

Dihydrogen Activation by Antiaromatic Pentaarylboroles

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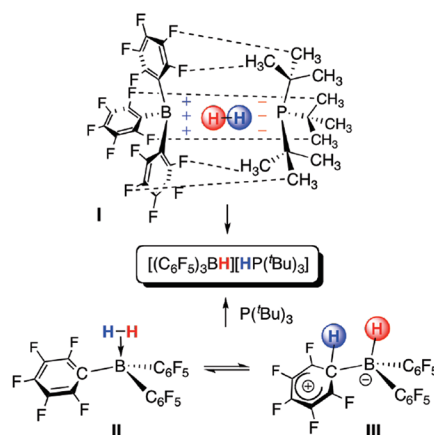
Abstract: Facile metal-free splitting of molecular hydrogen (H_2) is crucial for the utilization of H_2 without the need for toxic transition-metal-based catalysts. Frustrated Lewis pairs (FLPs) are a new class of hydrogen activators wherein interactions with both a Lewis acid and a Lewis base heterolytically disrupt the hydrogen–hydrogen bond. Here we describe the activation of hydrogen exclusively by a boron-based Lewis acid, perfluoropentaphenylborole. This antiaromatic compound reacts extremely rapidly with H_2 in both solution and the solid state to yield boracyclopent-3-ene products resulting from addition of hydrogen atoms to the carbons α to boron in the starting borole. The disruption of antiaromaticity upon reaction of the borole with H_2 provides a significant thermodynamic driving force for this new metal-free hydrogen-splitting reaction.

The splitting of the simplest nonpolar molecule, dihydrogen (H_2), is a critical chemical reaction that is most commonly accomplished by a transition-metal center in homogeneous, heterogeneous, or biological catalysts via homolytic oxidative addition or heterolytic processes.¹ Recently, interest in more environmentally benign, transition-metal-free systems for activation of dihydrogen^{2–4} has spiked,⁵ primarily spurred by the development of the “frustrated Lewis pair” (FLP) concept.^{6–8} In FLPs, Lewis acid/base combinations that are sterically prevented from forming strong classical adducts can heterolytically activate H_2 . Highly Lewis acidic perfluoroarylboranes,^{9,10} such as $B(C_6F_5)_3$, are typically employed as the hydride acceptor, while bulky phosphines,¹¹ amines/imines,^{12,13} or carbenes^{14,15} serve as the Lewis base proton acceptor.

The mechanistic details of hydrogen activation by FLPs are still a subject of debate, although computational investigations point to an “encounter complex” (**I**, Scheme 1) stabilized by noncovalent interactions and dispersion forces^{16,17} that creates an electric field in the pocket of the FLP where a dative bond would form in a satisfied Lewis acid/base pair. This electric field polarizes H_2 , leading to cleavage of the $H-H$ bond.¹⁸ Despite the in silico support for this picture, spectroscopic evidence for the encounter complex is lacking.

An alternate view involves an adduct between borane and H_2 (**II**) that is related to transition metal– H_2 σ complexes.¹⁹ Intermediate **II** could be deprotonated directly or proceed to **III**, an intermediate analogous to protonated fluorobenzenes, via heterolytic addition of H_2 across a $B-C$ bond.^{20,21} This has been proposed as the initial step in the addition of H_2 to Stephan’s seminal phosphinoborane hydrogen activation system⁴ and is supported computationally.²² This mechanism is conceptually related to that developed for the $B(C_6F_5)_3$ -catalyzed hydrosilylation of carbonyl^{23–25} and imine²⁶ functions and the dehydrosilylation of alcohols.²⁷ In

Scheme 1



that mechanism, the Lewis acidic borane activates the silane toward nucleophilic attack by the substrate by partially abstracting the silane hydrogen via a borane–silane adduct related to **II**. While the mechanism of $B(C_6F_5)_3$ -catalyzed hydrosilylation is well-established, the involvement of **II** in FLP H_2 splitting remains unproven, even though computations suggest that **II** is energetically viable relative to the reactants.⁶

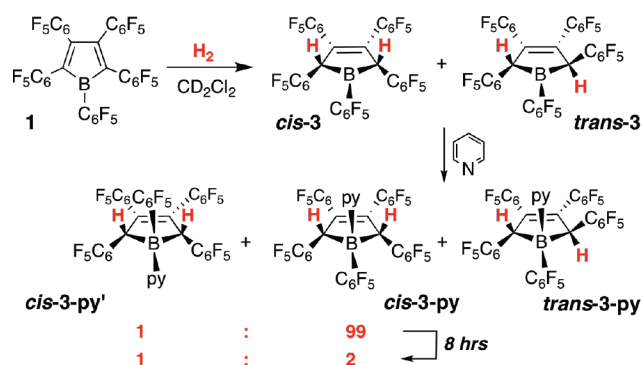
Mechanistic details aside, it is clear that a high level of Lewis acidity at the boron center is required²⁸ in order to achieve hydrogen activation in these systems; unfluorinated triphenylborane, $B(C_6H_5)_3$, for example, is much less effective as an FLP partner.⁶ Recently, we reported the synthesis and characterization of perfluoropentaphenylborole (**1**),²⁹ a new perfluoroarylborane with exceptional Lewis acid strength as a consequence of both fluoroaryl substitution and the antiaromaticity of the four- π -electron borole ring.³⁰ Its reactivity in the context of the FLP paradigm was therefore worthy of exploration.

Borole **1** is sparingly soluble in nondonor solvents, and even weakly Lewis basic solvents form adducts.²⁹ Halogenated solvents are most useful, but mixtures of **1** and tBu_3P in CD_2Cl_2 exhibit reactions that involve chloride transfer to **1**, indicative of $C-Cl$ bond activation. In C_6D_5Br , however, **1** and tBu_3P do not activate the solvent, and no indication of conventional adduct formation is apparent either spectroscopically or visually (the intense color of pentaarylboroles³¹ is quenched upon ligation of boron). Exposure of this mixture to H_2 , however, resulted in a rapid reaction. Surprisingly, a mixture of products was observed, and the expected phosphonium borate ion pair $[(C_6F_5)_4C_4B(H)C_6F_5][HP(tBu)_3]^+$ (**2**) was a *minor* component (<15%) of the reaction product mixture.

This observation led us to investigate the reactivity of **1** with H_2 in the *absence* of tBu_3P . Rapid reaction (less than 1 min) in CD_2Cl_2 , C_6D_5Br , or C_7D_8 was indicated by the decolorization of these solutions or suspensions; indeed, even exposure of microcrystalline solid samples of **1** to an atmosphere of H_2 resulted in conversion to an off-white solid within 20 min.

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Scheme 2



The products are the two major species observed in the reaction performed in the presence of tBu_3P , which were identified as the *cis* and *trans* isomers of the boracyclopent-3-ene heterocycles **3** that result upon formal addition of hydrogen to the carbons α to boron in borole **1** (Scheme 2). This was deduced on the basis of multinuclear NMR spectroscopy, derivatization to the pyridine adducts **3-py**, and X-ray crystallographic characterization of *cis*-**3** and *trans*-**3-py**.

The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of products **3** shows a broad resonance at 78.5 ± 1.0 ppm, consistent with a three-coordinate borane center and distinct from the 66.0 ppm resonance associated with **1**. The ^1H NMR spectrum (Figure S1 in the Supporting Information) shows two singlets in a 2:1 ratio at 5.14 and 4.83 ppm, which were assigned to the *trans* and *cis* isomers of **3**, respectively, on the basis of the changes in the spectrum upon addition of pyridine (Figure S1). The signal at 5.13 ppm was split into two equal-intensity peaks at 5.67 and 5.06 ppm for the now inequivalent protons of *trans*-**3-py**, while that at 4.82 ppm was transformed into two singlets at 4.09 and 4.98 ppm, the latter barely observable initially. Over 8 h, this signal grew in until it was present at half the intensity of the resonance at 4.09 ppm. On the basis of NOE experiments, the kinetically favored isomer of *cis*-**3-py** is that with pyridine oriented *cis* to the two α protons (Figure S2). Isomerization to the thermodynamic mixture of *cis*-**3-py** isomers occurs by reversible dissociation and recoordination of pyridine. For the reaction of **1** with H_2 in solution, *trans*-**3** is kinetically favored, but for reactions of solid **1** with H_2 , *cis*-**3** is the dominant product by a 10:1 margin. Density functional theory (DFT) computations showed that *trans*-**3** is thermodynamically favored by 6.2 kcal mol $^{-1}$ (Table S1 in the Supporting Information). Heating solutions of the two isomers to 50 °C in the dark for 12 h had no effect on the kinetic ratios. However, irradiation of solutions enriched in *cis*-**3** at 254 nm for 4 days resulted in complete conversion to the more stable *trans*-**3** isomer via an unknown mechanism.

The structures of *cis*-**3** and *trans*-**3-py** were confirmed by X-ray crystallography.³² A thermal ellipsoid diagram of the former compound is shown in Figure 1 along with selected metrical parameters; that of the latter is given in Figure S3. The C_4B ring in *cis*-**3** features a trigonal-planar boron center [sum of angles = 359.2(6)°] and a $\text{C}=\text{C}$ double bond between C2 and C3 [1.326(5) Å]. The hydrogen atoms on C1 and C4 were located on the difference map and their positions refined: the C1 and C4 carbons are clearly pyramidalized [the sums of non-hydrogen angles about C1 and C4 are 331.9(5) and 340.6(5)°, respectively], and the α -carbon C_6F_5 rings lie below the C_4B plane. Although the *trans*-**3** isomer can be produced in pure form photochemically, suitable crystals were not obtained; instead, this isomer's structure was confirmed via characterization of its pyridine adduct. The hydrogen atoms on C1 and C4 were again located and refined, and their positioning *trans*

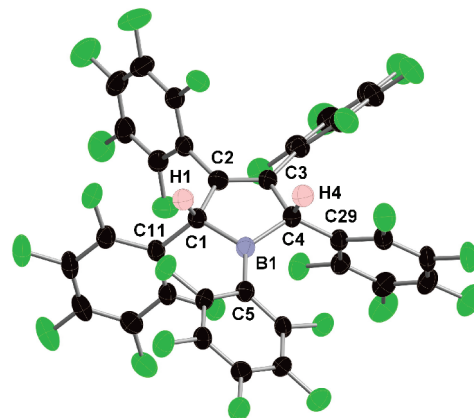
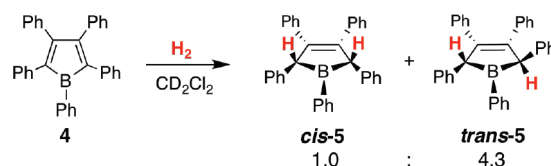


Figure 1. Thermal ellipsoid diagram (50%) of *cis*-**3**. Selected bond distances (Å): B1–C1, 1.585(6); C1–C2, 1.533(5); C2–C3, 1.326(5); C3–C4, 1.529(5); B1–C4, 1.586(6). Selected bond angles (deg): C1–B1–C5, 124.4(3); C1–B1–C4, 106.2(3); C4–B1–C5, 128.6(4); B1–C1–C11, 115.7(3); B1–C1–C2, 103.1(3); C2–C1–C11, 113.1(3); B1–C4–C29, 124.3(3); B1–C4–C3, 102.8(3); C3–C4–C29, 113.5(3).

to each other on the C_4B ring was also evident from the orientation of the C1 and C4 C_6F_5 rings on opposite sides of the C_4B plane.

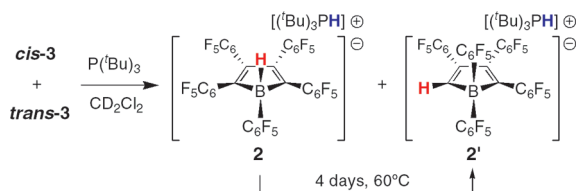
The reaction between **1** and H_2 in the absence of an external base shows that **1** is capable of forming a reactive adduct with H_2 . DFT computations showed that the LUMO of **1** is associated with the boron center and the two α carbons (Figure S4), but the low solubility of **1** has precluded low-temperature NMR experiments aimed at observing an H_2 adduct of **1** spectroscopically. However, DFT computations located a minimized-energy structure for the H_2 adduct of **1** that is only 0.5 kcal mol $^{-1}$ less stable than the reactants (Figure S5). Since the H_2 adduct of $\text{B}(\text{C}_6\text{F}_5)_3$ itself (i.e., **II**) reacts only by dissociation of H_2 (unless there is a proton acceptor on one of the fluorinated aryl rings⁴), it appears that disruption of antiaromaticity in the borole ring³⁰ provides a driving force for the remarkably facile reaction of **1** with H_2 to give compounds **3**. The energetic destabilization of four- π -electron five-membered borole rings in comparison with related aromatic systems has been estimated to be 10–20 kcal mol $^{-1}$,^{33,34} thus, the combination of antiaromaticity and high Lewis acidity in **1** leads to rapid H–H bond activation in the absence of an external Lewis base partner. Indeed, the extra driving force provided by antiaromaticity permits H_2 activation in more weakly Lewis acidic pentaarylboroles: the reaction of *unfluorinated* pentaphenylborole (**4**)³¹ with H_2 , although slower, produces *cis*-**5** and *trans*-**5** in a 1.0:4.3 ratio over 2–3 h (Scheme 3). Interestingly, no H_2 adduct with **4** could be found by DFT calculations, suggesting that in this case H_2 binding to the less Lewis acidic boron center may be rate-limiting.

Scheme 3



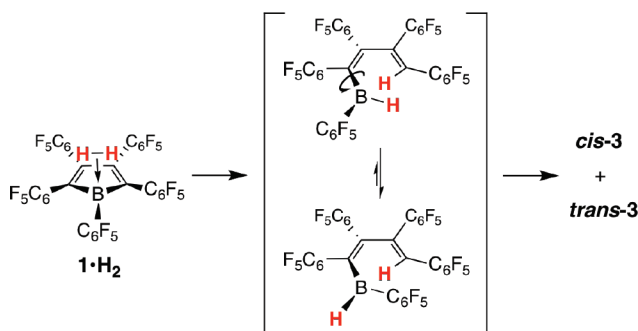
Attempts to reverse the addition of H_2 to Lewis acidic borole **1** thermally or photochemically were unsuccessful, and no deuterium incorporation into compounds **3** was observed under any conditions upon exposure of their solutions to 4 atm D_2 . Interestingly, when mixtures of *cis/trans*-**3** were treated with tBu_3P (1 equiv per boron), conversion to the phosphonium borates **2** and **2'** occurred (Scheme 4).

Scheme 4



Isomer **2'** is the thermodynamic product of this reaction; pure samples exhibit 1H NMR spectral signature resonances for the P–H (5.02 ppm, $^1J_{PH} = 426$ Hz) and C–H (broad, 7.16 ppm, $^1J_{CH} = 149.3$ Hz) protons. Furthermore, **2'** exhibits a resonance at 169.9 ppm in the ^{13}C NMR spectrum (1:1:1:1 quartet, $^1J_{CB} = 56$ Hz) and resonances for four inequivalent C_6F_5 groups in the ^{19}F NMR spectrum in the expected 2:1:1:1 ratio. It is likely that this reaction is initiated by direct deprotonation of a benzylic proton in boracycles **3** by the phosphine base rather than reversible formation of the H_2 adduct of **1** from **3**. Nonetheless, conversion of *cis*/*trans*-**3** to hydrido borate **2** suggests a possible H_2 delivery pathway via this ion pair⁶ using catalytic amounts of a bulky Lewis base.

Scheme 5



In summary, we have reported a facile metal-free hydrogen splitting reaction at Lewis acidic, antiaromatic pentaarylborole boron centers. The details of the mechanism of the reaction are yet to be determined, but the presence of the *trans* isomers of **3** and **5** as the major isomers in solution suggests that the H_2 adducts under go B– C_α bond cleavage followed by rapid cyclization to a mixture of boracyclopent-3-ene products (Scheme 5). Photochemically generated *cis*-1,3-butadienylboranes similar to those depicted in Scheme 5 have been shown to rapidly cyclize to boracyclopent-3-enes.^{35,36} That this reaction occurs so rapidly in the absence of a frustrated Lewis base partner has implications for the mechanism of H_2 splitting by FLPs. Kinetic, thermodynamic, and computational investigations that will address these issues in detail are underway; the greater solubility of unfluorinated pentaphenylborole **4** and the more forgiving time scale of its reaction with H_2 make it ideal for further study.

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Supporting Information Available: Crystallographic data for *cis*-**3** and *trans*-**3-py** (CIF) and additional experimental, spectroscopic, and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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