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Direct observation of a borane-silane complex involved in frustrated Lewis-pair-mediated hydrosilylations

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Abstract: Perfluorarylborane Lewis acids catalyze the addition of silicon-hydrogen bonds across C=C, C=N and C=O double bonds. This “metal-free” hydrosilation has been proposed to occur via borane activation of the silane Si-H bond, rather than through classical Lewis acid/base adducts with the substrate. However, the key borane/silane adduct has never been experimentally observed. Here, it is shown that the strongly Lewis acidic, antiaromatic 1,2,3-*tris*(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-borandene forms an observable, isolable adduct with triethylsilane. The equilibrium for adduct formation has been studied quantitatively through variable temperature NMR spectroscopic investigations. The interaction of the silane with the borane occurs through the Si-H bond, as evidenced by trends in the silicon-hydrogen coupling constant and the IR stretching frequency of the Si-H bond, as well as by X-ray crystallography and theoretical calculations. The adduct’s reactivity with nucleophiles and its efficacy in the hydrosilation of olefins demonstrate conclusively the role of this species in metal free, “frustrated Lewis pair” hydrosilation reactions.

Homogeneous catalytic processes necessitating a bond activation step typically require transition metal-based catalysts in order to achieve turnover. Accordingly, many catalysts from metals across the transition period are known that conduct the hydrosilation and/or hydrogenation of unsaturated organic functions such as C=O, C=N and C=C bonds. In such systems, the Si-H or H-H bonds are activated via oxidative addition or sigma bond metathesis processes at the transition metal center as a key first step in the catalytic cycle.¹

While such catalysts offer many advantages, two drawbacks are the high cost and toxicity of metals most typically employed in such applications. There has therefore been significant interest in developing highly active, selective catalysts based on more economical and less harmful elements such as first row transition metals² or main group elements.^{3,4} With regard to the latter class of “metal-free” catalysts, the primary challenge lies in coaxing main group element compounds into mediating the critical bond activation step necessary for catalytic turnover.⁵

In this context, our observation in the mid 1990’s that the strongly Lewis acidic organoborane *tris*-pentafluorophenyl borane, B(C₆F₅)₃,⁶ was a highly active catalyst for the hydrosilation of carbonyl⁷ and imine⁸ functions has proven to be a key discovery in the development of metal-free catalyst systems for the addition of Si-H⁹⁻¹³ and subsequently H-H¹⁴⁻¹⁶ across a number of unsaturated bonds. Although we initially surmised that B(C₆F₅)₃ was serving to activate the carbonyl group via a classical Lewis acid-Lewis base interaction, kinetic and mechanistic studies strongly suggested that, although such adducts are quite thermodynamically favored,^{17,18} the true role of the borane was to activate the *silane*,^{7,19} as depicted in Fig. 1. The putative borane-silane adduct **I** is then susceptible to attack at silicon by the Lewis basic substrate, resulting in the bond activation intermediate **III**. This type of bond cleavage has come to be termed “frustrated Lewis

pair” (FLP) bond activation.^{20,21} In the hydrogenation chemistry, the role of an $\text{H}_2 \cdot \text{B}(\text{C}_6\text{F}_5)_3$ adduct (**I**, $\text{E} = \text{H}$) is still in question,²² and proposals that involve the formation of a weak “encounter complex” **II**, stabilized by secondary $\text{C-H} \cdots \text{F}$ interactions, prior to FLP activation of H_2 via **III** have strong computational support.^{23,24} Whether the path to **III** involves an $\text{EH} \cdot \text{B}(\text{C}_6\text{F}_5)_3$ adduct **I** or an encounter complex **II**, the bond activation transition state leads to an ion pair **IV** which proceeds to product upon transfer of hydride from the $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ to the substrate carbon, regenerating the $\text{B}(\text{C}_6\text{F}_5)_3$ catalyst.

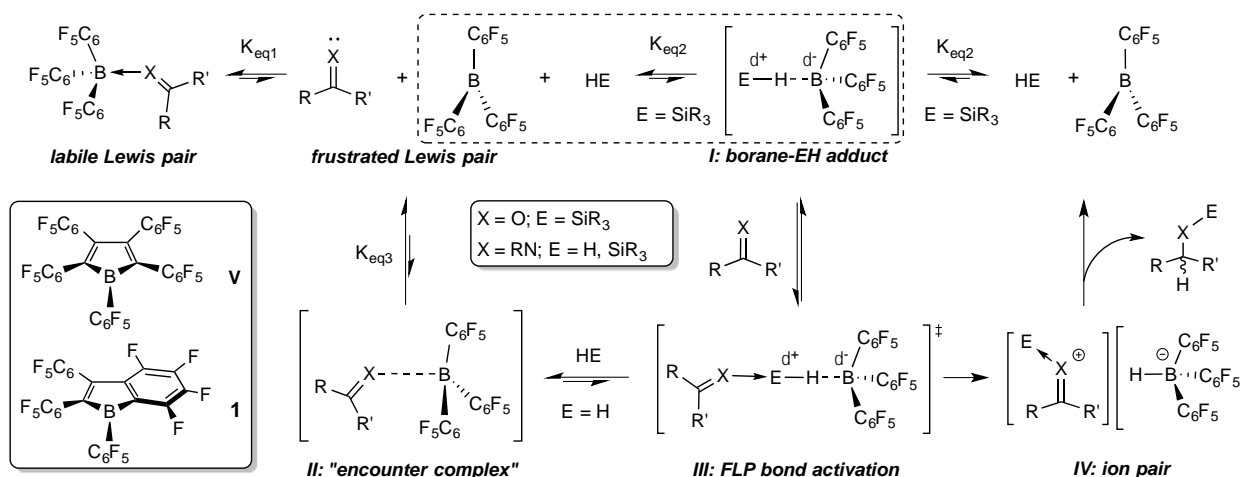


Figure 1. The mechanism of “frustrated” Lewis pair activation of Si-H and H-H bonds.

The various important equilibria involved in the activation and cleavage of Si-H and H-H bonds by Lewis acid/base pairs are depicted. While formation of classical Lewis acid/base adducts (K_{eq1}) may be favored, free Lewis acid may also interact with E-H to form a borane/E-H adduct which is the key intermediate in FLP activation of these bonds. This equilibrium, K_{eq2} is highlighted by the box with dashed lines. Such adducts **I** have not been experimentally observed. Inset: structures of antiaromatic borole **V** and boraindene **1**.

Much experimental and computational²⁵ support for this general mechanistic proposal has appeared in the years since our first disclosure of this chemistry. In addition to our own kinetic and labeling investigations,^{7,19} Oestreich has used stereo pure silanes to elegantly demonstrate that the Walden inversion at silicon that the mechanism predicts via structure **I** for $\text{E} = \text{R}_3\text{Si}$

indeed operative.^{26,27} Furthermore, in some cases, the ion pair intermediate **IV** can be observed spectroscopically.^{8,28}

This cumulative body of evidence has resulted in a high degree of acceptance for this mechanism in the literature, but the specific nature of the adducts **I**, or encounter complexes of type **II**, remain experimentally opaque.^{22,29} It has been observed that $\text{B}(\text{C}_6\text{F}_5)_3$ reacts slowly with Et_3SiH ^{30,31} to give *bis*-pentafluorophenyl borane, $\text{HB}(\text{C}_6\text{F}_5)_2$,³² along with $\text{Et}_3\text{SiC}_6\text{F}_5$, a process in which a borane-silane adduct is implicated. However, extensive attempts to detect this adduct through low temperature spectroscopic studies^{19,33} consistently failed to provide convincing evidence for its presence in solution. In other words, $K_{\text{eq}2}$ in Scheme 1 appears to strongly disfavor formation of adduct **I** for the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$. We were thus intrigued by a recent report from Berke *et al.*³⁴ in which they claimed to have observed substantial amounts of $\text{Et}_3\text{Si-H} \rightarrow \text{B}(\text{C}_6\text{F}_5)_3$ in solution via ²⁹Si NMR spectroscopy at 233 K. Noting, however, that their procedures did not appear to involve careful drying of the borane before use, it seemed likely that the peak assigned to this adduct is due in fact to $\text{Et}_3\text{SiOSiEt}_3$, formed rapidly when wet borane^{35,36} is treated with silane via rapid dehydrogenative silation of water.^{37,38} We confirmed this postulate by recording the ²⁹Si NMR spectrum of an authentic sample of $\text{Et}_3\text{SiOSiEt}_3$. Thus, this report of detection of the $\text{Et}_3\text{Si-H} \rightarrow \text{B}(\text{C}_6\text{F}_5)_3$ adduct³⁴ must be viewed as erroneous, and these species remain experimentally elusive.

In order to tilt the equilibrium $K_{\text{eq}2}$ in favor of the borane silane adduct **I**, the use of either a more Lewis basic silane or a more Lewis acidic borane might be contemplated. Since the latitude for increasing the Lewis basicity of the silane is rather narrow,³⁹ we have explored the latter strategy. To this end, we have utilized antiaromaticity in combination with perfluorination to prepare even more strongly Lewis acidic boranes than $\text{B}(\text{C}_6\text{F}_5)_3$. For example, we have shown

that perfluoropentaphenylborole⁴⁰ (**V**, Fig. 1, inset) is an extremely Lewis acidic compound that binds CO⁴¹ and activates dihydrogen towards H-H bond cleavage.^{42,43} In the latter reaction, an adduct of H₂ with **V** is clearly implicated. Borole **V** also undergoes less well defined reactions with silanes that involve cleavage of the Si-H bond,⁴⁴ but due to the compound's low solubility in non-donor solvents, we have been unable to conduct low temperature spectroscopic studies aimed at detecting either an H₂ or a silane adduct of **V**. Accordingly, we recently reported the synthesis of 1,2,3-*tris*(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-boraindene,⁴⁵ **1** (Fig. 1), a borane of essentially equal Lewis acid strength as **V**, but substantially more soluble than **V** in typical inert solvents. Here we describe its behavior in the presence of triethylsilane, Et₃SiH, and fully demonstrate the viability of borane-silane adducts **I**.

Results and discussion

The synthesis and characterization of boraindene **1** has been previously described.⁴⁵ It is a red solid that retains this color in toluene solution; the color is due to a weak absorption in the visible at 465 nm ($\epsilon = 900 \text{ M}^{-1}\text{cm}^{-1}$, see Supplementary Fig. S1) that is due to a forbidden $\pi \rightarrow n$ transition involving the empty p orbital on the Lewis acidic boron center. Upon complexation of a Lewis base, this absorption is disrupted and the color of the resulting adducts are pale yellow. Thus, Lewis acid/base adduct formation involving **1** is apparent with the naked eye by this red to yellow color change.

To explore the potential for adduct formation between **1** and Et₃SiH ($K_{\text{eq}2}$, Fig 2a), 1-2 equivalents of silane were added to a red solution of **1** in *d*₈-toluene. No visible change in color was observed at room temperature (Fig 2b) and little change to the components of the solution, as judged by ¹⁹F and ¹H NMR spectroscopy, was recorded. The thirteen separate resonances in

the ^{19}F NMR spectrum of **1** remained essentially unperturbed, while the signal for the Si-H moiety in Et_3SiH was a sharp septet at 3.79 ppm, essentially the same chemical shift as observed in pure samples of Et_3SiH . These observations showed that, while adduct formation was not favored under these conditions, boraindene **1** is stable towards reactions with silane that lead to ring opening processes observed for **V** and related compounds.⁴⁴ Therefore, when a reversible red to yellow color change was evident upon cooling this solution to 195 K (Fig. 2b), the coordination of silane to the boraindene to form adduct **2** was strongly implicated. We therefore followed up this encouraging qualitative evidence with a detailed spectroscopic, structural and computational study, aimed at establishing thermodynamic parameters for the equilibrium $K_{\text{eq}2}$ and characterizing borane/silane adduct **2**.

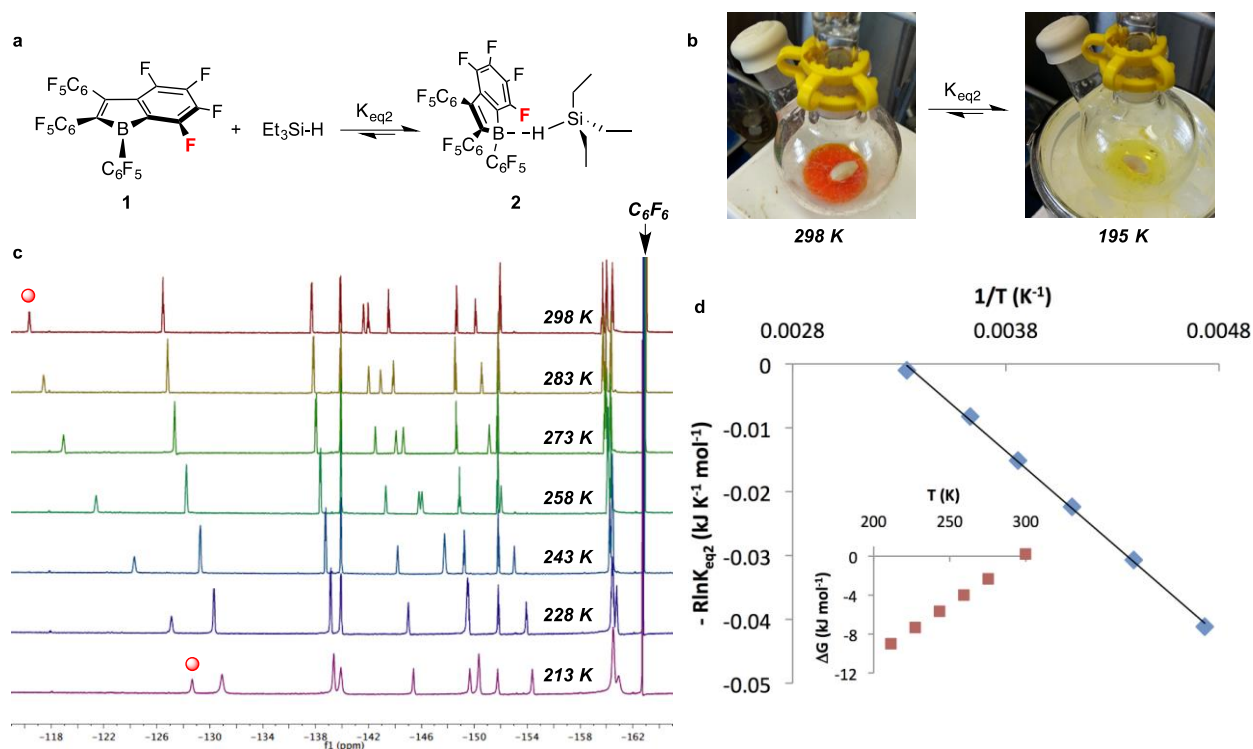


Figure 2. Equilibrium formation of borane-silane adduct 2. **a**, Schematic representation of adduct formation between 1,2,3-*tris*(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-boraindene, **1**, and triethylsilane, an example of equilibrium $K_{\text{eq}2}$ as depicted in Fig. 1. **b**, Visible color change observed upon cooling solutions of **1** and Et_3SiH from room temperature to 195 K with dry

ice/acetone; upon warming the red color of **1** returns. **c**, Variable temperature ^{19}F NMR spectra of this mixture, internally referenced to C_6F_6 , illustrating the significant perturbation in the chemical shift of the fluorine atom *ortho* to the boraindene boron atom (resonance marked by red circle). **d**, Van't Hoff analysis of the equilibrium, yielding thermodynamic parameters of $\Delta\text{H}^\circ = -29.7(3) \text{ kJ mol}^{-1}$ and $\Delta\text{S}^\circ = -100(1) \text{ J mol}^{-1} \text{ K}^{-1}$ for $\text{K}_{\text{eq}2}$; inset gives a plot of ΔG° vs. temperature.

Variable temperature ^{19}F NMR experiments were conducted on solutions of **1** with varying amounts of Et_3SiH in *d*₈-toluene. As the temperature is lowered, most of the resonances in the ^{19}F NMR spectrum shift slightly upfield, but the chemical shift for the fluorine *ortho* to boron on the boraindenyl core (colored red in Fig. 2a) is significantly perturbed as adduct formation is favored at lower temperatures (Fig. 2c). The drifting of this resonance is completely reversible as the temperature is lowered and raised. A similar phenomenon is observed in a series of ^{19}F NMR spectra recorded at room temperature with varying amounts of excess silane added (Supplementary Fig. S2). Both experiments indicate that, as the equilibrium shifts towards the adduct **2**, the chemical shift of the *ortho* fluorine atom moves closer to its absolute value in **2**. Since the position of the resonance for the *ortho*-F is a weighted average of the chemical shift of this fluorine in the free boraindene **1** and the adduct **2**, this series of spectra can be utilized to extract the mole fraction of each species and evaluate the equilibrium constant $\text{K}_{\text{eq}2}$. This was done by titrating 26 mM solutions of **1** with measured amounts of added silane at six different temperatures. Treatment of this data using the binding isotherm equation allowed for determination of $\text{K}_{\text{eq}2}$ at these temperatures (see Supplementary Fig. S3 and Table S1), facilitating a Van't Hoff analysis (Fig. 2d), which yields thermodynamic parameters of $\Delta\text{H}^\circ = -29.7(3) \text{ kJ mol}^{-1}$ and $\Delta\text{S}^\circ = -100(1) \text{ J mol}^{-1} \text{ K}^{-1}$ for $\text{K}_{\text{eq}2}$. The enthalpy associated with silane binding is approximately double that calculated for the binding of Et_3SiH to $\text{B}(\text{C}_6\text{F}_5)_3$ ^{25,33} but still rather weak, and the unfavorable entropic term renders the equilibrium approximately

thermoneutral at room temperature (Fig. 2c, inset), completely consistent with our macroscopic and spectroscopic observations.

We depict the adduct as being bonded via a Si-H••B bridge; this is consistent with computed structures for adducts involving B(C₆F₅)₃.^{25,33} The variable temperature

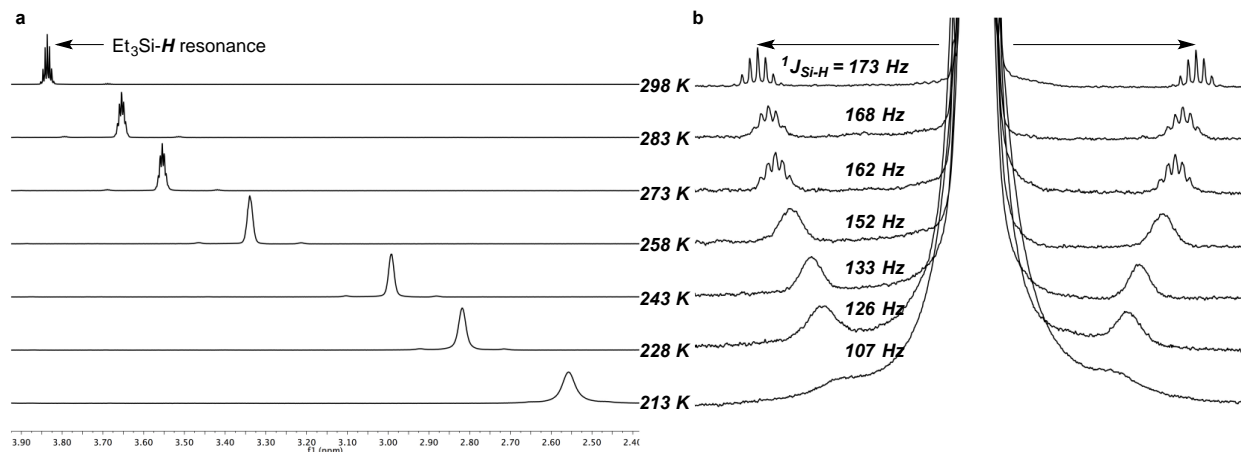


Figure 3. Partial proton NMR spectrum of solutions of **1 and Et₃Si-H.** **a**, Region of the spectrum showing the upfield shift for the Si-H resonance as the temperature is lowered and the equilibrium K_{eq2} favors adduct **2**. **b**, Overlaid and expanded resonance showing the steady contraction in the one-bond silicon-hydrogen coupling constant as the shifts towards adduct **2**.

¹H NMR and IR spectra for **2** provide experimental support for this assignment. As the temperature is lowered from 298 to 213 K, the signal for the silane hydrogen in the ¹H NMR spectrum moves more than 1 ppm upfield (Fig. 3a). An expansion of this signal to render the ²⁹Si satellites visible shows clearly that, as the temperature is lowered and the equilibrium shifts towards **2**, the value for the ¹J_{Si-H} coupling constant drops smoothly from 177 Hz in free Et₃Si-H to a value of 107(2) Hz at 213 K (Fig 3b). A lowering of this coupling constant would be expected⁴⁶ as the Si-H bond weakens upon interaction with the boron center. It was also anticipated that the stretching frequency of the Si-H bond would be impacted upon adduct

formation and indeed, a broad band at 1918 cm^{-1} is observed in solid samples of **2** precipitated from solutions of **1** in neat Et_3SiH at 195 K (Supplementary Fig. 4a). The $\nu_{\text{Si-H}}$ stretch for free silane is a sharp band at 2103 cm^{-1} ; the broadness of the band in **2** is typical of such $\nu_{\text{asSi-H-E}}$ moieties.⁴⁷ Furthermore, when samples of d_1 -**2** are prepared using $\text{Et}_3\text{Si-D}$, this band shifts from its position at 1918 cm^{-1} to $\approx 1400\text{ cm}^{-1}$ in the fingerprint region of the spectrum (Supplementary Fig. 4d).

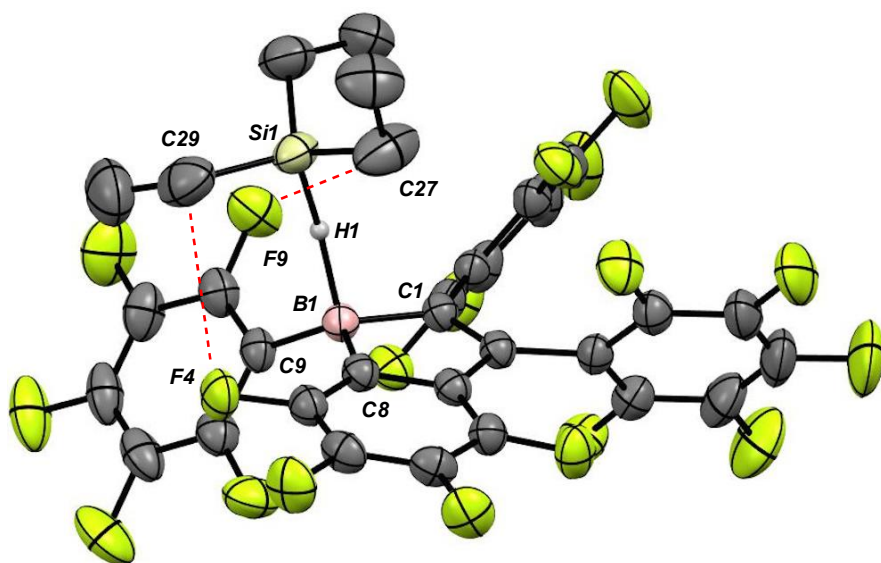


Figure 4. Crystal structure of boraindene-silane adduct **2 (50% probability ellipsoids.** Only the bridging hydrogen atom H1 is shown. Boron, silicon, carbon, fluorine and hydrogen atoms are in pink, light green, charcoal grey, lime green and grey, respectively. Red dashes indicate the close, non-bonded contacts. Selected bond lengths (\AA), non-bonded distances (\AA) and bond angles (deg): [calculated values]: B1-C1 = 1.616(3) [1.607], B1-C8 = 1.608(3) [1.594], B1-C9 = 1.605(3) [1.597], B1-H1 = 1.46(2) [1.402], Si1-H1 = 1.51(2) [1.608], F4-C29 = 3.262(2) [4.717], F9-C27 = 3.138(3) [3.171], C1-B1-C8 = $100.58(15)$ [100.91], C1-B1-C9 = $122.89(16)$ [121.061], C8-B1-C9 = $120.84(17)$ [122.57], B1-H1-Si1 = 157 [154.45].

The fact that we were able to perform IR spectroscopy on *solid* samples of **2** encouraged us to pursue the compound's crystallization for the purpose of structural analysis by X-ray diffraction. When neat Et_3SiH was layered onto a toluene solution of boraindene **1** at -35°C in a 5 mm glass

tube and allowed to slowly diffuse together, X-ray quality crystals were obtained and the structure determined; a thermal ellipsoid depiction of the molecular structure is given in Fig. 4 along with selected metrical parameters. In **2**, the silane binds the borane via the Si-H bond, forming a somewhat bent Si(1)-H(1)-B(1) bridge (157°). The bridging hydrogen H1 was found and refined on the difference map, providing Si1-H1 and B1-H1 bond distances of 1.51(2) and 1.46(2) Å, respectively. Thus, the hydrogen remains mainly associated with silicon, since typical Si-H distances are ≈ 1.48 Å,⁴⁶ while B-H distances in perfluoroaryl hydridoborate anions are around 1.14 Å,⁴⁸ and **2** can be viewed as a Lewis acid/base adduct rather than an ion pair of the form $[\text{Et}_3\text{Si}]^+[\text{HB}(\text{Ar}^{\text{F}})_3]^-$. Although the interaction is weak, the boron center is significantly pyramidalized relative to the planar boron in **1**,⁴⁵ with the sum of the C-B-C angles amounting to $344.3(2)^\circ$. The adduct also appears stabilized by secondary C-H...F Van der Waals interactions as evidenced by close contacts between F9 and C27 (3.138(3) Å) and F4 and C29 (3.262(2) Å). The adduct **2** was further studied by density functional theory (see Supplementary Information). Most of the optimized structural parameters of **2** correspond well with those in the crystal structure (Fig. 4, caption), but the calculated Si1-H1 bond length and the non-bonded distances between the F and C atoms are longer than in the X-ray structure. This can be explained by the uncertainty in the location of the bridging hydrogen in the difference density map and crystal packing effects that are not accounted for in gas phase calculations. We note that an atoms-in-molecules analysis⁴⁹ of the Si1-H1 bond critical point in **2** yields properties comparable to those for the Si-H bond in the free silane, indicating locally similar electronic structures. In contrast, the data for the B1-H1 bond critical point in **2** differ considerably from results obtained for the anion $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$, which supports the view of **2** as a Lewis acid/base adduct. The calculated

enthalpy associated with silane binding, $\Delta H^{\circ}_{\text{calc}}$, is -21 kJ mol^{-1} which is in agreement with the value obtained from the Van't Hoff analysis; the corresponding $\Delta G^{\circ}_{\text{calc}}$ is 32 kJ mol^{-1} .

To probe the stability of **2** further, calculations were carried out to compare the bonding in **2** to that in the Et_3SiH adduct with $\text{B}(\text{C}_6\text{F}_5)_3$ (*i.e.*, **I**, Fig. 1) and in the hypothetical adduct with perfluoroarylborole **V** (denoted **VI**). The calculated enthalpies and Gibbs energies (Table 1) show that adduct **I** is clearly the weakest of the three, while adduct **VI** is predicted to be as strongly bound as **2**. A further decomposition of the borane-silane bonding interaction allows quantification of the energy components arising from distortion of fragment geometries (ΔE_{dist}) and electronic (bonding) effects that stabilize the adducts (ΔE_{inst}). Adduct **I** has the smallest distortion energy but is nevertheless the least bound due to its weakest bonding interaction. While the distortion energies in **2** and, in particular, **VI** are greater than in **I**, the difference is more than compensated by stronger bonding interactions between the boraindene/borole and silane. The data in Table 1 also suggests that the Lewis-acidity of the investigated boranes decreases in the series $\text{V} > \mathbf{1} > \text{B}(\text{C}_6\text{F}_5)_3$, a notion corroborated by calculated hydride affinities of -593 , -564 and -538 kJ mol^{-1} , respectively. Thus, a fine balance between steric and electronic effects, rather than the high Lewis acidity of **1** alone, explain the stability of the adduct **2**.

Table 1 The calculated bonding enthalpies ($\Delta H^{\circ}_{\text{calc}}$), Gibbs energies ($\Delta G^{\circ}_{\text{calc}}$), distortion energies (ΔE_{dist}) and instantaneous interaction energies (ΔE_{inst}) of the adducts **2**, **I** and **VI**.^{a, b}

adduct	$\Delta H^{\circ}_{\text{calc}}$	$\Delta G^{\circ}_{\text{calc}}$	ΔE_{dist}	ΔE_{inst}
2	-21	32	75	-102
I	-6	56	68	-79
VI	-20	42	103	-129

^a Energies are given in kJ mol^{-1} . ^b The sum of ΔE_{dist} and ΔE_{inst} equals ΔH_{calc} at 0 K temperature.

The characterization of **2** in both solution and the solid state represents the first direct evidence for the long-proposed activation of silane by perfluoroarylboranes.⁷ While intramolecular Si-H••B interactions have been noted,⁵⁰ the intermolecular silane borane adduct **2** is explicitly relevant to metal-free, “frustrated Lewis pair”²⁰ mediated hydrosilations of unsaturated functions. To demonstrate that adduct **2** reacts in ways that are consistent with the mechanistic proposals of Fig. 1, we examined its reactivity towards a simple nucleophile and tested the efficacy of **1** as a catalyst for the hydrosilation of olefins (Fig. 5). When boraindene **1** and silane were dissolved in toluene and cooled to -78°C, one equivalent of dry *bis*-(triphenylphosphine)iminium chloride, [PPN]⁺[Cl]⁻, was added to form, immediately and quantitatively, the [PPN]⁺ salt of the hydridoborate anion, **3**, and Et₃SiCl (Fig. 5a). The latter was identified by comparison with an authentic sample, while **3** exhibited ¹¹B NMR (-16.2 ppm) and ¹H NMR (1.6 ppm, ¹J_{BH} = 90 Hz) data consistent with formation of a hydridoborate.⁴⁸ The chloroborate **4** that might be expected to form competitively (Fig. 5a) was not observed; this was confirmed by synthesizing it separately from **1** and [PPN]⁺[Cl]⁻. Furthermore, a control experiment in which **4** was treated with excess Et₃SiH showed that this is not a viable pathway to **3**. In fact, when the boraindene **1**/Et₃SiH mixture is treated with [PPN]⁺[Cl]⁻ at room temperature, the hydridoborate **3** is the exclusive boron containing product. From equilibrium thermodynamic data, under these conditions, the speciation of **2** in solution is less than 5% relative to free boraindene **1**, suggesting that the borane silane adduct reacts with chloride ion at least 20 times faster than the free boraindene. On the face of it, this seems quite surprising, but is in line with the high rates hydrosilation of imine and carbonyl functions by B(C₆F₅)₃; clearly, these borane silane adducts are highly reactive towards nucleophiles.

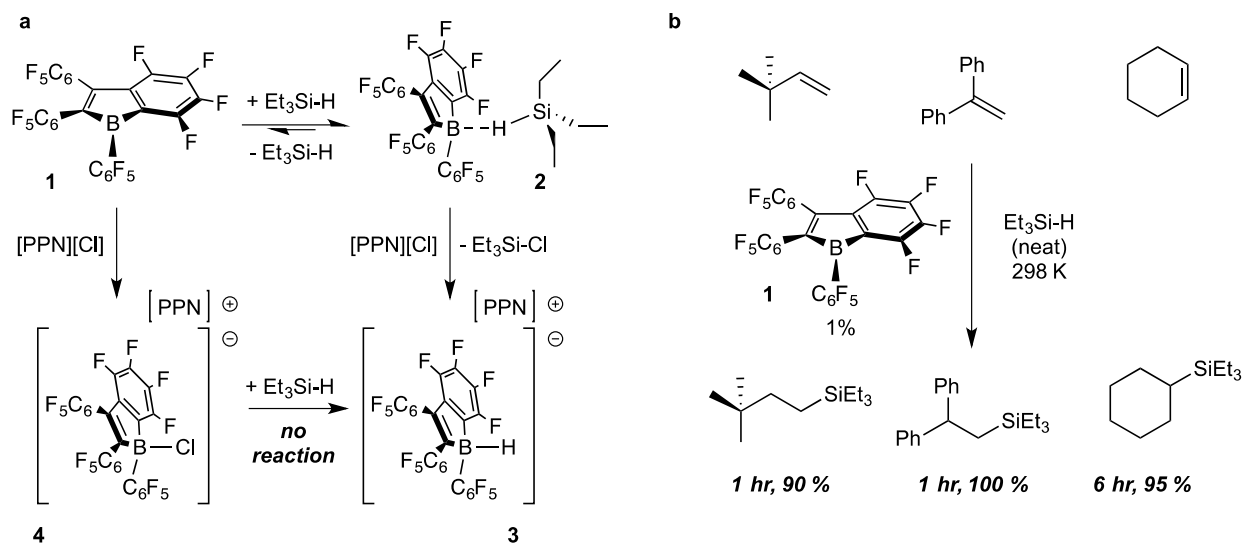


Figure 5. Reactivity of boraindene silane adduct 2. a, Schematic representation of the reactivity of both **1** and **2** with PPN chloride. b, Catalytic hydrosilation of the olefins *tert*-butyl ethylene, 1,1-diphenylethylene and cyclohexene by boraindene **1** using Et_3SiH ; yields given are estimated by NMR spectroscopy.

The scope and utility of boraindene **1** as a hydrosilation or hydrogenation⁴⁵ catalyst is under active investigation, but initial results indicate that it is highly active for the hydrosilation of olefins that lack polar functionalities. Gevorgyan and co-workers demonstrated in 2002 that $\text{B}(\text{C}_6\text{F}_5)_3$ is active for such hydrosilations, albeit at high catalyst loadings (10 mol %) and long reaction times (> 10 hours).⁹ As shown in Fig. 5b, boraindene **1** is a highly active catalyst for the hydrosilation of *tert*-butyl ethylene, 1,1-diphenyl ethylene and cyclohexene using Et_3SiH at loadings of only 1 mol%. The reactions are carried out in neat silane at room temperature and are complete in 1-6 hours. Qualitatively, boraindene **1** is a more active catalyst for this reaction than $\text{B}(\text{C}_6\text{F}_5)_3$, presumably because of the more favorable equilibrium constant $K_{\text{eq}2}$ for borane-silane adduct formation in **1** vs $\text{B}(\text{C}_6\text{F}_5)_3$.

Methods

1,2,3-tris(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-boraindene 1 was prepared as described elsewhere⁴⁶; triethylsilane was purchased from Sigma-Aldrich and dried via distillation under vacuum from calcium hydride. Unless explicitly stated otherwise, all operations were carried out under a purified argon atmosphere using either inert-atmosphere-glovebox or vacuum-line techniques. Dichloromethane was dried over and distilled from CaH₂, then distilled from molecular sieves after at least three days. Toluene, hexanes and benzene were dried over and distilled from sodium/benzophenone. Argon was passed through a Matheson TriGas cartridge (model M641-02) prior to use to remove traces of water and oxygen. All NMR analyses (¹H, ¹³C{¹H} DEPT-Q, ¹¹B, ¹⁹F, ³¹P) were performed on either a Bruker 400 MHz or 600 MHz instrument. The X-ray crystallography analysis was performed on suitable crystals coated in Paratone oil and mounted on a Bruker Smart APEX II with a three-circle diffractometer. Full descriptions of the methods used for data accumulation and analysis, as well as representative NMR and infrared spectra and computational results, are given in the Supplementary Information.

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Author contributions

A.Y.H. and W.E.P. conceived and designed the experiments, A.Y.H. performed the experiments, and determined the X-ray structure, H.M.T. and A.M. conceived and designed the computational work, J.H. and A.M. executed the calculations and performed data analyses. A.Y.H., W.E.P. and A.M. co-wrote the paper with input from J.H. and H.M.T.

Additional information

The authors declare no competing financial interests. Supplementary information and chemical compound information accompany this paper at www.nature.com/naturechemistry. Reprints and permission information is available online at <http://npg.nature.com/reprintsandpermissions/>.

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References

- 1 Hartwig, J. F. *Organotransition Metal Chemistry - From Bonding to Catalysis*. (University Science Books, 2010).
- 2 Bullock, R. M. Abundant Metals Give Precious Hydrogenation Performance. *Science* **342**, 1054-1055 (2013).
- 3 Frey, G. D., Lavallo, V., Donnadiu, B., Schoeller, W. W. & Bertrand, G. Facile Splitting of Hydrogen and Ammonia by Nucleophilic Activation at a Single Carbon Center. *Science* **316**, 439-441 (2007).
- 4 Welch, G. C., Juan, R. R. S., Masuda, J. D. & Stephan, D. W. Reversible, Metal-Free Hydrogen Activation. *Science* **314**, 1124-1126 (2006).
- 5 Spikes, G. H., Fettinger, J. C. & Power, P. P. Facile Activation of Dihydrogen by an Unsaturated Heavier Main Group Compound. *J. Am. Chem. Soc.* **127**, 12232-12233 (2005).
- 6 Massey, A. G., Park, A. J. & Stone, F. G. A. *Proc. Chem. Soc.*, 212 (1963).
- 7 Parks, D. J. & Piers, W. E. Tris(pentafluorophenyl)boron-catalyzed hydrosilation of aromatic aldehydes, ketones, and esters. *J. Am. Chem. Soc.* **118**, 9440-9441 (1996).
- 8 Blackwell, J. M., Sonmor, E. R., Scoccitti, T. & Piers, W. E. B(C₆F₅)₃-catalyzed hydrosilation of imines via silyliminium intermediates. *Org. Lett.* **2**, 3921-3923 (2000).
- 9 Rubin, M., Schwier, T. & Gevorgyan, V. Highly Efficient B(C₆F₅)₃-Catalyzed Hydrosilylation of Olefins. *J. Org. Chem.* **67**, 1936-1940 (2002).
- 10 Blackwell, J. M., Morrison, D. J. & Piers, W. E. B(C₆F₅)₃ catalyzed hydrosilation of enones and silyl enol ethers. *Tetrahedron* **58**, 8247-8254 (2002).

- 11 Berkefeld, A., Piers, W. E. & Parvez, M. Tandem Frustrated Lewis
Pair/Tris(pentafluorophenyl)borane-Catalyzed Deoxygenative Hydrosilylation of Carbon
Dioxide. *J. Am. Chem. Soc.* **132**, 10660-10661 (2010).
- 12 Müther, K., Mohr, J. & Oestreich, M. Silylium Ion Promoted Reduction of Imines with
Hydrosilanes. *Organometallics* **32**, 6643-6646 (2013).
- 13 Chen, D., Leich, V., Pan, F. & Klankermayer, J. Enantioselective Hydrosilylation with
Chiral Frustrated Lewis Pairs. *Chem. Eur. J.* **18**, 5184-5187 (2012).
- 14 Chase, P. A., Welch, G. C., Jurca, T. & Stephan, D. W. Metal-Free Catalytic
Hydrogenation. *Angew. Chem. Int. Ed.* **46**, 8050-8053 (2007).
- 15 Chase, P. A., Jurca, T. & Stephan, D. W. Lewis acid-catalyzed hydrogenation:
B(C₆F₅)₃-mediated reduction of imines and nitriles with H₂. *Chem. Commun.*, 1701-
1703 (2008).
- 16 Chernichenko, K. *et al.* A frustrated-Lewis-pair approach to catalytic reduction of
alkynes to cis-alkenes. *Nat Chem* **5**, 718-723 (2013).
- 17 Parks, D. J., Piers, W. E., Parvez, M., Atencio, R. & Zaworotko, M. J. Synthesis and
solution and solid-state structures of tris(pentafluorophenyl)borane adducts of PhC(O)X
(X = H, Me, OEt, NPr₂i). *Organometallics* **17**, 1369-1377 (1998).
- 18 Blackwell, J. M., Piers, W. E., Parvez, M. & McDonald, R. Solution and solid-state
characteristics of imine adducts with tris(pentafluorophenyl)borane. *Organometallics* **21**,
1400-1407 (2002).
- 19 Parks, D. J., Blackwell, J. M. & Piers, W. E. Studies on the mechanism of B(C₆F₅)₃-
catalyzed hydrosilation of carbonyl functions. *J. Org. Chem.* **65**, 3090-3098 (2000).
- 20 Stephan, D. W. "Frustrated Lewis pairs"; a concept for new reactivity and catalysis. *Org.*
Biomol. Chem. **6**, 1535-1539 (2008).
- 21 Stephan, D. W. & Erker, G. Frustrated Lewis Pairs: Metal-free Hydrogen Activation and
More. *Angew. Chem. Int. Ed.* **49**, 46-76 (2010).
- 22 Piers, W. E., Marwitz, A. J. V. & Mercier, L. G. Mechanistic Aspects of Bond Activation
with Perfluoroarylboranes. *Inorg. Chem.* **50**, 12252-12262 (2011).
- 23 Grimme, S., Kruse, H., Goerigk, L. & Erker, G. The Mechanism of Dihydrogen
Activation by Frustrated Lewis Pairs Revisited. *Angew. Chem. Int. Ed.* **49**, 1402-1405
(2010).
- 24 Rokob, T. A., Bakó, I., Stirling, A., Hamza, A. & Pápai, I. Reactivity Models of
Hydrogen Activation by Frustrated Lewis Pairs: Synergistic Electron Transfers or
Polarization by Electric Field? *J. Am. Chem. Soc.* **135**, 4425-4437 (2013).
- 25 Sakata, K. & Fujimoto, H. Quantum Chemical Study of B(C₆F₅)₃-Catalyzed
Hydrosilylation of Carbonyl Group. *J. Org. Chem.* **78**, 12505-12512 (2013).
- 26 Rendler, S. & Oestreich, M. Conclusive Evidence for an S_N2-Si Mechanism in the
B(C₆F₅)₃-Catalyzed Hydrosilylation of Carbonyl Compounds: Implications for the
Related Hydrogenation. *Angew. Chem. Int. Ed.* **47**, 5997-6000 (2008).
- 27 Hog, D. T. & Oestreich, M. B(C₆F₅)₃-Catalyzed Reduction of Ketones and Imines Using
Silicon-Stereogenic Silanes: Stereinduction by Single-Point Binding. *Eur. J. Org. Chem.*
2009, 5047-5056 (2009).
- 28 Hermeke, J., Mewald, M. & Oestreich, M. Experimental Analysis of the Catalytic Cycle
of the Borane-Promoted Imine Reduction with Hydrosilanes: Spectroscopic Detection of
Unexpected Intermediates and a Refined Mechanism. *J. Am. Chem. Soc.* **135**, 17537-
17546 (2013).

- 29 Marwitz, A. J. V., Dutton, J. L., Mercier, L. G. & Piers, W. E. Dihydrogen Activation with tBu₃P/B(C₆F₅)₃: A Chemically Competent Indirect Mechanism via in Situ-Generated p-tBu₂P–C₆F₄–B(C₆F₅)₂. *J. Am. Chem. Soc.* **133**, 10026-10029 (2011).
- 30 Parks, D. J., Piers, W. E. & Yap, G. P. A. Synthesis, Properties, and Hydroboration Activity of the Highly Electrophilic Borane Bis(pentafluorophenyl)borane, HB(C₆F₅)₂. *Organometallics* **17**, 5492-5503 (1998).
- 31 Nikonov, G. I., Vyboishchikov, S. F. & Shirobokov, O. G. Facile Activation of H-H and Si-H Bonds by Boranes. *J. Am. Chem. Soc.* **134**, 5488-5491 (2012).
- 32 Parks, D. J., von H. Spence, R. E. & Piers, W. E. Bis(pentafluorophenyl)borane: Synthesis, Properties, and Hydroboration Chemistry of a Highly Electrophilic Borane Reagent. *Angew. Chem. Int. Ed. Engl.* **34**, 809-811 (1995).
- 33 Chojnowski, J. *et al.* Mechanism of the B(C₆F₅)₃-Catalyzed Reaction of Silyl Hydrides with Alkoxysilanes. Kinetic and Spectroscopic Studies. *Organometallics* **24**, 6077-6084 (2005).
- 34 Jiang, Y. *et al.* The “Catalytic Nitrosyl Effect”: NO Bending Boosting the Efficiency of Rhenium Based Alkene Hydrogenations. *J. Am. Chem. Soc.* **135**, 4088-4102 (2013).
- 35 Bergquist, C. *et al.* Aqua, Alcohol, and Acetonitrile Adducts of Tris(perfluorophenyl)borane: Evaluation of Brønsted Acidity and Ligand Lability with Experimental and Computational Methods. *J. Am. Chem. Soc.* **122**, 10581-10590 (2000).
- 36 Beringhelli, T., Maggioni, D. & D'Alfonso, G. ¹H and ¹⁹F NMR Investigation of the Reaction of B(C₆F₅)₃ with Water in Toluene Solution. *Organometallics* **20**, 4927-4938 (2001).
- 37 Blackwell, J. M., Foster, K. L., Beck, V. H. & Piers, W. E. B(C₆F₅)₃-catalyzed silylation of alcohols: A mild, general method for synthesis of silyl ethers. *J. Org. Chem.* **64**, 4887-4892 (1999).
- 38 Gevorgyan, V., Rubin, M., Benson, S., Liu, J.-X. & Yamamoto, Y. A Novel B(C₆F₅)₃-Catalyzed Reduction of Alcohols and Cleavage of Aryl and Alkyl Ethers with Hydrosilanes. *J. Org. Chem.* **65**, 6179-6186 (2000).
- 39 Richter, D., Tan, Y., Antipova, A., Zhu, X.-Q. & Mayr, H. Kinetics of Hydride Abstractions from 2-Arylbenzimidazolines. *Chemistry – An Asian Journal* **4**, 1824-1829 (2009).
- 40 Fan, C., Piers, W. E. & Parvez, M. Perfluoropentaphenylborole. *Angew. Chem. Int. Ed.* **48**, 2955-2958 (2009).
- 41 Fukazawa, A. *et al.* Reaction of pentaarylboreles with carbon monoxide: an isolable organoboron carbonyl complex. *Chemical Science* **3**, 1814-1818 (2012).
- 42 Fan, C., Mercier, L. G., Piers, W. E., Tuononen, H. M. & Parvez, M. Dihydrogen Activation by Antiaromatic Pentaarylboreles. *J. Am. Chem. Soc.* **132**, 9604-9606 (2010).
- 43 Houghton, A. Y., Karttunen, V. A., Fan, C., Piers, W. E. & Tuononen, H. M. Mechanistic Studies on the Metal-Free Activation of Dihydrogen by Antiaromatic Pentarylboreles. *J. Am. Chem. Soc.* **135**, 941-947 (2012).
- 44 Braunschweig, H., Damme, A., Hörl, C., Kupfer, T. & Wahler, J. Si–H Bond Activation at the Boron Center of Pentaphenylborole. *Organometallics* **32**, 6800-6803 (2013).
- 45 Houghton, A. Y., Karttunen, V. A., Piers, W. E. & Tuononen, H. M. Hydrogen activation with perfluorinated organoboreles: 1,2,3-tris(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-boreindene. *Chem. Commun.* **50**, 1295-1298 (2014).

- 46 Corey, J. Y. & Braddock-Wilking, J. Reactions of Hydrosilanes with Transition-Metal Complexes: Formation of Stable Transition-Metal Silyl Compounds. *Chem. Rev.* **99**, 175-292 (1998).
- 47 Nava, M. & Reed, C. A. Triethylsilyl Perfluoro-Tetraphenylborate, [Et₃Si⁺][F₂₀-BPh₄⁻], a Widely Used Nonexistent Compound. *Organometallics* **30**, 4798-4800 (2011).
- 48 Berkefeld, A. *et al.* Carbon Monoxide Activation via O-Bound CO Using Decamethylscandocinium–Hydridoborate Ion Pairs. *J. Am. Chem. Soc.* **134**, 10843-10851 (2012).
- 49 Bader, R. F. W. *Atoms in Molecules: A Quantum Theory.*, (Oxford University Press, 1990).
- 50 Wrackmeyer, B., Milius, W. & Tok, O. L. Reaction of Alkyn-1-yl(diorganyl)silanes with 1-Boraadamantane: Si-H-B Bridges Confirmed by the Molecular Structure in the Solid State and in Solution. *Chem. Eur. J.* **9**, 4732-4738 (2003).