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Dihydrogen Activation by Antiaromatic Pentaarylboroles.

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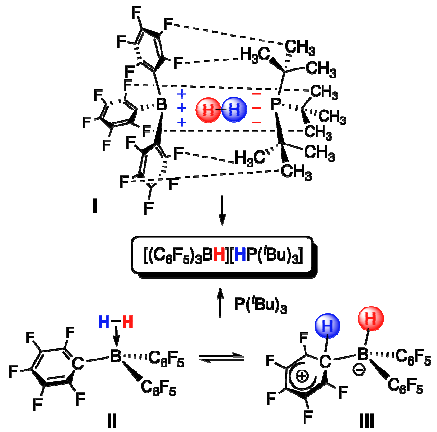
The splitting of the simplest non-polar molecule dihydrogen (H_2) is a critical chemical reaction that is most commonly accomplished by a transition metal center in homogeneous, heterogeneous or biological catalysts via homolytic oxidative addition or heterolytic processes.[1] Recently, interest in more environmentally benign, transition metal-free systems for activation of dihydrogen[2-4] has spiked,[5] primarily spurred by the development of the "Frustrated Lewis Pairs" (FLPs) concept.[6-8] In FLPs, Lewis acid/base combinations sterically prevented from forming strong classical adducts are capable of heterolytically activating 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 non-covalent 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.

Scheme 1

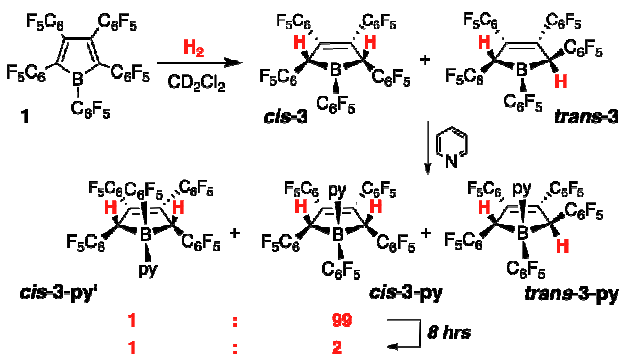


An alternate view involves an adduct between borane and H_2, (**II**), related to transition metal H_2 sigma complexes.[19] Intermediate **II** could be deprotonated directly, or proceed to **III** via heterolytic addition of H_2 across a B-C bond, an intermediate analogous to protonated fluorobenzenes.[20-21] This has been proposed as the initial step in the addition of H_2 to Stephan's seminal phosphinoborane hydrogen activation system,[4] and supported computationally.[22] This mechanism is conceptually related to that developed for the $B(C_6F_5)_3$ catalyzed hydrosilation of carbonyl[23-25] and imine[26] functions and the dehydrosilation of alcohols.[27] Here, the Lewis acidic borane activates the silane towards 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 hydrosilation is well established, the involvement of **II** in FLP H_2 splitting remains unproven even though computations suggest **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 perfluoropentaphenyl borole, **1**,[29] a new perfluoroarylborane with exceptional Lewis acid strength as a consequence of both fluoroaryl substitution and the antiaromaticity of the 4π borole ring.[30] Its reactivity in the context of the FLP paradigm was therefore worthy of exploration.

Borole **1** is sparingly soluble in non-donor 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 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.

Scheme 2



This observation led us to investigate the reactivity of **1** with H_2 in the *absence* of ^{t}Bu$_3$P. Rapid reaction in CD_2Cl_2, C_6D_5Br or C_7D_8 (less than one minute) 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 minutes.

The products are the two major species observed in the reaction performed in the presence of $^tBu_3P$ and 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 and via 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 (Fig. S1) shows two singlets in a 2:1 ratio at 5.14 and 4.83 ppm assigned to the *trans* and *cis* isomers of **3**, respectively, on the basis of the changes in the spectrum upon addition of pyridine (Fig. S1). The signal at 5.13 ppm splits 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 transforms into two singlets at 4.09 and 4.98 ppm, the latter barely observable initially. Over eight hours, this signal grows in until 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 a protons (Fig 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. DFT computations show that ***trans*-3** is thermodynamically favored by 6.2 kcal mol^{-1} (Table S1). Heating solutions of the two isomers to 50°C in the dark for twelve hours had no effect on the kinetic ratios. However, irradiation of solutions enriched in ***cis*-3** at 254 nm for four days results in complete conversion to the more stable ***trans*-3** isomer via an unknown mechanism.

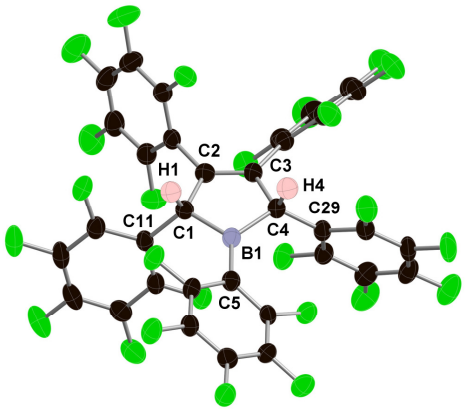
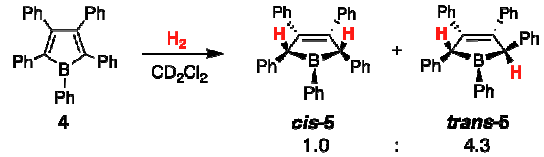


Figure 1. Thermal ellipsoid diagram (50%) of ***cis*-3**. Selected bond distances (Å): B1-C1, 1.585(6); C1-C2, 1.533(5); C2-C3, 1.326(5); C3-C4, 1.529(5), B1-C4, 1.586(6). Selected bond angles (°): C1-B1-C5, 124.4(3); C1-B1-C4, 106.2(3); C4-B1-C5, 128.6(4); B1-C1-C11, 115.7(3); B1-C1-C2, 103.1(3); C2-C1-C11,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

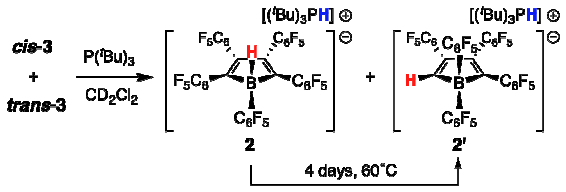
The structures of ***cis*-3** and ***trans*-3-py** were confirmed by X-ray crystallography;[32] a thermal ellipsoid diagram of the former compound is shown in Fig. 1, with selected metrical parameters; that of the latter is given in the SI (Fig. S3). The C_4B ring in ***cis*-3** features a trigonal planar 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 (sum of non-hydrogen angles about C1: 331.9(5)°; C4: 340.6(5)°) 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* to each other on the C_4B ring is evident also 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 show that the LUMO of **1** is associated with the boron center and the two α carbons, (Fig. 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 locate a minimized energy structure for the H_2 adduct of **1** that is only 0.5 kcal mol^{-1} less stable than the reactants (Fig. 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 4π five membered borole rings compared to 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 hours (Scheme 3). Interestingly, no H_2 adduct with **4** is found by DFT calculations, suggesting that here, H_2 binding to the less Lewis acidic boron center may be rate limiting.

Scheme 3

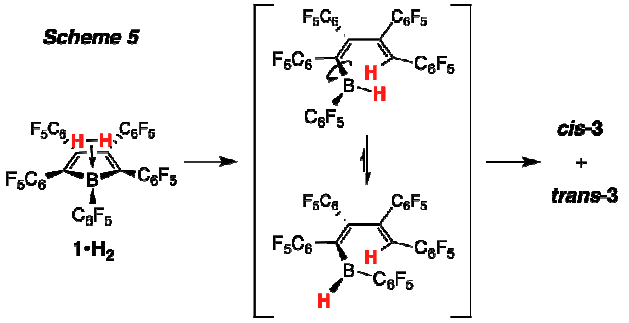


Scheme 4



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** under any conditions upon exposure of their solutions to four atmospheres of D_2 was observed. Interestingly, when mixtures of ***cis/trans*-3** were treated with $^tBu_3P$ (one equivalent per boron), conversion to the phosphonium borates **2** and **2'** occurred (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. Likely, 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 report 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 isomer in solution suggests that the H_2 adducts under go B-C$_\alpha$ 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 shown in the Scheme 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 timescale of its reaction with H_2, make it ideal for further study.

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Supporting Information Available. Crystallographic data files for ***cis*-3** and ***trans*-3-py**, additional experimental, spectroscopic and computational details.

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