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Dihydrogen Activation by Antiaromatic Pentaarylboroles

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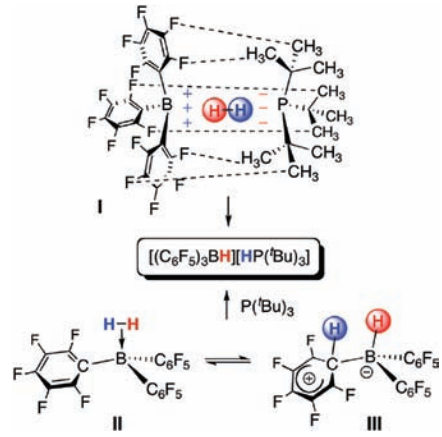
Abstract: Facile metal-free splitting of molecular hydrogen (H_2) is crucial for the utilization of H_2 without the need for toxic transition-metal-based catalysts. Frustrated Lewis pairs (FLPs) are a new class of hydrogen activators wherein interactions with both a Lewis acid and a Lewis base heterolytically 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 system[4] 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 imine[26] 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 required[28] 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 ^{t}Bu$_3$P 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 ^{t}Bu$_3$P do not activate the solvent, and no indication of conventional adduct formation is apparent either spectroscopically or visually (the intense color of pentaarylboroles[31] 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 ^{t}Bu$_3$P. 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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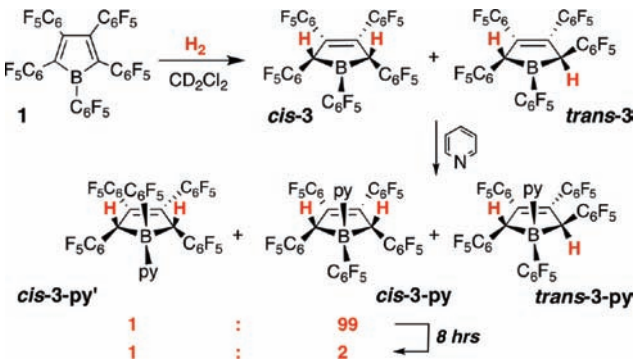
Scheme 2



The products are the two major species observed in the reaction performed in the presence of $^{t}Bu_3P$, 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 $^{11}B\{^1H\}$ 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 C═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

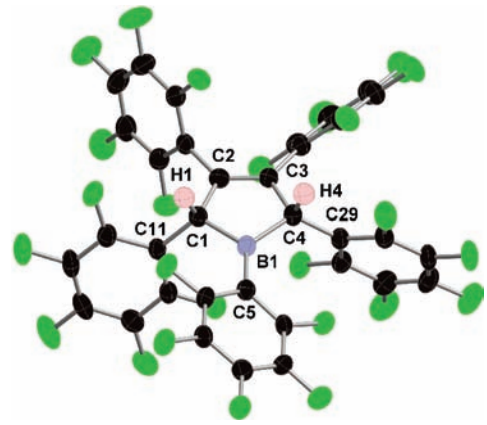
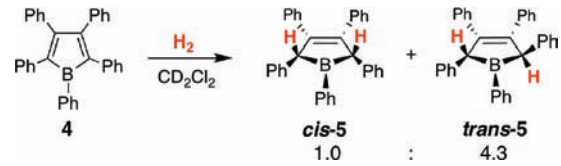


Figure 1. Thermal ellipsoid diagram (50%) of *cis*-**3**. Selected bond distances (Å): B1−C1, 1.585(6); C1−C2, 1.533(5); C2−C3, 1.326(5); C3−C4, 1.529(5); B1−C4, 1.586(6). Selected bond angles (deg): C1−B1−C5, 124.4(3); C1−B1−C4, 106.2(3); C4−B1−C5, 128.6(4); B1−C1−C11, 115.7(3); B1−C1−C2, 103.1(3);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

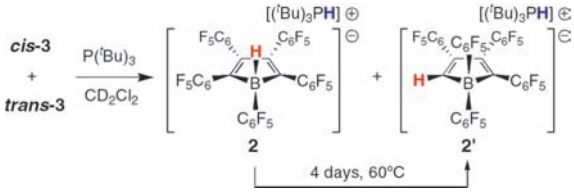
The reaction between **1** and H_2 in the absence of an external base shows that **1** is capable of forming a reactive adduct with H_2. DFT computations showed that the LUMO of **1** is associated with the boron center and the two α carbons (Figure S4), but the low solubility of **1** has precluded 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 $B(C_6F_5)_3$ itself (i.e., **II**) reacts only by dissociation of H_2 (unless there is a proton acceptor on one of the fluorinated aryl rings[4]), it appears that disruption of antiaromaticity in the borole ring[30] 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



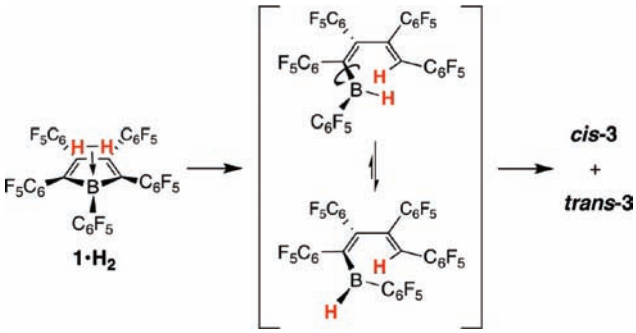
Attempts to reverse the addition of H_2 to Lewis acidic borole **1** thermally or photochemically were unsuccessful, and no deuterium incorporation into compounds **3** was observed under any conditions upon exposure of their solutions to 4 atm D_2. Interestingly, when mixtures of *cis*/*trans*-**3** were treated with $^{t}Bu_3P$ (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 ^{1}H 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 pair[6] 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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