Mechanistic Studies on the Metal Free Activation of Dihydrogen by Antiaromatic Pentarylboroles

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ABSTRACT: The perfluoro and perprotiopentaphenyl boroles 1 and 2 react with dihydrogen to effect H-H bond cleavage and formation of boracyclopentene products. The mechanism of this reaction has been studied experimentally through evaluation of the kinetic properties of the slower reaction between 2 and H₂. The reaction is first order in both [borole] and [H₂] with activation parameters of ΔH² = 34(8) kJ mol⁻¹ and ΔS² = -146(25) J mol⁻¹ K⁻¹. A minimal kinetic isotope effect of 1.10(5) was observed, suggesting rate limiting binding of H₂ to the boron center of the borole. To explain the stereochemistry of the observed products, a ring-opening/ring-closing mechanism is proposed and supported by the separate synthesis of a proposed intermediate and its observed conversion to product. Furthermore, extensive DFT mapping of the reaction mechanism supports the plausibility of this proposal. The study illustrates a new mechanism for the activation of H₂ by a strong main group Lewis acid in the absence of an external base, a process driven in part by the antiaromaticity of the borole rings in 1 and 2.

Introduction

Despite the low polarity and high bond strength of the H-H bond in dihydrogen, it’s activation is remarkably facile in the presence of transition metal compounds via oxidative addition (OA),1,2 σ-bond metathesis3-4 (SBM) and electrophilic 1,2 addition type mechanisms.5,6 Thus, the catalytic addition of H₂ to a variety of unsaturated organic functions and the hydrogenolysis of many M-X bonds are well known and understood phenomena that are widely deployed reactions in the chemical industry.7

While transition metal catalyzed hydrogen utilization is of tremendous economic and practical importance, transition metals and their complexes can be costly and toxicity issues can also present challenges. Therefore, there has been significant interest in “metal-free” processes that do not require transition metals to activate and deliver hydrogen to substrates of interest.8 Main group element based compounds that cleave dihydrogen are less common, but a growing body of literature, beginning with the seminal discoveries of Power et al.,9 suggest that main group elements can also cleave dihydrogen via low energy pathways that synergistically depopulate the H-H σ bonding orbital while populating the H-H σ* antibonding orbital. For example, Bertrand and co-workers showed10 that stable singlet carbenes react rapidly with H₂ via a mechanism that is heterolytic in character but involves polarization of the H-H bond by donation of carbene electrons into its σ* orbital and transfer of hydride to the carbene carbon. In both the Power and Bertrand systems, application to catalytic hydrogenation is limited by the lack of reversibility in the hydrogen cleavage reaction.

In 2006, Stephan and co-workers found11 that sterically bulky Lewis acids combined with likewise sterically endowed Lewis bases are capable of activating H₂—reversibly—with remarkably low barriers. The acids are almost invariably perfluoraryl boranes of high Lewis acid strength, but wide variation in the nature of the Lewis base is possible and there are now many examples of this phenomenon in the literature.12 The mechanism by which these systems polarize the H-H bond has been probed in the seminal B(C₆F₅)₃/PR₃ (R = mesityl, ‘Bu) systems both experimentally13-14 and computationally15-17 and it is currently believed that a preformed “encounter complex”, held together by weak van der Waal’s interactions, creates a pocket in which the H₂ can bind; the electric field created by the empty orbital on the boron and the filled orbital on phosphorus splits the H-H bond heterolytically with a very low barrier.18 No experimental evidence for this encounter complex has yet been found, but the computational support for this picture is convincing for this particular system.

For bases with less symmetry complementarity, like imines18 or carbenes,19 similar encounter complexes have been described in silico but are somewhat less favored than those found for the borane/phosphine complexes. Thus, alternate mechanisms in these systems might be operative. For example, in a mechanism reminiscent of that proposed for B(C₆F₅)₃ catalyzed hydrosilation reactions,20-24 the highly Lewis acidic borane might bind hydrogen via the σ bonding electrons; the base may then deprotonate the coordinated H₂ to generate the ion pair that is the product of dihydrogen activation. This process bears resemblance to the binding and deprotonation of dihydrogen to transition metal complexes.25-27

In this context, then, our observation that the very highly Lewis acidic perfluoropentaphenyl borole28 complex reacts essentially instantly with dihydrogen29 to form the cis and trans isomers of the pentaarylboracyclopentenes, is significant. With no external base present, it seems clear that the H₂ must interact with the boron center in some fashion in order that this
In both reactions, the pyridine adduct, were isolated analytically pure. (Scheme 1).

Over the course of 4-5 hours with the less Lewis acidic (50-80˚C). Interestingly, solid samples of do not change upon heating the mixture to higher temperatures (50-80˚C). Although no structures have been determined, the fully fluorinated system I and its unfluorinated pentaarylborole analog 2.

### Results and Discussion

**Activation of H₂ by Pentaarylboreoles.** Reaction of the pentaarylboreoles I or 2 with 1 atm. of dihydrogen in methylene chloride occurs rapidly in the case of fully fluorinated I, and over the course of 4-5 hours with the less Lewis acidic 2 to yield the 1-bora-3-cyclopentene products 3 and 4, respectively (Scheme 1). The reactions are accompanied by a striking color change from the deep blue or purple colors of the boroles to light yellow as the cyclic borane products are formed. The nature of the isomers 3 were determined by a combination of ¹H NMR spectroscopy and X-ray crystallography of the borpentanes themselves and their pyridine adducts. Although no structures have been determined, the unfluorinated isomers of 4 exhibited similar chemical and spectral behavior to that observed for 3, and trans-4, as well as its pyridine adduct, were isolated analytically pure.

In both reactions, the trans isomer is favored; the numbers in parentheses indicate the relative amounts of each isomer under these ambient conditions. This ratio is a kinetic ratio and does not change upon heating the mixture to higher temperatures (50-80˚C). Interestingly, solid samples of 1 also react with H₂ to give the products, but under these conditions, the cis isomer of 3 is favored, being produced in a 10:1 ratio in comparison to the trans isomer. Irradiation of solutions of 3 thusly enriched in the cis isomer at 254 nm results in complete conversion to trans-3 after about four days. Therefore, the trans isomer is also the thermodynamically most favored isomer in these systems, a notion supported by DFT calculations (see below).

**Proposed Mechanism.** The reaction of boroles 1 and 2 has been probed mechanistically via kinetic studies, the separate generation of a key intermediate and demonstration that it proceeds to products, and DFT studies. A mechanism that is consistent with these investigations is shown in Scheme 2. The first step entails reversible formation of a borole dihydrogen adduct (I). This step is faster for the more Lewis acidic perfluorinated borole 1 and accounts for the qualitatively much faster rates of reaction of 1 with H₂ in comparison to that observed for 2. Attempts to observe these H₂ adducts met with failure; solubility issues thwarted the examination of solutions of either 1 or 2 under H₂ at low temperatures. At ambient temperatures, addition of the coordinated H₂ to an intraring B-C bond (step b) produces the reactive zwitterionic intermediate cis-II which features a carbocationic center that is stabilized by virtue of the fact that it is both benzylic and allylic; the adjacent borate center is probably also a stabilizing influence. Again, this intermediate is not observed directly, due to low energy decomposition pathways that either lead directly to the cis isomers of the product 1-bora-3-cyclopentenes as indicated by step c or to an interconverting pair of 1-bora-2,4-pentadienyl rotamers (cis/trans-III) via a B-C bond cleaving ring opening step (d). Note that this is the only path by which the trans isomers of 3 and 4 can form, since path c leads only to the cis isomers; path d must therefore be kinetically competitive with the seemingly more straightforward migration of hydride from cis-II to give cis-3/4. The rotomers of III are in rapid exchange by rotation about the B-C single bond (e) and each leads to one of the product isomers by a rapid conrotatory ring closure back to the
cyclic zwitterions cis/trans-II that lead to the observed products via 1,2-hydride migration. Compound 1 reacts too rapidly with H₂ at temperatures at which it exhibits reasonable solubility in CD₂Cl₂ to follow by NMR spectroscopy. Fortunately, the less Lewis acidic borole 2 has no such limitations and its reactivity with H₂ can be followed conveniently over the course of 3-6 hours to > 4 half lives using ¹H NMR spectroscopy. Methodology similar to that reported by Parkin and co-workers²⁸ was employed. In a typical procedure, an NMR tube was charged with a CD₂Cl₂ solution containing 2 and mesitylene as an internal standard. After degassing, dry H₂ was admitted to a defined pressure and temperature and the reaction followed by recording spectra every 5-10 minutes; between data collection the sample was agitated to ensure that the solution remained saturated. It should be noted that while the measurements indicated that the [H₂] in solution was roughly equal to that of the [2], the total H₂ in the 2.7 mL NMR tube was in at least tenfold excess of the total 2 (0.0080 mmol). This method therefore relied on the assumption that agitatio of the sample would replenish the dissolved H₂ much faster than the rate of reaction. That every trial obeyed a pseudo first-order rate law indicates that this is a valid assumption.

The proposed mechanism predicts that the reaction should be first order in both [H₂] and [2]. Indeed, by varying the pressure of H₂ from ca. 1 – 4 atm (10 – 40 times the amount of 2), the observed rate constant (k₀₀₃) changed in direct proportion to [H₂] (Figure 1). The slope of this ln vs. [H₂] plot is 1.01, indicating the order in [H₂] to be 1; plots of k₀₀₃ vs. [H₂]ⁿ (n = 1, 2, Figure S1) showed that only the n = 1 plot was linear, with a slope of 0.12 s⁻¹. First order behavior in 2 is evidenced by the fact that every reaction profile can be fitted to a pseudo first-order plot. These results are consistent with the second order, rate-limiting formation of the H₂ adduct I at least in the case of unfluorinated 2.

Figure 1. Plot of ln k₀₀₃ against ln [H₂] with [2] = 0.016M under ca. 1-3.8 atm H₂ in CD₂Cl₂ at 293 K for the determination of the reaction order in [H₂] using the isolation method.

A kinetic isotope effect (KIE) for this reaction was measured by two methods. First, the ratio of k₀₀₃ values for the separate reaction of 2 with H₂ and D₂ showed a small effect of 1.10(5) (Figure 2). Second, exposure of 2 to a 1:1 mixture of H₂:D₂ resulted in a 1.11(1):1 ratio of cis/trans-4 and d₁-cis/trans-4 products, corroborating the result. The reaction of fully fluorinated 1 with a 1:1 mixture of H₂:D₂ gave a slightly larger KIE of 1.2(1). The small KIEs observed are consistent with rate-limiting binding of H₂ followed by a faster step (b, Scheme 2) in which the H-H bond is cleaved.

Figure 2. Pseudo-first-order plots of the reaction between 2 and H₂ (red) and D₂ (blue) at various temperatures. In a final set of kinetic experiments, the activation parameters for the reaction were derived from an Eyring plot (Figure 3): ΔH‡ = 34(8) kJ mol⁻¹ and ΔS‡ = -146(25) J mol⁻¹ K⁻¹. Although the temperature range over which these measurements were conveniently made is quite narrow, the negative ΔS‡ value is consistent with a bimolecular process. Using these activation parameters, the ΔG‡ at 298K is 78(16) kJ mol⁻¹. While these kinetic experiments are consistent with the first steps in the proposed mechanism, the subsequent steps remain rather speculative. We thus sought to provide more evidence for the proposal through the separate synthesis of a 1-bora-2,4-pentadiene complex analogous to cis or trans III. Early attempts by Zweifel and co-workers⁰⁻³¹ to generate such boranes lead directly and rapidly to 1-bora-3-cyclopentenes analogous to products 3 and 4 herein, and so we have only succeeded in generating III (Ar = C₆H₅) in situ.

This was accomplished by the synthesis of the borinic ester 5 via the protic ring opening of 2 by treatment with one equivalent of phenol (Scheme 3). After exploring various hydroboration-based routes (as originally established by Zweifel), this proved the most convenient way to generate 5. Of significance is the fact that the π-donating phenoxy group on boron in 5 stabilizes this compound towards ring closing—so much so that 5 can be isolated as a pale yellow solid in 52% yield after recrystallization from hot toluene. The ¹³B NMR spectrum of 5 contains a broad signal that appears at 44.8 ppm, which is
comparable to that found for $\text{Ph}_2\text{B(OMe)}$ (45.2 ppm). Furthermore, a crystal suitable for X-ray analysis was obtained by slow evaporation from dichloromethane; its molecular structure and selected metrical parameters are given in Figure 4.

Figure 4. Thermal ellipsoid diagram (50%) of $5$. Selected bond lengths (Å) and angles (°): C1-C2 1.361 (3), C2-C3 1.486 (3), C3-C4 1.354 (3), B1-C1 1.571 (3), B1-O1 1.367 (3), B1-C11 1.568 (3); C1-B1-C11 122.05 (17), C1-B1-O1 122.05 (17), C11-B1-O1 114.76 (17), C1-C2-C3-C4 35.47.

Significantly, $5$ adopts a cisoid 1-bora-2,4-pentadienyl geometry, which is required for the electrocyclic cyclization to occur. Bond distances are as one would expect for localized double and single bonds; the short B1-O1 distance of 1.367 (3)Å is indicative of strong $\pi$ bonding in this linkage. The C1-C2-C3-C4 dihedral angle of 35.47(5)° orients the $\pi$ bond between C3 and C4 towards the trigonal plane about B1; the non-bonding distance between C4 and B1 is only 2.79Å.

As shown in Scheme 3, treatment of $5$ with one equivalent of DIBAI-H rapidly gave $\text{trans-4}$ (exclusively) as evidenced by the emergence of the singlet at 4.85 ppm in the $^1$H NMR spectrum characteristic of this compound. Addition of a few drops of pyridine resulted in the quantitative conversion to the pyridine adduct of $\text{trans-4-py}$ generated from $2$ and $\text{H}_2$ (top) and $5$ and DIBAI-H (bottom).

These experimental studies provide convincing support for the mechanism proposed in Scheme 1, but the facility of these reactions, and the limitations imposed by the physical properties of these sparingly soluble, highly Lewis acidic and reactive boroles necessarily dictates that aspects of the proposed mechanism remain experimentally opaque. Therefore, we turned to DFT calculations to probe the veracity of the overall mechanistic proposal and computed a complete energy surface for the reactions of both $1$ and $2$ with dihydrogen.

DFT Calculations

The mechanism outlined in Scheme 2 was examined in detail at the PBE1PBE/def-TZVP level of theory, employing the polarizable continuum model for the treatment of solvent effects (methylene chloride). The acquired solution state energies are presented in Figure 6 for both the fluorinated ($1$) and unfluorinated ($2$) pentaphenylborole.

Figure 5. Comparison of the $^1$H NMR of $\text{trans-4}$ and the corresponding pyridine adduct $\text{trans-4-py}$ generated from $2$ and $\text{H}_2$ (top) and $5$ and DIBAI-H (bottom).

The initial step on the reaction pathway is the reversible formation of a stable adduct ($\text{I}$) between the borole and a molecule of dihydrogen (step a in Scheme 2). This step is endergonic for both boroles, around 20 kJ mol$^{-1}$ less so for the fully fluorinated system. Furthermore, the energy of the transition state ($\text{TS0}$) is virtually on par with that of the adduct. Consequently, these intermediates can release $\text{H}_2$ or access a transition state ($\text{TS1}$) leading to addition of $\text{H}_2$ across an internal B-C bond to give intermediates $\text{cis-II}$ (step b in Scheme 2). In this transformation, the $\pi$-electrons of the antiaromatic system function as an internal Lewis base, resulting in an overall heterolytic cleavage of the H-H bond. The energies for $\text{TS1}$ are only 61 kJ mol$^{-1}$ for $1$ and 74 kJ mol$^{-1}$ for $2$, in agreement with the experimentally observed reaction rates and the experimentally determined activation energy of 78(16) kJ mol$^{-1}$ for borole $2$. 

flect the fact that in the $\text{H}_2$ reaction with $2$, the $\text{cis}$ isomer arises exclusively via path c depicted in Scheme 1.
Continuing from the intermediates cis-II, the reactions can follow two alternate mechanisms whose transition states TS2 and TS3 have very similar energies. This indicates that both pathways are equally probable, in agreement with the observed formation of both cis and trans isomers. The transition states TS2 and TS3 are not only close in energy to each other but also to cis-II, which suggests that the intermediate is short-lived and that formation of intermediates cis-II is effectively irreversible.

The TS2 involves a hydride transfer from boron to carbon (step e in Scheme 2) and leads to the formation of the cis-3/4 products. However, the internal B-C bond lengths are significantly divergent in the cis-II structure: 1.566 Å vs 1.731 Å for the fluorinated system and 1.584 Å vs 1.711 Å in the phenyl substituted borole. Consequently, TS3 leads to B-C bond cleavage and ring opening (step d) to yield the cis-1-bora-2,4-pentadienyl rotamer (cis-III) which is the first intermediate on the pathway leading to products trans-3/4. The transformation of the cis-III rotamer to the corresponding trans isomer proceeds through TS4 (step e) with activation barriers of only 28 and 30 kJ mol⁻¹ for boroles 1 and 2, respectively. A subsequent, virtually barrierless (TS5), ring closure yields the trans-II intermediate (step f), which readily undergoes hydride migration from boron to carbon (TS6, analogous to step e) to give the trans-3/4 products, thus completing the reaction pathway. In agreement with the photochemical experiments, the trans-3 product is found to be more stable than the corresponding cis isomer for the fully fluorinated compound 1 (by 21 kJ/mol).

As is evident from Figure 6, the relative energies of transition states TS2-TS6 are significantly below that of the initial adduct I and the transition state of the rate limiting step TS1. Although the kinetic isotope effects observed are quite small, the low concentration of adduct I and the highly asynchronous geometry for the H-H cleavage in TS1 (Figure 7) are consistent with this observation. Indeed, in agreement with the kinetic isotope effect measurements, the reaction profiles shown in Figure 2 were found to be essentially independent of the isotope used in the calculations: substituting hydrogen in H₂ with deuterium had only a very minor (around 0-2 kJ mol⁻¹) effect on the relative Gibbs free energies calculated for both I and TS1.

A comparison of the two reaction profiles in Figure 6 shows that the overall energetics of the mechanism are largely independent of the identity of the borole as in many steps the blue and red lines overlap or are otherwise very close to each other. The biggest differences between the two profiles are observed for the trans-3/4 product as well as for the initial adduct I and the transition state TS1. In each of these cases, the fully fluorinated system is about 20 kJ mol⁻¹ more stable than its phenyl analogue, suggesting that the difference in Gibbs energy could be related to the short F···H and F···B contacts observed in the optimized structures. This was examined by conducting calculations on boroles which had their phenyl substituents only partially fluorinated.

Figure 6. Calculated Gibbs free energies (kJ mol⁻¹) for the reaction of boroles 1 (blue) and 2 (red) with H₂. The TS2 involves a hydride transfer from boron to carbon (step e in Scheme 2) and leads to the formation of the cis-3/4 products. However, the internal B-C bond lengths are significantly divergent in the cis-II structure: 1.566 Å vs 1.731 Å for the fluorinated system and 1.584 Å vs 1.711 Å in the phenyl substituted borole. Consequently, TS3 leads to B-C bond cleavage and ring opening (step d) to yield the cis-1-bora-2,4-pentadienyl rotamer (cis-III) which is the first intermediate on the pathway leading to products trans-3/4. The transformation of the cis-III rotamer to the corresponding trans isomer proceeds through TS4 (step e) with activation barriers of only 28 and 30 kJ mol⁻¹ for boroles 1 and 2, respectively. A subsequent, virtually barrierless (TS5), ring closure yields the trans-II intermediate (step f), which readily undergoes hydride migration from boron to carbon (TS6, analogous to step e) to give the trans-3/4 products, thus completing the reaction pathway. In agreement with the photochemical experiments, the trans-3 product is found to be more stable than the corresponding cis isomer for the fully fluorinated compound 1 (by 21 kJ/mol).

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Figure 7. Computed structures for the H₂ adduct I for the fully fluorinated borole 1 (top) and the transition state TS1 (bottom) for addition of H₂ across the internal B(1)-C(1) bond to form cis-II. Selected bond lengths (Å): (top) H(1)-H(2) = 0.814; F(1)-H(1) = 2.166, F(2)-H(2) = 2.309; C(1)-H(1) = 2.056; C(2)-H(2) = 2.111; B(1)-H(1) = 1.438 ; B(1)-H(2) = 1.443. (bottom) H(1)-H(2) = 1.057; F(1)-H(1) = 2.266, F(2)-H(2) = 2.391; C(1)-H(1) = 1.450; C(2)-H(2) = 2.142; B(1)-H(1) = 1.328 ; B(1)-H(2) = 1.304.

The calculations show that for 1, the structures I and TS1 gain extra stabilization from two short F···H contacts (2.106 – 2.391 Å) that make an approx. 10 kJ mol⁻¹ total contribution to their relative energies. Consequently, the first step on the reaction pathway is faster for the borole 1 not just because of its greater Lewis acidity but also because of the possibility to form van der Waals interactions that its phenyl substituted analogue 2 inevitably lacks. In a similar fashion, the lower relative energy of trans-3 compared to both trans-4 and cis-3 results in part from the two short F···B contacts (2.716 Å) in its structure. Selective F-to-H replacements showed that the combined effect of these interactions to the relative energy is 8 kJ mol⁻¹ which accounts for almost half of the difference between trans-3 and trans-4 structures.

As a whole, the results from theoretical calculations add considerable support for the pathway presented in Scheme 2. Nevertheless, in an effort to test the plausibility of alternate
mechanistic possibilities, we performed a more comprehensive scan of the potential energy surfaces of 1 and 2 with H₂. As expected, the environment at and around the boron atom was found to be the single reactive site in both boroles. However, we were able to characterize an additional transition state in which H₂ adds to the external B-C bond involving the aromatic substituent bound to the boron center. Significantly, these transition states were found to be 72 and 46 kJ mol⁻¹ higher in energy than the TS1 of boroles 1 and 2, respectively. Furthermore, following the internal reaction coordinate towards products clearly showed that the characterized transition state leads to breakup of the B-C bond and subsequent formation of a borole with a B-H functionality and a molecule of benzene/pentafluorobenzene. Since neither ArH₂ nor products arising from the highly reactive H-borole 43, 40 were observed, this pathway is not competitive in the reaction of boroles with H₂.

**Conclusions.**

The facile reaction of dihydrogen with antiaromatic boroles 1 and 2 illustrates that strongly Lewis acidic main group Lewis acids can bind hydrogen and activate it in the absence of an external Lewis base. Although dihydrogen addsucts of Lewis acid centers incapable of π backbonding are ephemeral, these reactions show that, when a thermodynamic driving force is present, such adducts can lead to reactivity other than simple release of the bound H₂. Here, the antiaromaticity associated with the borole ring are likely contributors to this driving force. For other Lewis acidic boranes, such as B(C₆F₅)₃, adducts with H₂ have been shown computationally to lie in energetic minima, but are not thought to lie on the reaction coordinate for hydrogen splitting in the presence of a bulky trialkylphosphine Lewis base such as PPh₃. Little, however, is known regarding the mechanism of H₂ activation by B(C₆F₅)₃ in partnership with other, non-Cₓ, symmetric Lewis bases. The role of H₂ addsucts of boranes may be more pronounced in the mechanisms involving these systems.

The work described here suggests that an H₂ adduct of a pen-taaryl borole might be observable experimentally under the right conditions. Unfortunately, the solubility properties of 1 and 2 (particularly 1) have precluded us from pursuing low temperature spectroscopic studies. With solubilizing groups, such studies may yield interesting results; efforts along these lines are currently underway.

**Experimental Section.**

General procedures are detailed in the Supporting Information.

**Kinetics Experiments.** A J. Young NMR tube was charged with a CD₃Cl solution (0.5 mL) containing 2 (0.016 M) and mesitylene (0.004 M) as an internal standard. The solution was then subjected to three freeze-pump-thaw cycles and allowed to equilibrate at a given temperature. At this time H₂ was then subjected to three freeze-pump-thaw cycles and allowed to equilibrate to room temperature. Agitation of the NMR tube first, followed by H₂. All three tubes were agitated with a modified Kugelrohr apparatus overnight. The ²H NMR spectra of each mixture were recorded and the ratio of H₂:D₂ products obtained by integration of appropriate signals.

**Synthesis of 5.** A solution of phenol (47 mg, 0.50 mmol) in dichloromethane (10 mL) was added to a cold (0 °C) solution of pentaphenylborole 2 (222 mg, 0.50 mmol) in dichloromethane (20 mL) via syringe over 30 minutes. The purple solution turned pale yellow almost immediately, and the ice bath was removed. After 30 minutes the volatiles were removed in vacuo, and yellow solid was recrystallized from hot toluene and washed with cold hexanes (2 x 3 mL). A pale yellow powder was obtained (140 mg, 52% yield). Crystals suitable for X-ray analysis were grown from slow evaporation from dichloromethane. ¹H NMR (400 MHz, CDCl₃): δ = 7.90 (m, 2H, ArH), 7.41 (m, 1H, ArH), 7.33 (m, 2H, ArH), 7.19 – 6.87 (m, 20H, ArH + C₆H₅-H), 6.83 (m, 2H, ArH), 6.76 (m, 2H, ArH), 6.70 (m, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ = 155.66, 152.88, 146.95, 145.64, 142.26, 139.31, 138.14, 136.70, 135.11, 131.98, 131.07, 130.80, 130.73, 130.55, 130.10, 129.08, 127.78, 127.69, 127.48, 127.40, 127.28, 127.08, 126.86, 126.48, 125.94, 124.26, 139.16. (Two peaks for the carbons bonded to boron were not observed due to the quadrupolar relaxation). ¹¹B NMR (128 MHz, CDCl₃): δ = 45 brs. HRMS (TOF MS El+): Calculated for C₅₀H₄₀BO 558.2468, found 538.2450.

**Reaction of 5 with DiBAl-H and pyridine.** A solution of 5 (26 mg, 0.050 mmol) in CD₃Cl (~0.7 mL) was mixed with DiBAl-H (50 uL, 1.0 M in hexanes) and shaken. After 20 minutes, two drops of pyridine were added to the NMR tube and the ¹H NMR spectrum recorded.

**Reaction of 2 with H₂ then pyridine.** In a J. Young NMR tube, a solution of 2 (5 mg, 0.01 mmol) in CD₃Cl (~0.7 mL) was degassed at -78°C and then charged with H₂ gas (ca. 1 atm). The tube was then rotated on a modified Kugelrohr
apparatus for 10 hours. Two drops of pyridine were added to the tube and the $^1$H NMR spectrum recorded.

**Computational Details.** All calculations were done with the program packages Turbomole 6.3,44 and Gaussian99.45 Geometries of the studied systems were optimized both in the gas phase as well as in solution (methylene chloride) using the PBE1PBE density functional48-50 in combination with Ahlrichs’ TZVP basis sets.47 The polarizable continuum model, as implemented in Gaussian 09, was used for the treatment of solvent effects.48 The nature of stationary points found was assessed by calculating full Hessian matrices. To ensure that the calculated energetics are not significantly dependent of the employed basis set, the reaction profile of borole 1 was recalculated in the gas phase using Ahlrichs’ de2TZVP basis sets.49,50 Doubling the size of the basis sets resulted in only minor 1-10 kJ mol$^{-1}$ changes to the relative energies. The program gOpenMo1 was used for all visualizations of molecular structures.51,52

**ASSOCIATED CONTENT**

**Supporting Information.** Crystallographic data files for 5 (CCDC 912008) as well as relative energies and xyz coordinates of the calculated structures and the full list of authors for reference 42. This material is available free of charge via the Internet at http://pubs.acs.org.

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**REFERENCES**

38. For the unfluorinated system, trans-4 is also the most stable (by 10 kJ/mol) but irradiation of cis-trans-4 mixtures leads to extensive decomposition.