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# Metal-free Catalytic Hydrogenolysis of Silyl Triflates and Halides into Hydrosilanes

Gabriel Durin, Albane Fontaine, Jean-Claude Berthet, Emmanuel Nicolas, Pierre Thuéry and Thibault Cantat\*

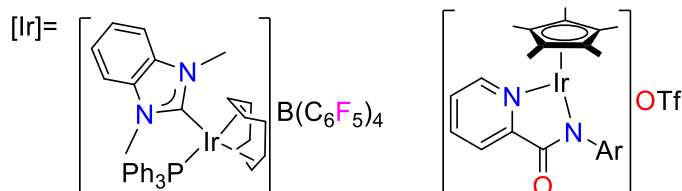
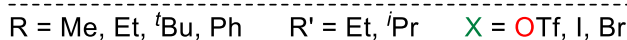
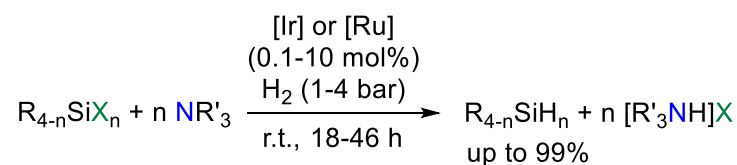
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## Abstract

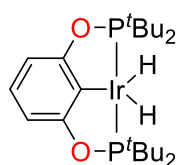
The metal-free catalytic hydrogenolysis of silyl triflates and halides (I, Br) to hydrosilanes is unlocked by using arylborane Lewis acids as catalysts. In the presence of a nitrogen base, the catalyst acts as a Frustrated Lewis Pair (FLP) able to split  $H_2$  and generate a boron hydride intermediate capable of reducing (pseudo)halosilanes. This metal-free organocatalytic system is competitive with metal-based catalysts and enables the formation of a variety of hydrosilanes at r.t. in high yields (>85 %) under a low pressure of  $H_2$  ( $\leq 10$  bar).

## Introduction

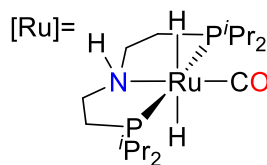
Hydrosilanes are useful compounds for the production of a variety of organosilicon compounds through hydrosilylation of alkenes or dehydrocoupling reactions.<sup>[1]</sup> They also promote, in mild conditions, the reduction of functional groups such as esters<sup>[2]</sup> or amides<sup>[3]</sup> with high selectivity. In comparison with apolar dihydrogen, the more reducing redox couple  $E^0(Si(OEt)_4(l)/SiH_4(g)$  ( $-0.51$  V vs. NHE) and the polarized and weaker Si–H bond ( $BDE_{Si-H} = 95$  kcal.mol<sup>-1</sup> <  $BDE_{H-H} = 104$  kcal.mol<sup>-1</sup>) offer some thermodynamic and kinetic advantages<sup>[4]</sup> relevant for the reduction of oxygenated chemical feedstocks (lignin, plastics and CO<sub>2</sub>) to chemical fuels and value-added products.<sup>[5]</sup> Because classical routes for the production of hydrosilanes are energy demanding,<sup>[1b, 6]</sup> alternative catalytic syntheses that transform Si–X (X = halides, alkoxides) precursors into Si–H groups are appealing. This endeavor has motivated the recent development of catalytic hydrogenolysis routes to hydrosilanes: in the presence of a suitable base, able to facilitate the thermodynamics of the reaction, Si–X bonds (X = OTf, I, Br, Cl) were successfully reduced to Si–H bonds. Yet, the catalysts reported so far by the groups of Shimada, Schneider and Cantat,<sup>[7]</sup> all use catalytic systems based on molecular complexes of noble metals (Ir, Ru) (Scheme 1, top). To improve the sustainability of this reaction and gain fundamental insights into the generation of hydrosilanes, we have sought to unlock the first metal-free catalytic reduction Si–X into Si–H bonds under  $H_2$ . Using boranes as catalysts, hydrosilanes (Me<sub>3</sub>SiH, Et<sub>3</sub>SiH, Ph<sub>3</sub>SiH and <sup>i</sup>Pr<sub>2</sub>SiH<sub>2</sub>) were generated in yields up to 91 %, in the presence of an amine base.



**Shimada 2017-2018**

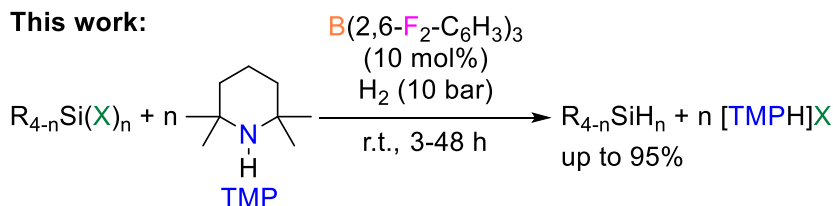


**Cantat 2021**



**Schneider 2018**

**This work:**



**Scheme 1.** Examples of catalytic routes that convert silyl halides and triflates into hydrosilanes with H<sub>2</sub> as hydride source.

Mechanistic investigations derived from the iridium and ruthenium catalyzed hydrogenolysis of Si–X bonds have shown that the generation of a metal hydride from H<sub>2</sub> is key to yield a hydrosilane by hydride transfer to the silicon atom.<sup>[7c-e]</sup> To perform this transformation without a metal, we have sought to use borohydrides as hydrogen transfer reagents. Indeed, borohydrides are known to convert halosilanes into hydrosilanes, as reported by the groups of Klejnot or Nakazawa for instance, who highlighted the stoichiometric reduction of chlorosilanes into hydrosilanes with lithium or sodium borohydride.<sup>[8]</sup> Moreover, borohydride species can be generated from H<sub>2</sub> using Frustrated Lewis Pairs (FLP) chemistry as demonstrated by Stephan and others if an appropriate Lewis base is present.<sup>[9]</sup> The catalytic hydrogenation of organic functionalities using FLPs has been reported for alkynes,<sup>[10]</sup> alkenes,<sup>[11]</sup> ketones,<sup>[12]</sup> silyl enol ethers,<sup>[13]</sup> anilines,<sup>[14]</sup> imines,<sup>[15]</sup> enamines,<sup>[16]</sup> amides,<sup>[17]</sup> aza-Morita–Baylis–Hillman adducts,<sup>[18]</sup> esters,<sup>[19]</sup> and recently for the hydrodehalogenation of benzylhalides.<sup>[20]</sup> In the case of silyl halides and pseudohalides, the presence of a stoichiometric quantity of a nitrogen base is necessary since the reaction is otherwise endergonic.<sup>[7c-e]</sup> Interestingly, the group of Rieger reported the cleavage of H<sub>2</sub> with B/N Frustrated Lewis Pairs (amines and perfluorinated triarylboranes).<sup>[21]</sup> The group of O'Hare later demonstrated that the generated borohydride is capable of reducing CO<sub>2</sub>.<sup>[22]</sup> This result prompted us to consider aryl boranes as catalysts for

the hydrogenolysis of Si–X into Si–H bonds, together with a stoichiometric amount of nitrogen bases, effectively forming an FLP system in solution.

Using B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (10 mol%) and TMP (2,2,6,6-tetramethylpiperidine) (1.1 equiv.), only traces of Me<sub>3</sub>SiH were obtained from Me<sub>3</sub>SiOTf under 10 bar of H<sub>2</sub> at r.t. in CD<sub>2</sub>Cl<sub>2</sub> (Table 1, entry 1). The reactivity of a variety of boranes, *i.e.* BPh<sub>3</sub>, B(4-F-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, B(2-F-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, B(2,6-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> and HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> with distinct Lewis acidities<sup>[23]</sup> was thus evaluated. The catalytic performance increased slightly with Piers borane<sup>[24]</sup> HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> which afforded 21 % NMR yield of Me<sub>3</sub>SiH (Table 1, entry 2). In contrast, B(2,6-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> and B(2-F-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub> proved to be significantly more reactive, affording Me<sub>3</sub>SiH in excellent yields (88 and 85 % respectively) (Table 1, entries 3 and 4). Compounds BPh<sub>3</sub> and its *para*-F analogue, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, displayed a low efficiency with a poor Me<sub>3</sub>SiH yield of 4 % (Table 1, entries 5 and 6). With the most reactive FLP system, *i.e.* the TMP/ B(2,6-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (Table 1, entry 4), a reduction in the yield of Me<sub>3</sub>SiH was observed either by decreasing the H<sub>2</sub> pressure from 10 to 5 bar (88 to 66 % yield, see ESI Section 2.1.6) or the borane catalyst loading from 10 to 5 mol% (67 % yield, see ESI Section 2.1.7). These results represent the first examples of the metal-free hydrogenolysis of (pseudo)halosilanes.

**Table 1.** Screening of borane catalysts for the hydrogenolysis of Me<sub>3</sub>SiOTf.<sup>[a]</sup>

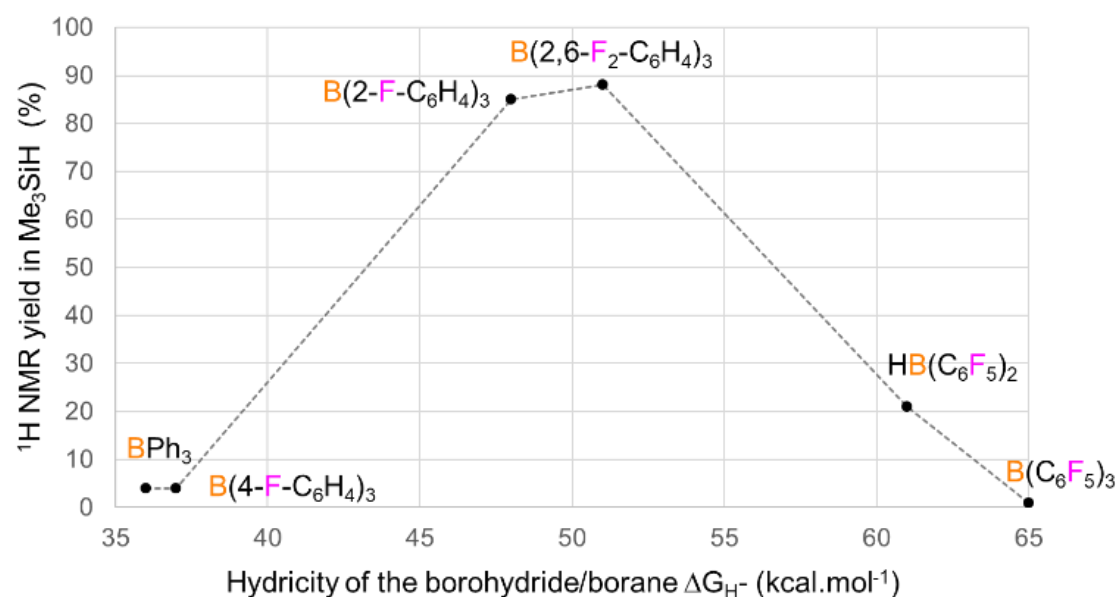
$$\text{Me}_3\text{SiOTf} + \text{TMP} \xrightarrow[\text{CD}_2\text{Cl}_2, \text{ r.t., 24 h}]{\text{cat. (10 mol\%)} \atop \text{H}_2 \text{ (10 bar)}} \text{Me}_3\text{SiH} + [\text{TMPH}]\text{OTf}$$

Entry	Borane	Computed hydricity <sup>[25]</sup> [kcal.mol <sup>-1</sup> ]	Conv. <sup>[b]</sup> [%]	Yield (Select.) <sup>[b]</sup> [%]
1	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	65	<1	traces
2	HB(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	61	21	21 (99)
3	B(2,6-F <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> ) <sub>3</sub>	51	95	88 (92)
4	B(2-F-C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	48 <sup>[c]</sup>	96	85 (88)
5	B(4-F-C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	37	4	4 (99)
6	BPh <sub>3</sub>	36	5	4 (80)

<sup>[a]</sup> General conditions: Me<sub>3</sub>SiOTf (0.1 mmol), TMP (0.11 mmol), borane (10 μmol), CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL), H<sub>2</sub> (10 bar), 25 °C. <sup>[b]</sup>Conversions, selectivities, and yields were determined through integration of the Me<sub>3</sub>Si– signals by <sup>1</sup>H NMR versus an internal standard (1,3,5-trimethylbenzene). <sup>[c]</sup>This value was calculated for this work.

The NMR yields of Me<sub>3</sub>SiH were plotted against the hydricity of the different borane catalysts, which corresponds to the energy required to release a hydride ion H<sup>–</sup> from a putative borohydride [R<sub>3</sub>BH]<sup>–</sup> (Figure 1). B–H hydricity values can be obtained from the hydricity scale computed by Heiden *et al.* for main group hydrides;<sup>[25]</sup> they quantify the stability of the borohydrides and assist in the evaluation of their reducing power. Figure 1 highlights a volcano-type distribution similar to those resulting from the Sabatier principle for heterogeneous catalysts.<sup>[26]</sup> It reveals that borohydrides having the lowest hydricities, such as [HBPh<sub>3</sub>]<sup>–</sup> (36 kcal.mol<sup>-1</sup>), or the highest, such as [H<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>–</sup> and [HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>–</sup> (61 and 65 kcal.mol<sup>-1</sup>), afford poor yields in hydrosilane. This plot reveals that a balance must be achieved for an

efficient catalytic turnover, where the borane is acidic enough to yield a borohydride from the activation of H<sub>2</sub>, yet still able to transfer a hydride ligand to silicon in a subsequent step.



**Figure 1.** Volcano plot with NMR yield, obtained from Table 2, plotted against the hydricity<sup>[25]</sup> of the different arylborane catalysts.

**Table 2.** Screening of bases for the hydrogenolysis of Me<sub>3</sub>SiOTf in CD<sub>2</sub>Cl<sub>2</sub>.<sup>[a]</sup>

$$\text{Me}_3\text{SiOTf} + \text{Base} \xrightarrow[\text{CD}_2\text{Cl}_2, \text{ r.t., 24 h}]{\text{B(2,6-F}_2\text{-C}_6\text{H}_3)_3 \text{ (10 mol\%)} \\ \text{H}_2 \text{ (10 bar)}} \text{Me}_3\text{SiH} + [\text{HBase}]\text{OTf}$$

Entry	Base	pKa <sup>[b]</sup>	Conv. <sup>[c]</sup> [%]	Yield (Select.) <sup>[c]</sup> [%]
1	2,6-lutidine	14.1	22	15 (68)
2	<i>i</i> Pr <sub>2</sub> NEt	18.1	48	18 (38)
3	NEt <sub>3</sub>	18.8	82	55 (67)
4	TMP	18.6	95	88 (92)
5	PMP	18.2	39	24 (62)

<sup>[a]</sup> General conditions: Me<sub>3</sub>SiOTf (0.1 mmol), base (0.11 mmol), B(2,6-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (10 μmol), CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL), H<sub>2</sub> (10 bar), 25 °C <sup>[b]</sup>pKa in MeCN. <sup>[27]</sup> <sup>[c]</sup>Conversions, selectivities, and yields were determined by <sup>1</sup>H NMR spectroscopy, through integration of the Me<sub>3</sub>Si signals versus an internal standard (1,3,5-trimethylbenzene).

The role of the nitrogen base was then evaluated by considering a variety of classical and sterically congested amines,<sup>[22, 28]</sup> *i.e.* 2,6-lutidine, trialkylamines NEt<sub>3</sub> and *i*Pr<sub>2</sub>NEt, and piperidines (TMP and PMP = 1,2,2,6,6-pentamethylpiperidine) using the conditions depicted in Table 2. With 2,6-lutidine, the reaction led to the formation of Me<sub>3</sub>SiH in 15 % yield after 24 h at r.t. (Table 2, entry 1).<sup>[29]</sup> Replacing 2,6-lutidine with trialkylamines NEt<sub>3</sub> or *i*Pr<sub>2</sub>NEt increased the yield in Me<sub>3</sub>SiH (18 and 55 %, respectively) (Table 2, entries 2 and 3). This yield reached 88 % with the bulky piperidine TMP (Table 2, entry 4 or Table 1, entry 3) but dropped to 24 % with the N-methylated derivative of TMP (1,2,2,6,6-pentamethylpiperidine, PMP), thus underlining a possible influence of the NH group (Table 2, entry 5). A plausible explanation for such a behavior might be the presence of hydrogen bonding N–H•••F interactions between

the secondary amine and the fluorine atoms on the triarylborane, reminiscent of the adduct described by Bourissou *et al.*,<sup>[30]</sup> which pre-organizes the FLP for a more efficient activation of H<sub>2</sub> and overall, a more favorable catalytic process.<sup>[31]</sup>

The most productive bases have a pK<sub>a</sub> greater than 18, while 2,6-lutidine (pK<sub>a</sub> = 14) afforded the lowest yield in Me<sub>3</sub>SiH. Nonetheless, as noted previously with transition metal catalysts,<sup>[7d]</sup> the Brønsted basicity is not the sole parameter influencing the reactivity of the nitrogen base: NEt<sub>3</sub> and <sup>i</sup>Pr<sub>2</sub>NEt are readily trapped by Me<sub>3</sub>SiOTf to form the silylated ammonium salts [R<sub>3</sub>NSiMe<sub>3</sub>][OTf], which has a decreased reactivity compared to the free silyl triflate. These silylated ammonium salts were, in contrast, not observed with the piperidines for which the hydrogenolysis proceeded in CD<sub>2</sub>Cl<sub>2</sub> with gradual precipitation of the insoluble [TMPH][OTf] or partially soluble [PMPH][OTf] salts (Table 2, entries 4 and 5). When performed with stirring, the reaction proved to be faster in benzene than in dichloromethane, reaching a maximum yield of 91 % after 3 h instead of 24 h using the TMP/B(2,6-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> pair (ESI, Section 2.1.5).

The generality of this catalytic system using these optimized conditions was evaluated with a series of silyl triflates and halides (Table 3). Similar to Me<sub>3</sub>SiOTf, Et<sub>3</sub>SiOTf was almost fully converted into Et<sub>3</sub>SiH (90 % yield) with excellent selectivity within 3 h (Table 3, entries 1 and 2). Formation of the bulky Ph<sub>3</sub>SiH was much slower and required 48 h to reach 88 % yield from Ph<sub>3</sub>SiOTf (Table 3, entry 3). The double hydrogenolysis of the bis triflate <sup>i</sup>Pr<sub>2</sub>Si(OTf)<sub>2</sub> was twice as fast as the hydrogenolysis of Ph<sub>3</sub>SiOTf and provided <sup>i</sup>Pr<sub>2</sub>SiH<sub>2</sub> in 86 % yield (Table 3, entry 4). Attempts to synthesize <sup>i</sup>Pr<sub>2</sub>SiH(OTf) by using only 1.1 equivalent of TMP afforded <sup>i</sup>Pr<sub>2</sub>SiH<sub>2</sub> as the major product (41 %) with low yields of the desired <sup>i</sup>Pr<sub>2</sub>SiH(OTf) (9 %) (Table 3, entry 5). Compared to Me<sub>3</sub>SiOTf, the reduction of Me<sub>3</sub>SiI and Me<sub>3</sub>SiBr was slower requiring 7 h and 16 h to reach 88 % and 71 % yields in Me<sub>3</sub>SiH, respectively (Table 3, entries 6-7). Finally, only traces of hydrosilane could be detected in the hydrogenolysis of Me<sub>3</sub>SiCl (Table 3, entry 8). These findings are consistent with the trends obtained using organometallic catalysts for the hydrogenolysis of (pseudo)halosilanes, pointing to a more difficult cleavage of the Si-Cl bond.<sup>[7c, 7e]</sup>

The hydrogenolysis of (pseudo)halosilanes is somewhat more efficient using the borane catalyst compared to the known Ir and Ru catalysts, which require prolonged reaction times and higher temperatures. For example, Me<sub>3</sub>SiH was obtained in 11 % yield from Me<sub>3</sub>SiBr using an iridium amido catalyst and <sup>i</sup>Pr<sub>2</sub>NEt after 48 h at 60 °C.<sup>[7a]</sup> In the case of Ru(II) bearing a cooperative ligand, improved performances are reported: Me<sub>3</sub>SiH was obtained in 85 % yield from Me<sub>3</sub>SiOTf after 18 h at r.t., with only 1 mol% catalyst loading. These results are close to the 91 % yield obtained after 3 h with 10 mol% loading for our borane-catalyzed reaction (Table 3, entry 1).

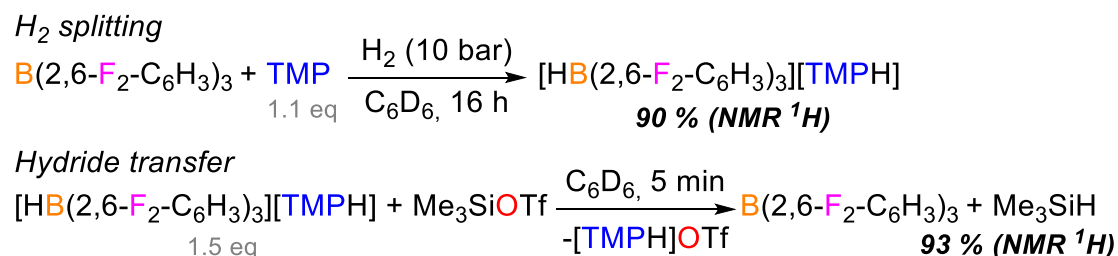
To gain insights into the mechanism of the reaction, stoichiometric experiments have been conducted (Scheme 2). In line with the findings of Paradies *et al.*,<sup>[32]</sup> [HB(2,6-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>][TMPH] could be generated in 90 % yield by reacting B(2,6-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> and TMP (1.1 equiv.) under 10 bar of H<sub>2</sub> at r.t. in C<sub>6</sub>D<sub>6</sub>. Addition of Me<sub>3</sub>SiOTf to this solution yielded Me<sub>3</sub>SiH (93 % yield) within 5 minutes at r.t., together with B(2,6-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> and a white deposit of [TMPH][OTf].

Table 3. Scope of the reaction.<sup>[a]</sup>

$$\text{R}_{4-n}\text{SiX}_n + \text{TMP} \xrightarrow[\text{C}_6\text{D}_6, \text{ r.t.}]{\text{B(2,6-F}_2\text{-C}_6\text{H}_3)_3 \text{ (10 mol\%)} \\ \text{H}_2 \text{ (10 bar)}} \text{R}_{4-n}\text{SiH}_n\text{X}_{n-1} + [\text{TMPH}]\text{X}$$

Entry	Reagent R <sub>4-n</sub> SiX <sub>n</sub>	Product R <sub>4-n</sub> SiH <sub>n</sub> X <sub>n-1</sub>	Reaction time [h]	Conv. <sup>[b]</sup> [%]	Yield (Select.) <sup>[b]</sup> [%]
1	Me <sub>3</sub> SiOTf	Me <sub>3</sub> SiH	3	96	91 (95)
2	Et <sub>3</sub> SiOTf	Et <sub>3</sub> SiH	3	93	90 (97)
3	Ph <sub>3</sub> SiOTf	Ph <sub>3</sub> SiH	48	89	88 (99)
4 <sup>[c,d]</sup>	<i>i</i> Pr <sub>2</sub> Si(OTf) <sub>2</sub>	<i>i</i> Pr <sub>2</sub> SiH <sub>2</sub>	24	94	86 (91)
		<i>i</i> Pr <sub>2</sub> SiH <sub>2</sub>			41 (68)
5 <sup>[d]</sup>	<i>i</i> Pr <sub>2</sub> Si(OTf) <sub>2</sub>	<i>i</i> Pr <sub>2</sub> SiHOTf	24	60	9 (15)
6	Me <sub>3</sub> SiI	Me <sub>3</sub> SiH	7	89	88 (99)
7	Me <sub>3</sub> SiBr	Me <sub>3</sub> SiH	16	87	71 (82)
8	Me <sub>3</sub> SiCl	Me <sub>3</sub> SiH	48	<1	traces

<sup>[a]</sup> General conditions: R<sub>4-n</sub>SiX<sub>n</sub> (0.1 mmol), TMP (0.11 mmol), B(2,6-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (10 μmol), C<sub>6</sub>D<sub>6</sub> (0.5 mL), H<sub>2</sub> (10 bar), 25 °C <sup>[b]</sup> Conversions, selectivities, and yields were determined by <sup>1</sup>H NMR spectroscopy, through integration of the R<sub>4-n</sub>Si signals versus the internal standard 1,3,5-trimethylbenzene. <sup>[c]</sup> 0.22 mmol of TMP was used. <sup>[d]</sup> In CD<sub>2</sub>Cl<sub>2</sub>.

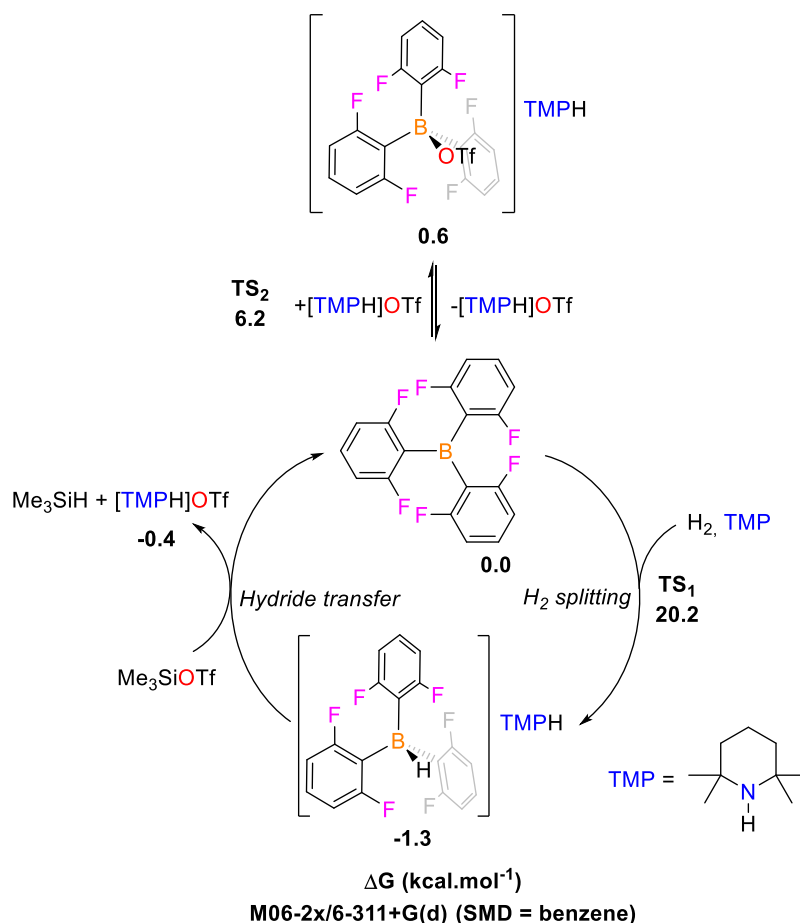


**Scheme 2.** Stoichiometric experiment for the H<sub>2</sub> splitting by the FLP B(2,6-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>/TMP and further hydride transfer into Me<sub>3</sub>SiOTf.

These two reactions suggest a mechanism in two steps depicted in Scheme 3, which is supported by DFT calculations at the M06-2X/6-311+G(d) level of theory (using the SMD model to account for the solvation effects due to benzene). The activation of H<sub>2</sub> is exergonic (ΔG = − 1.3 kcal.mol<sup>−1</sup>) and proceeds *via* transition state TS<sub>1</sub> (ΔG<sup>‡</sup> = 20.2 kcal.mol<sup>−1</sup>) to yield the ion pair [HB(2,6-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>][TMPH]. This complex transfers its hydride in a barrierless endergonic step (ΔG = + 1.3 kcal.mol<sup>−1</sup>), affording Me<sub>3</sub>SiH, free borane B(2,6-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>, and the salt [TMPH][OTf] as by-product. Since boranes are strong oxophiles, the triflate salt is able to coordinate to the free borane, to form the off-cycle adduct [(TfO)B(2,6-F<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>]<sup>−</sup> (ΔG = + 0.6 kcal.mol<sup>−1</sup>). This equilibrium might in turn slow down the catalysis, due to quenching of the vacant site of the Lewis acid catalyst.

Overall, the rate determining step is the splitting of H<sub>2</sub> with an energetic span of 20.2 kcal.mol<sup>−1</sup> (TS<sub>1</sub>) consistent with the catalytic experimental conditions (10 bar H<sub>2</sub>, r.t., 3 h for full

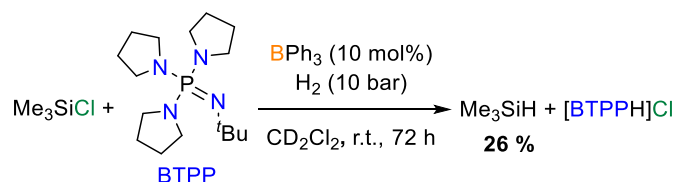
completion at 10 mol% catalytic loading). A kinetic study based on the time-scale normalization method described by Burés<sup>[33]</sup> was performed and revealed a partial order of 1 for the base and 0 for the silyl triflate (see ESI, section 2.3). Such values are in agreement with the DFT calculations and the experiments. A complex order (ca. 0.1) for the borane was also found which shows the detrimental influence of the interaction between  $B(2,6-F_2-C_6H_3)_3$  and  $TfO^-$ .



**Scheme 3.** Computed mechanism for the hydrogenolysis of  $Me_3SiOTf$  with the FLP ( $TMP/B(2,6-F_2-C_6H_3)_3$ ) (M06-2X/6-311+G(d) level of theory, solvent (benzene) effects are taken into account with SMD).

Capitalizing on this mechanistic knowledge, we next targeted the hydrogenolysis of chlorosilanes, an appealing yet challenging class of substrates.<sup>[7]</sup> Regardless of the nature of the base,  $B(2,6-F_2-C_6H_3)_3$  proved unproductive in the conversion of  $Me_3SiCl$  to  $Me_3SiH$ . Nonetheless, as  $Me_3SiCl$  has a lower reactivity than  $Me_3SiOTf$ , we have considered a mildly acidic borane ( $BPh_3$ ) in the presence of the strong phosphazene base BTPP (*tert*-butylimino-tri(pyrrolidino)phosphorane) to split  $H_2$  and generate a highly reactive borohydride (hydricity of 36 kcal.mol<sup>-1</sup>)<sup>[25]</sup> (Scheme 4). When that particular combination was used, 28 % of  $Me_3SiCl$  was converted after 72 h, forming  $Me_3SiH$  in 26 % yield. To try to improve this reaction, chloride abstractors were added to the reaction mixture.<sup>[7b, 7c]</sup> While NaI and Na[BPh<sub>4</sub>] did not show any influence (25 and 26 % yield respectively), the addition of NaOTf had a positive effect on the reaction yield, and  $Me_3SiH$  was formed in 52 % yield after 72 h. This particular reaction will be further studied and optimized.





**Scheme 4.** Hydrogenolysis of  $\text{Me}_3\text{SiCl}$  with the phosphazene BTTP and  $\text{BPh}_3$ .

In summary, we have developed an unprecedented transition metal free catalytic route for the hydrogenolysis of silyl triflates and halides (I, Br), using di- and triarylboranes as catalysts. A delicate balance of the Lewis acidity of the borane catalyst is essential for efficient catalysis. In the presence of the base, the catalyst acts as a B/N FLP and the combination of  $\text{B}(2,6\text{-F}_2\text{-C}_6\text{H}_3)_3$  and TMP proved the most efficient to afford hydrosilanes in high yields at room temperature and under a low pressure (10 bar  $\text{H}_2$ ). Experimental reactions, kinetic data and theoretical calculations support a two-step mechanism with the rate-determining step being the heterolytic splitting of  $\text{H}_2$ . This result paves the way for new catalytic systems for the sustainable synthesis of hydrosilanes, a necessary step towards a closed silicon cycle.

## Conflict of interest

The authors declare no conflict of interest.

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