Hydrosilylation

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Chemoselective Silylative Reduction of Conjugated Nitriles under Metal-Free Catalytic Conditions: β-Silyl Amines and Enamines**

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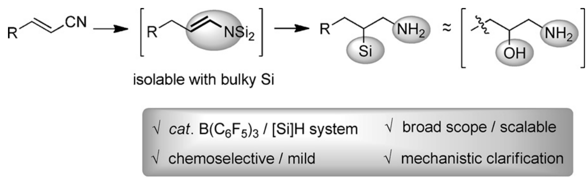
Dedicated to Professor Mahn-Joo Kim on the occasion of his 60th birthday

Abstract: *The $B(C_6F_5)_3$-catalyzed silylative reduction of conjugated nitriles has been developed to afford synthetically valuable β-silyl amines. The reaction is chemoselective and proceeds under mild conditions. Mechanistic elucidation indicates that it proceeds by rapid double hydrosilylation of the conjugated nitrile to an enamine intermediate which is subsequently reduced to the β-silyl amine, thus forming a new $C(sp^3)$–Si bond. Based on this mechanistic understanding, a preparative route to enamines was also established using bulky silanes.*

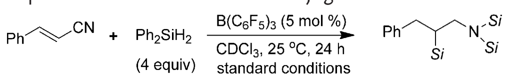
Functional-group-containing organosilanes are known to be highly useful as synthetic intermediates in organic synthesis[1,2] and as monomeric units for crosslinking in industrial polymer chemistry.[3] One convenient approach to those compounds is to utilize hydrosilylation of olefins containing functional groups,[4] thus allowing selective installation of $C(sp^3)$–Si bonds in the molecular backbone.[3a,5] Since carbon–silicon bonds are readily converted into hydroxy groups under oxidative conditions, we anticipated that 1,*n*-amino alcohols ($n = 2$ or 3), which are key components in synthetic and medicinal chemistry,[6] could be accessed by selective hydrosilylation of (conjugated) nitriles followed by oxidation. Several preparative methods of hydrogenation or hydrosilylation are available for the reduction of nitriles to primary amines.[7] In contrast, tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] and its derivatives have been used in the reduction of olefins, imines, ethers, carbonyls, and N-heteroarenes with either hydrosilanes[5a,c,8] or hydrogen.[9] In spite of the broad substrate scope of the boron catalysis, reduction of (conjugated) nitriles still remains little explored. Along these lines, Stephan and co-workers reported an elegant example showing that frustrated Lewis pairs (FLP) generated in situ from phosphine and borane can hydrogenate nitrile–boron adducts.[10] While conjugated nitriles are known to be partially reduced to α-silylated nitriles under metal-catalyzed conditions,[11] a chemoselective reduction to silylated amines is unprecedented to the best of our knowledge.

Recently, we developed a silylative reduction of quinolines to form a new $C(sp^3)$–Si bond, β to the nitrogen atom of tetrahydroquinoline products, with excellent chemo-, regio-, and stereoselectivity.[12] In this context, we anticipated that conjugated nitriles would undergo silylative reduction to afford β-silyl amines, a synthetic equivalent to β-amino alcohols (Scheme 1). Described herein is the successful realization of this transformation and mechanistic elucidation to reveal a stepwise pathway which offers an additional opportunity to establish a facile route to isolable enamine compounds.



Scheme 1. Silylative reduction of conjugated nitriles.

Table 1: Optimization of reduction of conjugated nitriles.[a]



Entry	Changes from the "standard conditions"	Yield [%]
1	none	86
2	$CHCl_3$ solvent in Schlenk flask	85
3	$CHCl_3$ in reaction vial	82
4	3 mol% of $B(C_6F_5)_3$ instead of 5 mol% (36 h)	81
5	6 h instead of 24 h	34
6	CD_2Cl_2 instead of $CDCl_3$	66
7	[D8]Toluene instead of $CDCl_3$	71
8	Et_2SiH_2 (4 equiv) instead of Ph_2SiH_2 (30 min)	93
9	$PhMeSiH_2$ (4 equiv) instead of Ph_2SiH_2 (2 h)	73
10	$PhMe_2SiH$ (4 equiv) instead of Ph_2SiH_2	<1
11	Et_3SiH (4 equiv) instead of Ph_2SiH_2	<1
12	$PhSiH_3$ instead of Ph_2SiH_2	29

[a] Reactions were carried out on a 0.5 mmol scale and yields were determined by ^1H NMR spectroscopy (1,1,2,2-tetrachloroethane used as the internal standard).

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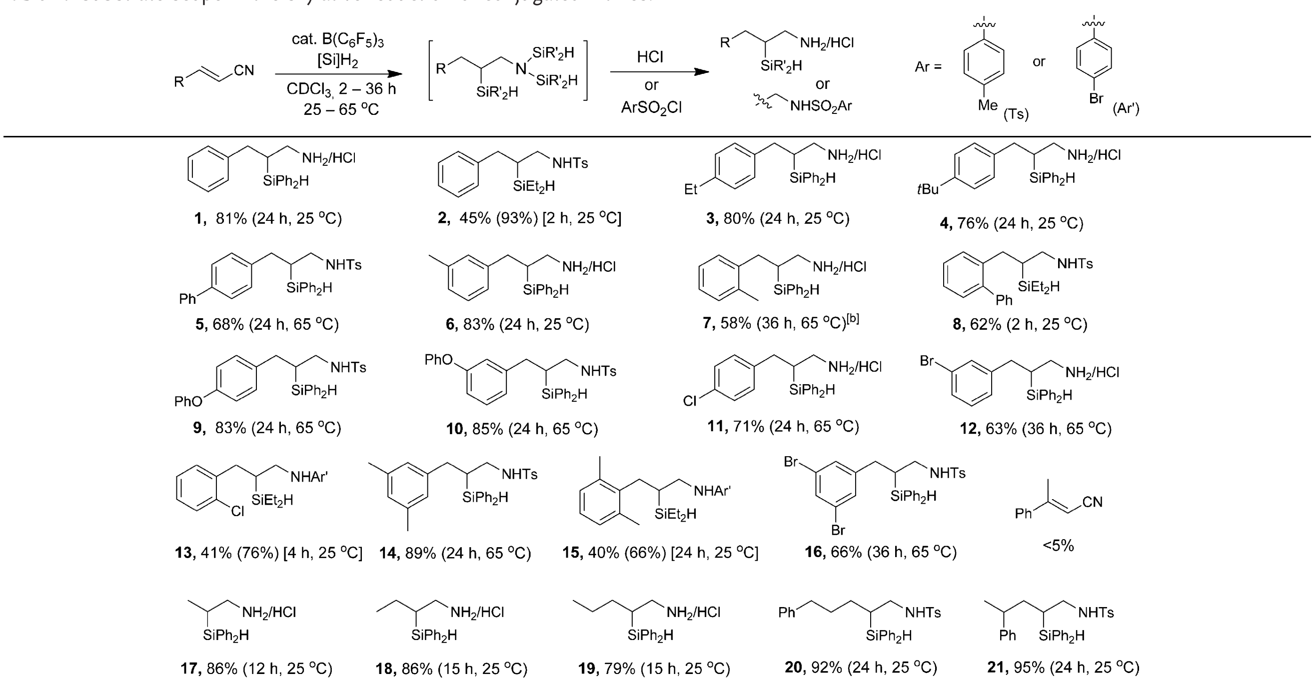
We commenced our optimization study from a silylative reduction of conjugated nitriles using cinnamonitrile as a model substrate (Table 1; also see the Supporting Information for details). While the reaction was found to be facile with 4 equivalents of diphenylsilane (Ph_2SiH_2) in the presence of the $B(C_6F_5)_3$ catalyst (5 mol %) in $CDCl_3$ at room temperature to afford the β-silyl-*N*,*N*-disilylamine, as determined by ^{1}H NMR analysis (entry 1), additional reaction parameters were examined under various reaction conditions. A similar range of efficiency was observed for reactions run either in a Schlenk flask or reaction vial (entries 2 and 3). While the product yield was still satisfactory with a lower loading of the catalyst (entry 4), the efficiency turned out to be more sensitive to the reaction time (entry 5), and solvents other than chloroform were less effective (entries 6 and 7). Significantly, the silylative reduction of cinnamonitrile was more efficient when diethylsilane (Et_2SiH_2) was employed to give the β-diethylsilyl-*N*,*N*-diethylsilylamine product, even under shorter reaction times (93 %, 30 min; entry 8), whereas the use of phenylmethylsilane resulted in moderate product yield (entry 9). Since these β-diethylsilyl and β-phenylmethylsilyl products were found to be less stable than the corresponding β-diphenylsilyl analogues, the silylative reduction of conjugated nitriles was carried out with diphenylsilane in most cases. In addition, the reaction was less effective when different types of silanes (e.g. mono- or trihydrosilanes) were employed as the reducing reagent (entries 10–12).

With the optimal reaction conditions in hand, we subsequently investigated the scope with respect to the α,β-unsaturated nitriles (Table 2). As described above, cinnamonitrile reacted efficiently with either diphenylsilane or diethylsilane to afford the corresponding products in good yields (**1** and **2**, respectively). While the former product was isolated as a hydrochloride salt, the latter one was converted in situ into its *N*-(*p*-toluenesulfonyl) derivative. It needs to be mentioned that the moderate yield of **2** (45 %) was mainly the result of the low efficiency of the conversion of the crude reaction mixture into its sulfonamide. The structure of **2** was confirmed by an X-ray crystallographic analysis.

Cinnamonitrile compounds having substituents on the phenyl moiety were converted into the corresponding products in high yields irrespective of their electronic properties. For instance, substrates bearing ethyl, *tert*-butyl, and phenyl substituents at the *para* position underwent the silylative reduction in satisfactory yields (**3**–**5**; Table 2). In contrast, the position of the substituents influenced the reaction efficiency to some extent, as seen in the formation of the products **6**–**8**. In the case of sterically demanding substrates, such as *ortho*-methylcinnamonitrile, the reaction with diphenylsilane (Ph_2SiH_2) was carried out at 65 °C to obtain a reasonable yield of **7**. Interestingly, the use of diethylsilane instead of diphenylsilane allowed the reaction of *ortho*-phenylcinnamonitrile to proceed at room temperature, thus giving an analogous product (**8**) in good yield. The present reaction conditions were compatible with a range of functional groups such as phenoxy and halides (**9**–**13**).[8c,13] Cinnamonitriles having multiple substituents also reacted smoothly to give the desired products in moderate to good yields (**14**–**16**). Again, the moderate yields of the isolated products were mainly a result of the subsequent conversion of the initially generated β-silyl-*N*,*N*-disilylamines into the corresponding N-sulfonamides. In contrast, reactions of disubstituted substrates such as β-methylcinnamonitrile were observed to be negligible under the optimized reaction conditions.

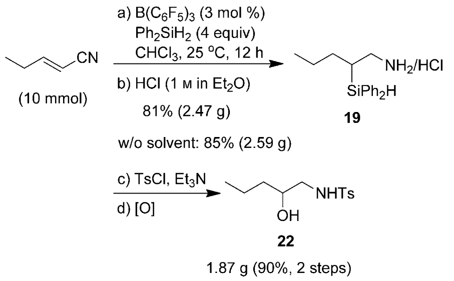
Table 2: Substrate scope in the silylative reduction of conjugated nitriles.[a]



[a] Substrate (0.5 mmol), silane (4 equiv), and $B(C_6F_5)_3$ (5 mol %). Yield of isolated product given and value within parentheses is the yield of the initially formed β-silyl-*N*,*N*-disilylamine using 1,1,2,2-tetrachloroethane as an internal standard. [b] $B(C_6F_5)_3$ (7 mol %).

The scope of more challenging substrates, including conjugated aliphatic nitriles, was next examined. We were pleased to observe that acrylonitrile was efficiently reacted with diphenylsilane at 25 °C to give 2-silyl-1-propylamine, which was isolated as the HCl salt in good yield (**17**; Table 2). Likewise, additional derivatives bearing longer aliphatic chains also underwent the desired reaction with high efficiency (**18**–**19**). Phenyl-substituted conjugated aliphatic nitriles displayed high reactivity at room temperature, thus leading to the corresponding sulfonamide products in excellent yields (**20**–**21**).

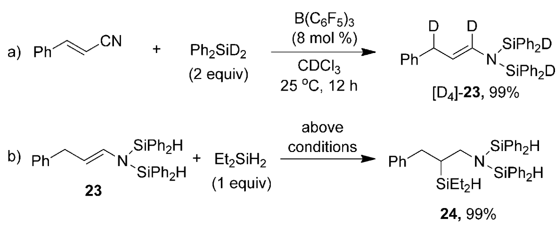
The present silylative reduction procedure was convenient to carry out on a gram scale (Scheme 2). When 1-cyano-1-butene (10 mmol) was reacted with diphenylsilane under the



Scheme 2. Synthetic applications.

optimal reaction conditions, 2-silyl-1-pentylamine was obtained as the HCl salt in 81 % yield (**19**; 2.47 g) using 3 mol % of the $B(C_6F_5)_3$ catalyst at 25 °C in chloroform. The reaction was also facile under neat conditions (85 %, 2.59 g). The obtained amine salt was converted into its sulfonamide derivative, which was subsequently oxidized under the Tamao conditions[14] to deliver the β-hydroxy *N*-sulfonamide **22** in good yield (90 % in two steps). It should be mentioned that the two post reactions could be performed in one pot without isolating a tosylated intermediate.

This silylative reduction of conjugated nitriles to β-silylamines obviously involves three hydrosilylations across the olefinic double and cyano triple bond. A series of mechanistic experiments was performed to shed light on the mechanistic considerations (Scheme 3). When 2 equivalents of diphenylsilane were reacted with cinnamonitrile, a partially reduced compound (*N*,*N*-disilylenamine; **23**) was obtained in high yield, and characterized by NMR spectrosocopy (^{1}H and ^{29}Si) and mass analyses. Moreover, with the employment of Ph_2SiD_2, deuterium was observed to be incorporated (> 95 %) at the α- and γ-position of enamine [D$_4$]-**23**, but



Scheme 3. Sequential reduction with silanes.

without detection at the β-position (Scheme 3 a). This result suggests that a hydrosilylation on the conjugated C=C bond does not occur under the standard reaction conditions. Instead, it is more reasonable to assume that 1,4-hydrosilylation across conjugated nitriles is operative in the initial stage. When the in situ generated enamine **23** was treated with Et_2SiH_2 (1 equiv), the (β-diethylsilyl)amino species **24** was obtained quantitatively, and thus indicated that the new C(sp^3)−Si bond forms at a late stage via an enamine intermediate (Scheme 3 b). Additionally, it suggests that the new C(sp^3)−Si bond formation does not occur through an intramolecular migration of the N-silyl group of **23** to the β-position.

The reaction progress was monitored by ^{1}H NMR spectroscopy and time-resolved IR (Figure 1). When cinnamonitrile (**I**) was treated with diethylsilane (3.3 equiv) in the presence of the $B(C_6F_5)_3$ catalyst, the triple hydrosilylation was found to proceed cleanly through an enamine intermediate (**II**), thus eventually leading to the β-silyl-*N*,*N*-disilylamine product **III. I** was consumed completely within 10 minutes at 25 °C with concomitant accumulation of **II**. Interestingly, however, conversion of **II** into the final product **III** was not observed during this period of intermediate formation. Only after a full consumption of cinnamonitrile did the final hydrosilylation of **II** start to proceed (Figure 1 a), thus suggesting that the formation of an enamine is fast while the hydrosilylation on this intermediate is much slower. A similar observation was also made by time-resolved IR (Figure 1 b). A new cyano (C≡N) peak at 2316 cm^{-1} was monitored during the reaction progress and it was distinct from the free cinnamonitrile peak (2226 cm^{-1}) in the absence

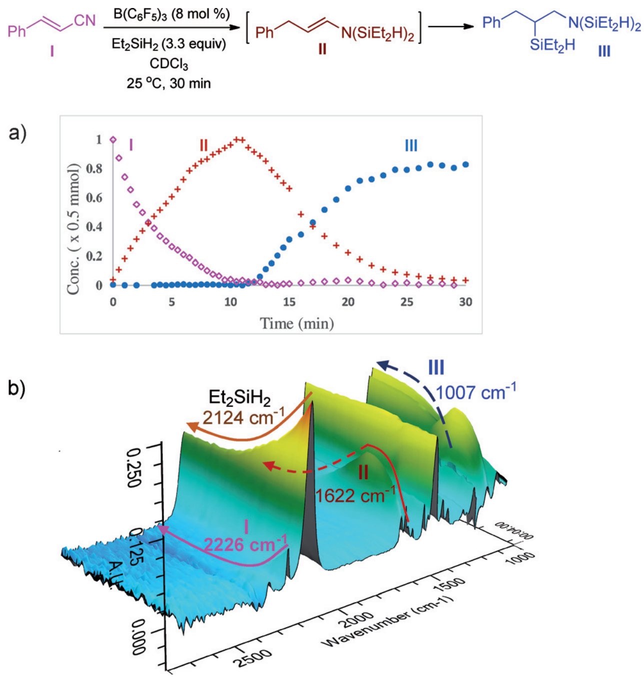
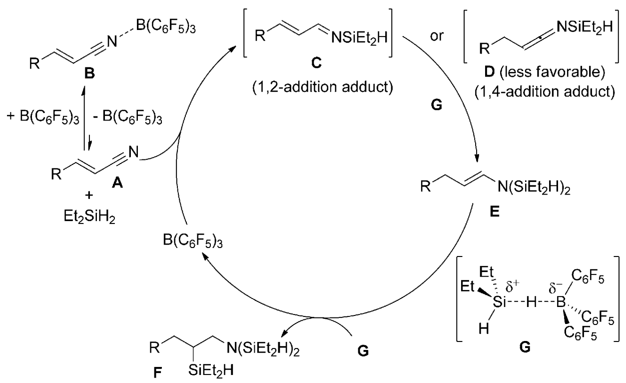


Figure 1. Monitoring of the reaction progress by a) ^{1}H NMR spectroscopy and b) time-resolved IR spectroscopy.

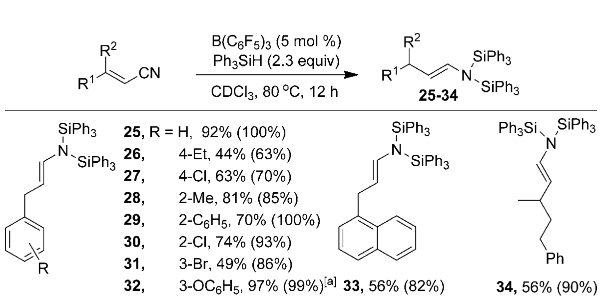
of $B(C_6F_5)_3$. In accordance with the literature,[15] the peak of 2316 cm^{-1} was assigned to a nitrile–borane complex which is believed to be a resting species.

Based on the above observations and literature precedent indicating a stepwise process of multiple hydrosilylation of enones,[8e,10a,12,13c,16] we propose a mechanistic pathway of the borane-catalyzed silylative reduction of conjugated nitriles (Scheme 4).[12,17] The first hydrosilylation of the conjugated nitrile is assumed to proceed through either a [1,2]- or [1,4]-addition manner, thus leading to the vinylimine **C**[18] and N-silyl ketene imine **D**,[19] respectively, with the former being energetically more favorable according to DFT calculations (see the Supporting Information for details). It is noteworthy that the second hydrosilylation affords an isolable N,N-disilylenamine intermediate **E** irrespective of whether it starts from **C** or **D**. The final silylative reduction of **E** is believed to be slowest in the proposed catalytic cycle, thus delivering the desired product with the concomitant regeneration of $B(C_6F_5)_3$ catalyst.

The above mechanistic understanding led us to envision that synthetically valuable enamine compounds[20] can be obtained presumably by tuning the stoichiometry and steric bulkiness of silanes. Indeed, we were delighted to find that the use of bulky triphenylsilane as a reducing reagent resulted in the chemoselective reduction to stop at the enamine stage (Scheme 5). When cinnamonitrile was treated with Ph_3SiH (2.3 equiv) in the presence of $B(C_6F_5)_3$ catalyst (5 mol%), the *N,N*-disilylenamine **25** was isolated in 92% yield. Likewise, *para*-substituted derivatives of cinnamonitrile underwent partial reduction to afford the corresponding enamines, albeit in moderate yields (**26** and **27**). Substrates bearing substituents at either the *ortho* or *meta* position also underwent the reaction with high efficiency (**28**–**33**). Moreover, this approach was readily extended to conjugated aliphatic nitriles having a β-substituent to afford the corresponding 3-substituted enamine (**34**). However, reaction of substrates having ketone or ester groups did not afford the desired products under the present reaction conditions.



Scheme 4. Mechanistic proposal for the borane-catalyzed silylative reduction of conjugated nitriles.



Scheme 5. Partial reduction of conjugated nitriles to enamines. Reaction conditions: substrate (0.5 mmol) and silane (2.3 equiv). Yield of the isolated product is shown, with that of the product in the crude reaction mixture given within parentheses (determined by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard). [a] $B(C_6F_5)_3$ (10 mol%).

In summary, the $B(C_6F_5)_3$-catalyzed chemoselective and mild silylative reduction of conjugated nitriles has been developed to afford synthetically valuable β-silyl amines. Mechanistic details were elucidated to reveal that it proceeds by rapid double hydrosilylation of conjugated nitriles to an enamine intermediate, which is subsequently reduced to a β-silyl amine, thus forming a new $C(sp^3)$–Si bond. Based on this mechanistic understanding, a preparative route to enamines was also established using bulky silanes.

Keywords: boron · conjugation · hydrosilylation · reduction · synthetic methods

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