A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
International Edition
www.angewandte.org

**Title:** Me3Si−SiMe2[o-CON(i-Pr)2-C6H4]: A New Unsymmetrical Disilane Reagent for Regio- and Stereoselective Bis-silylation of Alkynes

**Authors:** Zhen Lei Song, Peihong Xiao, Yanjun Cao, Yingying Gui, and Lu Gao

**To be cited as:** *Angew. Chem. Int. Ed.* 10.1002/anie.201800513
*Angew. Chem.* 10.1002/ange.201800513

**Link to VoR:** http://dx.doi.org/10.1002/anie.201800513
http://dx.doi.org/10.1002/ange.201800513

WILEY-VCH

Angewandte Communications

**Organosilanes**

DOI: 10.1002/anie.201((will be filled in by the editorial staff))

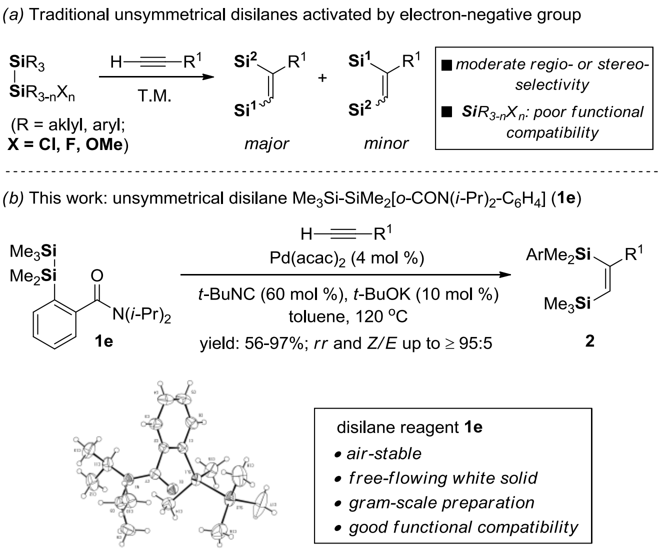
# $Me_3Si{-}SiMe_2[o\text{-}CON(i\text{-}Pr)_2\text{-}C_6H_4]$: A New Unsymmetrical Disilane Reagent for Regio- and Stereoselective Bis-silylation of Alkynes**

*Peihong Xiao, Yanjun Cao, Yingying Gui, Lu Gao, and Zhenlei Song**

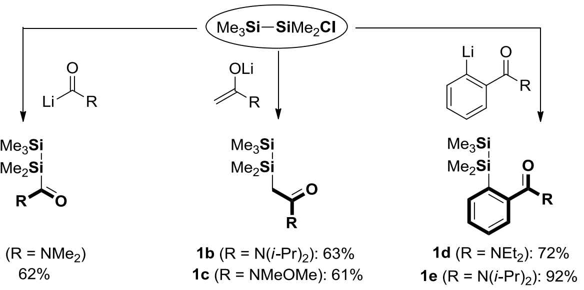
***Abstract**: The air-stable unsymmetrical disilane $Me_3Si{-}SiMe_2[o\text{-}CON(i\text{-}Pr)_2C_6H_4]$ has been developed for bis-silylation of alkynes. This reagent tolerates a range of functional groups, providing Z-vinyl disilanes in high yields. The phenyl ring-tethered amide group is proposed to direct oxidative addition of Pd(0) into the Si-Si bond, that might facilitate formation of a six-membered Pd cycle, leading to the observed good to excellent regioselectivity.*

**D**isilane is one of the most important organosilane reagents in both industry and academia.[1] It has been widely used in the formation of vinyl,[2] allyl,[3] aryl[4] and acyl silanes,[5] silyl halides,[6] and protection of alcohols to silyl ethers.[7] A particularly attractive use is transition metal-catalyzed bis-silylation of unsaturated C−C bonds, since two Si−C bonds can be constructed in one step. Generally, intermolecular bis-silylation of alkynes is conducted using symmetric disilanes with two identical silyl groups.[2a-2l] While this approach avoids regioselectivity problems, it limits downstream transformations because the two silyl groups are difficult to differentiate chemoselectively. Using unsymmetrical disilanes can potentially solve this problem. However, the regio- and stereoselective control during bis-silylation is a notoriously difficult task. The challenge can be evident from prior studies (Scheme 1a).[8] Moderate regio- or stereoselectivity were frequently obtained using unsymmetrical disilanes, in which one of the two silicons is activated by electro-negative substituents such as halide or methoxy group. In addition, the strong Lewis acidity of the halogenated silicon center renders these unsymmetrical reagents toxic, moisture-sensitive and intolerant of various Lewis base functional groups. This severely limits the use of these bis-silylation reagents in organic synthesis. Therefore, new disilane reagents are highly demanded that are easy to handle, tolerant of a broad range of functional groups, and able to provide high regio- and stereochemical control.

Amide has been used widely as a good directing group in many transition metal-catalyzed transformations.[9] The reactions generally take advantage of the strong ability of amide to coordinate with transition metals, thereby facilitating activation of the neighboring bond to form a metal cycle species. We envisioned that introducing an amide group into one of the silicon in disilane might allow us to develop a new type of unsymmetrical disilane reagents. Amide-directed Si-Si bond activation would be distinct from the traditional approach of activating disilanes by introducing an electron-negative substituent, and it might improve regio- and stereoselectivity in alkyne bis-silylation. Here we report the new unsymmetrical disilane $Me_3Si{-}SiMe_2[o\text{-}CON(i\text{-}Pr)_2C_6H_4]$ (**1e**, Scheme 1b), in which the disilane and amide moieties are tethered by a phenyl ring. This reagent is an air-stable white solid and can be prepared practically on gram scale. It tolerates a range of functionalities including Lewis basic groups in bis-silylation of terminal alkynes, giving *Z*-vinyl disilanes in high yields with good regio- and stereoselectivity.



***Scheme 1**.* (a) Bis-silylation of alkynes using traditional unsymmetrical disilanes activated by electron-negative groups. (b) Bis-silylation of alkynes using $Me_3Si{-}SiMe_2[o\text{-}CON(i\text{-}Pr)_2\text{-}C_6H_4]$ (**1e**).



***Scheme 2**.* Syntheses of disilanes **1a-1e**.

Our studies began by synthesizing the amide-substituted disilane reagents **1a-1e** from $Me_3Si\text{-}SiMe_2Cl$. These reagents were prepared via nucleophilic addition with the corresponding organolithium reagents (Scheme 2).[10] The resulting disilanes are much more air-stable than $Me_3Si\text{-}SiMe_2Cl$. The disilanes can be categorized according to the position of the amide moiety attached to the internal silicon: (a) **1a** is a unique acylsilane, with the amide moiety

---

[*] P. H. Xiao, Y. J. Cao, Y. Y. Gui, Dr. L. Gao, Prof. Dr. Z. L. Song
Sichuan Engineering Laboratory for Plant-Sourced Drug and Research Center for Drug Industrial Technology
West China School of Pharmacy, Sichuan University
Chengdu, 610041 (China)
E-mail: zhenleisong@scu.edu.cn

Prof. Dr. Z. L. Song
State Key Laboratory of Elemento-organic Chemistry, Nankai University, Tianjin, 300071 (China)

[**] We are grateful for financial support from the NSFC (21622202, 21502125).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201xxxxxx.

attached directly to silicon; (b) **1b** and **1c** are α-silyl amides, in which the disilane and amide groups are tethered by a methylene group; (c) **1d** and **1e**[11] are β-silyl amides, in which the disilane and amide moieties are tethered using a phenyl ring as a linkage.

***Table 1.*** Screening of Disilanes **1a**-**1e** for Bis-silylation of Phenylacetylene[a]

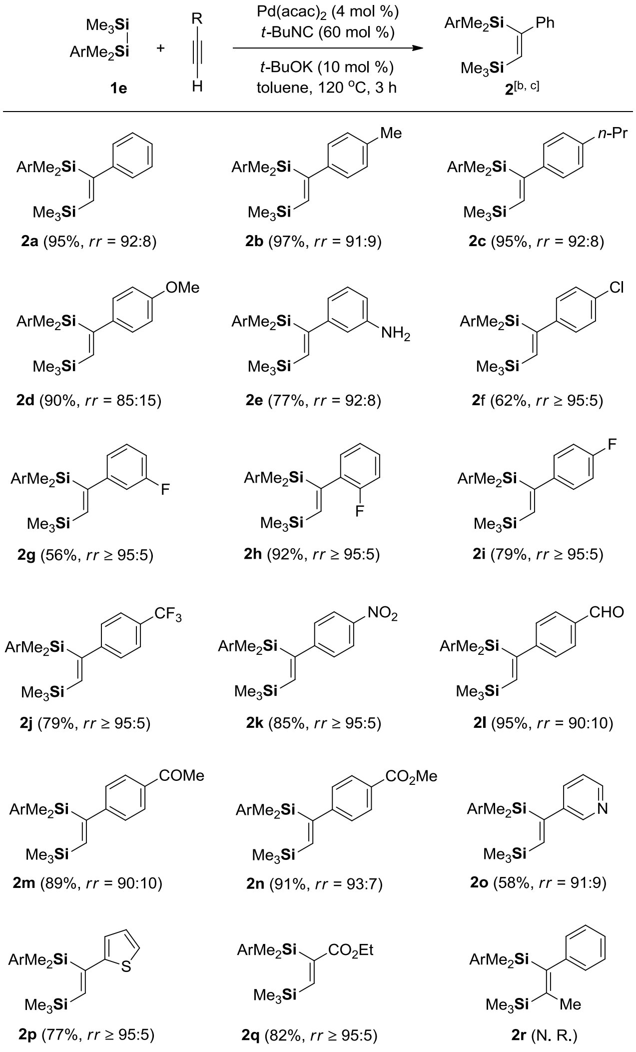
| Entry | $Si^1$-$Si^2$ | Catalyst | Additive | Yield[c] | **2**:**3**[d] |
|---|---|---|---|---|---|
| 1 | **1a** | $Pd(acac)_2$ | w/o | N.R. | N.D. |
| 2 | **1a** | $Pd(acac)_2$ | *t*-BuOK (10 mol %) | 65% | 62:38 |
| 3 | **1b** | $Pd(acac)_2$ | *t*-BuOK (10 mol %) | 32% | 75:25 |
| 4 | **1c** | $Pd(acac)_2$ | *t*-BuOK (10 mol %) | N.R. | N.D. |
| 5 | **1d** | $Pd(acac)_2$ | *t*-BuOK (10 mol %) | 59% | 87:13 |
| 6 | **1e** | $Pd(acac)_2$ | *t*-BuOK (10 mol %) | 95% | 92:8 |
| 7 | **1e** | $Pd(acac)_2$ | w/o | <5% | N.D. |
| 8 | **1e** | $Pd(acac)_2$ | NaOMe (10 mol %) | 91% | 90:10 |
| 9 | **1e** | $Pd(acac)_2$ | $K_2CO_3$ (10 mol %) | <5% | N.D |
| 10 | **1e** | $Pd(OAc)_2$ | *t*-BuOK (10 mol %) | 45% | 87:13 |
| 11 | **1e** | $Pd(PPh_3)_4$ | *t*-BuOK (10 mol %) | N.R. | N.D. |

[a] Reaction conditions: disilane **1** (0.20 mmol), phenylacetylene (0.60 mmol), *t*-BuNC (0.12 mmol), palladium catalyst (4 mol %), 2.0 mL of toluene, 120 °C, 3 h. [b] Regio- and stereochemistry was assigned based on NOE experiments of **2a** generated from **1e**. [c] Isolated yields. [d] Ratios were determined from crude $^1H$ NMR.

With disilanes **1a**-**1e** in hand, we examined the bis-silylation of phenylacetylene (Table 1). The reaction was initially carried out with acylsilane **1a** and under the conditions developed by Ito:[12] 4 mol % of $Pd(acac)_2$ as catalyst, 60 mol % of *t*-BuNC as ligand in toluene solvent at 120 ℃. Unfortunately, no desired bis-silylation was detected (entry 1). We added 10 mol % of *t*-BuOK as additive with the expectation that base might be capable of activating the Si-Si bond to facilitate bis-silylation. The efficiency was dramatically improved to give *Z*-vinyl disilanes in 65% yield as a 62:38 mixture of regioisomers **2** and **3** (entry 2). The methylene-tethered α-silyl amides **1b** and **1c** appeared to retard or even inhibit bis-silylation (entries 4 and 5). In sharp contrast, reaction of disilanes **1d** and **1e**, in which the phenyl ring is a linker, provided a remarkable improvement of regioselectivity than that of acylsilane **1a** (entries 5 and 6). Screening different substituents on the amide group revealed the bulkier *i*-Pr group to be superior to the Et group, providing the optimal yield of 95% and regioselectivity of 92:8 (entry 6). Similar to the result shown in entry 1, bis-silylation of phenylacetylene with **1e** was barely detected without addition of *t*-BuOK (entry 7). Replacing *t*-BuOK with NaOMe led to comparable yield and regioselectivity (entry 8), while the additive $K_2CO_3$ was ineffective for bis-silylation (entry 9). Palladium catalyst also showed a distinct impact on bis-silylation. Using $Pd(OAc)_2$ as catalyst decreased yield and regioselectivity (entry 10), while $Pd(PPh_3)_4$ did not catalyze bis-silylation at all (entry 11).

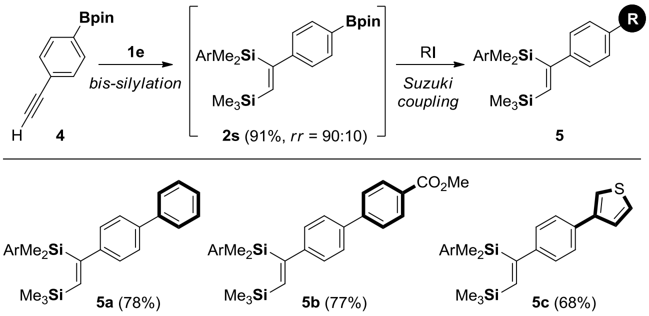
A range of alkynes was further tested in bis-silylation reactions with disilane **1e** (Table 2). The reaction proved useful for synthesizing styrene-type vinyl disilanes **2b**-**2e**, in which the phenyl ring is substituted with various electron-donating groups. It is noteworthy that the Lewis basic aniline group, which may be incompatible with halogenated disilanes such as $Me_3Si$-$SiMe_2Cl$, showed a good tolerance to **1e**, giving **2e** in 77% yield with 92:8 regioselectivity. The reaction also afforded **2f**-**2n** containing a phenyl ring substituted with a range of electron-withdrawing groups such as halide, $CF_3$, $NO_2$ and carbonyl groups. These substitutions generally resulted in higher regioselectivity than that obtained with phenylacetylene carrying an electron-donating group. Changing the position of the substitution on the phenyl ring did not affect the high regioselectivity (**2g**-**2i**), although it did affect yield to some extent. The approach also proved efficient at synthesizing **2o** and **2p** from a heterocycle-substituted alkyne, or **2q** from an ester group-activated alkyne. However, the internal alkyne, which is sterically more demanding than terminal alkyne, is currently not suitable to synthesize **2r** by our approach with **1e**.

***Table 2.*** Scope of Alkynes to Synthesize Vinyl Disilanes **2**[a]



**2a** (95%, *rr* = 92:8) **2b** (97%, *rr* = 91:9) **2c** (95%, *rr* = 92:8)
**2d** (90%, *rr* = 85:15) **2e** (77%, *rr* = 92:8) **2f** (62%, *rr* ≥ 95:5)
**2g** (56%, *rr* ≥ 95:5) **2h** (92%, *rr* ≥ 95:5) **2i** (79%, *rr* ≥ 95:5)
**2j** (79%, *rr* ≥ 95:5) **2k** (85%, *rr* ≥ 95:5) **2l** (95%, *rr* = 90:10)
**2m** (89%, *rr* = 90:10) **2n** (91%, *rr* = 93:7) **2o** (58%, *rr* = 91:9)
**2p** (77%, *rr* ≥ 95:5) **2q** (82%, *rr* ≥ 95:5) **2r** (N. R.)

[a] Reaction conditions: **1e** (0.20 mmol), alkyne (0.60 mmol), *t*-BuNC (0.12 mmol), *t*-BuOK (0.02 mmol), $Pd(acac)_2$ (4 mol %), 2.0 mL of toluene, 120 °C, 3 h. [b] Isolated yields. [c] Ratios were determined from crude $^1H$ NMR.

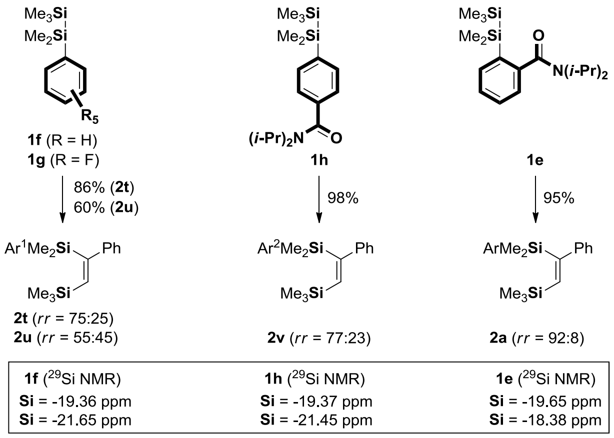


**5a** (78%) **5b** (77%) **5c** (68%)

Sequential one-pot reaction conditions: **1e**, $Pd(acac)_2$ (4 mol %), *t*-BuNC (60 mol %), *t*-BuOK (10 mol %), toluene, 120 °C, 3 h; then RI, $Pd(PPh_3)_4$ (4 mol %), $K_2CO_3$ (2.0 eq), DMF, 90 °C, 3 h.

***Scheme 3***. A sequential one-pot bis-silylation/Suzuki cross-coupling process to synthesize **5a**-**5c**.

The synthetic potential of our approach was further illustrated when we achieved the bis-silylation of alkynes **4** containing a *p*-Bpin-substituted phenyl ring. Disilane **1e** showed good compatibility with the Bpin group, giving **2s** in 91% yield with 90:10 regioselectivity (Scheme 3). This clean bis-silylation allowed us to realize a sequential one-pot bis-silylation/Suzuki cross-coupling[13] process. Once the bis-silylation was complete and had formed **2s**, a solution of aryl iodide, $Pd(PPh_3)_4$ and $K_2CO_3$ in DMF were added to the same reaction tube. In this way, biaryl-substituted vinyl disilanes **5a-5c** were generated in 68-78% yields.

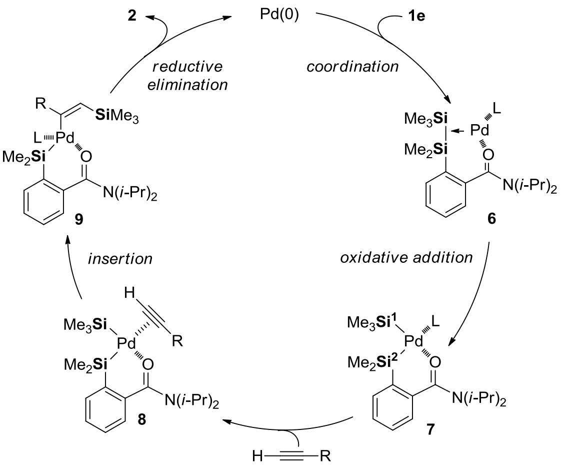


***Scheme 4.*** Control experiments using disilanes **1e**, **1f**, **1g** and **1h**.

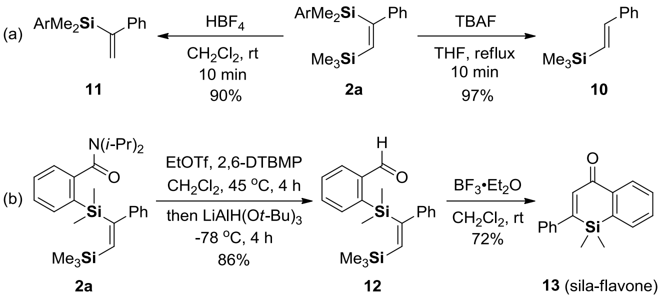
To gain a deeper understanding of the unique reactivity of disilane **1e**, we performed a control experiment using **1f** containing a phenyl ring, and **1g** containing a highly electronegative $C_6F_5$ group (Scheme 4). Bis-silylation of phenylacetylene with **1f** and **1g** led, respectively, to **2t** and **2u** with regioselectivity of 75:25 and 55:45. Both ratios were much lower than the 92:8 obtained using **1e**. These results clearly indicate that the presence of the amide group on the phenyl ring is crucial for high regioselectivity. A similarly moderate ratio of 77:23 was also observed using **1h**, which contains a CON(*i*-Pr)$_2$ group on the phenyl ring but at the *para* position. This result suggests that the electron-withdrawing effect of amide should not account for the high regioselectivity of the reaction with **1e**. Contrary to expectations, $^{29}$Si NMR studies of **1e**, **1f** [14] and **1h** showed no evidence that the amide group in **1e** activates the internal silicon by forming a penta-coordinated silicate.[15] *Ortho*-substitution of the amide in **1e** did affect the chemical shift of the internal silicon, but not in the expected direction: the corresponding $^{29}$Si chemical shift (-18.38 ppm) in **1e** is downfield 3.3 ppm than that of **1f** (-21.65 ppm) and 3.1 ppm than that of **1h** (-21.45 ppm),[16] in contrast to the upfield shift expected if a penta-coordinated silicate forms.[17]

Based on our experimental results, we propose the catalytic cycle outlined in Scheme 5. The reaction should be initiated by oxidative addition of the Si-Si bond to Pd(0). This step is facilitated most likely by the amide-directed intramolecular approach **6**. *t*-BuOK might attack the silicon centers to form silicates, thus activating the Si-Si bond.[18] In the resulting complex **7**, the Pd-Si$^2$ bond is embedded in a six-membered Pd cycle, while the Pd-Si$^1$ bond is an *exo*-cyclic orientation. Thus, the subsequent alkyne insertion via **8** would proceed regioselectively into the Pd-Si$^1$ bond to give **9**, in which the Pd is attached to the internal carbon of the alkyne.[19] Finally, the vinyl Pd species **9** undergoes reductive elimination to afford **2** as the major or single regioisomer, thereby regenerating the Pd catalyst.

The two silyl groups in *Z*-vinyl disilane **2a** can easily be differentiated. As shown in Scheme 6a, the SiMe$_2$[*o*-CON(*i*-Pr)$_2$C$_6$H$_4$] moiety appeared being more reactive to fluoride anion than SiMe$_3$. **2a** underwent chemoselective desilylation with TBAF to give vinyl silane **10** in 97% yield. On the other hand, acid-promoted desilylation of **2a** led exclusively to elimination of the SiMe$_3$ group, affording **11** in 90% yield. In addition, the benzamide moiety is not only a directing group, it can also be used to transform vinyl disilane into structurally interesting cyclic organosilanes (Scheme 6b). For example, aldehyde **12**, generated by reduction of **2a**,[20] underwent $BF_3$•$OEt_2$-promoted cyclization/oxidation to give sila-flavone **13** in 72% yield. This compound mimics biologically important flavone,[21] so it may have interesting reactivities or bioactivities.



***Scheme 5***. Proposed catalytic cycle of bis-silylation of alkyne with **1e**.



***Scheme 6***. (a) Chemoselective desilylation of **2a**; (b) Synthesis of **13** from **2a**.

In summary, we have developed the new unsymmetrical disilane reagent Me$_3$Si−SiMe$_2$[*o*-CON(*i*-Pr)$_2$C$_6$H$_4$], which is an air-stable white solid and can be prepared on the gram scale. This reagent shows good functional compatibility in bis-silylation of terminal alkynes, giving *Z*-vinyl disilanes in good yields. The phenyl ring-tethered amide group is proposed to direct oxidative addition of the Si-Si bond to Pd(0), facilitating formation of a six-membered Pd cycle responsible for the observed high regio- and stereoselectivity. More detailed studies and application of this useful activation mode in organosilane-involved transformations are underway.

Received: ((will be filled in by the editorial staff))

**Keywords:** Disilanes • Bis-silylation • Amide • Alkynes • Vinyl Silanes

---

[1] For reviews, see: a) K. A. Horn, *Chem. Rev.* **1995**, *95*, 1317−1350; b) H. K. Sharma, K. H. Pannell, *Chem. Rev.* **1995**, *95*, 1351−1374; c) L. B. Han, M. Tanaka, *Chem. Commun.* **1999**, 395−402; d) R. Zimmer, C. U.

Dinesh, E. Nandanan, F. A. Khan, *Chem. Rev.* **2000**, *100*, 3067−3126; e) M. Suginome, Y. Ito, *Chem. Rev.* **2000**, *100*, 3221−3256; f) M. Suginome, Y. Ito, *J. Organomet. Chem.* **2003**, *685*, 218−229.

[2] From alkynes: a) H. Okinoshima, K. Yamamoto, M. Kumada, *J. Organomet. Chem.* **1975**, *86*, C27−C30; b) H. Sakurai, Y. Kamiyama, Y. Nakadaira, *J. Am. Chem. Soc.* **1975**, *97*, 931−932; c) K. Tamao, T. Hayashi, M. Kumada, *J. Organomet. Chem.* **1976**, *114*, C19−C22; d) H. Matsumoto, I. Matsubara, T. Kato, K. Shono, H. Watanabe, Y. Nagai, *J. Organomet. Chem.* **1980**, *199*, 43−47; e) T. Kusumoto, T. Hiyama, *Tetrahedron Lett.* **1987**, *28*, 1807−1810; f) H. Yamashita, M. Catellani, M. Tanaka, *Chem. Lett.* **1991**, *20*, 241−244; g) M. Murakami, M. Suginome, K. Fujimoto, Y. Ito, *Angew. Chem. Int. Ed.* **1993**, *32*, 1473−1475; *Angew. Chem.* **1993**, *105*, 1542−1544; h) M. Suginome, A. Matsumoto, Y. Ito, *J. Org. Chem.* **1996**, *61*, 4884−4885; i) M. Suginome, A. Takama, Y. Ito, *J. Am. Chem. Soc.* **1998**, *120*, 1930−1931; j) C. Gryparis, M. Kidonakis, M. Stratakis, *Org. Lett.* **2013**, *15*, 6038−6041; k) M. B. Ansell, D. E. Roberts, F. G. N. Cloke, O. Navarro, J. Spencer, *Angew. Chem. Int. Ed.* **2015**, *54*, 5578 –5582; *Angew.Chem.* **2015**, *127*, 5670 –5674. From vinyl halides: l) Y. Hatanaka, T. Hiyama, *Tetrahedron Lett.* **1987**, *28*, 4715−4718. For recent works, see: m) M. Ahmad, A. C. Gaumont, M. Durandetti, J. Maddaluno, *Angew. Chem. Int. Ed.* **2017**, *56*, 2464–2468；*Angew. Chem.* **2017**, *129*, 2504–2508; n) J. L. Pan, C. Chen, Z. G. Ma, J. Zhou, L. R. Wang, S. Y. Zhang, *Org. Lett.* **2017**, *19*, 5216−5219.

[3] a) H. Okinoshima, K. Yamamoto, M. Kumada, *J. Am. Chem. Soc.* **1972**, *94*, 9263−9264; b) K. Tamao, S. Okazaki, M. Kumada, *J. Organomet. Chem.* **1978**, *146*, 87−93; c) B. M. Trost, J. I. Yoshida, M. Lautena, *J. Am. Chem. Soc.* **1983**, *105*, 4494−4496; d) J. R. Hwu, L. C. Lin, B. R. Liaw, *J. Am. Chem. Soc.* **1988**, *110*, 7252−7254; e) Y. Tsuji, R. M. Lago, S. Tomohiro, H. Tsuneishi, *Organometallics* **1992**, *11*, 2353−2355; f) Y. Matsumoto, A. Ohno, T. Hayashi, *Organometallics* **1992**, *12*, 4051−4055; g) Y. Obora, Y. Tsuji, T. Kawamura, *J. Am. Chem. Soc.* **1993**, *115*, 10414−10415; h) N. Selander, J. R. Paasch, K. J. Szabó, *J. Am. Chem. Soc.* **2011**, *133*, 409−411.

[4] a) H. Matsumoto, S. Nagashima, K. Yoshihara, Y. Nagai, *J. Organomet. Chem.* **1975**, *85*, C1−C3; b) E. Shirakawa, T. Kurahashi, H. Yoshida, T. Hiyama, *Chem. Commun.* **2000**, 1895−1896; c) M. Murata, M. Ishikura, M. Nagata, S. Watanabe, Y. Masuda, *Org. Lett.* **2002**, *4*, 1843−1845; d) A. Postigo, R. A. Rossi, *Org. Lett.* **2001**, *3*, 1197−1200; e) S. E. Denmark, J. M. Kallemeyn, *Org. Lett.* **2003**, *5*, 3483−3486; f) E. Mcneill, T. E. Barder, S. L. Buchwald, *Org. Lett.* **2007**, *9*, 3785–3788; g) M. Tobisu, Y. Kita, Y. Ano, N. Chatani, *J. Am. Chem. Soc.* **2008**, *130*, 15982−15989; h) T. A. Su, J. R. Widawsky, H.-X. Li, R. S. Klausen, J. L. Leighton, M. L. Steigerwald, L. Venkataraman, C. Nuckolls, *J. Am. Chem. Soc.* **2013**, *135*, 18331−18334; i) Z. X. Liu, H. C. Tan, T. R. Fu, Y. Xia, D. Qiu, Y. Zhang, J. B. Wang, *J. Am. Chem. Soc.* **2015**, *137*, 12800−12803; j) N. T. Kim, H.-X. Li, L. Venkataraman, J. L. Leighton, *J. Am. Chem. Soc.* **2016**, *138*, 11505−11508.

[5] a) K. Yamamoto, A. Hayashi, S. Suzuki, J. Tsuji, *Organometallics* **1987**, *6*, 974−979; b) Y. Obora, Y. Tsuji, T. Kawamura, *J. Am. Chem. Soc.* **1995**, *117*, 9814−9821.

[6] M. Ishikawa, J. Ikadai, A. Naka, J. Ohshita, A. Kunai, K. Yoshizawa, S. Y. Kang, T. Yamabe, *Organometallics* **2001**, *20*, 1059–1061.

[7] a) A. Studer, M. Bossart, T. Vasella, *Org. Lett.* **2000**, *2*, 985–988; b) E. Shirakawa, K. Hironaka, H. Otsuka, T. Hayashi, *Chem. Commun.* **2006**, 3927–3929.

[8] a) H. Watanabe, M. Kobayashi, K. Higuchi, Y. Nagai, *J. Organomet. Chem.* **1980**, *186*, 51−62; b) H. Watanabe, M. Kobayashi, M. Saito, Y. Nagai, *J. Organomet. Chem.*, **1981**, *216*, 149−157; c) F. Ozawa, M. Sugawara, T. Hayashi, *Organometallics* **1994**, *13*, 3237−3243.

[9] For a latest review, see: a) R. Y. Zhu, M. E. Farmer, Y. Q. Chen, J. Q. Yu, *Angew. Chem. Int. Ed.* **2016**, *55*, 10578–10599; *Angew.Chem.* **2016**, *128*, 10734 –10756. For selected examples, see: b) B. H. Ye, N. Cramer, *Science* **2012**, *338*, 504–506; c) D. G. Yu, F. de Azambuja, T. Gensch, C. G. Daniliuc, F. Glorius, *Angew. Chem. Int. Ed.* **2014**, *53*, 9650–9654; *Angew. Chem.* **2014**, *126*, 9804–9809; d) Y. J. Liu, H. Xu, W. J. Kong, M. Shang, H. X. Dai, J. Q. Yu, *Nature* **2014**, *515*, 389–393; e) S. Z. Wu, R. Zeng, C. L. Fu, Y. H. Yu, X. Zhang, S. M. Ma, *Chem. Sci.* **2015**, *6*, 2275–2285; f) N. Tezuka, K. Shimojo, K. Hirano, S. Komagawa, K. Yoshida, C. Wang, K. Miyamoto, T. Saito, R. Takita, M. Uchiyama, *J. Am. Chem. Soc.* **2016**, *138*, 9166−9171; g) B. J. Groendyke, D. I. AbuSalim, S. P. Cook, *J. Am. Chem. Soc.* **2016**, *138*, 12771−12774; h) J. C. K. Chu, T. Rovis, *Nature* **2016**, *539*, 272−275. i) Y. J. Liu, Y. H. Liu, Z. Z. Zhang, S. Y. Yan, K. Chen, B. F. Shi, *Angew. Chem. Int. Ed.* **2016**, 55, 13859-13862; *Angew. Chem.* **2016**, 128, 1-5.

[10] For the preparation of **1a**-**1c**, see: a) S. Urayama, S. Inoue, Y. Sato, *J. Organomet. Chem.* **1988**, *354*, 155−160; b) Z. G. Huang, L. Gao , Z. L. Song, *Tetrahedron Letts*. **2016**, *57*, 2861−2864. For the preparation of **1d** and **1e**, see: c) P. Beak, S. T. Kerrick, D. J. Gallagher, *J. Am. Chem. Soc.* **1993**, *115*, 10628−10636.

[11] CCDC 1816350 [**1e**] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] Y. Ito, M. Suginome, M. Murakami, *J. Org. Chem.* **1991**, *56*, 1948−1951.

[13] a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457−2483; b) S. R. Chemler, D. Trauner, S. J. Danishefsky, *Angew. Chem. Int. Ed.* **2001**, *40*, 4544−4568; *Angew. Chem.* **2001**, *113*, 4676 − 4701.

[14] K. G. Sharp, P. A. Sutor, E. A. Williams, J. D. Cargioli, T. C. Farrar, K. Ishibitsu, *J. Am. Chem. Soc.* **1976**, *98*, 1977−1979.

[15] For selected reviews, see: a) R. R. Holmes, *Chem. Rev.* **1990**, *90*, 17−31; b) C. Chuit, R. J. P. Corriu, C. Reye, J. C. Young, *Chem. Rev.* **1993**, *93*, 1371−1448; For selected examples of amides-type of penta-coordinate silicate: c) C. H. Yoder, C. M. Ryan, G. F. Martin, P. S. Ho, *J. Organomet. Chem.* **1980**, *190*, 1−7; d) I. D. Kalikhman, V. A. Pestunovich, B. A. Gostevskii, O. B. Bannikova, M. G. Voronkov, *J. Organomet. Chem.* **1988**, *338*, 169−180.

[16] The downfield chemical shift of the internal silicon in **1e** than that of **1f** and **1h** might be attributed to other factors such as the steric effect of amide group.

[17] For a review, see: a) E. A. Williams, In *The Chemistry of Organic Silicon Compounds*; S. Patai, Z. Rappoport, Eds.; John Wiley & Sons: Chichester, **1989**; pp 511−554. For selected examples, see: b) C. Brellère, F. Carré, R. J. P. Corriu, M. Poirier, G. Royo, *Organometallics* **1986**, *5*, 388−390; c) H. H. Karsch, F. Bienlein, A. Sladek, M. Heckel, K. Burger, *J. Am. Chem. Soc.* **1995**, *117*, 5160−5161; d) I. Kalikhman, S. Krivonos, A. Ellern, D. Kost, *Organometallics* **1996**, *15*, 5073−5076.

[18] We currently prefer that *t*-BuOK might facilitate the approach by activating the Si−Si bond. But, we cannot confirm this role because *t*-BuOK could also potentially react with terminal alkyne or even catalyst. More detailed studies are ongoing in our group.

[19] F. Ozawa, J. Kamite, *Organometallics* **1998**, *17*, 5630−5639.

[20] P. H. Xiao, Z. X. Tang, K. Wang, H. Chen, Q. Y. Guo, Y. Chu, L. Gao, Z. L. Song, *J. Org. Chem.* **2017**, DOI: 10.1021/acs.joc.7b02868.

[21] a) M. Narwal, J. Koivunen, T. Haikarainen, E. Obaji, O. E. Legala, H. Venkannagari, P. Joensuu, T. Pihlajaniemi, L. Lehtiö, *J. Med. Chem.* **2013**, *56*, 7880–7889.

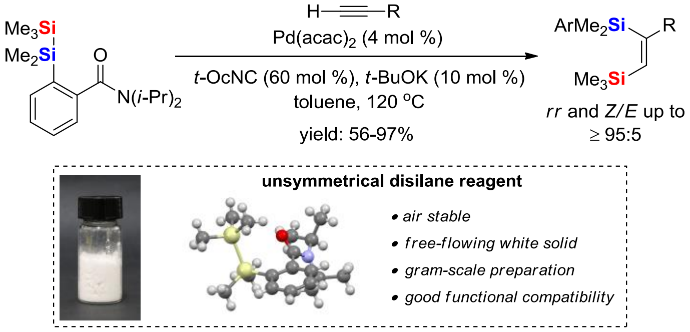
**Entry for the Table of Contents** (Please choose one layout)

**_Organosilanes_**

Peihong Xiao, Yanjun Cao, Yingying Gui, Lu Gao, and Zhenlei Song*

__________ **Page – Page**

### $Me_3Si{-}SiMe_2[o\text{-}CON(i\text{-}Pr)_2\text{-}C_6H_4]$: A New Unsymmetrical Disilane Reagent for Regio- and Stereoselective Bis-silylation of Alkynes



The air-stable unsymmetrical disilane $Me_3Si{-}SiMe_2[o\text{-}CON(i\text{-}Pr)_2C_6H_4]$ has been developed for bis-silylation of alkynes. This reagent tolerates a range of functional groups, providing *Z*-vinyl disilanes in high yields. The phenyl ring-tethered amide group is proposed to direct oxidative addition of Pd(0) into the Si-Si bond, that might facilitate formation of a six-membered Pd cycle, leading to the observed good to excellent regioselectivity.