B(C$_6$F$_5$)$_3$-Catalyzed Reductive Amination using Hydrosilanes

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S *Supporting Information*

ABSTRACT: In contrast to the established dogma that B(C$_6$F$_5$)$_3$ is irreversibly poisoned by excess H$_2$O/amine (or imine) bases, B(C$_6$F$_5$)$_3$ is actually a water-tolerant catalyst for the reductive amination of primary and secondary arylamines with aldehydes and ketones in "wet solvents" at raised temperatures and using only 1.2 equiv of Me$_2$PhSiH as reductant. Arylamines/ N-arylimines do not result in the irreversible deprotonation of H$_2$O−B(C$_6$F$_5$)$_3$, allowing sufficient B(C$_6$F$_5$)$_3$ to be evolved at raised temperatures to effect catalytic reductions. Stronger Brønsted basic amines such as ^{t}BuNH$_2$ (and derived imines) result in irreversible formation of [HO−B(C$_6$F$_5$)$_3$]$^-$ from H$_2$O−B(C$_6$F$_5$)$_3$, precluding the formation of B(C$_6$F$_5$)$_3$ at raised temperatures and thus preventing any imine reduction. A substrate scope exploration using 1 mol % nonpurified B(C$_6$F$_5$)$_3$ and "wet solvents" demonstrates that this is an operationally simple and effective methodology for the production of secondary and tertiary arylamines in high yield, with imine reduction proceeding in preference to other possible reactions catalyzed by B(C$_6$F$_5$)$_3$, including the dehydrosilylation of H$_2$O and the reduction of carbonyl moieties (e.g., esters).

KEYWORDS: *"frustrated Lewis pairs", water tolerance, reductive amination, metal-free, amines*
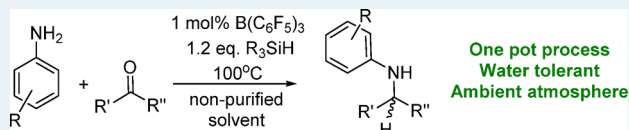
■ INTRODUCTION

The past decade has witnessed spectacular advances in metal-free catalytic reductions, particularly using "frustrated Lewis pairs" (FLPs).[1] Numerous advances built on the pioneering work of Piers (using hydrosilanes)[2] and Stephan (using H$_2$)[3] have led to B(C$_6$F$_5$)$_3$ (1) being established as a versatile reduction catalyst.[1,4] While 1 and its derivatives are effective metal-free catalysts for the reduction of imines,[1,2d,4] including enantioselective variants,[5] these procedures require prior synthesis and isolation of the imine and rigorous exclusion of H$_2$O in the subsequent reduction process. The latter necessitates anhydrous solvents and inert conditions or the in situ removal of low levels of H$_2$O from "wet" solvents/reagents using sacrificial hydrides or molecular sieves (Scheme 1, right).[6] These requirements have limited the wider uptake of 1 as a catalyst and also prevented the use of 1 as a catalyst for reductive amination where the imine is formed (along with 1 equiv of H$_2$O) and reduced in situ. Reductive amination is a one-pot method that is thus preferable from an efficiency

perspective and facilitates rapid access to amines that are ubiquitous functionalities in natural products, pharmaceuticals, and agrochemicals (such as imatinib).[7] While transition-metal catalysts have been used for reductive aminations,[8] a metal-free FLP-catalyzed process using H$_2$ or Si−H as reductant has limited precedence; to the best of our knowledge, only one example using 1 has been reported in which aniline/hexanal formally undergoes reductive amination to afford the amine in moderate (42%) conversion. However, this process uses 5 equiv of Si−H, presumably effecting H$_2$O dehydrosilylation and generating anhydrous conditions.[9]

Catalyst tolerance to H$_2$O is essential for reductive aminations, as imine (or enamine) formation produces 1 equiv of H$_2$O. However, borane Lewis acids such as 1 are highly oxophilic[10] and readily bind water, which leads to a significant enhancement in its Brønsted acidity.[11] In the presence of an appropriate Brønsted base 1-OH$_2$ undergoes deprotonation to form [1-OH]$^-$, which is catalytically inactive. In recent notable work water (and alcohol) tolerant reductions catalyzed by 1 (and derivatives) have been reported. However, to date these processes are limited to the reduction of weak Brønsted bases (relative to imines/amines) such as carbonyl moieties to alcohols.[12] Water-tolerant reductions of systems containing more Brønsted basic functional groups (e.g., anilines) catalyzed by 1 have not been reported, due to the perception that irreversible deprotonation of 1-OH$_2$ would occur, poisoning the catalyst.[12] Herein we report that B(C$_6$F$_5$)$_3$ is tolerant of excess water/arylamines, functioning as an effective catalyst for

Scheme 1. B(C$_6$F$_5$)$_3$-Catalyzed Reductive Amination (Left) and Hydrosilylation of Purified Imine (Right)
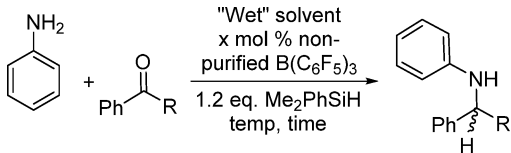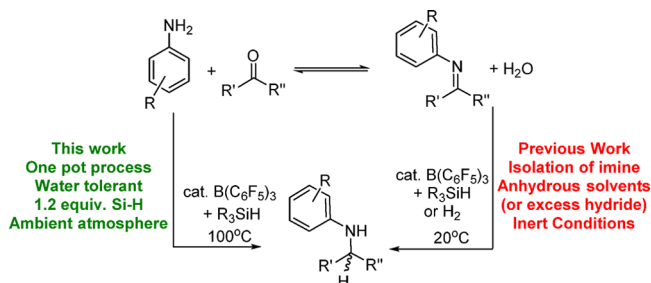
the reductive amination of a range of arylamines using only 1.2 equiv of silane as reductant.

RESULTS

As part of our ongoing investigations into water tolerant carbon Lewis acids in FLPs, a control reaction combining 5 mol % of **1**, 1 equiv of benzaldehyde, and 1.2 equiv of both aniline and Me$_2$PhSiH in o-dichlorobenzene (o-DCB) was investigated. Me$_2$PhSiH was used for direct comparison to the previously reported hydrosilylation of N-benzylideneaniline under anhydrous conditions.[2d] At 20 °C there was significant imine formation (>90%) but no reductive amination and no consumption of the silane, indicating that **1** is effectively poisoned (Table 1, entry 1). However, heating led to formation

Table 1. Reductive Amination Catalyzed by B(C$_6$F$_5$)$_3$[a]

	R	solvent	temp (°C)[a]	time (h)	amt of B(C$_6$F$_5$)$_3$ (mol %)	yield (%)[b]
1	H	o-DCB	20	20	5	0
2	H	o-DCB	60	2	5	52
3	H	o-DCB	100	0.25	5	94
4	H	CH$_2$Cl$_2$	60	2	5	80
5[c]	H	THF	80	1.5	5	90
6	H	CPME	100	0.5	5	96
7	H	CPME	100	1	1	95
8	H	o-DCB	100	0.5	1	90
9[d]	H	o-DCB	100	24	5	0
10[d]	Me	o-DCB	100	24	5	0
11	Me	o-DCB	100	1.5	1	64

[a]Reactions run in sealed tubes under an ambient atmosphere using "wet" solvents and nonpurified **1**. [b]Conversion by ^{1}H NMR spectroscopy vs mesitylene as internal standard. [c]0.95 equiv of Me$_2$PhSiH. [d]Ca. 4 atm of H$_2$ as reductant.

of the reduced product, N-benzylaniline, in good conversion. Subsequently, the reductive amination was found to proceed efficiently using nonpurified ("wet") o-DCB and nonpurified **1** under an ambient atmosphere at raised temperatures (Table 1 entries 2 and 3). Analogous reductive amination reactivity was observed when repeating the reaction in "wet" CH$_2$Cl$_2$ (entry 4), "wet" THF (entry 5), and "wet" cyclopentyl methyl ether (CPME) (entry 6), even with only 1 mol % of nonpurified **1** under ambient conditions (entry 7). While CPME is a more attractive solvent from a green chemistry perspective,[13] o-DCB was utilized hereon, as it facilitates in situ monitoring of the aliphatic region of the ^{1}H NMR spectra, enabling rapid substrate screening. The catalyzed reductive amination proceeds in the presence of >100 equiv of H$_2$O (relative to B(C$_6$F$_5$)$_3$, due to the presence of H$_2$O from the condensation reaction and from the "wet" solvent), as only 1.2 equiv of Me$_2$PhSiH is utilized, insufficient to both dry the reaction mixture (by dehydrosilylation of H$_2$O) and reduce the imine.

In a control reaction containing PhNH$_2$ but in the absence of benzaldehyde (precluding imine formation), the dehydrosilylation of H$_2$O in o-DCB catalyzed by **1** does proceed at 100 °C. Nevertheless, in these reductive aminations 1.2 equiv of Me$_2$PhSiH is sufficient for imine reduction, indicating that

imine reduction is kinetically favored over the dehydrosilylation of H$_2$O. Attempts to replace the hydrosilane reductant with H$_2$ (ca. 4 atm) under identical reductive amination conditions failed to produce any amine (entry 9). However, as the reduction of isolated benzylideneaniline with 5 mol % of purified **1** and ca. 4 atm of H$_2$ in anhydrous o-DCB was found to be extremely slow and low yielding at 100 °C, α-methylbenzylideneaniline was utilized as an alternative test substrate. Under anhydrous conditions this imine is reduced in good conversion using 10 mol % of purified **1** and ca. 4 atm of H$_2$ (>95% after 48 h at 100 °C). In contrast, combining acetophenone and aniline with 10 mol % of **1** under ca. 4 atm of H$_2$ and heating for 24 h at 100 °C led to no reductive amination (by ^{1}H NMR spectroscopy). The analogous reductive amination of acetophenone and aniline using 1 mol % of **1** and 1.2 equiv of Me$_2$PhSiH as reductant proceeded rapidly to give the desired amine (entry 11). The disparity between H$_2$ and Me$_2$PhSiH reactions is attributed to kinetic factors, as similar ^{19}F NMR spectra are observed (see the Supporting Information), indicating that **1** is not irreversibly poisoned in either case (consistent with hydrosilylation being rapid under anhydrous conditions while hydrogenation with ca. 4 atm of H$_2$ is slow even in the absence of H$_2$O). A drastic rate retardation by 20 equiv of H$_2$O with respect to **1** was also observed in the recently reported water tolerant carbonyl hydrogenation.[12c] Borane **1** is essential, as while **1-OH$_2$** forms readily in wet solvents and has a pK$_a$ similar to that of HCl,[11] the use of a range of strong Brønsted acids (including H$_2$SO$_4$, HNO$_3$, HCl, and CF$_3$COOH, with the last previously used to promote hydrosilane reductions of C=O)[14] as catalysts at 5 mol % loading led to no reductive amination of benzaldehyde/aniline/Me$_2$PhSiH mixtures on heating to 100 °C (20 h). The ability of **1** to catalyze reductive aminations expands the limited list of examples where B(C$_6$F$_5$)$_3$ can be used for σ-bond activation in the presence of excess H$_2$O/base mixtures to moderately basic arylamines and N-arylimines.[12] However, it is significant that more basic amines, e.g., ^{t}BuNH$_2$, do not undergo reductive amination catalyzed by **1** using Me$_2$PhSiH under identical conditions.

To provide more insight, particularly into the amine disparity, the model reaction was analyzed at each stage by ^{1}H, ^{19}F, and ^{11}B NMR spectroscopy (Figure 1). This was performed with 5 mol % of **1** (see the Supporting Information)
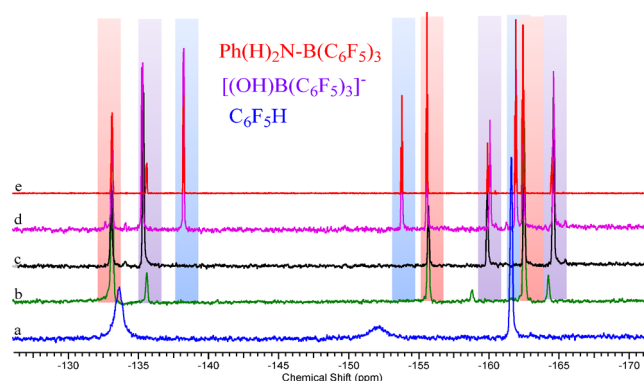

Figure 1. ^{19}F NMR spectra in wet o-DCB (with a capillary insert of d_6-DMSO) of the in situ reaction mixture showing (a) 1 equiv of B(C$_6$F$_5$)$_3$·xH$_2$O, (b) +1 equiv of aniline, (c) +1 equiv of benzaldehyde, (d) heating to 100 °C for 18 h, and (e) +1.2 equiv of Me$_2$PhSiH after heating to 100 °C for 2 h.

and stoichiometric **1** (to facilitate observation of [11]B resonances). The ^{19}F NMR spectra for both loadings of **1** reveal that the same major species are present at each stage, albeit with the resonances for **1-OH₂** shifting depending on the ratio **1**:H₂O as previously reported.[11] On combination of equimolar aniline and **1-OH₂** in "wet" o-DCB two compounds are observed: **1-NH₂Ph** and [**1-OH**]⁻ (Figure 1, spectrum b). A change in their relative ratio is then observed on addition of 1 equiv of benzaldehyde, with [**1-OH**]⁻ increasing (spectrum c). At this point significant N-benzylideneaniline is observed in the ^{1}H NMR spectrum, indicating a reduction in the concentration of aniline and an increase in that of H₂O consistent with the observed change in the **1-NH₂Ph**:[**1-OH**]⁻ ratio. It should be noted that coordination of N-benzylideneaniline to **1** is not observed at any point throughout this reaction sequence. Anion [**1-OH**]⁻ corresponds to an [11]B resonance at −4.8 ppm (observed in the stoichiometric in **1** reaction), significantly upfield from **1-OH₂** (δ^{11}_B +4.6 ppm in difluorobenzene),[12d,15] while **1-NH₂Ph** has δ^{11}_B −6.4 ppm (see the Supporting Information). Aniline dissociates rapidly from **1** at room temperature (confirmed by the addition of benzaldehyde to **1-NH₂Ph** leading to rapid imine formation); therefore, the persistence of **1-NH₂Ph** in the reaction mixture is not due to kinetic factors. This conclusion was further supported by heating the reaction mixture to 100 °C for 18 h (spectrum d), which led to changes in the ratio of **1-NH₂Ph** and [**1-OH**]⁻ along with slow formation of C₆F₅H (by ^{19}F NMR spectroscopy); crucially significant amounts of **1-NH₂Ph** and [**1-OH**]⁻ both remained after heating. The addition of Me₂PhSiH to the reaction mixture and further heating then resulted in imine reduction (by ^{1}H NMR spectroscopy). The activity observed in these sequential reactions at both 100 and 5 mol % loadings is attributed to **1-NH₂Ph** or [**1-OH**]⁻ (after protonation to form **1-OH₂**), releasing a critical concentration of the active catalyst **1** at raised temperatures.

Previously, N-benzylidene-$tert$-butylamine has been hydrosilylated using catalytic **1** and Me₂PhSiH under anhydrous conditions.[2d] Attempting the reductive amination of [t]BuNH₂ and benzaldehyde with **1-OH₂**/Me₂PhSiH resulted in no reduction under a range of conditions. Examination of the ^{19}F NMR spectrum of **1**/tBuNH₂ mixtures in "wet" o-DCB (Figure 2, spectrum a) revealed that [**1-OH**]⁻ was the major C₆F₅-containing species observable (with and without
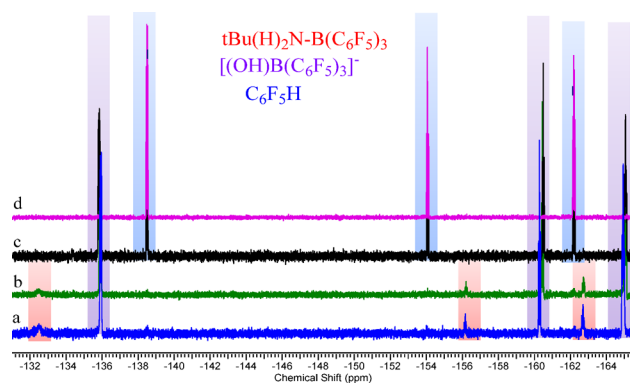
benzaldehyde; Figure 2, spectrum b) and after heating to 100 °C became the only B(C₆F₅)₃ containing species observable (Figure 2, spectrum c). Significant N-benzylidene-$tert$-butylamine was observed in the ^{1}H NMR spectrum, confirming imine formation. Under these conditions [**1-OH**]⁻ forms effectively irreversibly, as indicated by the absence of imine reduction on addition of Me₂PhSiH and heating to 100 °C for 24 h (there is no consumption of silane by ^{29}Si NMR spectroscopy). This confirms that [**1-OH**]⁻ does not react with Me₂PhSiH at raised temperatures. The effective poisoning of catalyst **1** is further indicated by the imine-free reaction, where **1-OH₂**/tBuNH₂/Me₂PhSiH mixtures in "wet" o-DCB do not lead to H₂O dehydrosilylation or consumption of any silane even on prolonged heating at 100 °C. Dehydrosilylation therefore does not proceed in the presence of stoichiometric [t]BuNH₂, whereas it does in the presence of PhNH₂. Heating the [t]BuNH₂-containing reaction mixture to 100 °C only leads to decomposition of [**1-OH**]⁻ to C₆F₅H and unidentified boron species. The reactivity disparity is attributed to the greater Brønsted basicity of [t]BuNH₂/benzylidene-$tert$-butylamine relative to aniline, which does not irreversibly deprotonate **1-OH₂** (Scheme 2, left). Reversible deprotonation

Scheme 2. Disparate Equilibrium Positions on Combining Aniline or $tert$-Butylamine with Benzaldehyde and 1 in Wet o-DCB
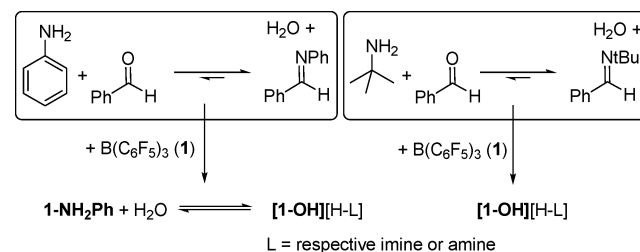

of **1-OH₂** is essential for catalytic activity, as it enables the release of sufficient **1** at raised temperatures (from **1-OH₂** or **1-NH₂Ph**). These observations are related to the recent reports on water tolerant carbonyl hydrogenation using **1** and weakly basic conditions, where the key factor is also the deprotonation of **1-OH₂** being reversible.[12]

It is noteworthy that the basicity and the nucleophilicity of the amine are both important. The conjugate acids of [n]BuNH₂ and [t]BuNH₂ have similar pK_a values (10.59 and 10.55, respectively),[16] and their respective imines have similar Brønsted basicities, yet these two amines result in different outcomes. On combination of **1**, [n]BuNH₂, and benzaldehyde **1-[n]BuN=C(H)Ph** is the major product observed by NMR spectroscopy. This is not a kinetic product, as adding [n]BuNH₂/benzaldehyde to **1-OH₂** initially forms predominantly [**1-OH**]⁻ but subsequent heating to 100 °C produces mixtures containing predominantly **1-[n]BuN=C(H)Ph** (along with C₆F₅H). The lower steric bulk of n-butyl relative to $tert$-butyl presumably makes the dative bond in **1-[n]BuN=C(H)Ph** stronger and thus alters the relative energetics, the equilibrium position, and thus the species observed post-heating to 100 °C. Irrespective of this, [n]BuNH₂/benzaldehyde mixtures do not undergo reductive amination catalyzed by **1** (or **1-OH₂**). This is attributed to N-benzylidene-n-butylamine coordinating strongly to **1** (^{19}F resonances for **1-[n]BuN=C(H)Ph** persist on prolonged heating in the presence of Me₂PhSiH). This observation is consistent with previous reports in which **1** does not catalyze the

Figure 2. ^{19}F NMR spectra in wet o-DCB (with a capillary insert of d_6-DMSO) of the in situ reaction mixture showing (a) 1 equiv of B(C₆F₅)₃·xH₂O + 1 equiv of [t]BuNH₂, (b) +1 equiv of benzaldehyde, (c) heating to 100 °C for 2 h, and (d) +1.2 equiv of Me₂PhSiH after heating to 100 °C for 2 h.

hydrosilylation of the sterically similar imine benzylidenemethylamine under anhydrous conditions due to its strong coordination to **1**.[2d]

These NMR spectroscopic studies allow the key requirements for successful reductive amination using **1**/Me₂PhSiH at raised temperatures to be defined as (i) the amine and corresponding imine need to be of sufficiently low Brønsted basicity to reversibly deprotonate **1-OH₂** and (ii) the amine and imine need to be of sufficiently low nucleophilicity to reversibly bind to **1**. When these requirements are fulfilled, a critical concentration of **1** is present at high temperatures to activate the silane to nucleophilic attack, as previously elucidated.[2e−g,17] The nucleophile attacking $R_3Si-H-B(C_6F_5)_3$ may be an imine or H_2O, the latter forming $[Me_2PhSi-OH_2][H\text{-}1]$, which could then protonate the imine. The silylated or protonated iminium cation would then be reduced by hydride transfer from $[1\text{-}H]^-$ (Scheme 3). Attempts to observe intermediates (e.g., silylated

**Scheme 3. Proposed Reductive Amination Pathways**
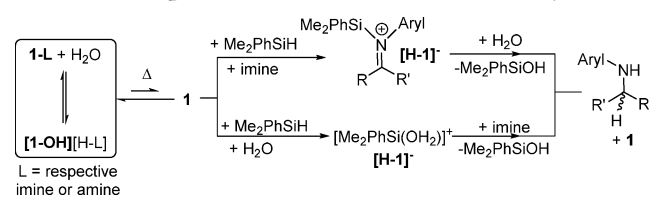
iminium cations or silylated amines) over a range of temperatures were not successful, as the hydrolysis of Me₂PhSi-protected amines is rapid under these conditions even at 20 °C; thus, either mechanism could be operating at 100 °C (Scheme 3). The expected silicon byproducts, Me₂PhSiOH and (PhMe₂Si)₂O, are observed by ²⁹Si NMR spectroscopy. Attempts to observe a silylated intermediate with bulkier silanes, for example Ph₃SiH, were also unsuccessful. Furthermore, hydrolysis of *N*-SiPh₃-substituted amines also occurs more rapidly than the reductive amination reaction using Ph₃SiH under these conditions.

Despite being slower than the reduction of isolated *N*-benzylideneaniline under anhydrous conditions,[2d] $B(C_6F_5)_3$-catalyzed reductive amination is attractive due to the simplicity of the procedure (all reactants are used as received without any additional purification and combined at the start), compatibility with green solvents (CPME), and the low catalyst loading. With the requirements for reductive amination in hand, the scope of this process catalyzed by 1 mol % of nonpurified **1** and using 1.2 equiv of Me₂PhSiH in wet *o*-DCB was explored (Table 2).

A range of functionalized benzaldehydes were compatible (**2a−f**) with in situ conversions, and isolated yields (e.g., **2d**) were moderate to good. Diaryl, aryl alkyl, and dialkyl ketones (**2g−i**) were amenable to reductive amination. However, acetaldehyde and butyraldehyde produced complex mixtures in which the desired product was only a minor component. The inclusion of electron-withdrawing and electron-donating substituents on the aromatic aldehyde and the aniline was also realized (e.g., **2j−m**). It is notable that the more Brønsted basic and nucleophilic *p*-methoxyaniline (PMP) was viable in reductive amination under these conditions, albeit requiring 1.5 h. The longer reaction time is attributable to a lower concentration of catalyst **1** at raised temperatures, with in situ ¹⁹F NMR spectroscopy revealing a higher proportion of [**1-OH**]⁻ (relative to **1-NH₂Aryl**) for *p*-methoxyaniline in

Table 2. Reductive Amination Substrate Scope
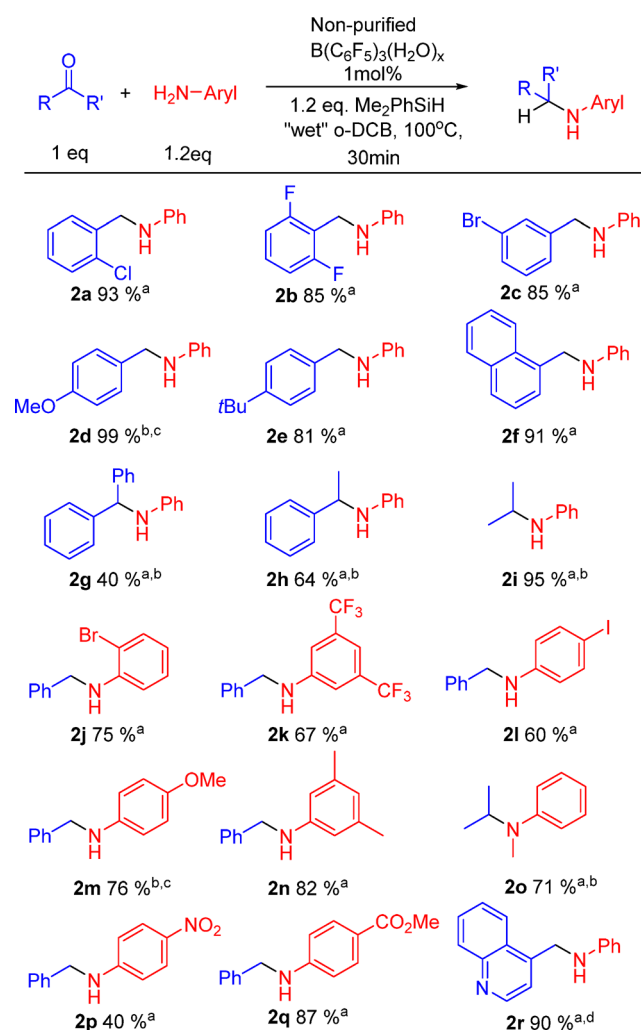
*a*Yield calculated by ¹H NMR spectroscopy using mesitylene as an internal standard. *b*1.5 h. *c*Isolated yield. *d*20 h.

comparison to that observed for aniline (preheating). This is consistent with the greater Brønsted basicity of PMP. Compatibility with PMP is significant, as it generates a masked N−H moiety which can be readily deprotected to provide access to the parent primary amine. The reductive amination of a secondary arylamine also was achieved, with in situ enamine formation and reduction proceeding in good yield (**2o**). Nitro groups on the arylamine are also amenable (**2p**), but in lower yield, due to an imine formation equilibrium position favoring benzaldehyde (significant carbonyl reduction is observed). We also explored functional groups that may interfere with reductive amination catalyzed by **1**. This revealed that reductive amination proceeds in preference to ester hydrosilylation (**2q**)[2] and that exogenous base (in the form of a substituted quinoline) is compatible (**2r**). It should be noted that the formation of **2r** required 20 h at 100 °C with the additional Brønsted base shifting the equilibrium position toward [**1-OH**]⁻, thereby reducing the quantity of **1** present at high temperature.

To probe further the effect of exogenous base on the reductive amination methodology, 1 equiv of PMes₃ was added as a non-nucleophilic base to the reaction of PhNH₂/benzaldehyde/Me₂PhSiH catalyzed by 5 mol % of **1**. This

resulted in a drastic change to the ^{19}F NMR spectrum preheating (relative to the PMes$_3$-free reaction), with only [**1-OH**]$^-$ observed ([HPMes$_3$]$^+$ is also observed in the ^{31}P NMR spectrum). Nevertheless, on heating this mixture to 100 °C reductive amination still proceeds, albeit slowly, indicating that the protonation of [**1-OH**]$^-$ by [HPMes$_3$]$^+$ also proceeds under these conditions to generate **1-OH$_2$** and subsequently catalytically active **1**.

Finally, the scope of the methodology was further extended to form biologically important N-substituted isoindolinones starting from 2-carboxybenzaldehyde and aniline.[18] This process involves an amination/amidation sequence and was successful on a gram scale using 5 mol % of nonpurified **1** and 1.2 equiv of Me$_2$PhSiH in "wet" o-DCB to produce *N*-Ph-isoindolinone in 92% yield (1.24 g; Scheme 4), isolated without column chromatography.

Scheme 4. Catalyzed Formation of *N*-Ph-isoindolinone[a]
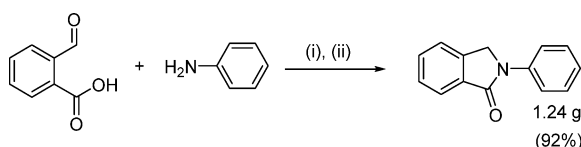
[a]Legend: (i) "wet" o-DCB, 15 min; (ii) 5 mol % of **1-OH$_2$**, 1.2 equiv of Me$_2$PhSiH, 100 °C, 1 h.

CONCLUSION

In summary, B(C$_6$F$_5$)$_3$ is a highly effective and water tolerant catalyst for the reductive amination of primary and secondary arylamines at raised temperatures using nonpurified solvents and reagents. This process uses only 1.2 equiv of Me$_2$PhSiH; thus, under these conditions imine reduction is faster than H$_2$O dehydrosilylation. The key to this successful reductive amination is the fact that arylamines (and their derived imines) do not irreversibly deprotonate H$_2$O–B(C$_6$F$_5$)$_3$ and do not form strong dative bonds to B(C$_6$F$_5$)$_3$, two outcomes that would otherwise preclude catalysis. This operationally simple reductive amination methodology represents a rare example of B(C$_6$F$_5$)$_3$ being effective for σ-bond activation in the presence of (super) stoichiometric H$_2$O and moderate amounts of Brønsted bases. Furthermore, it extends significantly the Lewis bases compatible with H$_2$O–B(C$_6$F$_5$)$_3$ (i.e., that form [HO–B(C$_6$F$_5$)$_3$]$^-$ reversibly) to arylamines, N-arylimines, quinolines, and PMes$_3$.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b02896.

Full experimental details and NMR spectra (PDF)

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Notes
The authors declare no competing financial interest.

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