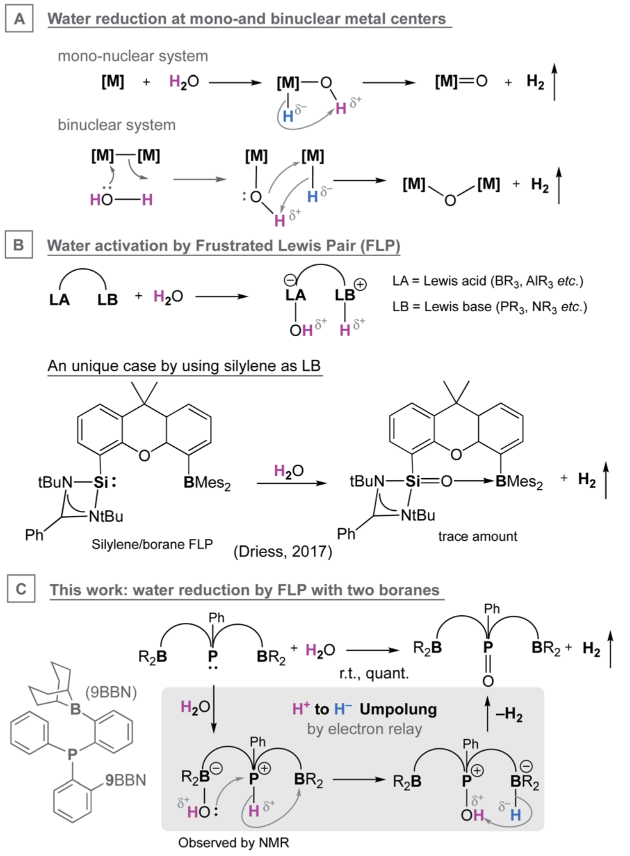


Chart 1 Metal- (A) and p-block element (B and C)-based mechanisms for water activation and reduction.

reaction stops at the HO–H bond cleavage step.[36–44] By using both low-valent p-block elements and FLP chemistry, Driess and coworkers reported a metal-free water reduction example, from an intramolecular silylene/borane system (Chart 1B).[45] However, since silylene is in a highly reduced form, this water reduction is not entirely unexpected. The necessity of borane in the water reduction was not discussed explicitly in the report, though its involvement in H_2 generation was proposed based on the calculated reaction mechanism.

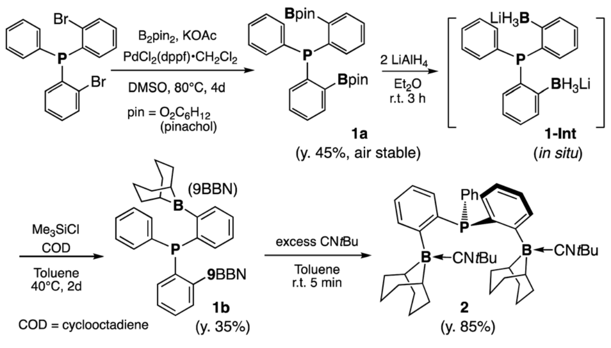
Herein we report a new FLP design for metal-free water reduction based on phosphine and borane functionalities. While triphenyl phosphine does not react with water under ambient conditions, we found that a bisborane-functionalized triaryl phosphine can instantaneously and quantitatively reduce water to generate dihydrogen and phosphine oxide.[46–49] This reaction features an electron relay mechanism among the borane-phosphine-borane centers, which allowed an umpolung of a proton in water to a hydride on borane driven at a phosphonium center. This then led to formation of phosphine oxide and H_2, leaving both Lewis acidic boranes intact after the reaction.

Discussion

During the systematic development of group 13 ligands for transition metal complexes, we set out to synthesize an *ortho*-phenylene linked bis(borane)-phosphine (BPB) ligand. We envisioned that the rigid and π-rich aryl linker would increase the stability and reactivity in comparison to previously reported systems.[50] We were able to obtain the air-stable, colorless crystalline pinacolboranyl derivative (BPB-pin), **1a**, from bis(2-bromophenyl)(phenyl)-phosphine[51] *via* Miyaura–Ishiyama borylation with bis(pinacolato)diboron (B_2pin_2) in 45% yield (Scheme 1, see the ESI† for full structural and spectroscopic data).[52] Following the strategy developed by Wagner,[53] **1a** was converted to the dialkyl-substituted 9BBN derivative **1b** in 34% yield. The formation of the lithium boron hydride intermediate (**1-Int**) was detected by a proton-coupling ^{11}B NMR experiment of the reaction mixture, which showed a broad quartet at −26.1 ppm, confirming the three hydrides bound to the boron centre ($^1J_{BH}$ = 59 Hz, ESI 4.2†). Single-crystals of **1-Int** were also obtained, which revealed a $(\mathbf{1\text{-}Int})_4LiCl$ cluster structure (see the ESI†).

Compound **1b** is a highly reactive crystalline solid. Its $^{31}P\{^1H\}$ NMR spectrum showed a sharp singlet at −7.0 ppm. The $^{11}B\{^1H\}$ NMR spectrum showed a broad singlet at 79.2 ppm, similar to that of Bourissou's phosphorus/borane ambiphilic ligand bearing the cyclohexylborane moiety.[54] The down-field ^{11}B NMR signal suggests a highly Lewis acidic borane center with no strong intra- or intermolecular coordination from the phosphine moiety. Attempts to obtain single crystals of **1b** were not successful in our hands. However, its isocyanide-Lewis adduct **2** could be obtained as colorless crystals in 85% yield (Scheme 1). X-ray analysis of a single crystal of **2** showed the molecular structure of **1b** with each borane coordinated by an isocyanide moiety (Fig. 1b). The solution NMR spectrum of **2** was fully consistent with its solid-state structure, showing no dissociation of the Lewis base in solution at room temperature.

Compound **1b** did not react with H_2 under ambient conditions. However, it reacted with H_2O at room temperature with vigorous evolution of gas (Fig. 2). The ^1H NMR spectrum of the reaction mixture showed a singlet at 4.47 ppm, assignable to H_2. An analogous reaction with D_2O in toluene led to clean generation of D_2, detected by ^2H NMR. These results confirmed that both hydrogen atoms in the generated dihydrogen are from the water molecule (Fig. 2). In addition, phosphine oxide **3** was isolated in 97% yield. The solid-state structure of **3** showed a POBCC 5-membered ring,[55] with a short P–O distance of



Scheme 1 Synthetic pathway to bis(boranylphenyl)phenyl phosphine derivatives **1a**, **1b** and **2**.

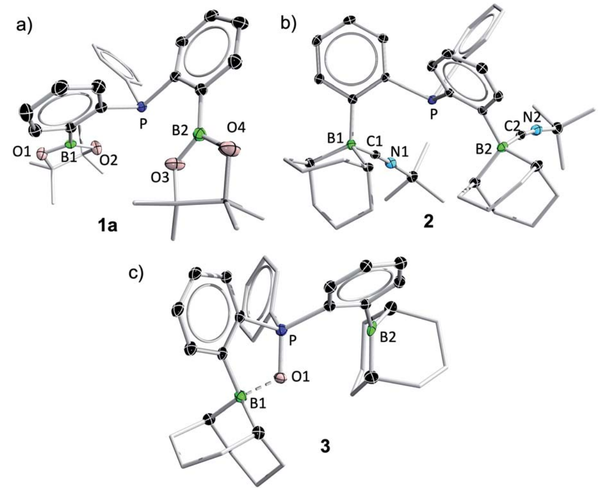


Fig. 1 Solid-state structures of **1a** (a), **2** (b) and **3** (c). Thermal ellipsoids are drawn at 30% probability. Peripheral ellipsoids are omitted for clarity. CCDC: 2096462 (**1a**), 2096464 (**2**), 2096465 (**3**). See the ESI for **1-int**, CCDC 2096463 and **3**$\cdot H_2O$, CCDC 2109052.†

1.5322(13) Å and a remarkably long B1–O distance of 1.633(2) Å. The tetrahedral geometry at B1 ($\Sigma B1^{CCC} = 339.9°$) suggests a definite B–O interaction. In solution however, only one boron signal at 48.2 ppm could be observed at room temperature, which broadened into the baseline below 0 °C (see spectra in the ESI†). The ^{1}H NMR spectrum also suggested a symmetrical structure in solution at room temperature. These revealed a fluxional coordination of the oxide to both borane centres. The $^{31}P\{^{1}H\}$ NMR signal of compound **3** showed a sharp signal at 60.4 ppm. Interestingly, compound **3** does not react with additional H_2O under an inert atmosphere but decomposes readily in air at room temperature.

Although FLPs are well known for heterolytic bond cleavages in water[36–44] and dihydrogen,[56–61] to the best of our knowledge, there is only one exmple of water reduction by metal-free FLP systems (Chart 1C). A control reaction of free PPh_3 and BCy_3 in a 1 : 2 ratio at 50 °C in benzene did not yield any H_2 overnight (see spectra in the ESI†), which means the architecture of the rigid phenylene backbone and the proximity of two boranes are essential for this reaction. In addition, numerous examples of phenylene linked phosphine/borane FLPs for small molecule activation studies have been reported previously. However, water reduction has not been described.[62–76]

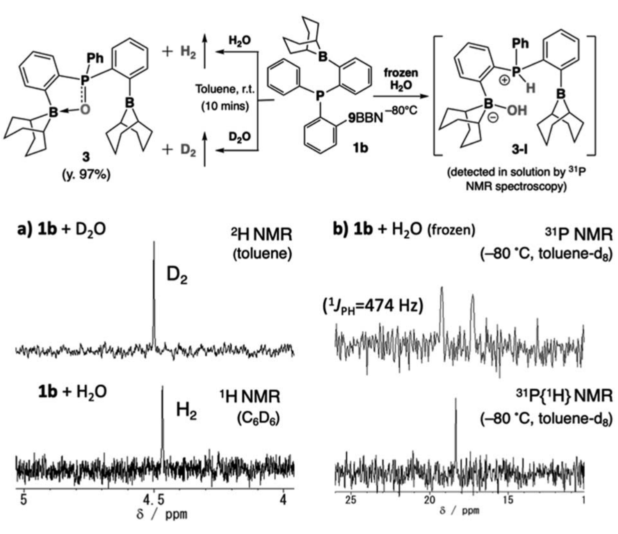


Fig. 2 Reaction schemes and NMR spectra of **1b** with H_2O and D_2O at room temperature (a) and with frozen water at −80 °C (b).

In the search for possible HO–H bond splitting intermediates like those observed in FLP chemistry,[36–44] a toluene-d_8 solution of **1b** was frozen while water was added by syringe. The $^{31}P\{^{1}H\}$ NMR measurement of the reaction mixture at −80 °C revealed a small singlet at 18.3 ppm which splits into a doublet ($^{1}J_{PH} = 474$ Hz) in a subsequent ^{31}P NMR measurement, confirming the generation of a phosphonium ($[Ar_3PH]^+$) intermediate (Fig. 2b). This signal could not be observed at temperatures higher than −30 °C, where the reaction proceeds too quickly. Attempts to isolate a similar O–H bond cleavage product from the reaction of **1b** and methanol were not successful. A large excess of methanol (*ca.* 50 equiv.) was needed for an observable change in the NMR reactions with **1b**, where the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture revealed a singlet which splits into a doublet in a proton-coupled ^{31}P NMR experiment (see spectra in the ESI†). Removal of solvent led to a complete recovery of **1b**. This suggested that the cleavage of the MeO–H bond by **1b** is slightly uphill energetically, and **1b** and the activation product (**4**, see the ESI†) are in equilibrium in solution.

To obtain more insights into the mechanistic details on the water reduction by **1b**, we performed theoretical calculations at the SMD(benzene):ω-B97XD/6-311G(d) level (see the ESI† for computational details). The calculated reaction mechanism (Fig. 3) suggests that the water activation starts with its coordination to one borane to give adduct **H1** ($\Delta G_{R1} = +4.7$ kcal mol^{-1}). Then the phosphine serves as a base to deprotonate the coordinated HO–H bond (*via* transition state **TSH1**, $\Delta G_1^{\ddagger} = +7.7$ kcal mol^{-1}) which generates intermediate **H2** (observed by NMR at −80 °C as **3-I**, $\Delta G_{R2} = -1.2$ kcal mol^{-1}). The resulting phosphonium cation now behaves as an electrophile[77] to receive the pair of electrons of the hydroxyl group while transferring the first hydrogen as a hydride to the second boron (**TSH2**, $\Delta G_2^{\ddagger} = +14.5$ kcal mol^{-1}) in a concerted fashion to form **H3** ($\Delta G_{R3} = +8.6$ kcal mol^{-1}). This is followed by the decoordination of hydroxyl from the first boron (**TSH3**, $\Delta G_3^{\ddagger} = +1.0$ kcal mol^{-1}) generating rotamer **H4** ($\Delta G_{R4} = -2.5$ kcal mol^{-1}) which keeps closer the hydrogens to finally lead to formation of H_2 (*via* **TSH4**, $\Delta G_4^{\ddagger} = +1.2$ kcal mol^{-1}) and the phosphine oxide **3** ($\Delta G_{R5} = -31.7$ kcal mol^{-1}). Overall, this reaction is exergonic ($\Delta G_R^0 = -22.1$ kcal mol^{-1}). The calculated total energy barrier of +18.0 kcal mol^{-1} is in line with our reported reaction conditions. **H2** was also observed experimentally at −80 °C by NMR experiments.

The natural bond orbital (NBO) charges of the phosphorus atom and the transferred hydrogen atom between **H2** and **H3** reflected the charge transfer corresponding to oxidation and reduction respectively, showing a simultaneous increase in the charge of P and decrease in that of H (Fig. 3b). Also, our theoretical calculations suggest that there is a fluxional coordination

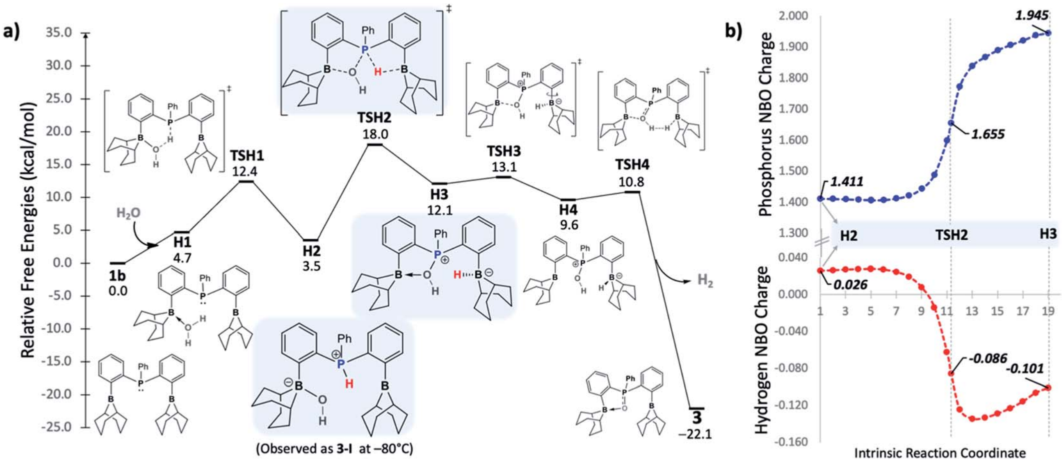


Fig. 3 Proposed reaction mechanism for the formation of 3 calculated at the SMD(benzene): ω-B97XD/6-311G(d) level (298 K) (a) and NBO charges of the phosphorus and transfer of hydrogen atoms from **H2** (observed in the NMR spectrum as **3-I**) to **H3** (b).

of the oxygen to each boron atom in **3** (see Fig. S5†) with a low barrier energy of 8.4 kcal mol^{-1}, indicating a weak O–B coordination which is consistent with the experimental observations.

Following the same mechanistic route as described above, the reaction of **1b** with MeOH (see Fig. S7†) was also investigated computationally. The coordination of methanol to the first boron gives adduct **Me1** ($\Delta G_{R1} = -0.4$ kcal mol^{-1}) followed by the proton transfer leading to intermediate **4** (**Me2** in Fig. S7,† $\Delta G_{R2} = 4.1$ kcal mol^{-1}) through **TSMe1** ($\Delta G_1^{\ddagger} = +6.5$ kcal mol^{-1}) which are accessible at room temperature. However, the following reaction steps are very high in energy and the reaction stops at this point. In general, the reduction of MeOH by **1b** to produce CH_4 and **3** must overcome a total energy barrier of 58.4 kcal mol^{-1} and, therefore, is practically unreachable. The reaction to afford the MeO–H bond cleavage intermediate (**4**) is exergonic, and because of the excess of methanol, this intermediate could be detected by NMR spectroscopy but could not be isolated.

Conclusions

This work reports a 9-BBN derivative of a bisborane-functionalized phosphine which reduces water to dihydrogen at room temperature in a stoichiometric reaction to produce phosphine oxide as the sole by-product. Computational investigations revealed that phosphine initially serves as a Lewis base to split water by deprotonation cooperatively with one borane. The resulting phosphonium then serves as a Lewis acid to accept the borane-bound hydroxide to facilitate a hydride transfer to the 2nd borane.

Although triphenyl phosphine and trialkyl/aryl boranes are not particularly reactive in comparison to other derivatives often employed in FLP chemistry, the preorganization of the borane-phosphine-borane framework in **1b** is very important to coordinate the phosphine/phosphonium bifunctionality, taking advantage of phosphorus' ability of hypervalent bonding and its non-polar P–H bond for the umpolung of proton to hydride. This simple design of a bisborane-functionalized phosphine FLP has demonstrated a new working paradigm for metal-free water reduction, showing a new strategy for generation of hydride at a main-group element from water that was previously only possible at metal centres.

Data availability

Crystallographic data for compounds **1a**, **1-Int**, **1b**, **2** and **3·H_2O** has been deposited at the CCDC under 2096462–2096465, and 2109052. They can be obtained from [https://www.ccdc.cam.ac.uk/structures/?]. Computational details, spectroscopic data supporting this article have been uploaded as part of the supplementary information.

Author contributions

RS came up with the molecular design and supervised the development of the synthesis and reactivity studies with help from YY and MN. YJ developed the synthesis of **1a**. TO improved the synthesis of **1a**, developed the synthesis of **1b** and discovered the water reduction reaction. TO carried out the synthesis and characterization of all the compounds reported in this paper. LIL-F carried out all the computational studies under close supervision of JOCJ-H with additional help from JBF. NT carried out GC analysis of reaction mixtures to confirm the presence of H_2. RS and TO wrote the initial MS draft and LIL-F and JOCJ-H added the computational part of the study. All authors contributed to the discussion of the results and finalization of this manuscript.

Conflicts of interest

There are no conflicts to declare.

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