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# Facile Activation of H−H and Si−H Bonds by Boranes

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*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 storage[1] 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 digermyne[3] 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 reversibly[9] 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 experimental[11] and computational studies.[7,12] In contrast, calculations of the reaction between $H_2$ and $BH_3$ were shown[13] to give a weakly bound $BH_3{\cdot}H_2$ 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

$$R_3Si\text{-}D + H_2 \rightarrow R_3Si\text{-}H + HD \qquad (1)$$

(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 workers[7] 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 $SiR_3^+$ cation[17] 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 $[(Et_3Si)_2(\mu\text{-}H)]^+$ ion[19] 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···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 $\Delta E_e$ at MP2/6-311G** and CCSD/6-311++G**//MP2/6-311G** Levels and $\Delta G°_{298}$ CCSD COSMO (in kcal·mol$^{-1}$)**

| | | $\Delta E_e$ | | |
|---|---|---|---|---|
| | process | MP2 | CCSD | $\Delta G°_{298}$ CCSD COSMO$^a$ |
| 1. | $Et_3SiH + B(C_6F_5)_3 \rightarrow [Et_3Si]^+ + [HB(C_6F_5)_3]^-$ | 106.9 | 99.8 | 59.6 |
| 2. | $Et_3SiH + C_6H_6 + B(C_6F_5)_3 \rightarrow [Et_3Si]^+ \cdot C_6H_6 + [HB(C_6F_5)_3]^-$ | 73.0 | 70.8 | 50.1 |
| 3. | $2Et_3SiH + B(C_6F_5)_3 \rightarrow (Et_3Si)_2H^+ + [HB(C_6F_5)_3]^-$ | 70.5 | 63.8 | 44.2 |
| 4. | $Et_3SiH + B(C_6F_5)_3 \rightarrow [Et_2HSi]^+ + [EtB(C_6F_5)_3]^-$ | 125.6 | 117.1 | 74.0 |
| 5. | $Et_3SiH + B(C_6F_5)_3 \rightarrow Et_3SiH \cdot B(C_6F_5)_3$ | −17.7 | −18.8 | −4.4 |
| 6 | $Et_3SiH \cdot B(C_6F_5)_3 \rightarrow Et_3Si(C_6F_5) + HB(C_6F_5)_2$; barrier | 18.3 | 24.5 | 27.8 |
| 7. | $Et_3SiH + B(C_6F_5)_3 \rightarrow Et_3Si(C_6F_5) + HB(C_6F_5)_2$ | 4.6 | 4.7 | 6.1 |
| 8. | $H_2 + HB(C_6F_5)_2 \rightarrow H_2 + HB(C_6F_5)_2$ (degenerate exchange); barrier | 12.2 | 15.1 | 23.5 |
| 9. | $Et_3SiH + HB(C_6F_5)_2 \rightarrow Et_3SiH \cdot HB(C_6F_5)_2$; adduct | −17.2 | −15.6 | −1.4 |
| 10. | $Et_3SiH \cdot HB(C_6F_5)_2 \rightarrow Et_3SiH \cdot HB(C_6F_5)_2$; adduct (degenerate exchange); barrier | 1.8 | 3.4 | 5.1 |
| 11. | $Et_3SiH + HB(C_6F_5)_2 \rightarrow Et_3Si\text{-}B(C_6F_5)_2 + H_2$; | 4.6 | 5.9 | 8.6 |
| | barrier | 7.4 | 9.1 | 21.7 |
| 12. | $PhH + HB(C_6F_5)_2 \rightarrow Ph\text{-}B(C_6F_5)_2 + H_2$; | −6.6 | −3.6 | −3.7 |
| | barrier | 14.6 | 21.5 | 31.3 |
| 13. | $H_2 + BH_3 \rightarrow H_2 \cdot BH_3$; adduct | −3.8 | −2.3 | 10.4 |
| 14. | $H_2 + BH_3 \rightarrow H_2 + BH_3$ (degenerate exchange); barrier | 2.6 | 5.1 | 18.1 |
| 15. | $BH_3 \cdot THF \rightarrow BH_3 + THF$ | 25.4 | 21.9 | 5.9 |

[a] An estimate at the CCSD/6-311++G**//MP2/6-311G** level taking into account solvent effects (benzene).

induction period was observed for the $H_2$/silane exchange (Figure 1). Also, it was shown previously[20] that thermolysis of $Et_3SiH$ with $B(C_6F_5)_3$ at 60 °C for 3 days gives a secondary borane according to the equation

$$Et_3SiH + B(C_6F_5)_3 \rightarrow HB(C_6F_5)_2 + Et_3Si(C_6F_5)$$

We found that this H/C exchange process occurs via formation of the $Et_3Si{-}H \cdots B(C_6F_5)_3$ adduct followed by a $\sigma$-bond metathesis (Figure 2a) with the calculated activation free energy $\Delta^{\ddagger}G°_{298}$ = 27.8 kcal·mol$^{-1}$. In the $\sigma$-bond metathesis, the cleavage of old $\sigma$ bonds (e.g., C−B and Si−H) occurs simultaneously with the formation of new $\sigma$ 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 ($PhSiH_3$) and secondary silanes ($PhMeSiH_2$) and is observed already within a few hours at room temperature (9% yield of $HB(C_6F_5)_2$ overnight in the case of $PhMeSiH_2$, and 5% yield of $HB(C_6F_5)_2$ overnight in the case of $PhMe_2SiH$, according to $^{19}F$ NMR).[22] These observations are in line with the ease of the boron-catalyzed $H_2/DSiR_3$ exchange (*vide supra*). It is, therefore, reasonable to assume that $HB(C_6F_5)_2$ formed *in situ* is the true catalyst of the hydrogen/silane and silane/silane exchanges. Indeed, when $HB(C_6F_5)_2$ was used as a catalyst for the $H_2/PhSiD_3$ exchange, 70% exchange was reached without an induction period in <13.5 h (cf. 14.5% after 24 h in Figure 1).

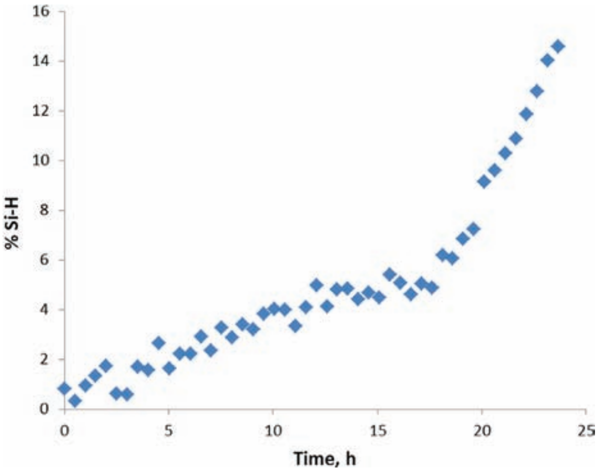


**Figure 1.** Formation of protiosilane in the solution of $PhSiD_3$ in $C_6D_6$ under hydrogen atmosphere in the presence of $B(C_6F_5)_3$. 100% conversion corresponds to the exchange of all three deuteriums of $PhSiD_3$ for protons.

According to calculations, $HB(C_6F_5)_2$ does not form a stable adduct with $H_2$ either, but undergoes a direct degenerate 2+2 $\sigma$-bond metathesis via a nearly symmetric transition state $(\eta^2\text{-}H_3)B(C_6F_5)_2$ (Table 1, Figure 2b) with a moderate $\Delta^{\ddagger}G°_{298}$ barrier of 23.5 kcal·mol$^{-1}$. The feasibility of such metathesis was further proved experimentally by the direct reaction of $BD_3 \cdot THF$ in THF/$C_6D_6$ 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 $BH_xD_y \cdot THF$ was confirmed by $^1H{-}^{11}B$ HSQC NMR experiment.

Quantum mechanical calculations established that dissociation of the $BH_3 \cdot THF$ adduct proceeds easily ($\Delta G°_{298}$ = 5.9 kcal·mol$^{-1}$). The subsequent degenerate $H_2/BH_3$ exchange occurs with a reasonable barrier of 18.1 kcal·mol$^{-1}$. For the latter process we did find a loosely bound adduct $H_2 \cdot BH_3$ (Table 1), in accord with the previous calculations.[13]

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

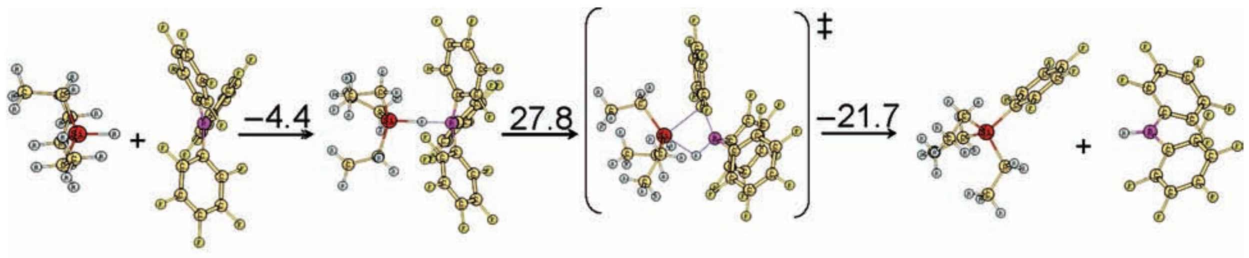
$$HB(C_6F_5)_2 + Et_3SiH \rightarrow HB(C_6F_5)_2 + Et_3SiH$$

requires a low $\Delta^{\ddagger}G°_{298}$ barrier of 5.1 kcal·mol$^{-1}$ (Table 1), which eventually accounts for the experimentally observed isotope exchange between $H_2$ and the deuterium atom in $Et_3SiD$.

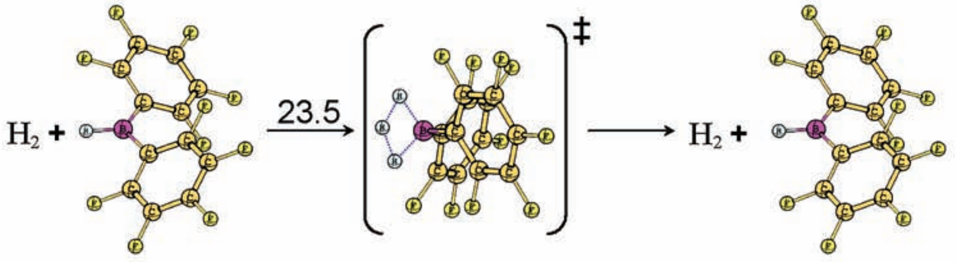
Apart from the hydrogen *exchange*, we have also looked at the possibility of productive dehydrogenative B−Si *coupling*,

$$Et_3SiH + HB(C_6F_5)_2 \rightarrow Et_3Si\text{-}B(C_6F_5)_2 + H_2$$

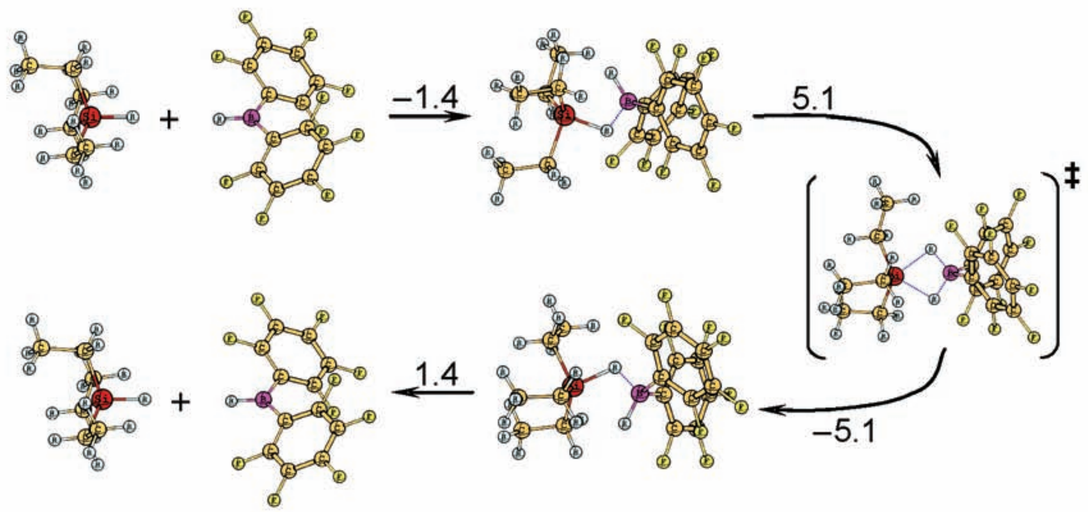
(Figure 2d), that would afford synthetically useful silylboranes.[23] According to calculations, the reaction is energetically uphill ($\Delta G°_{298}$ = +8.6 kcal·mol$^{-1}$) but still has an affordable barrier ($\Delta^{\ddagger}G°_{298}$ = 21.7 kcal·mol$^{-1}$, Table 1). Such a coupling may therefore 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 coupling[24] between benzene and borane (in this example $HB(C_6F_5)_2$) is thermodynamically feasible ($\Delta G°_{298}$ = −3.7 kcal·mol$^{-1}$) but proceeds with a large barrier ($\Delta^{\ddagger}G°_{298}$ = 31.3 kcal·mol$^{-1}$, Table 1). This kinetic hurdle is in agreement with the fact that transition-metal



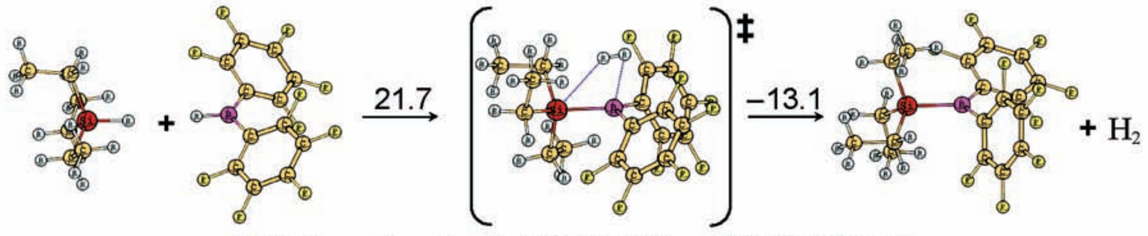
**(a)** $Et_3SiH + B(C_6F_5)_3 \rightleftarrows Et_3SiH{\cdot}B(C_6F_5)_3$ adduct $\rightarrow Et_3Si(C_6F_5) + HB(C_6F_5)_2$



**(b)** $H_2 + HB(C_6F_5)_2 \rightleftarrows H_2 + HB(C_6F_5)_2$ degenerate hydrogen exchange



**(c)** $Et_3SiH + HB(C_6F_5)_2 \rightleftarrows Et_3SiH{\cdot}HB(C_6F_5)_2$ adduct $\rightleftarrows Et_3SiH + HB(C_6F_5)_2$ degenerate silane-borane hydrogen exchange



**(d)** Silylborane formation $Et_3SiH + HB(C_6F_5)_2 \rightarrow (Et_3Si)B(C_6F_5) + H_2$

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

catalysts are needed for dehydrogenative coupling of arenes Ar−H and boranes $HB(OR)_2$ to give arylboranes $Ar{-}B(OR)_2$.[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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## REFERENCES

(1) (a) Eberle, U.; Felderhoff, M.; Schüth, F. *Angew. Chem., Int. Ed.* **2009**, *48*, 6608. (b) Campbell, P. G.; Zakharov, L. N.; Grant, D. J.; Dixon, D. A.; Liu, S.-Y. *J. Am. Chem. Soc.* **2010**, *132*, 3289. (c) Geier, S. J.; Gilbert, T. M.; Stephan, D. W. *J. Am. Chem. Soc.* **2008**, *130*, 12632.

(2) (a) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 8050. (b) Chen, D.; Klankermayer, J. *Chem. Commun.* **2008**, 2130. (c) Li, B.; Xu, Z. *J. Am. Chem. Soc.* **2009**, *131*, 16380. (d) Heiden, Z.; Stephan, D. W. *Chem. Commun.* **2011**, *47*, 5729. (e) Erős, G.; Mehdi, H.; Pápai, I.; Rokob, T. A.; Király, P.; Tárkányi, G.; Soós, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 6559.

(3) Spikes, G. H.; Fettinger, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232.

(4) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439.

(5) Stephan, D. W. *Org. Biol. Chem.* **2008**, *6*, 1535.

(6) (a) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46. (b) Kenward, A. L.; Piers, W. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 38.

(7) (a) Rokob, T. A.; Hamza, A.; Stirling, A.; Pápai, I. *J. Am. Chem. Soc.* **2009**, *131*, 2029. (b) Rokob, T. A.; Hamza, A.; Stirling, A.; Soós, T.; Pápai, I. *Angew. Chem., Int. Ed.* **2008**, *47*, 2435. (c) Grimme, S.; Kruse, H.; Goerigk, L.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 1402.

(8) The Piers group found evidence that activation of $H_2$ by the $PBu^{t}_{3}/B(C_6F_5)_3$ pair can be catalyzed by $Bu^{t}_{3}P(C_6F_4)B(C_6F_5)_2$ formed *in situ*: Marwitz, A. J. V.; Dutton, J. L.; Mercier, L. G.; Piers, W. E. *zJ. Am. Chem. Soc.* **2011**, *133*, 10026.

(9) Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124.

(10) Fan, C.; Mercier, L. G.; Piers, W. E.; Tuononen, H. M.; Parvez, M. *J. Am. Chem. Soc.* **2010**, *132*, 9604.

(11) Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129*, 1880.

(12) Tertiary boranes react with dihydrogen upon thermolysis (160−200 °C) in high-pressure autoclaves (200−300 atm) to give secondary and primary boranes: (a) Köster, R. *Angew. Chem.* **1956**, *68*, 383. (b) Köster, R.; Brüno, G.; Binger, P. *Ann. Chem.* **1962**, *644*, 1.

(13) For an example of high-level calculations, see: Schuurman, M. S.; Allen, W. D.; Schleyer, P. v. R.; Schaefer, H. F. *J. Chem. Phys.* **2005**, *122*, 104302.

(14) Tague, T. J.; Andrews, L. *J. Am. Chem. Soc.* **1994**, *116*, 4970.

(15) $BH_5$ intermediate was also postulated to be formed upon hydrolysis of $BH_4^-$: (a) Mesmer, R. E.; Jolly, W. L. *Inorg. Chem.* **1962**, *1*, 608. (b) Kreevoy, M. M.; J. Hutchins, E. C. *J. Am. Chem. Soc.* **1972**, *94*, 6371. (c) Olah, G. A.; Westerman, P. W.; Mo, Y. K.; Klopman, G. *J. Am. Chem. Soc.* **1972**, *94*, 7859. (d) Davis, R. E.; Bromels, E. B.; Kibby, C. L. *J. Am. Chem. Soc.* **1962**, *84*, 885.

(16) Nageswara Rao, B. D.; Anders, L. R. *Phys. Rev.* **1965**, *140*, A112.

(17) Analogous formation of $SiEt_3^+$ was previously suggested to account for the borane-catalyzed silane/silane exchange and borane-catalyzed hydrosilylation: (a) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090. (b) Berkefeld, A.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2010**, *132*, 10660. (c) Blackwell, J. M.; Morrison, D. J.; Piers, W. E. *Tetrahedron* **2002**, *58*, 8247. (d) For the reaction of hydrogen with silylium ions, see: Schäfer, A.; Reißmann, M.; Schäfer, A.; Saak, W.; Haase, D.; Müller, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 12636.

(18) Lambert, J. B.; Zhang, S.; Stren, C. L.; Huffman, J. C. *Science* **1997**, *275*, 39.

(19) Hoffmann, S. P.; Kato, T.; Tham, F. S.; Reed, C. A. *Chem. Commun.* **2005**, 767.

(20) Parks, D. J.; Piers, W. E.; Yap, G. P. A *Organometallics* **1998**, *17*, 5492.

(21) $\sigma$-Bond metathesis is a well-established mechanism in transition metal chemistry, e.g.: Hartwig, J. *Organotransition Metal Chemistry. From Bonding to Catalysis*; University Science Books: Mill Valley, CA, 2010.

(22) $R_3Si(C_6F_5)$ was observed by $^{19}F$ NMR as another coproduct.

(23) The silylboranes are interesting reagents for making functionalized materials via Si−B bond additions. See, for example: Oshima, K.; Ohmura, T.; Suginome, M. *J. Am. Chem. Soc.* **2011**, *133*, 7324.

(24) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890.

(25) (a) Inverson, C. N.; Smith, M. R. *J. Am. Chem. Soc.* **1999**, *121*, 7696. (b) Cho, J.-Y.; Kin Tse, M.; Holmes, D.; Maleczka, R. E. Jr.; Smith, M. R. III *Science* **2002**, *295*, 305. (c) Chen, H.; Schlecht, S.; Semple, T. C.; Hartwig, J. F. *Science* **2000**, *287*, 1995.

## NOTE ADDED IN PROOF

A similar H/D exchange has been very recently observed by Wang et al. for the system $H_2/DB(2,4,6\text{-}(F_3C)_2C_6H_2)_2$ (Lu, Z.; Cheng, Z.; Chen, Z.; Weng, L.; Li, Z.H.; Wang, H. *Angew. Chem. Int. Ed.* **2011**, *50*, 12227).