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$B(C_6F_5)_3$-Catalyzed Hydrosilation of Imines via Silyliminium Intermediates

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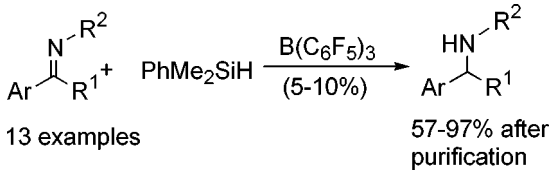
ABSTRACT



A broad range of benzaldimines and ketimines can be hydrosilated efficiently, employing $B(C_6F_5)_3$ as a catalyst in conjunction with $PhMe_2SiH$. Spectral evidence supports the intermediacy of a silyliminium cation with a hydridoborate counterion formed via abstraction of a hydride from $PhMe_2SiH$ by $B(C_6F_5)_3$ in the presence of imines.

Although used primarily as an olefin polymerization cocatalyst,[1] applications of the commercially available borane, $B(C_6F_5)_3$, in organic synthesis are growing.[2] While it is proposed to operate in a typical carbonyl-activating capacity in aldol and Diels−Alder type reactions,[2a] in the hydrosilation and allylstannation reactions it mediates, mechanistic studies suggest its role is to activate the group 14 reagent rather than the carbonyl or alcohol substrate.[3] For silanes, the silicon center assumes silylium character as the borane abstracts the silane hydride; substrate then displaces $[HB(C_6F_5)_3]^-$, producing an ion pair which collapses to the observed products. In these reactions, silylium intermediates have not been directly observed.[4]

The reduction of imines to amines is an important transformation in organic chemistry.[5] Most methods involve borohydride reagents or transition metal hydrogenation catalysts; few general methods employing main group Lewis acid *catalysts* have appeared.[5] In this Letter, we report the use of $B(C_6F_5)_3$ as a mild, effective catalyst for the hydrosilation of imine functions. In addition to demonstrating the scope of $B(C_6F_5)_3$-mediated imine reduction, we present convincing spectral evidence for the intermediacy of a silyliminium[6,7]/hydridoborate ion pair,[8] supporting the mechanistic proposals advanced for carbonyl hydrosilation.[3a,b]

(1) Chen, Y.-X. E.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

(2) For example, see: (a) Ishihara, K.; Yamamoto, H. *Eur. J. Org. Chem.* **1999**, 527. (b) Ooi, T.; Uraguchi, D.; Kagoshima, N.; Maruoka, K. *J. Am. Chem. Soc.* **1998**, *120*, 5327. (c) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 6179. (d) Gevorgyan, V.; Liu, J.-X.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1997**, 37. (e) Ishihara, K.; Hanaki, N.; Funahasi, M.; Miyata, M.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1721.

(3) (a) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440. (b) Park, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090. (c) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887. (d) Blackwell, J. M.; Piers, W. E.; Parvez, M. Org. *Lett.* **2000**, *2*, 695.

(4) Stannyloxonium intermediates have, however, been observed by NMR spectroscopy, see ref 3d.

(5) For recent reviews on imine reductions, see (a) Kobayashi, S.; Ishitani, H. *Chem. Rev.* **1999**, *99*, 1069. (b) Hutchins, R. O.; Hutchins, M. K. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 8, p 25.

(6) For proposed intermediacy of silyliminium cations, see: (a) Jahangir; MacLean, D. B.; Brook, M. A.; Holland, H. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1608. (b) Johannsen, M.; Jorgensen, K. A.; Helmchen, G. *J. Am. Chem. Soc.* **1998**, *120*, 7637. For a proposed stannyliminium intermediate, see: Suwa, T.; Shibata, I.; Nishino, K.; Baba, A. *Org. Lett.* **1999**, *1*, 1579.

(7) Silylnitrilium, silylpyridinium, and silylimidazolium cations have been characterized, see: Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1191 and references therein.

(8) Abstraction of hydride from stannanes by $B(C_6F_5)_3$ has been proposed, see: Lambert, J. B.; Kuhlmann, B. *J. Chem. Soc., Chem. Commun.* **1992**, 931. However, no direct spectral evidence has been provided yet for silanes.

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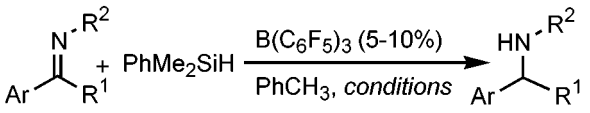
Table 1. Hydrosilation of Imines to Amines



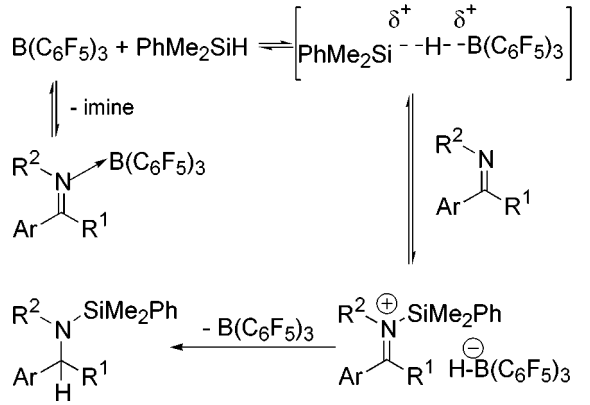
entry	R	R^1	R^2	*conditions*	yield
1	Ph	H	SO_2Ph	r.t., 30 min	93%
2	Ph	H	^{t}Boc	r.t., 30 min	60%[a]
3	Ph	H	Ph	r.t., 60 min	95%
4	Ph	H	Bn	70 °C, 3 h	91%
5	Ph	H	4-MeOPh	70 °C, 1.5 h	>95%[b]
6	Ph	H	2-MeOPh	r.t., 2 h	86%
7	4-MeOPh	H	Bn	70 °C, 17.5 h	97%
8	Ph	H	Me	70 °C, 48 h	n.r.
9	Ph	H	allyl	70 °C, 26 h	57%
10	Ph	H	^{t}Bu	r.t., 30 min	80%
11	Ph	Me	Bn	r.t., 4h	95%
12			Bn	r.t., 23 h	95%
13	Ph	Ph	Bn	r.t., 96 h	96%

[a] Two-step yield from PhCH(N^{t}Boc)SO_2Ph after desulfonylation with K_2CO_3. [b] Unable to completely purify from silane impurities.

As detailed in Table 1, a variety of benzaldimines and ketimines are hydrosilated in good to excellent isolated yield (of desilated amine) by employing 5−10 mol % of $B(C_6F_5)_3$ and a stoichiometric amount of $PhMe_2SiH$.[9] These substrates differ primarily in the nitrogen substitutent R^2 and produce a diverse range of amines with R^2 = SO_2Ph, ^{t}Boc, Bn, Ph, 2- and 4-MeOPh, allyl, and ^{t}Bu.[10] The rates for hydrosilation of aldimines vary considerably, ranging from 30 min at room temperature (entries 1 and 2) to 26 h at 70 °C (entry 9), depending on the nature of R^2.

The qualitative reactivity trends observed in Table 1 are consistent with a mechanism analogous to that found for hydrosilation and allylstannation of carbonyls.[3b,d] Thus, as shown in Scheme 1, abstraction of a hydride from the silane by $B(C_6F_5)_3$ in the presence of the imine substrate can lead to the silyliminium/hydridoborate ion pair, which either collapses to product or reacts with another equivalent of silane.

Scheme 1. Proposed Mechanism for Hydrosilation of Imines



Several observations support this picture of the reaction. Generally, the less basic imines of Table 1 are hydrosilated more readily than the more basic examples. This implies that when more borane is free to activate the silane reagent, reduction is facilitated. For example, when R^2 is strongly electron withdrawing, as in entries 1 and 2 of Table 1, the hydrosilation is rapid and exothermic. Indeed, by ^{19}F NMR spectroscopy, the imine substrate of E1 does not complex to $B(C_6F_5)_3$ in solution. Comparison of E3 and E5 shows that increasing the basicity of the imine through incorporation of a *para*-OMe group slows the reaction considerably. Furthermore, as the steric size of the R^2 substituent increases in the order E8, E9, E4, and E10, the reduction rate increases dramatically. Again, when R^2 is ^{t}Bu (E10), no complexation between the imine substrate and $B(C_6F_5)_3$ in the absence of silane is detected by ^{19}F NMR spectroscopy, indicating that most of the borane catalyst is available to activate the silane. In contrast, for R^2 = Me, no reduction is observed even under forcing conditions. In this case, the imine coordinates strongly to the borane catalyst,[11] effectively shutting down the reaction. Finally, the ketimine of E11 is hydrosilated under milder conditions than those of the corresponding aldimine (E4), again reflective of the relative basicities of these two substrates toward $B(C_6F_5)_3$.

The chemistry involving the ketimine derived from benzophenone (E13) provides convincing support for the mechanism depicted in Scheme 1. The rate of hydrosilation of this substrate seemed anomalously slow in light of the trends discussed above. We thus chose to examine this particular reaction more closely via NMR spectroscopy. When Ph_2C═NBn, $PhMe_2SiH$, and $B(C_6F_5)_3$ are mixed in equimolar ratios in C_6D_6, formation of a liquid clathrate at the bottom of the NMR tube occurs rapidly,[12] indicative of formation of an ion pair of some sort. NMR spectroscopy can be performed directly on this liquid clathrate, using occluded solvent as a deuterium lock. ^{19}F and ^{11}B NMR spectroscopy are consistent with the presence of a hydridoborate anion.[13] Observation of a cross-peak in a $^1H-^{11}B$ HETCOR experiment confirms the direct H−B bonding required. The ^{29}Si

(9) **General Procedure for Hydrosilation of Imines:** To an oven-dried round-bottom flask containing imine (1.0 mmol) in 1 mL of dry $PhCH_3$ under an Ar atmosphere was added $B(C_6F_5)_3$ (26 mg (5 mol %) or 51 mg (10 mol %)). To this solution was then added $PhMe_2SiH$ (1.05 mmol) via syringe. The reaction mixture was then stirred at room temperature or heated to 70 °C in an oil bath for the required period of time. Reactions were monitored by GC-MS to determine when they were complete. Upon completion, the reaction mixtures were immediately columned using hexanes/ethyl acetate mixtures as eluent. The desilated amines were isolated, with ^1H NMR then being used to assess purity (see Supporting Information).

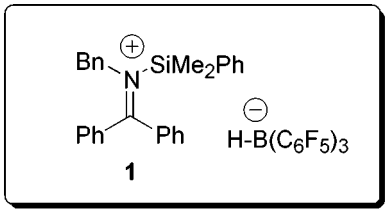
(10) For nitrogen deprotection strategies for these functional groups, see: Greene, T. W.; Wuts, P. G. *Protecive Groups in Organic Synthesis*, 2nd ed.; John Wiley and Sons: New York, 1991.

(11) A paper describing $B(C_6F_5)_3$ adducts of imines is in preparation.

(12) Lambert has also reported this behavior when generating solvent-coordinated silylium-type species, see: Lambert, J. B.; Zhang, S.; Ciro, C. M. *Organometallics* **1994**, *13*, 2430.

(13) For a detailed description of the use of ^{19}F and ^{11}B NMR spectroscopy as diagnostics for coordination number and charge on boron in $B(C_6F_5)_3$ derivatives, see ref 3d and references therein.

NMR data is also in line with a coordinated silylium species.[7] Silyliminium ion pair **1** (Figure 1) represents the key intermediate proposed in Scheme 1 and confirms the viability of



^{19}F: δ_o = -132.4 ppm, δ_p = -163.8 ppm,
δ_m = -166.6 ppm; $\Delta_{p\text{-}m}$ = 2.8 ppm

^{11}B: δ = -24 ppm

^{29}Si: δ = 27 ppm

^{1}H: $\delta_{B\text{-}H}$ = 4.2-5.2 ppm (br.)

Figure 1. Selected spectral data for silyliminium intermediate.

hydride abstraction by $B(C_6F_5)_3$ from silanes in the presence of a Lewis basic substrate.

To assess the importance of this species under catalytic conditions, we monitored the reaction of E13 by ^{1}H and ^{19}F NMR spectroscopy. As shown by the ^{19}F NMR spectra in Figure 2, when equimolar quantities of $PhMe_2SiH$ and $Ph_2C{=}NBn$ are mixed with 10 mol % of $B(C_6F_5)_3$, initially the borane is sequestered by the imine, leading to a complicated spectrum (Figure 2a). This spectrum of 15 separate resonances is due to the imine adduct of $B(C_6F_5)_3$, where all three C_6F_5 groups are inequivalent and experience restricted rotation about the B−C bonds.[11] Upon heating, a new set of signals, attributable to **1**, appear (Figure 2b) and eventually supplant the imine:borane adduct signals. As silated product is forming (as observed by ^{1}H NMR), only hydridoborate is observable in the ^{19}F NMR spectrum. Clearly, the $B(C_6F_5)_3$ in the system is tied up as **1** throughout the course of the reaction, raising the possibility that "$PhMe_2Si^+$", rather than $B(C_6F_5)_3$, is the catalytically active species. Work is still in progress to conclusively establish whether an additional equivalent of silane or hydridoborate delivers the hydride to consummate hydrosilation.

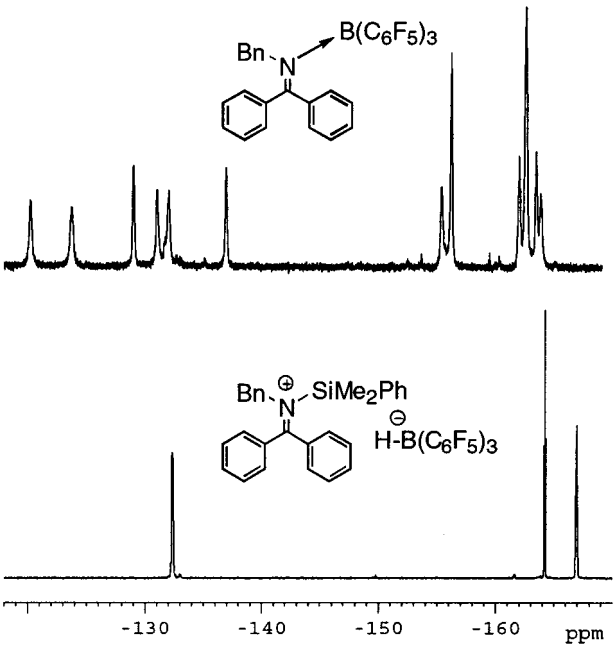


Figure 2. 282 MHz ^{19}F NMR spectra of reaction of 1:1 $PhMe_2SiH$:$Ph_2C{=}NBn$ + 10% $B(C_6F_5)_3$ at (a) rt after mixing and (b) 70 °C after 31 min.

In conclusion, we have developed a practical method for carrying out imine reduction via hydrosilation using commercially available $B(C_6F_5)_3$ as a catalyst. We have also begun to elucidate the mechanism for this reaction by showing that the reaction proceeds via activation of the imine by "$PhMe_2Si^+$" and not by $B(C_6F_5)_3$.

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Supporting Information Available: Experimental details, including complete spectral data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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