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B(C_6F_5)$_3$/Amine-Catalyzed C(sp)–H Silylation of Terminal Alkynes with Hydrosilanes: Experimental and Theoretical Studies

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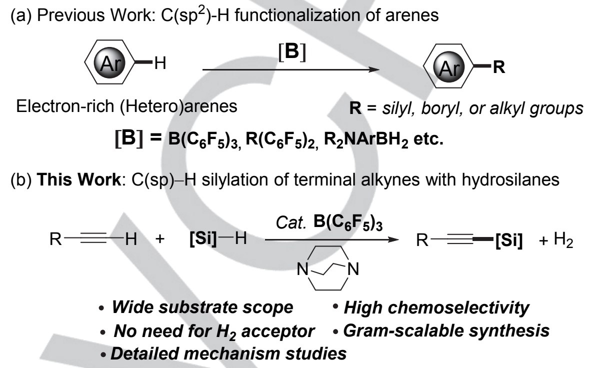
Abstract: Transition-metal-catalyzed C–H functionalization of organic compounds has proved to be a useful atom-efficient strategy in organic synthesis. In contrast, main-group-element-based catalytic processes for C–H functionalization have remained much underexplored to date. We herein report the catalytic C(sp)–H silylation of a wide range of terminal alkynes with hydrosilanes by a combination of B(C_6F_5)$_3$ and an organic base such as triethylenediamine (DABCO). This protocol constitutes the first example of boron-catalyzed C(sp)–H functionalization, offering a convenient route for the synthesis of a variety of alkynylsilanes. Experimental and computational studies have revealed that DABCO plays crucial dual roles (Lewis base and Brønsted base) in this catalytic transformation.

The catalytic activation and functionalization of C−H bonds by transition metal complexes have resulted in a wide variety of useful synthetic strategies for organic synthesis.[1,2] In endeavors to develop main-group-element-based catalytic processes for organic synthesis, boron catalysts, such as B(C_6F_5)$_3$, have recently received much attention.[3,4] However, studies on the catalytic C−H functionalization by boron catalysts are still limited.[5-8] Recently, the catalytic C(sp^2)−H borylation,[5] silylation,[6] alkylation[7] and deuteration[8] of (hetero)arenes by boron-based catalysts have been reported (Scheme 1a). As to C(sp)–H activation, the stoichiometric C–H cleavage of terminal alkynes by frustrated Lewis pairs (FLPs) has been achieved.[9] However, the catalytic transformation of a C(sp)–H bond by a boron catalyst has not been reported previously.

Alkynylsilanes are useful building blocks for the construction of C–C and C–X bonds[10] as well as for the synthesis of various functional materials.[11] The catalytic C(sp)–H silylation of terminal alkynes with hydrosilanes through release of H_2 is the most atom-efficient approach for the synthesis of alkynylsilanes. Previously, various transition metal[12] and alkali metal[13] catalysts, including the elegant work of Stoltz and Grubbs on KOH-based catalyst,[13e] have been reported for the synthesis of alkynylsilanes by the C(sp)–H silylation of terminal alkynes with hydrosilanes. However, challenges still exist despite recent advances. The development of new catalytic systems with different working mechanisms and wide substrate scope for the synthesis of alkynylsilanes is of great significance. We herein report the catalytic C(sp)–H silylation of a wide range of terminal alkynes with hydrosilanes by a combination of B(C_6F_5)$_3$ with an organic base such as triethylenediamine (DABCO) (Scheme 1b).



Scheme 1. Catalytic C–H functionalization by boron-based catalysts

We have recently found that B(C_6F_5)$_3$ can serve as an efficient catalyst for the C(sp^2)–H silylation[6b] of electron-rich arenes with hydrosilanes and the C–Si/Si–H cross metathesis[4j] of hydrosilanes. These results promoted us to explore the potential of B(C_6F_5)$_3$ as a catalyst for the C(sp)–H silylation of terminal alkynes with hydrosilanes. At first, we examined the reaction of phenylacetylene (**1a**) with diphenylsilane (**2a**) using B(C_6F_5)$_3$ as a catalyst under various conditions (Table 1 and Table S1). In the presence of 10 mol % of B(C_6F_5)$_3$, the reaction of **1a** with **2a** in toluene at 100 ºC did not give a silylation product (Table 1 entry 1), showing that the C(sp)–H silylation of a terminal alkyne significantly differs from the analogous C(sp^2)–H silylation of arenes. In contrast, addition of 1 equiv. of 2,6-lutidine to the reaction system afforded the alkyne C–H silylation product **3a** in 49% yield in 24 h (Table 1, entry 2). We then investigated the influence of various organic bases on this reaction. The use of Et_3N and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) gave a lower yield of **3a**, while 2,6-dicloropyridine or 2,6-di-t-butylpyridine did not work under the same conditions (Table 1, entries 3−6). When DABCO (triethylenediamine) was used as an additive, the desired product **3a** was isolated in 81% yield (Table 1 entry 7). It is also worth noting that even a catalytic amount of DABCO (10−20 mol %) could promote this transformation, although a slightly lower yield of **3a** (60−68%) was obtained, compared to that (85%) in the case of 1 equiv of DABCO (Table 1, entries 7, 8 and 9). In all of these reactions, hydrosilylation at the C≡C unit of **1a** was not observed.

Next, we examined the scope of hydrosilanes using **1a** as an alkyne partner in the presence of 10 mol % of B(C_6F_5)$_3$ and 1.0 equiv of DABCO at 100 ºC for 24 h. Some representative results are shown in Table 2. In addition to Ph_2SiH_2 (**2a**), a wide range of secondary hydrosilanes such as $PhMeSiH_2$, $Ph(PhCH_2)SiH_2$, $(n\text{-}Bu)_2SiH_2$, and Et_2SiH_2 were suitable for the C(sp)–H silylation of **1a**, affording the corresponding alkynylsilane products (**3a**-**3e**) in 65−81% yields. A gram-scale (5 mmol) reaction of **1a** with **2a** could be easily performed, affording **3a** in 77% isolated yield. In the case of primary hydrosilanes such as n-$C_{18}H_{37}SiH_3$ and

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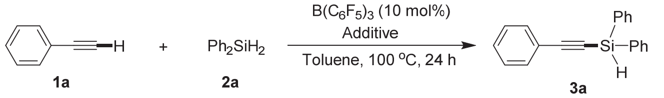
$PhSiH_3$, the target alkynylsilane products **3f** and **3g** were formed in 85% and 74% yields, respectively, as shown by ^1H NMR analyses. However, attempts to isolate a pure product in a significant yield by chromatography were not successful probably due to decomposition. A tertiary hydrosilane such as $PhMe_2SiH$ did not work for this transformation under the same conditions.

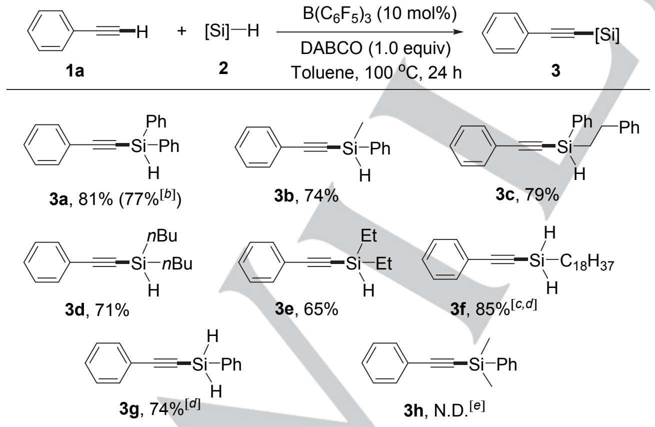
Table 1. Optimization of reaction conditions[a]



Entry	Additive	Yield (%)[b]
1	None	0
2	2,6-Lutidine (1.0 equiv.)	49
3	2,6-Dichloropyridine (1.0 equiv.)	Trace
4	2,6-Di-*t*-butylpyridine (1.0 equiv.)	N.D.[d]
5	Et_3N (1.0 equiv.)	25
6	DBU (1.0 equiv.)	10
7	DABCO (1.0 equiv.)	85 (81)[c]
8	DABCO (0.1 equiv.)	60
9	DABCO (0.2 equiv.)	68

[a] Conditions: **1a** (0.25 mmol), **2a** (0.75 mmol), $B(C_6F_5)_3$ (10.0 mol %), additive and toluene (1.0 mL) under N_2 at 100 °C for 24 h, unless otherwise noted. [b] Yield determined by ^1H NMR with CH_2Br_2 as an internal standard. [c] Isolated yield. [d] N.D. = Not detected. DABCO = triethylenediamine. DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene

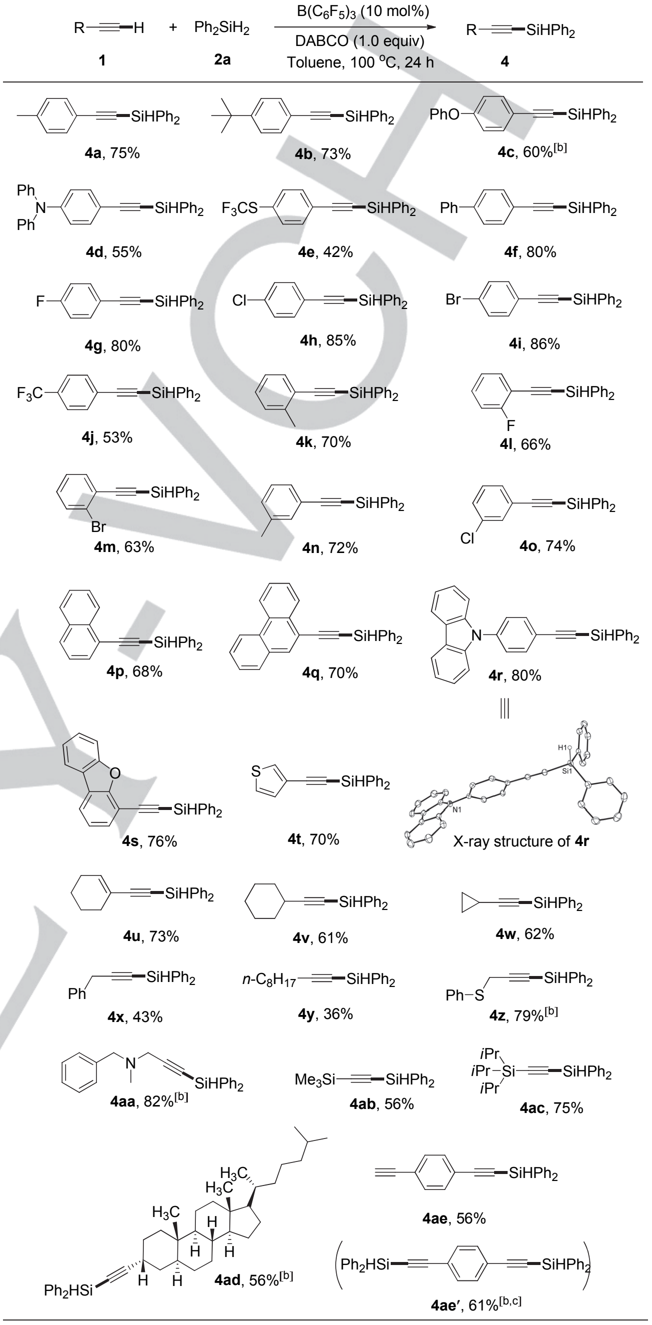
Table 2. Scope of hydrosilanes.[a]



3a, 81% (77%[b])
3b, 74%
3c, 79%
3d, 71%
3e, 65%
3f, 85%[c,d]
3g, 74%[d]
3h, N.D.[e]

[a] Conditions: **1a** (0.25 mmol), **2** (0.75 mmol), $B(C_6F_5)_3$ (10.0 mol%) , DABCO = triethylenediamine (1.0 equiv) and toluene (1.0 mL) under N_2 at 100 °C for 24 h, unless otherwise noted. Isolated yield. [b] 5 mmol scale, 48 h. [c] 12 h. [d] Yield determined by ^1H NMR with CH_2Br_2 as an internal standard. [e] Not detected.

Table 3. Scope of terminal alkynes[a,b]



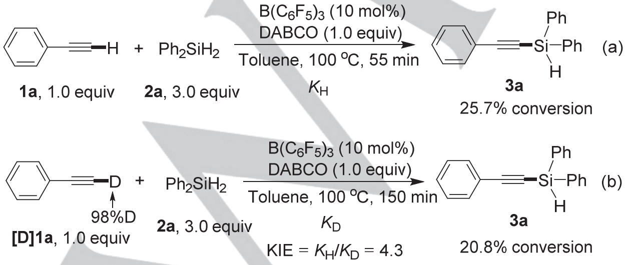
4a, 75%
4b, 73%
4c, 60%[b]
4d, 55%
4e, 42%
4f, 80%
4g, 80%
4h, 85%
4i, 86%
4j, 53%
4k, 70%
4l, 66%
4m, 63%
4n, 72%
4o, 74%
4p, 68%
4q, 70%
4r, 80%
4s, 76%
4t, 70%
X-ray structure of **4r**
4u, 73%
4v, 61%
4w, 62%
4x, 43%
4y, 36%
4z, 79%[b]
4aa, 82%[b]
4ab, 56%
4ac, 75%
4ad, 56%[b]
4ae, 56%
4ae′, 61%[b,c]

[a] Conditions: **1** (0.25 mmol), **2a** (0.75 mmol), $B(C_6F_5)_3$ (10.0 mol %), DABCO = triethylenediamine (1.0 equiv) and Toluene (1.0 mL) under N_2 at 100 °C for 24 h, unless otherwise noted. Isolated yield. [b] 48 h. [c] $B(C_6F_5)_3$ (20.0 mol %), DABCO (2.0 equiv) and **2a** (1.50 mmol).

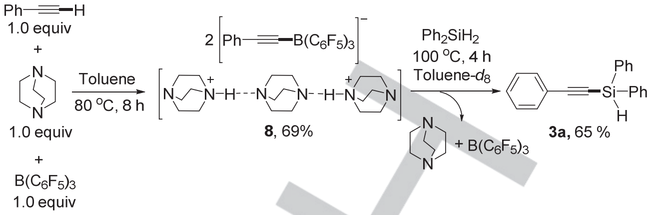
We then evaluated the scope of terminal alkynes by using diphenylsilane **2a** as a hydrosilane partner. Some representative results are summarized in Table 3. Phenylacetylenes bearing a wide range of functional groups such as alkyl, phenoxy, diphenylamino, halogen (F, Cl, Br), trifluoromethyl, and trifluoromethylthiol substituents at the phenyl ring were smoothly C−H silylated by **2a**, affording the corresponding alkynylsilane products (**4a**-**o**) in moderate to high yields. The bulky 1-

ethynylnaphthalene and 9-ethynylphenanthrene also worked well with **2a**, affording the desired products **4p** (68%) and **4q** (70%), respectively. Important heteroaromatic groups such as carbazolyl (**4r**), dibenzofuryl (**4s**) and thienyl (**4t**), which are often used as efficient donor units in materials science,[14] were compatible with this catalyst system. The solid structure of **4r** was confirmed by single-crystal X-ray diffraction analysis. Besides (hetero)aryl-substituted alkynes, terminal alkynes bearing cyclohexenyl (**4u**), cyclohexyl (**4v**), cyclopropyl (**4w**), benzyl (**4x**), *n*-octyl (**4y**), phenylthiomethyl (**4z**), aminomethyl (**4aa**), and silyl (**4ab**, **4ac**) substituents could also be efficiently C–H silylated with **2a**. In view of the wide existence of silicon-containing components in pharmaceuticals and natural products, the reaction of 3β-ethynylcholestane with **2a** was examined, which afforded the corresponding C–H silylation product **4ad** in 56% isolated yield. In the case of 1,4-diethynylbenzene, the monosilylation product **4ae** was formed in 56% yield together with 8% yield of the disilylation product **4ae'** under the standard conditions. When a further excess of the hydrosilane partner **2a** (6 equiv) was used, the disilylation product **4ae'** was obtained as a major product in 61% isolated yield. To demonstrate the synthetic usefulness of the alkynylsilane products, several transformations of **3a** were also examined as shown in the Supporting Information.

The ^{1}H NMR examination of the independent reactions of **1a** and **[D]1a** with **2a** at the initial stage revealed a significant kinetic isotope effect (KIE = k_H/k_D = 4.3) (Scheme 2), suggesting that the C(sp)–H bond cleavage of the terminal alkyne is involved in the rate-determining step in the present catalytic reaction. To gain more information on the present C–H silylation reaction mechanism, some stoichiometric reactions were examined. The reaction of phenylacetylene (**1a**) with DABCO and $B(C_6F_5)_3$ in a 1:1:1 feed ratio at 80 °C for 8 h gave an ion-pair product **8** in 69% yield through deprotonation and borylation of the terminal C–H unit of **1a** (Scheme 3).[9,15] Treatment of **8** with 2 equiv of Ph_2SiH_2 (**2a**) at 100 °C afforded the alkynylsilane product **3a** in 65% yield in 4 h (Scheme 3). The use of 5 mol % of **8** in the reaction of **1a** with **2a** gave **3a** in 46% yield (See Supporting Information). These results suggest that an ion-pair intermediate like **8** could be involved in the catalytic cycle. However, the density functional theory (DFT) studies showed that the reaction of an ion-pair intermediate like **8** with $PhSiH_3$ to give the alkynylsilane product has to overcome an energy barrier of as high as 43.7 kcal/mol (See Scheme S1 and Figure S2), which is energetically inaccessible under the present experiment conditions.



Scheme 2. Kinetic isotope effect experiments



Scheme 3. Isolation and transformation of an ion-pair compound **8**

It is well-known that a hydrosilane such as $PhSiH_3$ could be activated by $B(C_6F_5)_3$ through the "B···H" interaction to give an adduct $PhH_2Si–H···B(C_6F_5)_3$.[3,4] The DFT examination of a catalytic cycle involving such an adduct suggests that the reaction of $PhH_2Si–H···B(C_6F_5)_3$ with phenylacetylene to afford the desired C–H silylation product requires overcoming a rather high energy barrier (38.2 kcal/mol) (See Scheme S2 and Figure S3). Therefore, this reaction process may also be ruled out.

We then searched for a new pathway for the formation of the alkynylsilane product by DFT studies. As illustrated in Figure 1, phenylacetylene could easily be deprotonated by DABCO in the presence of $B(C_6F_5)_3$ via transition state **TS1** ($\Delta G^‡$ = 11.2 kcal/mol) to give a thermodynamically stable ion-pair intermediate (**A**),[9] which is equivalent to **8** obtained experimentally. The intermediate **A** could be viewed as a resting state, which may regenerate phenylacetylene, DABCO and $B(C_6F_5)_3$ by overcoming an energy barrier of 26.0 kcal/mol. The reaction of $B(C_6F_5)_3$ with $PhSiH_3$ could easily take place to give the adduct $PhH_2Si–H···B(C_6F_5)_3$ (**B**), as reported previously.[3,4] The reaction between **B** and DABCO through N–Si bond formation via **TS2** could give a more stable ion-pair species **C**. The role of DABCO in this process is to stabilize the cationic $PhSiH_2^+$ moiety. The subsequent reaction of **C** with phenylacetylene and DABCO through N···H and F···H. interactions would give **D**, which then yields the alkynylsilane product **3g** and an ion-pair species [DABCO–H]$^+$[HB(C$_6$F$_5$)$_3$]$^-$ (**E**) via **TS3** through deprotonation of PhC≡CH by DABCO and concerted C–Si bond formation. The relative high energy barrier (31.6 kcal/mol, **A**→**TS3**) for such deprotonation process could account for the experimental observation of KIE. The regeneration of $B(C_6F_5)_3$ could be effectively promoted by the entropy-driven elimination of H_2, although this process needs to overcome an energy barrier of 32.5 kcal/mol.

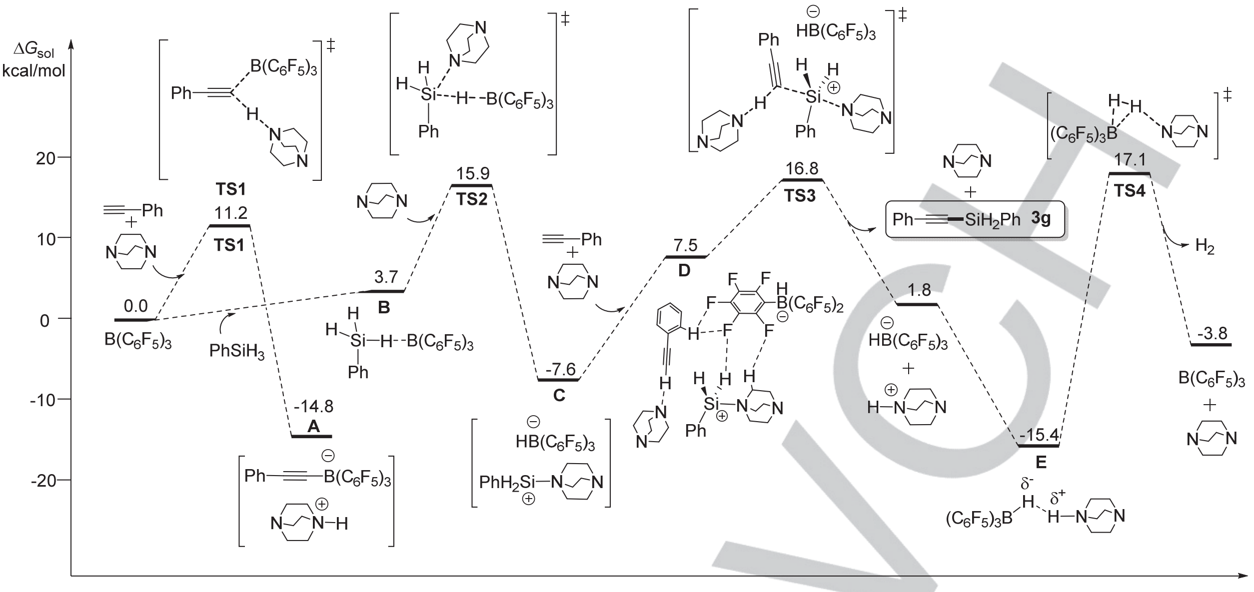
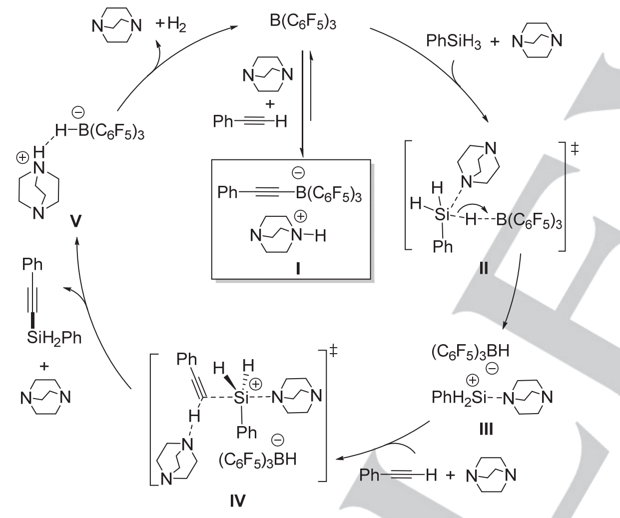


Figure 1. Energy profile (kcal/mol) for the $B(C_6F_5)_3$-catalyzed C(sp)–H silylation of PhC≡CH with $PhSiH_3$ calculated at the level of M06-2X(SMD, toluene)/6-311+G(d,p)//M06-2X/6-31G(d) (373.15 K, 1.0 atm).



Scheme 4. Proposed catalytic cycle based on experimental and DFT studies

Based on the above experimental and DFT studies, the most possibly operative mechanism for the present alkyne C–H silylation is shown in Scheme 4. The deprotonation of phenylacetylene by DABCO would easily give an ion-pair intermediate **I** (equivalent to **A** in Figure 1) in a reversible way. On the other hand, $PhSiH_3$ could be activated by $B(C_6F_5)_3$ with the assistance of DABCO to give an ion-pair intermediate **III** (which is equivalent to **C** in Figure 1) via a transition state like **II** (equivalent to **TS2** in Figure 1). The reaction of **III** with phenylacetylene and DABCO may give the alkynylsilane product via **IV** (equivalent to **TS3** in Figure 1) with release of DABCO and **V**. The elimination of H_2 from **V** would regenerate $B(C_6F_5)_3$ and DABCO. It is worth noting that DABCO plays two important roles in this transformation. One is acting as a Lewis base to stabilize the cationic $PhSiH_2^+$ species and the other is serving as a Brønsted base to deprotonate a terminal alkyne.

In summary, we have demonstrated for the first time that the combination of a boron Lewis acid such as $B(C_6F_5)_3$ and an organic base such as DABCO can serve as an excellent catalytic system for the C(sp)–H silylation of terminal alkynes with hydrosilanes. This protocol offers a novel route for the efficient synthesis of alkynylsilanes, featuring wide substrate scope, excellent chemoselectivity, good functionality tolerance, good scalability, and no need for H_2 acceptor. Experimental and computational studies have revealed that DABCO plays critically important roles in this catalytic transformation, thus offering unprecedented insights into the $B(C_6F_5)_3$-catalyed C–H silylation reactions.

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Keywords: Boron catalysis • Cross-dehydrogenative coupling • DFT study • Silylation • Synthetic method

[1] Selected reviews on C−H activation by late transition metal catalysts: a) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624−655; b) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147−1169; c) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879−5918; d) J. Wencel-Delord, F. Glorius, *Nature Chem.* **2013**, *5*, 369−375; e) Y. Segawa, T. Maekawa, K. Itami, *Angew. Chem. Int. Ed.* **2015**, *54*, 66−81; *Angew. Chem.* **2015**, *127*, 68–83; f) J. F. Hartwig, *J. Am. Chem. Soc.* **2016**, *138*, 2−24; g) R. Shang, L. Ilies, E. Nakamura, *Chem. Rev.* **2017**, *117*, 9086−9139.

[2] Selected reviews on C−H activation by early transition metal catalysts: a) K. R. D. Johnson, P. G. Hayes, *Chem. Soc. Rev.*, **2013**, *42*, 1947−1960; b) P. L. Arnold, M. W. McMullon, J. Rieb, F. E. Kühn, *Angew. Chem., Int. Ed.* **2015**, *54*, 82−100; *Angew. Chem.* **2015**, *127*, 84–103; c) M. Nishiura, F. Guo, Z. Hou, *Acc. Chem. Res.* **2015**, *48*, 2209–2220.

[3] Selected reviews: a) W. E. Piers, A. J. V. Marwitz, L. G. Mercier, *Inorg. Chem.* **2011***, 50,* 12252–12262; b) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400–6441; *Angew. Chem.* **2015**, *127*, 6498–6541; c) D. W. Stephan, *Acc. Chem. Res.* **2015**, *48*, 306–316; d) D. W. Stephan, *J. Am. Chem. Soc.* **2015**, *137*, 10018–10032; e) M. Oestreich, J. Hermeke, J. Mohr, *Chem. Soc. Rev.* **2015**, *44*, 2202–2220. f) D. W. Stephan, *Science* **2016**, *354*, aaf7229.1–8.

[4] Selected examples: a) D. J. Parks, W. E. Piers, *J. Am. Chem. Soc.* **1996**, *118*, 9440–9441; b) D. J. Parks, J. M. Blackwell, W. E. Piers, *J. Org. Chem.* **2000**, *65*, 3090–3098; c) S. Rendler, M. Oestreich, *Angew. Chem. Int. Ed.* **2008**, *47*, 5997–6000; d) K. Sakata, H. Fujimoto, *J. Org. Chem.* **2013**, *78*, 12505–12512; e) A. Y. Houghton, J. Hurmalainen, A. Mansikkamäki, W. E. Piers, H. M. Tuononen, *Nature Chem.* **2014**, *6*, 983–988; f) N. Gandhamsetty, S. Joung, S.-W. Park, S. Park, S. Chang, *J. Am. Chem. Soc.* **2014**, *136*, 16780–16783; g) A. Simonneau, M. Oestreich, *Nature Chem.* **2015**, *7*, 816–822; h) X. Ren, H. Du, *J. Am. Chem. Soc.* **2016**, *138*, 810–813; i) L. Süsse, J. Hermeke, M. Oestreich, *J. Am. Chem. Soc.* **2016**, *138*, 6940–6943; j) Y. Ma, L. Zhang, Y. Luo, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.* **2017**, *139*, 12434–12437. k) Y. Kim, R. B. Dateer, S. Chang, *Org. Lett.* **2017**, *19*, 190–193.

[5] a) M.-A. Légaré, M.-A. Courtemanche, É. Rochette, F.-G. Fontaine, *Science* **2015**, *349*, 513–516; b) K. Chernichenko, M. Lindqvist, B. Kótai, M. Nieger, K. Sorochkina, I. Pápai, T. Repo, *J. Am. Chem. Soc.* **2016**, *138*, 4860–4868; c) J. L. Lavergne, A. Jayaraman, L. C. M. Castro, É. Rochette, F.-G. Fontaine, *J. Am. Chem. Soc.* **2017**, *139*, 14714–14723; d) Q. Yin, H. F. T. Klare, M. Oestreich, *Angew. Chem. Int. Ed.* **2017**, *56*, 3712–3717; *Angew. Chem.* **2017**, *129*, 3766–3771; e) Y.-L. Liu, G. Kehr, C. G. Daniliuc, G. Erker, *Chem. Eur. J.* **2017***, 23,* 12141–12144.

[6] a) L. D. Curless, E. R. Clark, J. J. Dunsford, M. J. Ingleson, *Chem. Commun.* **2014**, *50*, 5270–5272; b) Y. Ma, B. Wang, L. Zhang, Z. Hou, *J. Am. Chem. Soc.* **2016**, *138*, 3663–3666; c) Q. Yin, H. F. T. Klare, M. Oestreich, *Angew. Chem. Int. Ed.* **2016**, *55*, 3204–3207; *Angew. Chem.* **2016**, *128*, 3256–3260; d) Y. Han, S. Zhang, J. He, Y. Zhang, *J. Am. Chem. Soc.* **2017**, *139*, 7399–7407. e) Y. Luo, H.-L. Teng, C. Xue, M. Nishiura, Z. Hou, *ACS Catal.* **2018**, *8*, 8027−8032.

[7] a) W. Li, T. Werner, *Org. Lett.* **2017**, *19*, 2568−2571; b) Z. Yu, Y. Li, J. Shi, B. Ma, L. Liu, J. Zhang, *Angew. Chem. Int. Ed.* **2016**, *55*, 14807−14811; *Angew. Chem.* **2016**, *128*, 15027–15031.

[8] W. Li, M.-M. Wang, Y. Hu, T. Werner, *Org. Lett.* **2017**, *19*, 5768−5771.

[9] a) M. A. Dureen, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 8396–8397; b) C. Jiang, O. Blacque, H. Berke, *Organometallics* **2010***, 29,* 125–133; c) T. Voss, T. Mahdi, E. Otten, R. Fröhlich, G. Kehr, D. W. Stephan, G. Erker, *Organometallics* **2012***, 31,* 2367–2378. d) H. Ye, Z. Lu, D. You, Z. Chen, Z. H. Li, H. Wang, *Angew. Chem. Int. Ed.* **2012**, *51*, 12047−12050; *Angew. Chem.* **2012**, *124*, 12213–12216. e) V. Iashin, K. Chernichenko, I. Pápai, T. Repo, *Angew. Chem. Int. Ed.* **2016**, *55*, 14146−14150; *Angew. Chem.* **2016**, *128*, 14352–14356.

[10] a) N. Sakai, R. Komatsu, N. Uchida, R. Ikeda, T. Konakahara, *Org. Lett.* **2010**, *12*, 1300–1303; b) K. Aikawa, Y. Hioki, K. Mikami, *Org. Lett.* **2010**, *12*, 5716–5719; c) B. M. Trost, M. T. Rudd, M. G. Costa, P. I. Lee, A. E. Pomerantz, *Org. Lett.* **2004**, *6*, 4235–4238; c) J. P. Brand, D. F. González, S. Nicolai, J. Waser, *Chem. Commun.* **2011**, *47*, 102–115.

[11] a) R. Gleiter, D. B. Werz, *Chem. Rev.* **2010**, *110*, 4447−4488; b) E. Langkopf, D. Schinzer, *Chem. Rev.* **1995**, *95*, 1375−1408; c) A. L. K. Shi Shun, R. R. Tykwinski, *Angew. Chem. Int. Ed.* **2006**, *45*, 1034−1057; *Angew. Chem.* **2006**, *118*, 1050–1073.

[12] Selected examples: a) M. G. Voronkov, N. I. Ushakova, I. I. Tsykhanskaya, V. B. Pukhnarevich, *J. Organomet. Chem.* **1984**, *264*, 39−48; b) R. Shimizu, R. Fuchikami, *Tetrahedron Lett.* **2000**, *41*, 907−910; c) T. Tsuchimoto, M. Fujii, Y. Iketani, M. Sekine, *Adv. Synth. Catal.* **2012**, *354*, 2959−2964; d) Yamaguchi, K.; Wang, Y.; Oishi, T.; Kuroda, Y.; Mizuno, N. *Angew. Chem. Int. Ed.* **2013**, *52*, 5627−5630; *Angew. Chem.* **2013**, *125*, 5737–5740.

[13] Selected examples: a) M. Itoh, M. Mitsuzuka, T. Utsumi, K. Iwata, K. Inoue, *J. Organomet. Chem.* **1994**, *476*, C30−C31; b) T. Baba, A. Kato, H. Yuasa, F. Toriyama, H. Handa, Y. Ono, *Catal. Today* **1998**, *44*, 271−276; c) J.-i. Ishikawa, K. Inoue, M. Itoh, *J. Organomet. Chem.* **1998**, *552*, 303−311; d) J.-i. Ishikawa, M. Itoh, *J. Catal.* **1999**, *185*, 454−461. e) A. A. Toutov, K. N. Betz, D. P. Schuman, W.-B. Liu, A. Fedorov, B. M. Stoltz, R. H. Grubbs, *J. Am. Chem. Soc.* **2017**, *139*, 1668–1674.

[14] A. Fukazawa, S. Yamaguchi, *Chem. Asian J.* **2009***, 4,* 1386–1400.

[15] For the solid structure of **8**, see Supporting Information (Figure S9).

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Boron catalysis

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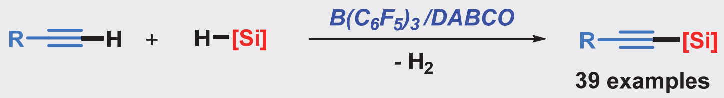

The combination of $B(C_6F_5)_3$ and an organic base such as triethylenediamine (DABCO) served as an excellent catalytic system for the C(sp)–H silylation of terminal alkynes with hydrosilanes, in which DABCO played crucial dual roles (Lewis base and Brønsted base) as revealed by experimental and DFT studies.

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