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Dihydrogen Activation by Antiaromatic Pentaarylboroles.

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The splitting of the simplest non-polar molecule dihydrogen (H₂) 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 dihydrogen³⁻⁴ has spiked,⁵ primarily spurred by the development of the “Frustrated Lewis Pairs” (FLPs) concept.⁶⁻⁷ In FLPs, Lewis acid/base combinations sterically prevented from forming strong classical adducts are capable of heterolytically activating H₂. Highly Lewis acidic perfluoroarylboranes,⁸⁻¹⁰ such as B(C₆F₃)₃, are typically employed as the hydride acceptor, while bulky phosphines,¹¹ amines/imines¹²⁻¹³ or carbenes¹⁴⁻¹⁵ 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 forces¹⁶⁻¹⁷ 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 H₂, 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 H₂, (II), related to transition metal H₂ sigma complexes.¹⁹ Intermediate II could be deprotonated directly, or proceed to III via heterolytic addition of H₂ 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 H₂ to Stephan’s seminal phosphinoborane hydrogen activation system,⁴ and supported computationally.²² This mechanism is conceptually related to that developed for the B(C₆F₃)₃ catalyst hydrosilation of carbonyl²³⁻²⁵ and imine²⁶ functions and the dehydroisolation 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(C₆F₃)₃ catalyzed hydrosilation is well established, the involvement of II in FLP H₂ 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 required²⁸ in order to achieve hydrogen activation in these systems; unfluorinated triphenylborane, B(C₆H₅)₃, for example, is much less effective as an FLP partner.⁹ Recently, we reported the synthesis and characterization of perfluoropentaphenyl borole, I,²⁹ a new perfluoroarylborane with exceptional Lewis acid strength as a consequence of both fluoraryl 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 I is sparingly soluble in non-donor solvents and even weakly Lewis basic solvents form adducts.²⁹ Halogenated solvents are most useful, but mixtures of I and 'Bu₃P in CDCl₃ exhibit reactions that involve chloride transfer to I, indicative of C-Cl bond activation. In C₆D₅Br, however, I and 'Bu₃P do not activate solvent and no indication of conventional adduct formation is apparent, either spectroscopically or visually (the intense color of the FLP H₂ adduct), however. Exposure of this mixture to H₂, however, resulted in a rapid reaction. Surprisingly, a mixture of products was observed and the expected phosphonium borate ion pair [(C₆F₃)₃C₆B(H/C₆F₃)·HP('Bu)₃], (2), was a minor component (<15%) of the reaction product mixture.

This observation led us to investigate the reactivity of I with H₂ in the absence of 'Bu₃P. Rapid reaction in CD₃Cl, CD₂DBr or C₆D₅ (less than one minute) was indicated by the decolorization of these solutions or suspensions; indeed, even exposure of microcrystalline solid samples of I to an
atmosphere of H₂ 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 Bu₃P 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($^{1}$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 at 78.5±1.0 ppm, consistent with a three coordinate isomerization to the thermodynamic mixture of isomers occurs by reversible dissociation and recoordination experiments, the kinetically favored isomer of intensity of the resonance at 4.09 ppm. On the basis of NOE eight hours, this signal grows in until present at half the X-ray crystallography; Figure 1. Thermal ellipsoid diagram (50%) of cis-3 and trans-3-py.

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 to the more stable atmosphere of H₂ and the two 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 H₂ in solution, trans-3 is kinetically favored, but for reactions of solid 1 with H₂, 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.

The structures of cis-3 and trans-3-py were confirmed by X-ray crystallography; 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 C4B 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 CₓF₃ rings lie below the CₓB 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 CₓB ring is evident also from the orientation of the C1 and C4 CₓF₃ rings on opposite sides of the CₓB plane.

The reaction between 1 and H₂ in the absence of an external base shows that 1 is capable of forming a reactive adduct with H₂. 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 H₂ adduct of 1 spectroscopically. However, DFT computations locate a minimized energy structure for the H₂ adduct of 1 that is only 0.5 kcal mol⁻¹ less stable than the reactants (Fig. S5). Since the H₂ adduct of B(CₓF₃), itself (i.e. II) reacts only by dissociation of H₂ (unless there is a proton acceptor on one of the fluorinated aryl rings⁵), it appears that disruption of antiaromaticity in the borole ring⁶ provides a driving force for the remarkably facile reaction of 1 with H₂ to give compounds 3. The energetic destabilization of 4tet five membered borole rings compared to related aromatic systems has been estimated to be ≈10-20 kcal mol⁻¹,⁷⁻⁹ 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 H₂ activation in more weakly Lewis acidic pentaarylboroles; the reaction of unfluorinated pentaphenylborole ⁴ with H₂, although slower, produces cis-5 and trans-5 in a 1.0:4.3 ratio over 2-3 hours (Scheme 3). Interestingly, no H₂ adduct with 4 is found by DFT calculations, suggesting that here, H₂ binding to the less Lewis acidic boron center may be rate limiting.

![Figure 1. Thermal ellipsoid diagram (50%) of cis-3.](image-url)

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**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-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; a thermal ellipsoid diagram of the
Attempts to reverse the addition of H₂ 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 D₂ was observed. Interestingly, when mixtures of cis/trans-3 were treated with Bu₃P (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, ¹J₁Hz = 426 Hz) and C-H (broad, 7.16 ppm, ¹J₁CH = 149.3 Hz) protons. Furthermore, 2' exhibits a resonance at 169.9 ppm in the ¹³C NMR spectrum (1:1:1 quartet, ¹J₁CH = 56 Hz) and resonances for four inequivalent C₂F₅ groups in the ¹⁹F NMR spectrum, in the expected 2:1:1:1 ratio. Likely, this reaction is initiated by direct deprotonation of a benzylic proton in boracies 3 by the phosphine base, rather than reversible formation of the H₂ adduct of 1 from 3. Nonetheless, conversion of cis/trans-3 to hydrido borate 2 suggests a possible H₂ delivery pathway via this ion pair⁵ using catalytic amounts of a bulky Lewis base.

In summary, we report a facile metal-free hydrogen splitting reaction at Lewis acidic, antiaromatic pentaarylbaboron 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 H₂ adducts under go B-Ca bond cleavage, followed by rapid cyclization to a mixture of boracyclpent-3-ene products (Scheme 5). Photochemically generated cis-1,3-buta dienylboranes similar to those shown in the Scheme have been shown to rapidly cyclize to boracyclopent-3-enes.⁶ That this reaction occurs so rapidly in the absence of a frustrated Lewis base partner has implications for the mechanism of H₂ 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 H₂, 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.

References.
32. Full crystallographic data for cis-3 and trans-3-py can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, under reference nos. CCDC-770705 and 770706, respectively, 2010.