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Direct and Transfer Hydrosilylation Reactions Catalyzed by Fully or Partially Fluorinated Triarylboranes: A Systematic Study

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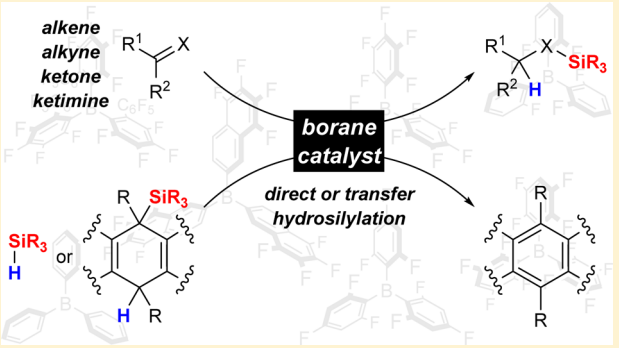
Supporting Information

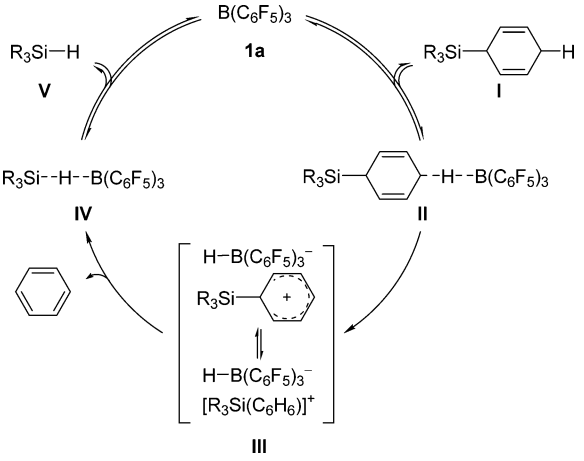
ABSTRACT: The present survey serves several purposes. Selected electron-deficient boron Lewis acids catalyze the release of hydrosilanes from cyclohexa-2,5-dien-1-yl-substituted silanes. The two-step process consists of a hydride abstraction to generate a silicon-stabilized Wheland complex and capture of the arene-stabilized silicon cation by the borohydride formed in the previous step. The same boron catalyst will then activate the Si–H bond for the reaction with representative π- and σ-donating substrates, alkenes/alkynes and ketones/ketimines, respectively. The net transformation is a transfer hydrosilylation, and the effect that the substitution pattern of the cyclohexa-1,4-diene core and the subsituents at the silicon atom exert on these hydrosilane surrogates is systematically investigated. The results are compared with those obtained employing the hydrosilane directly. Another part of this comprehensive analysis is dedicated to the comparison of literature-known fully or partially fluorinated triarylboranes in both the direct and the transfer hydrosilylation of the aforementioned substrates. The data are tabulated and color-coded, finally providing an overview of promising substrate/reductant/borane combinations. The often different reactivities of π- and σ-basic substrates are explained, and it is shown that the Lewis acidity of the boron atom, estimated by the Gutmann–Beckett method, is not the only decisive feature of these boron Lewis acids. Practical mechanistic models are presented to rationalize the interplay between the Lewis acidity and steric situation at the boron and, likewise, the silicon atom as well as the need for fluorination *ortho* to the boron atom in certain cases.



INTRODUCTION

Piers and co-workers demonstrated the ability of the strong Lewis acid tris(pentafluorophenyl)borane [$B(C_6F_5)_3$, **1a**][1,2] to activate Si–H bonds,[3] thereby promoting hydrosilylation of C=O[4] and C=N[5] motifs in catalytic fashion.[6] Historically known as potent polymerization cocatalysts,[7] C_6F_5-substituted boron Lewis acids have lately emerged as key components of frustrated Lewis pairs (FLPs) in the activation of small molecules.[8] Over the past few years, we have been involved in the Si–H bond activation chemistry of fluorinated boranes,[9] and we contributed to the understanding of the mechanisms of C=O[10] as well as C=N[11] hydrosilylation. More recently, we established an efficient protocol for the unprecedented ionic transfer hydrosilylation of alkenes using cyclohexa-2,5-dien-1-ylsilanes **I** as surrogates of otherwise gaseous, highly flammable, and potentially explosive hydrosilanes **V** such as Me_3SiH and Me_2SiH_2.[12] Catalytic in situ release of **V** from **I** is triggered by hydride abstraction from the bisallylic methylene group in **I** by $B(C_6F_5)_3$ (**1a**),[13] eventually forming hydrosilane **V** along with one molecule of benzene as a stoichiometric byproduct (Scheme 1). The process was recently shown to pass through a silicon-stabilized Wheland complex and/or benzene-stabilized silicon cation **III**.[14] The liberated hydrosilane **V** is then further activated by the same Lewis acid, and we have been able to

Scheme 1. Si–H Bond Activation with $B(C_6F_5)_3$ (Counterclockwise) and $B(C_6F_5)_3$-Catalyzed Release of Hydrosilanes from Cyclohexa-2,5-dien-1-ylsilanes (Clockwise)



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merge this new approach with $B(C_6F_5)_3$-catalyzed alkene hydrosilylation[12,15] and dehydrogenative Si−O coupling.[16,17]

The successful release of hydrosilanes from the unsubstituted cyclohexa-1,4-diene core (**I** → **V**) leads us now to gauge the factors that govern this transformation. Key questions are (1) how substitution at the cyclohexa-1,4-diene effects the hydride abstraction and the stabilization of the Wheland intermediate and (2) what degree of Lewis acidity of the electron-deficient borane is required in that hydride abstraction step. Extension of the silyl group scope from $R_{3-n}H_nSi$ (n = 0 and 1) to functionalized $Y_{3-n}R_nSi$ (n = 0 and 2) is another pivotal aspect. The choice of the boron Lewis acid would also be relevant in the subsequent Si−H bond activation step **IV**, and we realized at the outset of this project that there had not been a systematic study of fully and partially fluorinated boron-based catalysts in hydrosilylation reactions yet.[18] However, our investigation would only be meaningful with knowledge of the Lewis acid's ability to activate either the C−H bond in **I**, the Si−H bond in **V**, or both. Accordingly, our study also includes a systematic screening of representative $B(C_6F_5)_3$ congeners in the hydrosilylation of typical functional groups (C═C, C≡C, C═O, and C═N). The same substrates are then tested in the related transfer hydrosilylation processes. The net result is a useful roadmap to the identification of the optimal substrate/reductant/catalyst combination for direct and transfer hydrosilylation catalyzed by electron-deficient boranes.

RESULTS AND DISCUSSION

Variation of the Cyclohexa-1,4-diene Core. We prepared various cyclohexa-2,5-dien-1-ylsilane analogues with diverse substitution patterns as precursors for Me_3SiH (**2a**−**2f**, Figure 1). The intermediacy of Wheland complex **III** during the

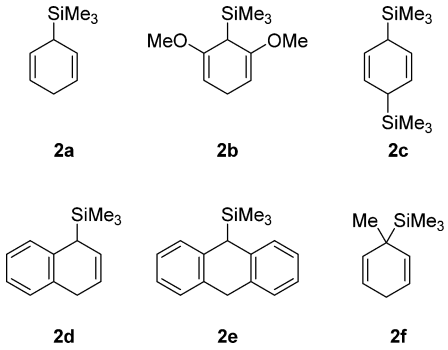
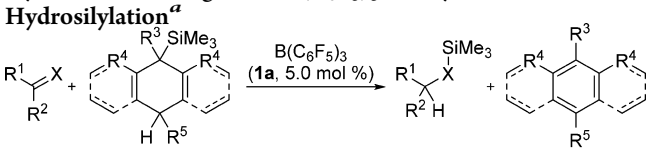


Figure 1. Variation of the substitution pattern at the cyclohexa-1,4-diene core.

release of hydrosilane **V** from surrogate **I** (Scheme 1, clockwise) suggests that substituents lending stabilization to **III** facilitate hydride abstraction (**I** → **III**) but will, in turn, negate the energy gained from rearomatization (**III** → benzene). These effects work in opposite directions, and surrogate **2b** with +M substituents in positions 2 and 6 will be particularly illustrative. Surrogate **2c** with another electropositive Me_3Si entity in position 4 combines stabilization by an additional β-silicon effect with steric congestion around the C−H bond. Annulation of benzene rings as in **2d** and **2e** extends the π system, lowering the energy of the Wheland complex even further. We were also interested in the effect of substitution *ipso* to the departing silicon group as in **2f**.

Table 1. Variation of the Cyclohexa-1,4-diene Core of the Hydrosilane Surrogate in $B(C_6F_5)_3$-Catalyzed Transfer Hydrosilylation[a]



4–7 2

Si–H \ Nu	Ph, Ph (4)	Ph, Ph (5)	Ph, O, Me (6)	Ph, N, Ph, Me (7)[b]
2a	98% r.t. 5 h●	96% r.t. 5 h●	64%[c] 90 °C 90 min●	93% 80 °C 3 h●
2b	0%[d] r.t. 5 min●	0%[d] r.t. 5 min●	quant.[e] r.t. 5 min●	93% r.t. 6 h●
2c	17%[e] r.t. 48 h●	24%[e] r.t. 48 h●	28%[e,f] 110 °C 24 h●	7%[e] 110 °C 48 h●
2d	91% r.t. 40 h●	83% r.t. 40 h●	25%[e,f] 90 °C 24 h●	32%[e] 80 °C 72 h●
2e	10%[e] 110 °C 38 h●	0% 110 °C 38 h●	0% 110 °C 48 h●	0% 110 °C 48 h●
2f	89%[e] r.t. 40 h●	88%[e] r.t. 40 h●	57%[e,f] 90 °C 24 h●	95% 80 °C 6 h●
Et_3SiH	87% 80 °C 8 h●	90% 80 °C 8 h●	93%[g] r.t. 3 h●	94% 80 °C 3 h●

[a]All reactions were performed in CH_2Cl_2 (at room temperature) or benzene (at elevated temperatures) at a substrate concentration of 1.0 M according to the general procedures (see the Experimental Section for details). Unless otherwise noted, isolated yields are given. Green dots denote hydrosilylation of substrate; yellow dots denote consumption of surrogate but no conversion of substrate; red dots denote no consumption of surrogate and substrate. [b]Yields after hydrolysis. [c]Full conversion of ketone **6** observed; diminished yield due to volatility of the silyl ether. [d]Full consumption of the surrogate observed. [e]Conversion of the substrate determined by GLC analysis using mesitylene as internal standard. [f]Formation of styrene observed as a result of the instability of the silyl ether. [g]Toluene used as solvent.

To obtain a comprehensive overview, we tested four typical substrates of different nucleophilicity (**4**−**7**, Table 1, columns 1−4).[19] As a reference, we performed these hydrosilylations directly with Et_3SiH (row 7), and reaction times and isolated yields are compared with unsubstituted surrogate **2a** (row 1). For transfer hydrosilylation of σ donors **6** and **7** elevated temperatures were required when using **2a** as silane source (row 1, columns 3 and 4), whereas π donors **4** or **5** reacted smoothly at room temperature (row 1, columns 1 and 2). We attribute this behavior to the formation of stronger Lewis acid−base adducts between **6**/**7** and **1a** compared to **4**/**5**, thereby deactivating the catalyst.

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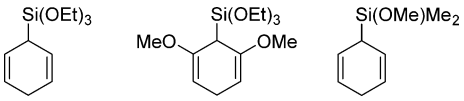
As expected, the substituent effects were indeed dramatic. Due to higher hydricity, MeO-substituted **2b** reacted readily at room temperature, and the transfer hydrosilylation of ketone **6** or ketimine **7** afforded the products in excellent yields (row 2, columns 3 and 4). Conversely, the reaction with alkene **4** and alkyne **5** was plagued with demethylation of **2b**,[20] and no hydrosilylation was seen (row 2, columns 1 and 2). These results nicely showcase the importance of the Lewis basicity, i.e., nucleophilicity, of the substrate; σ donors such as **6** and **7** and likewise the ether groups in **2b** outcompete π donors such as **4** and **5**. Surrogate **2c**, with the sterically shielded C−H bond, reacted poorly, independent of the substrate (row 3).

The effect of additional delocalization in the Wheland intermediate was demonstrated with benzannulated **2d** and **2e**. With 1,4-dihydronaphthalene-derived **2d**, transfer hydrosilylation worked in all cases (row 4), albeit significantly slower than with **2a** (row 1). Doubly benzannulated **2a** (= **2e**) did not participate in the transfer hydrosilylation (row 5), even at elevated temperature (110 °C); trace amounts of alkene hydrosilylation were obtained (row 5, column 1). These observations corroborate the notion that liberation of the silicon cation from those stabilized Wheland intermediates, i.e., rearomatization, is less favored. Finally, *ipso* substitution as in **2f** makes the surrogate less reactive than **2a** (row 6 vs row 1). However, the $B(C_6F_5)_3$-catalyzed degradation of **2f** produces toluene rather than benzene (from **2a**) and that might be viewed as an advantage.

Surrogates with Alkoxy-Substituted Silyl Groups. We were also interested in replacing alkoxy-substituted hydrosilanes, e.g., $(EtO)_3SiH$ and $(MeO)Me_2SiH$, with their corresponding surrogates to avoid handling these acutely toxic chemicals (**3a**−**3c**, Figure 2).

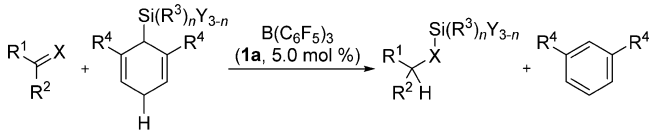


3a **3b** **3c**

Figure 2. Surrogates of alkoxy-substituted hydrosilanes.

The results of transfer hydrosilylations of the four typical substrate classes (Table 2, rows 1−3) were again compared with those obtained from the $B(C_6F_5)_3$-catalyzed hydrosilylation directly using $(EtO)_3SiH$ (row 4). Owing to their weak nucleophilicity, π-basic **4** and **5** did not undergo hydrosilylation, neither with **3a**−**3c** nor with $(EtO)_3SiH$ (columns 1 and 2). Decomposition of the cyclohexa-2,5-dien-1-ylsilanes **3a** and **3c** as well as partial demethylation of the methyl ether groups in **3b** was detected by ^{1}H NMR analysis. The sensitivity of alkoxy groups toward $B(C_6F_5)_3$ was further verified by treating $(EtO)_3SiH$ with a catalytic amount of **1a**; the reaction mixture turns into a gel within 5 min accompanied by vigorous gas evolution, presumably forming silicones along with ethane.[21] Conversely, the σ-donating substrates, ketone **8** as well as ketimine **7**, were cleanly converted into the silicate/alcohol and amine, respectively, not only with $(EtO)_3SiH$ but also with **3a** and **3c** (columns 3 and 4).[22] We were disappointed to find that, in contrast to Me_3Si-substituted derivative **2b**, **3b** did not act as a transfer reagent; just trace amounts of the reduced acceptors were detected at full conversion of surrogate **3b**.

Table 2. Transfer Hydrosilylation Using Surrogates with Alkoxy Groups at the Silicon Atom[a]



4–8 **3**

Si–H \ Nu	Ph, Ph (4)	Ph, Ph (5)	R, O, R' (6 or 8)	Ph, N, Me, Ph (7[b])
3a	0%[c,d] r.t. 5 min●	0%[c,d] r.t. 5 min●	80%[e] 80 °C 20 h●	81%[f] 80 °C 24 h●
3b	0%[c] 80 °C 3 h●	0%[c] 80 °C 3 h●	traces[c,e,g] r.t. 5 h●	traces[c] 80 °C 24 h●
3c	0%[c,d] r.t. 1.5 h●	0%[c,d] r.t. 1.5 h●	89%[e,h] 80 °C 20 h●	87% 80 °C 6 h●
$(EtO)_3SiH$	0%[d] r.t. 5 min●	0%[d] r.t. 5 min●	95%[e,g]/85%[i,j] r.t. 2 h/3 h●	64%[f,j] r.t. 90 min●

[a]All reactions were performed in CH_2Cl_2 (at room temperature) or benzene (at elevated temperatures) at a substrate concentration of 1.0 M according to the general procedures (see the Experimental Section for details). Unless otherwise noted, isolated yields are given. Green dots denote hydrosilylation of substrate; yellow dots denote consumption of surrogate but no conversion of substrate. [b]Yields after hydrolysis. [c]Full consumption of the surrogate observed. [d]Decomposition of the surrogate/silane monitored by ^{1}H NMR spectroscopy. [e]Cyclododecanone (**8**) used as the carbonyl compound. [f]Conversion of the substrate determined by GLC analysis using mesitylene as internal standard. Conversion was incomplete, and ^{1}H NMR measurements showed that not only unreacted **7** and the expected *N*-silylated amine are present but also the *N*-silylated enamine and the free amine.[11] [g]Benzene used as solvent. [h]Isolation of the corresponding alcohol. [i]Acetophenone (**6**) used as the carbonyl compound. [j]Toluene used as solvent.

Influence of the Boron Lewis Acid Catalyst. The Lewis acidity of the borane catalyst is another parameter that will influence both the hydride abstraction from cyclohexa-2,5-dien-1-ylsilanes (**I** → **III**) and the (subsequent) Si−H bond activation (**V** → **IV**). However, to date no systematic evaluation of partially or fully fluorinated triarylboranes in hydrosilylation reactions involving that borane-assisted Si−H bond cleavage has been conducted. Hence, we embarked on a comprehensive comparison of the performance of known electron-deficient triarylboranes **1a**−**1g** in our transfer hydrosilylation and the direct hydrosilylation of C═X reactants (Figure 3). To obtain a sufficiently precise measure of their Lewis acidities relative to archetypical $B(C_6F_5)_3$ (**1a**, 100%), we employed the established Gutmann−Beckett method (percentage values in parentheses; for details, see the Experimental Section and the Supporting Information).[28,29] As expected, the degree of fluorination correlated with the Lewis acidity of the boron atom,[30] and nonfluorinated $B(C_6H_5)_3$ (**1g**, 70%) was the weakest Lewis acid on the Gutmann−Beckett scale. Interestingly, fluorination in the *para* position had little effect on the electron deficiency at the boron atom (**1a**, 100% vs **1d**, 97%). Moreover, we also

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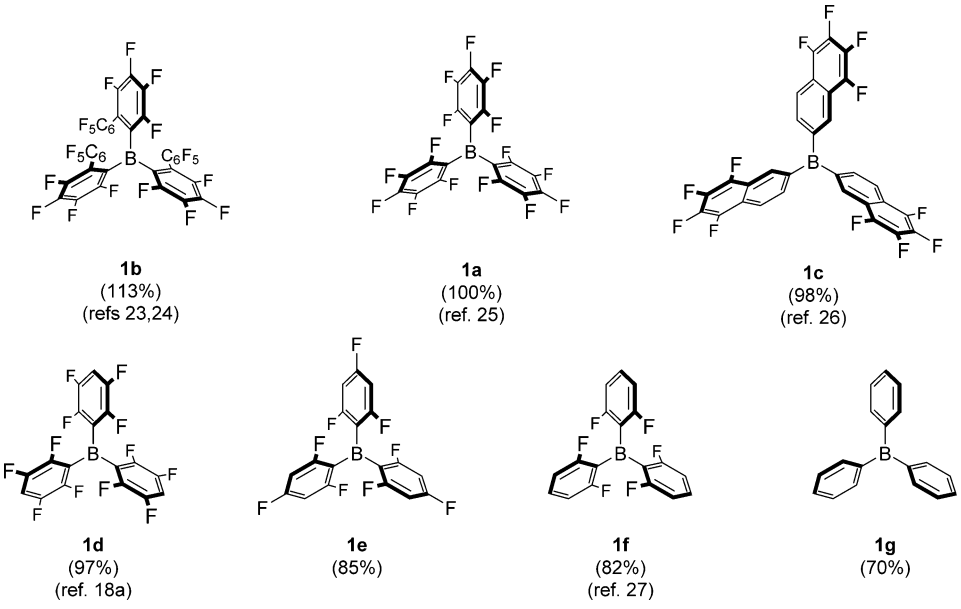

Figure 3. Partially or fully fluorinated triarylboranes investigated in this study and their Lewis acidities relative to $B(C_6F_5)_3$ (values in parentheses determined by the Gutmann–Beckett method).[18a,23−27]

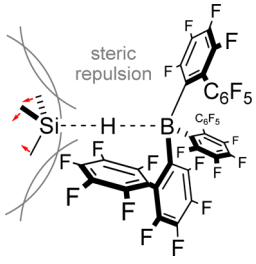

Figure 4. Large substituents at the boron atom in **1b** remotely creating steric congestion at the silicon atom.

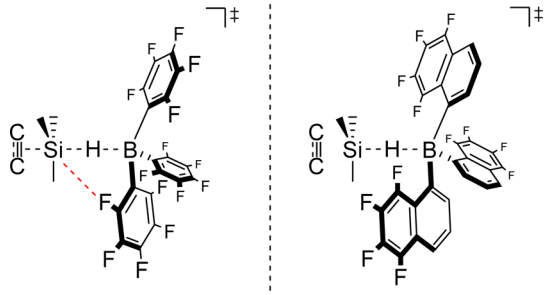

Figure 5. Enhanced Lewis acidity at the silicon atom as a result of Lewis base activation of Lewis acids through F–Si interaction.

included sterically encumbered tris(perfluoro-[1,1′-biphenyl]-2-yl)borane (**1b**)[31] and tris(5,6,7,8-tetrafluoronaphthalen-2-yl)-borane (**1c**),[26] which lacks fluorination in the proximity of the boron center.

The results of the comparative survey are collected in Table 3. Aside from benchmark borane **1a**, it was only **1d** that is able to catalyze both the direct and the transfer hydrosilylations of π-basic substrates **4** and **5** (rows 1–4). None of the less Lewis acidic boranes **1e**–**1g** were sufficiently reactive. Both **1b** and **1c**, with Lewis acidities similar to that of **1a** and **1d**, were equally unreactive. Steric congestion around the boron atom in **1b** is likely to account for its lack of reactivity. The η^1 coordination of the Si–H bond to the boron center will be less tight and, hence, the electrophilicity of the silicon atom will be diminished. Also, the associated "rehybridization" of the silicon atom from sp^3 to sp^2 will be less pronounced. Steric repulsion might even force the substituents at the silicon atom away from those of the boron Lewis acid, thereby sterically shielding the backside of the Si–H bond (Figure 4). As a result of that reduced electrophilicity and the augmented steric hindrance at the silicon atom, side-on attack of weakly π-basic **4** and **5** is disfavored. Conversely, nucleophilic attack of σ-donating **6**/**8** in an end-on manner is still possible.

However, steric repulsion alone cannot explain the inertness of less hindered **1c**, which is devoid of fluorine atoms *ortho* to the boron atom. Those seem to be an essential feature in the hydrosilylation of both C=C and C≡C bonds. Quantum-chemical calculations on the mechanism of carbonyl hydrosilylation showed that one of the *ortho* fluorine atoms in $B(C_6F_5)_3$ (**1a**) is in the coordination sphere of the silicon atom.[10b] That F–Si interaction renders the silicon atom pentacoordinated, thereby enhancing its Lewis acidity (Lewis base activation of Lewis acids)[32] and at the same time allowing for attack of weak π Lewis bases (Figure 5, left). The situation is different with borane **1c**, where the silicon atom is tetracoordinated and not sufficiently electrophilic to be attacked by π bonds (Figure 5, right).

Remarkably, the situation dramatically changed with the more nucleophilic σ donors **6**/**8** and **7** (rows 5–12). Except for $B(C_6H_5)_3$ (**1g**), partially fluorinated **1e** and **1f** displayed moderate to good reactivities in direct C=O and C=N hydrosilylations (columns 4 and 5, rows 5, 7, 9, and 11). The related transfer hydrosilylations were unsuccessful with **1f** as catalyst (column 5, rows 6, 8, 10, and 12), whereas **1e** afforded the reduced acceptor under harsh conditions in poor yields (column 4, rows 6, 8, 10, and 12).

The observed discrepancy between the Lewis acidities required for Si–H bond cleavage and C–H hydride abstraction in C=O and C=N (transfer) hydrosilylation is particularly noteworthy. The striking difference between equally Lewis acidic **1c** and **1d** suggests that the presence of *ortho* fluorine atoms is also crucial in the hydride abstraction step (**I** → **III**,

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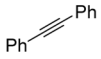
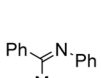
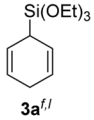
Table 3. Representative Electron-Deficient Triarylboranes as Catalysts in the Direct and Transfer Hydrosilylation of Typical π and σ Lewis Basic Substrates[a]

Nu	*Si*–H	**1b**[b]	**1c**	**1d**	**1e**	**1f**	**1g**
 **4**[c]	Et_3SiH	0% (80 °C, 24 h) ●	0% (110 °C, 24 h) ●	22%[d] (80 °C, 72 h) ●	0% (80 °C, 12 h) ●	0% (80 °C, 12 h) ●	0% (80 °C, 12 h) ●
	 **2a**	0% (r.t., 24 h) ●	0% (r.t., 48 h) ●	92% (r.t., 6 h) ●	0% (r.t., 46 h) ●	0% (r.t., 46 h) ●	0% (r.t., 46 h) ●
 **5**[c]	Et_3SiH	0% (80 °C, 24 h) ●	0% (r.t., 48 h) ●	13%[d] (80 °C, 48 h) ●	0% (110 °C, 48 h) ●	0% (110 °C, 48 h) ●	0% (110 °C, 48 h) ●
	 **2a**	0% (r.t, 24 h) ●	0% (r.t., 48 h) ●	91%[d] (r.t., 48 h) ●	0% (r.t., 43 h) ●	0% (r.t., 43 h) ●	0% (r.t., 23 h) ●
 **6** or **8**	Et_3SiH[e,f]	92%[g] (r.t., 2 h) ●	94%[h] (r.t., 3 h) ●	87% (r.t., 3 h) ●	91% (r.t., 3 h) ●	90% (r.t., 3 h) ●	9%[d,g] (110 °C, 48 h) ●
	 **2a**[e]	traces[d,f] (80 °C, 24 h) ●	0%[f,h] (80 °C, 24 h) ●	quant.[d,f] (80 °C, 4 h) ●	27%[d,g] (110 °C, 48 h) ●	0%[g] (110 °C, 48 h) ●	0%[g] (110 °C, 48 h) ●
	$(EtO)_3SiH$[e,g]	46%[i] (r.t., 96 h) ●	79%[d] (r.t., 48 h) ●	89% (r.t., 90 min) ●	86%[d] (r.t., 48 h) ●	70%[d] (80 °C, 96 h) ●	0% (110 °C, 48 h) ●
	 **3a**[g,j]	0% (80 °C, 48 h) ●	0% (80 °C, 48 h) ●	83%[d] (80 °C, 48 h) ●	traces[d] (110 °C, 48 h) ●	0% (110 °C, 48 h) ●	0% (110 °C, 48 h) ●
 **7**[k]	Et_3SiH[f]	56%[d] (80 °C, 48 h) ●	17%[d,f] (80 °C, 48 h) ●	96% (80 °C, 3 h) ●	71%[d] (80 °C, 48 h) ●	28%[d] (80 °C, 48 h) ●	traces[d] (110 °C, 48 h) ●
	 **2a**[f]	54%[d] (80 °C, 48 h) ●	8%[d,h] (80 °C, 48 h) ●	90% (80 °C, 2 h) ●	30%[d] (110 °C, 48 h) ●	3%[d] (110 °C, 48 h) ●	0% (110 °C, 48 h) ●
	$(EtO)_3SiH$[g,l]	77%[d] (80 °C, 48 h) ●	65%[d] (80 °C, 48 h) ●	31%[d] (r.t., 90 min) ●	53%[d] (80 °C, 48 h) ●	25%[d] (80 °C, 48 h) ●	7%[d] (110 °C, 48 h) ●
	 **3a**[f,l]	49%[d] (80 °C, 48 h) ●	12%[d] (80 °C, 48 h) ●	87%[d] (80 °C, 48 h) ●	10%[d] (110 °C, 48 h) ●	traces[d] (110 °C, 48 h) ●	0% (110 °C, 48 h) ●

[a]All reactions were performed with a catalyst loading of 5.0 mol % at a substrate concentration of 1.0 M according to the general procedures (see the Experimental Section for details). Unless otherwise noted, isolated yields are given. Green dots denote hydrosilylation of substrate; red dots denote no consumption of surrogate and substrate. [b]2.5 or 1.3 mol % of **1** used in the reactions with π-basic **4** and **5** and σ-basic **6**/**8** and **7**, respectively. [c]Performed in CH_2Cl_2 (at room temperature) or benzene (at elevated temperatures). [d]Conversion of the substrate determined by GLC analysis using mesitylene as internal standard. [e]Acetophenone (**6**) used as the carbonyl compound. [f]Benzene used as solvent. [g]Toluene used as solvent. [h]2.5 mol % of **1c** used. [i]Performed at a substrate concentration of 0.3 M. Conversion of the substrate determined by ^{1}H NMR spectroscopy using mesitylene as internal standard. Initially formed silyl ether decomposed. [j]Cyclododecanone (**8**) used as the carbonyl compound. [k]Yields after hydrolysis. [l]^{1}H NMR measurements showed that not only unreacted **7** and the expected *N*-silylated amine are present but also the *N*-silylated enamine and the free amine.[11]

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Scheme 1). However, a recent quantum-chemical analysis showed that this is in fact not the case. Instead, an *ortho* fluorine atom assists the release of hydrosilane **V** from $[R_3Si(C_6H_6)]^+[HB(C_6F_5)_3]^-$ with a F−Si interaction (**III** → **IV**, Scheme 1).[14]

CONCLUSION

To summarize, the present survey provides a useful roadmap of transfer and direct hydrosilylation reactions of typical substrates catalyzed by representative electron-deficient triarylboranes (**1a**−**1f**, Figure 3). Both weakly nucleophilic π Lewis bases (alkene **4** and alkyne **5**) and more nucleophilic σ Lewis bases (ketones **6**/**8** and ketimine **7**) were selected as test substrates in every screening. One part of our investigation is dedicated to the design of the hydrosilane surrogate in the transfer hydrosilylation by variation of the substitution pattern of the cyclohexa-1,4-diene core (as in **2a**−**2f**; Table 1) and installation of alkoxy groups at the silicon atom (as in **3a**−**3c**; Table 2). The major result from these experiments is that too strong stabilization of the Wheland intermediate hampers the release of the hydrosilane, even if the hydride abstraction is more facile. Also, the cyclohexa-2,5-dien-1-ylsilane must not be decorated with σ-donating groups such as ethers, as these outcompete π-basic substrates. Hence, alkenes and alkynes do not undergo transfer hydrosilylation in the presence of other Lewis basic functional groups. For example, ether cleavage is seen instead.

Another part of the present work compares the performance of fully and partially fluorinated triarylboranes **1** in the transfer and direct hydrosilylation of the aforementioned substrates (Table 3). These sets of experiments finally make long-needed data available. As expected, the Lewis acidity of **1** is crucial, and the reactivity of **1** in the Si−H bond activation correlates nicely with the relative Lewis acidities determined by the Gutmann−Beckett method if restricted to a certain class of Lewis bases, that is, π- or σ-donating substrates. The Lewis acid and the Lewis base act in concert, and either one is able to compensate the weakness of its counterpart. Hence, alkenes and alkynes require more Lewis acidic boranes **1**, whereas ketones and ketimines enable heterolytic Si−H bond cleavage with weaker Lewis acids **1**. With bulky aryl groups at the boron atom, steric hindrance also comes into play (Figure 4). The presence of fluorine atoms in the *ortho* position(s) to the boron atom appears to be essential in the Si−H bond activation **IV** (Figure 5 and Scheme 1)[10b] as well as in the silane release from intermediate **III** (Scheme 1).[14] These parameters must be well balanced with each class of substrates for the catalysis to proceed.

EXPERIMENTAL SECTION

General Remarks. All reactions were performed in flame-dried glassware using an MBraun glovebox or conventional Schlenk techniques under a static pressure of argon (glovebox) or nitrogen. Liquids and solutions were transferred with syringes. Solvents (benzene, CH_2Cl_2, THF, and toluene) were purified and dried following standard procedures. Technical grade solvents for extraction and chromatography (*tert*-butyl methyl ether, cyclohexane, and *n*-pentane) were distilled prior to use. C_6D_6, C_7D_8, and $CDCl_3$ (purchased from Eurisotop) were dried over 4 Å molecular sieves. *n*-Butyllithium (1.58 M in hexanes), *sec*-butyllithium (1.36−1.58 M in cyclohexane), *tert*-butyllithium (1.58−1.65 M in *n*-pentane), cyclohexa-1,4-diene, Me_3SiCl, $(EtO)_3SiCl$, $(MeO)Me_2SiCl$, hexamethylphosphoramide (HMPA), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU), and triethylamine were obtained from commercial sources and used without further purification. 1,1-Diphenylethylene (**4**), diphenylacetylene (**5**), acetophenone (**6**), and cyclododecanone (**8**) were distilled, degassed, and stored over 4 Å molecular sieves (if liquids) or dried overnight under high vacuum (if solids) and stored in a glovebox. Triphenylborane (**1g**) was recrystallized from benzene, dried overnight under high vacuum, and stored in a glovebox. Mesitylene was distilled from sodium, degassed, and stored over 4 Å molecular sieves in a glovebox. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) was distilled from sodium prior to use. Triarylboranes **1a**,[33] **1b**,[34] **1c**,[26] **1d**,[18b] **1e**,[18c] and **1f**,[35] cyclohexa-2,5-dien-1-ylsilane analogues **2a**,[12] **2c**,[36] **2e**,[37] and **2f**,[38] and (*E*)-phenyl(1-phenylethylidene)imine (**7**)[39] were synthesized according to reported procedures and stored in a glovebox (over 4 Å molecular sieves if liquids). 1,4-Dihydronaphthalene[40] and 1,5-dimethoxycyclohexa-1,4-diene[41] were prepared according to reported procedures and stored under a nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed on silica gel SIL G-25 glass plates from Machery-Nagel. Flash column chromatography was performed on silica gel 60 (40−63 μm, 230−400 mesh, ASTM) by Merck using the indicated solvents. MP EcoChrome Alumina N, Activity I, was purchased from MP Biomedicals Germany GmbH. ^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{29}Si, and ^{31}P NMR spectra were recorded in C_6D_6, C_7D_8, or $CDCl_3$ on Bruker AV400 and Bruker AV 500 instruments. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual solvent resonance as the internal standard (C_6D_5H, δ 7.16 ppm; $CHCl_3$, δ 7.26 ppm; $C_6D_6CD_2H$, δ 2.08 ppm for ^{1}H NMR and C_6D_6, δ 128.06 ppm; $CDCl_3$, δ 77.16 ppm; $C_6D_5CD_3$ δ 20.43 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, m_c = centrosymmetric multiplet), coupling constant (Hz), and integration. Infrared (IR) spectra were recorded on an Agilent Technologies Cary 630 FT-IR spectrophotometer equipped with an ATR unit and are reported in wavenumbers (cm^{-1}). Gas liquid chromatography−mass spectrometry (GLC-MS) was performed on an Agilent Technologies GC-System 5975C with an Agilent Technologies mass selective detector (EI) and an HP-5MS column. Gas liquid chromatography (GLC) was performed on an Agilent Technologies 7820A gas chromatograph equipped with an SE-54 capillary column (30 m × 0.32 mm, 0.25 μm film thickness) by CS-Chromatography Service using the following programs: N_2 carrier gas, column flow 1.7 mL/min, injection temperature 280 °C, detector temperature 300 °C; temperature program: start temperature 40 °C, heating rate 10 °C/min, final temperature 280 °C for 10 min. High-resolution mass spectrometry (HRMS) and elemental analysis were performed by the Analytical Facility at the Institut für Chemie, Technische Universität Berlin.

General Procedure for the Preparation of Surrogates 2d, 3a, and 3c (GP1). To a solution of the corresponding cyclohexa-1,4-diene (1.0 equiv) in THF (0.3−0.7 M) were added *s*BuLi (1.36−1.58 M in cyclohexane, 1.0−1.1 equiv) and TMEDA (1.0 equiv) dropwise at −78 °C. The resulting mixture was then warmed to −45 °C and maintained at this temperature for 3 h. The corresponding chlorosilane (1.0−1.1 equiv) in THF (0.70−2.5 M) was added dropwise at −45 °C, and the reaction mixture was then slowly warmed to room temperature. Saturated aqueous NH_4Cl solution was added, and the aqueous layer extracted with *tert*-butyl methyl ether (2×). The combined organic layers were washed with brine and water and dried over $MgSO_4$, and all volatiles removed in vacuo. The crude surrogates were purified by either flash column chromatography or distillation.

General Procedure for the Preparation of Surrogates 2b and 3b (GP2). To a solution of 1,5-dimethoxycyclohexa-1,4-diene (1.1−1.2 equiv) in THF (0.40−0.42 M) was added *t*BuLi (1.58−1.65 M in *n*-pentane, 1.1 equiv) dropwise at −78 °C. The resulting mixture was stirred at this temperature for 30 min, and HMPA or DMPU (1.1 equiv) was subsequently added dropwise. After stirring for 10 min, the corresponding chlorosilane (1.0 equiv) in THF (1.8−2.0 M) was slowly added at −78 °C. After 5 min, the cooling bath was removed, and the reaction mixture warmed to room temperature and then quenched with *n*-pentane and water. The aqueous layer was extracted with *tert*-butyl methyl ether (2×). The combined organic layers were washed with brine and water and dried over $MgSO_4$, and all volatiles

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removed in vacuo. The crude surrogates were purified by either flash column chromatography or distillation.

General Procedure for the Transfer Hydrosilylation (GP3). In a glovebox, a 1.3 mL GLC vial (for reactions at room temperature) or a 1.0 mL Ace pressure tube (for reactions at elevated temperatures) was charged with the indicated borane **1** (1.3−5.0 mol %) and dissolved in the indicated solvent. The substrate (1.0 equiv) and the hydrosilane surrogate (1.0−1.3 equiv) were weighed in a separate vial. Both reagents were dissolved in the indicated solvent, and the resulting solution was added to the catalyst. The reaction mixture (1.0 M) was then stirred at room temperature (inside the glovebox) or elevated temperatures (heated outside the glovebox) and monitored by GLC analysis. For product isolation, the mixture was filtered over a small silica gel or alumina column (1.0 cm, eluting with cyclohexane or *n*-pentane/*tert*-butyl methyl ether), and all volatiles were removed under reduced pressure. If necessary, the crude material was further purified by either flash column chromatography or Kugelrohr distillation.

General Procedure for the Preparation of Triethylphosphine Oxide Adducts of the Triarylboranes (GP4). In a glovebox, the indicated borane **1** (20 μmol) in C_6D_6 (0.5 mL) was mixed with triethylphosphine oxide (1.0 equiv) in C_6D_6 (0.5 mL). The sample was transferred to an NMR tube and directly subjected to NMR analysis.

*2,6-Dimethoxycyclohexa-2,5-dien-1-yltrimethylsilane (**2b**).* According to GP2, *t*BuLi (1.58 M in *n*-pentane, 9.1 mL, 14 mmol, 1.1 equiv) and DMPU (1.7 mL, 14 mmol, 1.1 equiv) were added to a solution of 1,5-dimethoxycyclohexa-1,4-diene (2.1 g, 15 mmol, 1.2 equiv) in THF (38 mL). After addition of a solution of Me_3SiCl (1.7 mL, 13 mmol, 1.0 equiv) in THF (7.5 mL), the reaction mixture was quenched with *n*-pentane (20 mL) and water (20 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (2 × 50 mL), and the combined organic layers were then washed with brine (50 mL) and water (50 mL) and dried over $MgSO_4$. The crude material was purified by flash column chromatography on silica gel using cyclohexane/*tert*-butyl methyl ether/triethylamine (70/1/0.7) as eluent, affording **2b** (95% purity, 1.73 g, 8.15 mmol, 60%) as a colorless oil.[42] R_f = 0.42 (cyclohexane/*tert*-butyl methyl ether, 25/1). GLC (SE-54): 12.4 min. IR (ATR): $\tilde{\nu}$ 3068, 2948, 2899, 2830, 1679, 1440, 1354, 1244, 1200, 1135, 1028, 995, 908, 835, 760, 707 cm^{-1}. HRMS (EI): calculated for $C_{11}H_{20}O_2Si$ $[M + H]^+$, 213.1305; found, 213.1304. ^1H NMR (500 MHz, C_6D_6): δ 0.20 (s, 9H), 2.68 (dd, *J* = 6.5, 3.9 Hz, 1H), 2.83 (ddt, *J* = 19.8, 4.9, 4.0 Hz, 1H), 2.91 (ddt, *J* = 19.8, 6.5, 2.4 Hz, 1H), 3.21 (s, 6H), 4.41 (dd, *J* = 5.0, 2.5 Hz, 2H) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ −1.3, 25.3, 36.5, 53.7, 88.2, 156.0 ppm. ^{29}Si NMR (99 MHz, C_6D_6): δ 6.8 ppm. Anal. Calcd for $C_{11}H_{20}O_2Si$: C, 62.21; H, 9.49. Found: C, 62.00; H, 9.70.

*1,4-Dihydronaphthalen-1-yltrimethylsilane (**2d**).* According to GP1, *s*BuLi (1.44 M in cyclohexane, 9.7 mL, 14 mmol, 1.1 equiv) and TMEDA (2.0 mL, 13 mmol, 1.0 equiv) were added to a solution of 1,4-dihydronaphthalene (84% purity, 2.0 g, 13 mmol, 1.0 equiv) in THF (40 mL). After addition of a solution of Me_3SiCl (1.8 mL, 14 mmol, 1.1 equiv) in THF (20 mL), the reaction mixture was quenched with a saturated aqueous NH_4Cl solution (20 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (2 × 25 mL), and the combined organic layers then washed with brine (25 mL) and water (25 mL) and dried over $MgSO_4$. The crude materal was purified by Kugelrohr distillation (10 mbar, 100 °C), affording **2d** (1.05 g, 5.19 mmol, 40%) as a colorless oil. R_f = 0.43 (cyclohexane). GLC (SE-54): 13.7 min. IR (ATR): $\tilde{\nu}$ 3029, 2953, 2896, 2861, 2820, 1648, 1486, 1451, 1289, 1244, 1089, 1005, 906, 822, 742, 695 cm^{-1}. HRMS (EI): calculated for $C_{13}H_{18}Si$ $[M]^{+\bullet}$, 202.11723; found, 202.11819. ^1H NMR (500 MHz, C_6D_6): δ −0.06 (s, 9H), 2.75−2.82 (m, 1H), 3.18 (ddd, *J* = 20.3, 5.3, 2.3 Hz, 1H), 3.24−3.33 (m, 1H), 5.69 (dddd, *J* = 9.9, 5.3, 2.2, 0.7 Hz, 1H), 5.86−5.92 (m, 1H), 6.86−6.90 (m, 1H), 6.97−7.01 (m, 1H), 7.02−7.10 (m, 2H) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ −2.7, 31.3, 36.5, 121.4, 125.3, 125.9, 127.6, 128.3, 128.8, 133.2, 137.5 ppm. ^{29}Si NMR (99 MHz, C_6D_6): δ 5.7 ppm. Anal. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97. Found: C, 77.19; H, 9.14.

*Cyclohexa-2,5-dien-1-yltriethoxysilane (**3a**).* According to GP1, *s*BuLi (1.58 M in cyclohexane, 19.0 mL, 30.0 mmol, 1.00 equiv) and TMEDA (4.5 mL, 30 mmol, 1.0 equiv) were added to a solution of cyclohexa-1,4-diene (2.8 mL, 30 mmol, 1.0 equiv) in THF (45 mL). After addition of a solution of $(EtO)_3SiCl$ (5.9 mL, 30 mmol, 1.0 equiv) in THF (12 mL), the reaction mixture was quenched with a saturated aqueous NH_4Cl solution (40 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (2 × 40 mL), and the combined organic layers were then washed with brine (40 mL) and water (40 mL) and dried over $MgSO_4$. The crude material was purified by fractional distillation (8 mbar, 55−65 °C), affording **3a** (3.90 g, 16.1 mmol, 54%) as a colorless liquid. R_f = 0.30 (cyclohexane/*tert*-butyl methyl ether, 25/1). GLC (SE-54): 12.4 min. IR (ATR): $\tilde{\nu}$ 3027, 2972, 2925, 2885, 2821, 1625, 1441, 1389, 1292, 1164, 1099, 1073, 952, 897, 782, 751 cm^{-1}. HRMS (APCI): calculated for $C_{12}H_{23}O_3Si$ $[M + H^+]$, 243.1411; found, 243.1405. ^1H NMR (500 MHz, C_6D_6): δ 1.17 (t, *J* = 7.0 Hz, 9H), 2.62−2.72 (m, 3H), 3.84 (q, *J* = 7.0 Hz, 6H), 5.55−5.63 (m, 2H), 5.90−5.99 (m, 2H) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ 18.6, 26.5, 28.2, 59.1, 122.5, 125.1 ppm. ^{29}Si NMR (99 MHz, C_6D_6): δ −57.6 ppm. Anal. Calcd for $C_{12}H_{22}O_3Si$: C, 59.46; H, 9.15. Found: C, 59.33; H, 9.38.

*2,6-Dimethoxycyclohexa-2,5-dien-1-yltriethoxysilane (**3b**).* According to GP2, *t*BuLi (1.65 M in *n*-pentane, 6.4 mL, 11 mmol, 1.1 equiv) and HMPA (1.9 mL, 11 mmol, 1.1 equiv) were added to a solution of 1,5-dimethoxycyclohexa-1,4-diene (1.47 g, 10.5 mmol, 1.05 equiv) in THF (25 mL). After addition of a solution of $(EtO)_3SiCl$ (2.0 mL, 10 mmol, 1.0 equiv) in THF (5.0 mL), the reaction mixture was quenched with *n*-pentane (15 mL) and water (15 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (2 × 40 mL), and the combined organic layers were then washed with brine (40 mL) and water (40 mL) and dried over $MgSO_4$. The crude material was purified by Kugelrohr distillation (0.5 mbar, 130−150 °C), affording **3b** (1.16 g, 3.84 mmol, 38%) as a colorless oil.[42] R_f = 0.15 (cyclohexane/*tert*-butyl methyl ether, 25/1). GLC (SE-54): 16.2 min. IR (ATR): $\tilde{\nu}$ 2972, 2927, 2893, 2830, 1683, 1654, 1462, 1439, 1388, 1352, 1235, 1202, 1136, 1100, 1074, 1029, 996, 956, 771, 743, 707, 683 cm^{-1}. HRMS (APCI): calculated for $C_{14}H_{27}O_5Si$ $[M + H^+]$, 303.1622; found, 303.1612. ^1H NMR (500 MHz, C_6D_6): δ 1.21 (t, *J* = 7.0 Hz, 9H), 2.80−2.90 (m, 1H), 2.92−3.08 (m, 2H), 3.31 (s, 6H), 3.93 (q, *J* = 7.0 Hz, 6H), 4.50 (dd, *J* = 5.2, 2.2 Hz, 2H) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ 18.6, 25.2, 33.8, 54.1, 59.0, 89.1, 154.8 ppm. ^{29}Si NMR (99 MHz, C_6D_6): δ −57.7 ppm. Anal. Calcd for $C_{14}H_{26}O_5Si$: C, 55.60; H, 8.67. Found: C, 55.84; H, 8.83.

*Cyclohexa-2,5-dien-1-yl(methoxy)dimethylsilane (**3c**).* According to GP1, *s*BuLi (1.36 M in cyclohexane, 7.4 mL, 10 mmol, 1.0 equiv) and TMEDA (1.5 mL, 10 mmol, 1.0 equiv) were added to a solution of cyclohexa-1,4-diene (0.93 mL, 10 mmol, 1.0 equiv) in THF (15 mL). After addition of a solution of $(MeO)Me_2SiCl$ (90% purity, 1.4 g, 10 mmol, 1.0 equiv) in THF (4.0 mL), the reaction mixture was quenched with a saturated aqueous NH_4Cl solution (15 mL). The aqueous layer was extracted with *tert*-butyl methyl ether (2 × 15 mL), and the combined organic layers were then washed with brine (15 mL) and water (15 mL) and dried over $MgSO_4$. The crude material was purified by Kugelrohr distillation (90 mbar, 115 °C), affording **3c** (560 mg, 3.3 mmol, 33%) as a colorless oil. R_f = 0.34 (cyclohexane/*tert*-butyl methyl ether, 25/1). GLC (SE-54): 8.6 min. IR (ATR): $\tilde{\nu}$ 3025, 2958, 2893, 2826, 1622, 1432, 1249, 1187, 1086, 1049, 936, 892, 822, 796, 756, 726 cm^{-1}. HRMS (APCI): calculated for $C_9H_{16}OSiNa$ $[M + Na^+]$, 191.0863; found, 191.0824. ^1H NMR (500 MHz, C_6D_6): δ 0.11 (s, 6H), 2.37−2.47 (m, 1H), 2.54−2.73 (m, 2H), 3.28 (s, 3H), 5.50−5.60 (m, 2H), 5.69−5.76 (m, 2H) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ −4.4, 26.7, 32.3, 50.6, 122.2, 125.8 ppm. ^{29}Si NMR (99 MHz, C_6D_6): δ 13.3 ppm. Anal. Calcd for $C_9H_{16}OSi$: C, 64.23; H, 9.58. Found: C, 63.62; H, 9.61.

*Tris(2,2′,2″-perfluorobiphenyl)borane Triethylphosphine Oxide Adduct (**1b**·Et₃PO).* Prepared from **1b** (19.1 mg, 20 μmol, 1.0 equiv) and triethylphosphine oxide (2.7 mg, 20 μmol, 1.0 equiv) according to GP4. ^1H NMR (500 MHz, C_6D_6): δ −0.10−0.40 (m, 9H), 0.79−1.10 (m, 6H) ppm. ^{11}B NMR (161 MHz, C_6D_6): δ 2.0 ppm. ^{19}F NMR (471 MHz, C_6D_6): δ −163.6, −162.2, −156.2, −154.5, −152.8, −136.7, −133.0, −132.0, −118.8 ppm. ^{31}P NMR (203 MHz, C_6D_6): δ 79.3 ppm.

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*Tris(2,3,5,6-tetrafluorophenyl)borane Triethylphosphine Oxide Adduct (**1d**·Et$_3$PO).* Prepared from **1d** (9.2 mg, 20 μmol, 1.0 equiv) and triethylphosphine oxide (2.7 mg, 20 μmol, 1.0 equiv) according to GP4. ^{1}H NMR (500 MHz, C_6D_6): δ 0.33 (dt, *J* = 18.4, 7.7 Hz, 9H), 1.04 (dq, *J* = 12.4, 7.6 Hz, 6H), 6.32−6.52 (m, 3H) ppm. ^{11}B NMR (161 MHz, C_6D_6): δ −1.5 ppm. ^{19}F NMR (471 MHz, C_6D_6): δ −141.2, −134.1 ppm. ^{31}P NMR (203 MHz, C_6D_6): δ 74.4 ppm.

*Tris(2,4,6-trifluorophenyl)borane Triethylphosphine Oxide Adduct (**1e**·Et$_3$PO).* Prepared from **1e** (8.1 mg, 20 μmol, 1.0 equiv) and triethylphosphine oxide (2.7 mg, 20 μmol, 1.0 equiv) according to GP4. ^{1}H NMR (500 MHz, C_6D_6): δ 0.44 (dt, *J* = 18.2, 7.7 Hz, 9H), 1.12 (dq, *J* = 12.2, 7.7 Hz, 6H), 6.44 (t, *J* = 8.5 Hz, 6H) ppm. ^{11}B NMR (161 MHz, C_6D_6): δ −1.1 ppm. ^{19}F NMR (471 MHz, C_6D_6): δ −114.1, −99.2 ppm. ^{31}P NMR (203 MHz, C_6D_6): δ 70.7 ppm.

*Tris(2,6-difluorophenyl)borane Triethylphosphine Oxide Adduct (**1f**·Et$_3$PO).* Prepared from **1f** (7.0 mg, 20 μmol, 1.0 equiv) and triethylphosphine oxide (2.7 mg, 20 μmol, 1.0 equiv) according to GP4. ^{1}H NMR (500 MHz, C_6D_6): δ 0.52 (dt, *J* = 17.9, 7.8 Hz, 9H), 1.25 (dq, *J* = 12.5, 7.6 Hz, 6H), 6.70 (t, *J* = 7.4 Hz, 6H), 6.77−6.87 (m, 3H) ppm. ^{11}B NMR (161 MHz, C_6D_6): δ −0.4 ppm. ^{19}F NMR (471 MHz, C_6D_6): δ −101.4 ppm. ^{31}P NMR (203 MHz, C_6D_6): δ 69.9 ppm.

*Triphenylborane Triethylphosphine Oxide Adduct (**1g**·Et$_3$PO).* Prepared from **1g** (4.8 mg, 20 μmol, 1.0 equiv) and triethylphosphine oxide (2.7 mg, 20 μmol, 1.0 equiv) according to GP4. ^{1}H NMR (500 MHz, C_6D_6): δ 0.48 (dt, *J* = 17.1, 7.8 Hz, 9H), 0.88 (dq, *J* = 12.1, 7.7 Hz, 6H), 7.26 (t, *J* = 7.3 Hz, 3H), 7.35 (t, *J* = 7.4 Hz, 6H), 7.78 (d, *J* = 7.8 Hz, 6H) ppm. ^{11}B NMR (161 MHz, C_6D_6): δ 18.1 ppm. ^{31}P NMR (203 MHz, C_6D_6): δ 66.4 ppm.

(2,2-Diphenylethyl)trimethylsilane. According to GP3, the reaction vial was charged with the indicated borane **1** (1.3−10 μmol, 1.3−5.0 mol %), dissolved in CH_2Cl_2 or benzene (50−100 μL), and a solution of the hydrosilane surrogate **2** (0.13−0.26 mmol, 1.3 equiv) and 1,1-diphenylethylene (**4**, 18−36 mg, 0.10−0.20 mmol, 1.0 equiv) in CH_2Cl_2 or benzene (50−100 μL). For isolation of the title compound, the crude material was filtered over a small silica gel column (1.0 cm, eluting with cyclohexane), and all volatiles were removed under reduced pressure, affording (2,2-diphenylethyl)trimethylsilane as a colorless oil. ^{1}H NMR (500 MHz, C_6D_6): δ −0.16 (s, 9H), 1.30 (d, *J* = 8.1 Hz, 2H), 4.02 (t, *J* = 8.1 Hz, 1H), 7.01 (tt, *J* = 7.3, 1.9 Hz, 2H), 7.08−7.14 (m, 4H), 7.15−7.22 (m, 4H) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ −1.1, 24.3, 47.7, 126.3, 128.0, 128.6, 147.5 ppm. ^{29}Si NMR (99 MHz, C_6D_6): δ 0.6 ppm. The analytical and spectroscopic data are in accordance with those reported.[12]

(2,2-Diphenylethyl)triethylsilane. According to GP3, an Ace pressure tube was charged with the indicated borane **1** (1.3−10 μmol, 1.3−5.0 mol %), dissolved in benzene or toluene (50−100 μL), and a solution of Et_3SiH (0.13−0.26 mmol, 1.3 equiv) and 1,1-diphenylethylene (**4**, 18−36 mg, 0.10−0.20 mmol, 1.0 equiv) in benzene or toluene (50−100 μL). For isolation of the title compound, the crude material was purified by flash column chromatography on silica gel (eluting with cyclohexane), and all volatiles were removed under reduced pressure, affording (2,2-diphenylethyl)triethylsilane as a colorless oil. ^{1}H NMR (500 MHz, C_6D_6): δ 0.38 (q, *J* = 7.9 Hz, 6H), 0.87 (t, *J* = 8.0 Hz, 9H), 1.39 (d, *J* = 7.9 Hz, 2H), 4.07 (t, *J* = 7.9 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 2H), 7.12 (t, *J* = 7.7 Hz, 4H), 7.23 (d, *J* = 7.5 Hz, 4H) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ 3.9, 7.6, 19.4, 47.6, 126.3, 127.9, 128.7, 147.7 ppm. ^{29}Si NMR (99 MHz, C_6D_6): δ 6.5 ppm. The analytical and spectroscopic data are in accordance with those reported.[12]

(Z)-(1,2-Diphenylvinyl)trimethylsilane. According to GP3, the reaction vial was charged with the indicated borane **1** (1.3−10 μmol, 1.3−5.0 mol %), dissolved in CH_2Cl_2 or benzene (50−100 μL), and a solution of the hydrosilane surrogate **2** (0.13−0.26 mmol, 1.3 equiv) and diphenylacetylene (**5**, 18−36 mg, 0.10−0.20 mmol, 1.0 equiv) in CH_2Cl_2 or benzene (50−100 μL). For isolation of the title compound, the crude material was purified by flash column chromatography on silica gel (eluting with cyclohexane), and all volatiles were removed under reduced pressure, affording (*Z*)-(1,2-diphenylvinyl)trimethylsilane as a colorless oil.[43] R_f = 0.38 (cyclohexane). GLC (SE-54): 17.9 min. IR (ATR): $\tilde{\nu}$ 3056, 3021, 2954, 2893, 1586, 1486, 1442, 1246, 1071, 1027, 944, 905, 831, 766, 688 cm^{-1}. HRMS (EI): calculated for $C_{17}H_{20}Si$ $[M]^{+\bullet}$, 252.1329; found, 252.1326. ^{1}H NMR (500 MHz, C_6D_6): δ 0.02 (s, 9H), 7.04−7.15 (m, 4H), 7.18−7.23 (m, 4H), 7.25−7.29 (m, 2H), 7.36 (s, 1H) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ 1.0, 126.2, 127.5, 127.6, 128.2, 128.4, 128.9, 140.4, 145.6, 147.6, 147.7 ppm. ^{29}Si NMR (99 MHz, C_6D_6): δ −7.1 ppm.

(Z)-(1,2-Diphenylvinyl)triethylsilane. According to GP3, the reaction vial was charged with the indicated borane **1** (1.3−10 μmol, 1.3−5.0 mol %), dissolved in CH_2Cl_2 or benzene (50−100 μL), and a solution of Et_3SiH (0.13−0.26 mmol, 1.3 equiv) and diphenylacetylene (**5**, 18−36 mg, 0.10−0.20 mmol, 1.0 equiv) in CH_2Cl_2 or benzene (50−100 μL). For isolation of the title compound, the crude material was purified by flash column chromatography on silica gel (eluting with cyclohexane), and all volatiles were removed under reduced pressure, affording (*Z*)-(1,2-diphenylvinyl)triethylsilane as a colorless oil. The double-bond geometry was assigned in analogy to that of (*Z*)-(1,2-diphenylvinyl)trimethylsilane. ^{1}H NMR (500 MHz, C_6D_6): δ 0.52 (q, *J* = 7.9 Hz, 6H), 0.87 (t, *J* = 7.9 Hz, 9H), 7.05−7.15 (m, 4H), 7.19−7.26 (m, 4H), 7.27−7.32 (m, 2H), 7.39 (s, 1H) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ 5.2, 7.9, 126.1, 127.6, 127.8, 128.1, 128.3, 128.7, 140.3, 145.6, 146.9, 147.9 ppm. ^{29}Si NMR (99 MHz, C_6D_6): δ −0.2 ppm. The analytical and spectroscopic data are in accordance with those reported.[44]

Trimethyl(1-phenylethoxy)silane. According to GP3, an Ace pressure tube was charged with the indicated borane **1** (1.3−10 μmol, 1.3−5.0 mol %), dissolved in benzene or toluene (50−100 μL), and a solution of the hydrosilane surrogate **2** (0.10−0.20 mmol, 1.0 equiv) and acetophenone (**6**, 12−24 mg, 0.10−0.20 mmol, 1.0 equiv) in benzene or toluene (50−100 μL). For isolation of the title compound, the crude material was filtered over a small alumina column (N, activity I, 1.0 cm, eluting with *n*-pentane/*tert*-butyl methyl ether, 25/1), and all volatiles were removed under reduced pressure, affording trimethyl(1-phenylethoxy)silane as a colorless oil. ^{1}H NMR (500 MHz, C_7D_8): δ 0.05 (s, 9H), 1.37 (d, *J* = 6.4 Hz, 3H), 4.73 (q, *J* = 6.4 Hz, 1H), 7.02−7.08 (m, 1H), 7.11−7.18 (m, 2H), 7.24−7.30 (m, 2H) ppm. ^{13}C NMR (126 MHz, C_7D_8): δ 0.2, 27.3, 71.1, 125.7, 127.2, 128.4, 147.0 ppm. ^{29}Si NMR (99 MHz, C_7D_8): δ 15.3 ppm. The analytical and spectroscopic data are in accordance with those reported.[45]

Triethyl(1-phenylethoxy)silane. According to GP3, the reaction vial was charged with the indicated borane **1** (1.3−10 μmol, 1.3−5.0 mol %), dissolved in benzene or toluene (50−100 μL), and a solution of the silane precursor **2** or Et_3SiH (0.10−0.20 mmol, 1.0 equiv) and acetophenone (**6**, 12−24 mg, 0.10−0.20 mmol, 1.0 equiv) in benzene or toluene (50−100 μL). For isolation of the title compound, the crude material was filtered over a small alumina column (N, activity I, 1.0 cm, eluting with cyclohexane/*tert*-butyl methyl ether, 25/1), and all volatiles were removed under reduced pressure, affording triethyl(1-phenylethoxy)silane as a colorless oil. ^{1}H NMR (500 MHz, C_6D_6): δ 0.57 (dq, *J* = 7.9, 3.3 Hz, 6H), 0.96 (t, *J* = 8.0 Hz, 9H), 1.41 (d, *J* = 6.3 Hz, 3H), 4.79 (q, *J* = 6.3 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 7.3 Hz, 2H) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ 5.3, 7.1, 27.6, 71.1, 125.6, 127.2, 128.5, 147.4 ppm. ^{29}Si NMR (99 MHz, C_6D_6): δ 17.5 ppm. The analytical and spectroscopic data are in accordance with those reported.[46]

Triethyl(1-phenylethyl)silicate. According to GP3, the reaction vial was charged with the indicated borane **1** (1.3−10 μmol, 1.3−5.0 mol %), dissolved in benzene or toluene (50−100 μL), and a solution of the hydrosilane surrogate **3** or $(EtO)_3SiH$ (0.10−0.20 mmol, 1.0 equiv) and acetophenone (**6**, 12−24 mg, 0.10−0.20 mmol, 1.0 equiv) in benzene or toluene (50−100 μL). For isolation of the title compound, the crude material was filtered over a small alumina column (N, activity I, 1.0 cm, eluting with cyclohexane/*tert*-butyl methyl ether, 25/1), and all volatiles were removed under reduced pressure, affording triethyl(1-phenylethyl)silicate as a colorless oil. R_f = 0.28 (cyclohexane/*tert*-butyl methyl ether, 25/1). GLC (SE-54): 14.1 min. IR (ATR): $\tilde{\nu}$ 2974, 2927, 2889, 1450, 1390, 1369, 1296, 1208, 1167, 1068, 1036, 963, 786, 697 cm^{-1}. HRMS (APCI): calculated for

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$C_{14}H_{25}O_3Si$ [M + H^+], 285.1517; found, 285.1516. ^{1}H NMR (500 MHz, C_6D_6): δ 1.14 (t, J = 7.0 Hz, 9H), 1.53 (d, J = 6.5 Hz, 3H), 3.76−3.93 (m, 6H), 5.26 (q, J = 6.4 Hz, 1H), 7.08 (t, J = 7.4 Hz, 1H), 7.19 (t, J = 7.7 Hz, 2H), 7.40 (d, J = 7.7 Hz, 2H) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ 18.4, 26.7, 59.4, 71.7, 125.7, 127.3, 128.5, 146.3 ppm. ^{29}Si NMR (99 MHz, C_6D_6): δ 117.0 ppm.

(Cyclododecyl)triethylsilicate. According to GP3, the reaction vial was charged with the indicated borane **1** (1.3−10 μmol, 1.3−5.0 mol %), dissolved in benzene or toluene (50−100 μL), and a solution of the hydrosilane surrogate **3** (0.10−0.20 mmol, 1.0 equiv) and cyclododecanone (**8**, 18−36 mg, 0.10−0.20 mmol, 1.0 equiv) in benzene or toluene (50−100 μL). For isolation of the title compound, the crude material was purified by Kugelrohr distillation (0.8 mbar, 140 °C), affording (cyclododecyl)triethylsilicate as a colorless oil. R_f = 0.25 (cyclohexane/*tert*-butyl methyl ether, 25/1). GLC (SE-54): 19.5 min. IR (ATR): $\tilde{\nu}$ 2973, 2928, 2862, 1469, 1444, 1389, 1294, 1167, 1076, 960, 882, 786, 726 cm^{-1}. HRMS (APCI): calculated for $C_{18}H_{38}O_4SiNa$ [M + Na^+], 369.2432; found, 369.2428. ^{1}H NMR (500 MHz, C_6D_6): δ 1.22 (t, J = 7.0 Hz, 9H), 1.25−1.50 (m, 16H), 1.51−1.61 (m, 2H), 1.62−1.72 (m, 2H), 1.75−1.86 (m, 2H), 3.92 (q, J = 7.0 Hz, 6H), 4.92−5.36 (m$_c$, 1H) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ 18.5, 21.4, 23.7, 23.9, 24.3, 24.8, 32.8, 59.3, 70.9 ppm. ^{29}Si NMR (99 MHz, C_6D_6): δ 117.0 ppm.

Cyclododecanol. According to GP3, an Ace pressure tube was charged with $B(C_6F_5)_3$ (**1a**) (5.1 mg, 10 μmol, 5.0 mol %) dissolved in benzene (0.1 mL). Then, a solution of hydrosilane surrogate **3c** (83% purity, 40.6 mg, 0.20 mmol, 1.0 equiv) and cyclododecanone (**8**, 36 mg, 0.20 mmol, 1.0 equiv) in benzene (0.1 mL) was added. The crude material was purified by flash column chromatography on silica gel (eluting with cyclohexane/*tert*-butyl methyl ether, 6/1), affording cyclododecanol as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25−1.50 (m, 20H), 1.59−1.76 (m, 2H), 3.78−3.92 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.2, 23.5, 23.6, 24.0, 24.4, 32.7, 69.5 ppm. The analytical and spectroscopic data are in accordance with those reported.[47]

N-Phenyl-N-(1-phenylethyl)amine. According to GP3, the reaction vial was charged with the indicated borane **1** (1.3−10 μmol, 1.3−5.0 mol %), dissolved in benzene or toluene (50−100 μL), and a solution of the hydrosilane (surrogate) (0.13−0.26 mmol, 1.3 equiv) and *N*-phenyl-*N*-(1-phenylethyl)imine (**7**, 20−39 mg, 0.10−0.20 mmol, 1.0 equiv) in benzene or toluene (50−100 μL). For isolation of the title compound, the crude material was purified by flash column chromatography on silica gel (eluting with cyclohexane/*tert*-butyl methyl ether, 40/1), affording *N*-phenyl-*N*-(1-phenylethyl)amine as a colorless oil. ^{1}H NMR (500 MHz, C_6D_6): δ 1.12 (d, J = 6.8 Hz, 3H), 3.52 (br s, 1H), 4.22 (q, J = 6.7 Hz, 1H), 6.40−6.47 (m, 2H), 6.65−6.71 (m, 1H), 7.01−7.10 (m, 3H), 7.11−7.20 (m, 4H) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ 24.9, 53.5, 113.8, 117.7, 126.1, 127.1, 128.9, 129.4, 145.7, 147.7 ppm. The analytical and spectroscopic data are in accordance with those reported.[11]

■ ASSOCIATED CONTENT

Supporting Information

Figures giving NMR spectra of the compounds synthesized in this paper and ^{31}P NMR chemical shifts for the estimation of the Lewis acidity by the Gutmann−Beckett method. 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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