

Facile Activation of H–H and Si–H Bonds by Boranes

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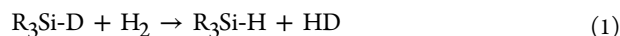
S Supporting Information

ABSTRACT: The borane $B(C_6F_5)_3$ is a precatalyst for H/D exchange between H_2 and deuterium-labeled silanes (D_3SiPh , $D_2SiMePh$, $DSiMe_2Ph$, $DSiEt_3$). Experimental and DFT studies reveal that $B(C_6F_5)_3$ itself cannot activate dihydrogen but converts to $HB(C_6F_5)_2$ under the action of hydrosilane. The latter species easily activates H–H and Si–H bonds by a σ -bond metathesis mechanism, which was further confirmed by the reactions of $BD_3 \cdot THF$ with H_2 .

Activation of hydrogen gas by non-transition-metal systems is an area of active research, both in the context of hydrogen storage¹ and for the development of metal-free hydrogenation/reduction catalysis.² There have been several recent breakthroughs in transition-metal-free H_2 activation: the irreversible hydrogenations of digermene³ and carbene,⁴ and the discovery of H_2 activation by frustrated Lewis pairs.^{5,6} In the latter case, the H_2 molecule is believed to be heterolytically split inside an $R_3P \cdots BAr_3$ cage to give the phosphonium ion R_3PH^+ and borate $HBAR_3^-$.^{7,8} This process can be done both reversibly⁹ and catalytically.^{2a,b,d} Activation of dihydrogen on a single boron center has been observed only very recently in the special case of irreversible hydrogenation of borole.¹⁰ At room temperature no reaction takes place between H_2 and tertiary boranes, such as the highly electrophilic $B(C_6F_5)_3$, according to experimental¹¹ and computational studies.^{7,12} In contrast, calculations of the reaction between H_2 and BH_3 were shown¹³ to give a weakly bound $BH_3 \cdots H_2$ adduct, and such a species was indeed generated by reacting boron atoms with hydrogen in an argon matrix.^{14,15}

Here we report an H/D exchange between the dihydrogen and silane catalyzed by boranes and provide evidence for the activation of H–H and Si–H bonds on a single boron center. We also provide evidence that the reaction proceeds via a σ -bond metathesis mechanism rather than by heterolytic bond cleavage.

Our initial observation was that $B(C_6F_5)_3$ catalyzes exchange between gaseous H_2 and deuterium-labeled silanes according to the equation



(where $R_3Si = D_2PhSi$, $DMePhSi$, Me_2PhSi , and Et_3Si), characterized by the appearance of the HD triplet at 4.54 ppm with a $J(H-D)$ spin–spin coupling constant of 43.2 Hz in the 1H NMR spectrum in C_6D_6 ,¹⁶ significant broadening of the Si–H signal, and appearance of the H_xD_ySi signal(s) in the case of primary and secondary silanes. There is a clear qualitative trend that bulkier silanes undergo the exchange slower, as

judged by the time required for the appearance of the HD and the extent of broadening of the SiH signal. After 1 day the extent of proton scrambling into $PhSiD_3$, $PhMeSiD_2$, and $PhMe_2SiD$ is 80%, 60%, and 30%, respectively. The electrophilicity of borane as a prerequisite for the exchange is evidenced in the BPh_3 -catalyzed reaction, which provides observable H/D exchange only after 1 month.

We were intrigued by the mechanism of this reaction, as previous reports by other workers⁷ as well as our own experimental and DFT studies demonstrate that $B(C_6F_5)_3$ does not form a stable adduct with dihydrogen. Our initial mechanistic suggestion for the reaction shown in eq 1 was that hydrogen activation may proceed on a SiR_3^+ cation¹⁷ formed *in situ* by hydride abstraction from $HSiR_3$ by $B(C_6F_5)_3$ (i.e., an ionic mechanism). However, our DFT calculations showed that such a process is energetically implausible in nonpolar media such as benzene (Table 1, entry 1). Under these conditions, silylium ion is not formed, even as a π -complex with benzene, $SiEt_3^+ \cdot C_6H_6$ ¹⁸ (Table 1, entry 2). Stabilization due to a Si–H–Si bridge formation to give the $[(Et_3Si)_2(\mu-H)]^+$ ion¹⁹ is not sufficient either (Table 1, entry 3). Alkyl abstraction by borane from triethylsilane is even less favorable than hydride abstraction (Table 1, entry 4).

During our further quest by *ab initio* calculations for a hydrogen-active intermediate, we found a stable adduct of the electrophilic borane $B(C_6F_5)_3$ with silane, $Et_3Si-H \cdots B(C_6F_5)_3$, which displays a short $B \cdots H$ distance of 1.398 Å and a noticeable elongation of the Si–H bond (1.554 Å in $Et_3SiH \cdot B(C_6F_5)_3$ vs 1.489 Å in Et_3SiH). Nonetheless, the $Et_3Si^{\delta+}-H^{\delta-}$ polarization caused by the adduct formation is not sufficient, and the adduct remains completely inert with respect to dihydrogen. Keeping in mind the known examples of dihydrogen activation by means of frustrated Lewis pairs,⁶ we also examined the possibility of an H–H activation by way of an $R_3Si^{\delta+}-H^{\delta-} \cdots H^{\delta+}-H^{\delta-} \cdots BAr_3$ complex, in which the R_3SiH and BAr_3 moieties would be kept together by a kind of a long-range intermolecular interaction.⁷ However, extensive calculations did not reveal any such intermediate.

The fact that both R_3SiH and BAr_3 , as well as their adduct, turned out to be inactive with respect to molecular hydrogen implies that there must be another species that actually reacts with H_2 . A number of experimental observations suggested the existence of an active intermediate. We noticed that broadening of the Si–H NMR signals upon addition of borane involves an induction period depending on the silane. Similarly, an

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Table 1. Relative Energies ΔE_e at MP2/6-311G** and CCSD/6-311++G**//MP2/6-311G** Levels and ΔG°_{298} CCSD COSMO (in kcal·mol⁻¹)

	process	ΔE_e		ΔG°_{298} CCSD COSMO ^a
		MP2	CCSD	
1.	$\text{Et}_3\text{SiH} + \text{B}(\text{C}_6\text{F}_5)_3 \rightarrow [\text{Et}_3\text{Si}]^+ + [\text{HB}(\text{C}_6\text{F}_5)_3]^-$	106.9	99.8	59.6
2.	$\text{Et}_3\text{SiH} + \text{C}_6\text{H}_6 + \text{B}(\text{C}_6\text{F}_5)_3 \rightarrow [\text{Et}_3\text{Si}]^+ \cdot \text{C}_6\text{H}_6 + [\text{HB}(\text{C}_6\text{F}_5)_3]^-$	73.0	70.8	50.1
3.	$2\text{Et}_3\text{SiH} + \text{B}(\text{C}_6\text{F}_5)_3 \rightarrow (\text{Et}_3\text{Si})_2\text{H}^+ + [\text{HB}(\text{C}_6\text{F}_5)_3]^-$	70.5	63.8	44.2
4.	$\text{Et}_3\text{SiH} + \text{B}(\text{C}_6\text{F}_5)_3 \rightarrow [\text{Et}_2\text{HSi}]^+ + [\text{EtB}(\text{C}_6\text{F}_5)_3]^-$	125.6	117.1	74.0
5.	$\text{Et}_3\text{SiH} + \text{B}(\text{C}_6\text{F}_5)_3 \rightarrow \text{Et}_3\text{SiH} \cdot \text{B}(\text{C}_6\text{F}_5)_3$	-17.7	-18.8	-4.4
6.	$\text{Et}_3\text{SiH} \cdot \text{B}(\text{C}_6\text{F}_5)_3 \rightarrow \text{Et}_3\text{Si}(\text{C}_6\text{F}_5) + \text{HB}(\text{C}_6\text{F}_5)_2$; barrier	18.3	24.5	27.8
7.	$\text{Et}_3\text{SiH} + \text{B}(\text{C}_6\text{F}_5)_3 \rightarrow \text{Et}_3\text{Si}(\text{C}_6\text{F}_5) + \text{HB}(\text{C}_6\text{F}_5)_2$	4.6	4.7	6.1
8.	$\text{H}_2 + \text{HB}(\text{C}_6\text{F}_5)_2 \rightarrow \text{H}_2 + \text{HB}(\text{C}_6\text{F}_5)_2$ (degenerate exchange); barrier	12.2	15.1	23.5
9.	$\text{Et}_3\text{SiH} + \text{HB}(\text{C}_6\text{F}_5)_2 \rightarrow \text{Et}_3\text{SiH} \cdot \text{HB}(\text{C}_6\text{F}_5)_2$; adduct	-17.2	-15.6	-1.4
10.	$\text{Et}_3\text{SiH} \cdot \text{HB}(\text{C}_6\text{F}_5)_2 \rightarrow \text{Et}_3\text{SiH} \cdot \text{HB}(\text{C}_6\text{F}_5)_2$; adduct (degenerate exchange); barrier	1.8	3.4	5.1
11.	$\text{Et}_3\text{SiH} + \text{HB}(\text{C}_6\text{F}_5)_2 \rightarrow \text{Et}_3\text{Si} \cdot \text{B}(\text{C}_6\text{F}_5)_2 + \text{H}_2$; barrier	4.6	5.9	8.6
		7.4	9.1	21.7
12.	$\text{PhH} + \text{HB}(\text{C}_6\text{F}_5)_2 \rightarrow \text{Ph} \cdot \text{B}(\text{C}_6\text{F}_5)_2 + \text{H}_2$; barrier	-6.6	-3.6	-3.7
		14.6	21.5	31.3
13.	$\text{H}_2 + \text{BH}_3 \rightarrow \text{H}_2 \cdot \text{BH}_3$; adduct	-3.8	-2.3	10.4
14.	$\text{H}_2 + \text{BH}_3 \rightarrow \text{H}_2 + \text{BH}_3$ (degenerate exchange); barrier	2.6	5.1	18.1
15.	$\text{BH}_3 \cdot \text{THF} \rightarrow \text{BH}_3 + \text{THF}$	25.4	21.9	5.9

^aAn estimate at the CCSD/6-311++G**//MP2/6-311G** level taking into account solvent effects (benzene).

induction period was observed for the H₂/silane exchange (Figure 1). Also, it was shown previously²⁰ that thermolysis of Et₃SiH with B(C₆F₅)₃ at 60 °C for 3 days gives a secondary borane according to the equation



We found that this H/C exchange process occurs via formation of the Et₃Si–H···B(C₆F₅)₃ adduct followed by a σ -bond metathesis (Figure 2a) with the calculated activation free energy $\Delta^\ddagger G^\circ_{298} = 27.8$ kcal·mol⁻¹. In the σ -bond metathesis, the cleavage of old σ bonds (e.g., C–B and Si–H) occurs simultaneously with the formation of new σ bonds (e.g., Si–C and B–H) in a concerted four-center transition state.²¹ Experimentally, we found that such an H/C exchange is much more facile for primary (PhSiH₃) and secondary silanes (PhMeSiH₂) and is observed already within a few hours at room temperature (9% yield of HB(C₆F₅)₂ overnight in the case of PhMeSiH₂, and 5% yield of HB(C₆F₅)₂ overnight in the case of PhMe₂SiH, according to ¹⁹F NMR).²² These observations are in line with the ease of the boron-catalyzed H₂/DSiR₃ exchange (*vide supra*). It is, therefore, reasonable to assume that HB(C₆F₅)₂ formed *in situ* is the true catalyst of the hydrogen/silane and silane/silane exchanges. Indeed, when

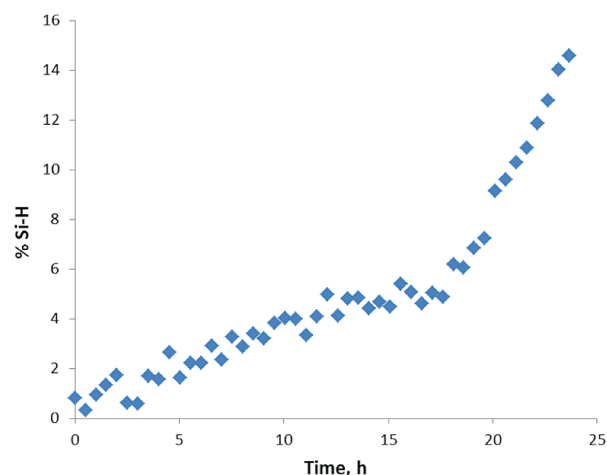


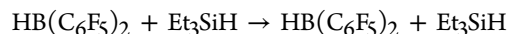
Figure 1. Formation of protosilane in the solution of PhSiD₃ in C₆D₆ under hydrogen atmosphere in the presence of B(C₆F₅)₃. 100% conversion corresponds to the exchange of all three deuteriums of PhSiD₃ for protons.

HB(C₆F₅)₂ was used as a catalyst for the H₂/PhSiD₃ exchange, 70% exchange was reached without an induction period in <13.5 h (cf. 14.5% after 24 h in Figure 1).

According to calculations, HB(C₆F₅)₂ does not form a stable adduct with H₂ either, but undergoes a direct degenerate 2+2 σ -bond metathesis via a nearly symmetric transition state ($\eta^2\text{-H}_2$)B(C₆F₅)₂ (Table 1, Figure 2b) with a moderate $\Delta^\ddagger G^\circ_{298}$ barrier of 23.5 kcal·mol⁻¹. The feasibility of such metathesis was further proved experimentally by the direct reaction of BD₃·THF in THF/C₆D₆ with hydrogen at atmospheric pressure, which results in very fast (<5 min) appearance of H–D in the ¹H and ²H NMR spectra. The concomitant formation of BH_xD_y·THF was confirmed by ¹H–¹¹B HSQC NMR experiment.

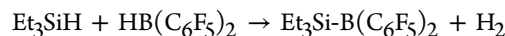
Quantum mechanical calculations established that dissociation of the BH₃·THF adduct proceeds easily ($\Delta G^\circ_{298} = 5.9$ kcal·mol⁻¹). The subsequent degenerate H₂/BH₃ exchange occurs with a reasonable barrier of 18.1 kcal·mol⁻¹. For the latter process we did find a loosely bound adduct H₂·BH₃ (Table 1), in accord with the previous calculations.¹³

A similar 2+2 degenerate hydride metathesis (Figure 2c),

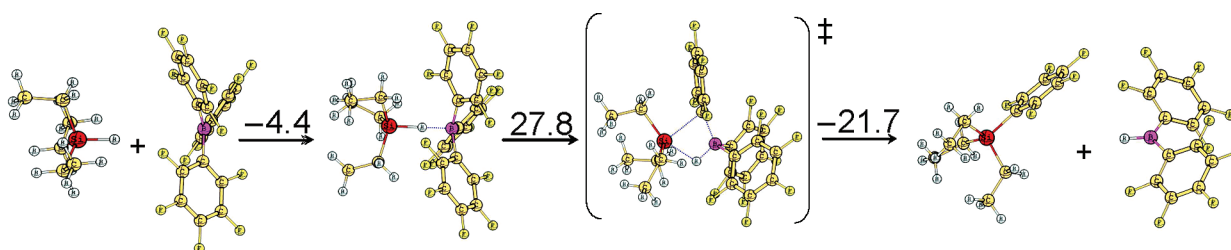


requires a low $\Delta^\ddagger G^\circ_{298}$ barrier of 5.1 kcal·mol⁻¹ (Table 1), which eventually accounts for the experimentally observed isotope exchange between H₂ and the deuterium atom in Et₃SiD.

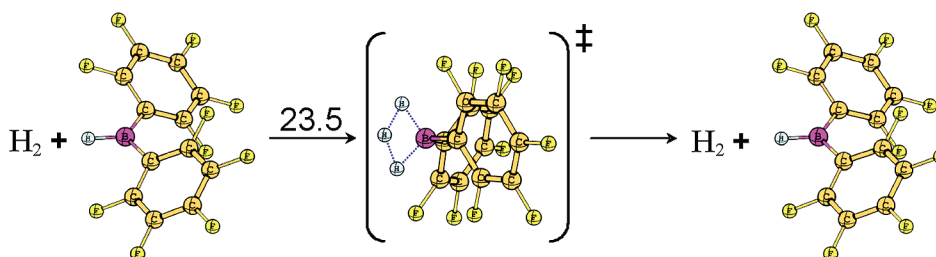
Apart from the hydrogen exchange, we have also looked at the possibility of productive dehydrogenative B–Si coupling,



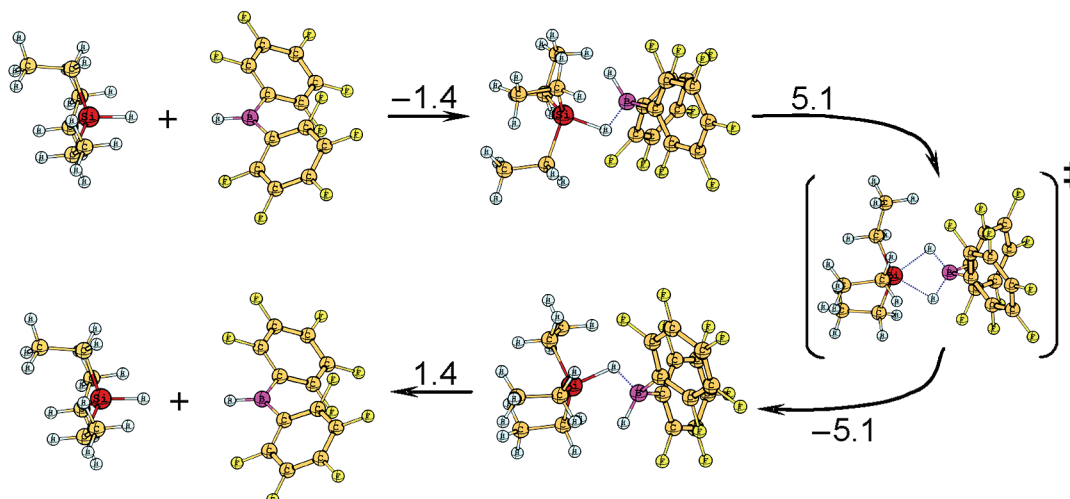
(Figure 2d), that would afford synthetically useful silylboranes.²³ According to calculations, the reaction is energetically uphill ($\Delta G^\circ_{298} = +8.6$ kcal·mol⁻¹) but still has an affordable barrier ($\Delta^\ddagger G^\circ_{298} = 21.7$ kcal·mol⁻¹, Table 1). Such a coupling may therefore become feasible if the evolved dihydrogen is consumed in a thermodynamically favorable process (e.g., in a reaction with an unsaturated substrate) or is removed from the reaction media. It is noteworthy that the synthetically important dehydrogenative B–C coupling²⁴ between benzene and borane (in this example HB(C₆F₅)₂) is thermodynamically feasible ($\Delta G^\circ_{298} = -3.7$ kcal·mol⁻¹) but proceeds with a large barrier ($\Delta^\ddagger G^\circ_{298} = 31.3$ kcal·mol⁻¹, Table 1). This kinetic hurdle is in agreement with the fact that transition-metal



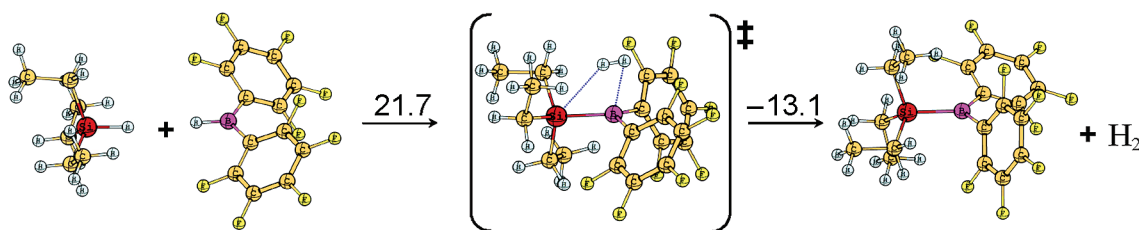
(a) $\text{Et}_3\text{SiH} + \text{B}(\text{C}_6\text{F}_5)_3 \rightleftharpoons \text{Et}_3\text{SiH} \cdot \text{B}(\text{C}_6\text{F}_5)_3 \text{ adduct} \rightarrow \text{Et}_3\text{Si}(\text{C}_6\text{F}_5) + \text{HB}(\text{C}_6\text{F}_5)_2$



(b) $\text{H}_2 + \text{HB}(\text{C}_6\text{F}_5)_2 \rightleftharpoons \text{H}_2 + \text{HB}(\text{C}_6\text{F}_5)_2$ degenerate hydrogen exchange



(c) $\text{Et}_3\text{SiH} + \text{HB}(\text{C}_6\text{F}_5)_2 \rightleftharpoons \text{Et}_3\text{SiH} \cdot \text{HB}(\text{C}_6\text{F}_5)_2 \text{ adduct} \rightleftharpoons \text{Et}_3\text{SiH} + \text{HB}(\text{C}_6\text{F}_5)_2$ degenerate silane-borane hydrogen exchange



(d) Silylborane formation $\text{Et}_3\text{SiH} + \text{HB}(\text{C}_6\text{F}_5)_2 \rightarrow (\text{Et}_3\text{Si})\text{B}(\text{C}_6\text{F}_5) + \text{H}_2$

Figure 2. σ -Bond metathesis reaction on boron centers. The numbers above the arrows are standard Gibbs energy changes (ΔG°_{298}) or barriers ($\Delta^\ddagger G^\circ_{298}$) in $\text{kcal} \cdot \text{mol}^{-1}$ calculated at the CCSD level taking into account solvation effects.

catalysts are needed for dehydrogenative coupling of arenes Ar-H and boranes $\text{HB}(\text{OR})_2$ to give arylboranes $\text{Ar-B}(\text{OR})_2$.^{24,25}

In summary, we have demonstrated activation of H-H and Si-H bonds on a single borane center and unveiled a mechanism based on a series of previously unrecognized direct σ -bond metatheses resulting in substituent exchange on the boron center.

■ ASSOCIATED CONTENT

Supporting Information

General experimental procedures and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED IN PROOF

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