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COMMUNICATION

A stable silylborane with diminished boron-Lewis acidity

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A new dimethyl(phenyl)silylborane having naphthalene-1,8-diaminato (dan) substituent on the boron center, PhMe$_2$Si–B(dan), was synthesized. Owing to the diminished boron-Lewis acidity, it is highly stable toward air. Synthetic application of the silylborane to catalytic silylboration and silylation of alkynes was also described.

Silylboranes have been useful reagents in modern synthetic organic chemistry,[1] which enjoy their versatility in installing silyl and/or boryl functionalities into organic frameworks depending on various catalytic and non-catalytic[2] transformations. The most popular and utilized silylborane is dimethyl(phenyl)silyl-containing one, PhMe$_2$Si–B(pin) (Fig. 1A),[3] whose silyl moiety serves as a synthetic equivalent of a hydroxy group through the Fleming–Tamao oxidation.[4] Despite the widespread usage, PhMe$_2$Si–B(pin) is highly air-sensitive,[5] and this can be attributed to facile generation of a silyl radical species via homolytic cleavage of the Si–B bond upon action with triplet oxygen,[6] which would lower synthetic practicality to some extent. The presence of the phenyl group on the silicon center may facilitate the cleavage process with stabilizing the generated silyl radical; trialkylsilylboranes, such as Et$_3$Si–B(pin)[7,8] and Me$_3$Si–B(pin)[9] (Fig. 1B), acquire air-resistant property, and thus can be isolated by silica gel column chromatography. Besides the electronic modification of the silicon moiety, a silylborane with steric bulk on the silicon center, (TMS)$_3$Si–B(pin) (Fig. 1B),[5] was also demonstrated to be stable to air. Since the above-described synthetic utility as a hydroxy group equivalent and the instability, both of which arise from the phenyl-substituted silicon moiety, are in a dilemma, a new approach for stabilizing silylboranes, especially based upon modification of a boron moiety, would be desirable. We report herein on synthesis of a stable dimethyl(phenyl)silylborane with diminished boron-Lewis acidity by introducing naphthalene-1,8-diaminato (dan) substituent on the boron center (Fig. 1C),[10,11] and on its utilization for platinum-catalyzed silylboration of alkynes[3a,12] bearing a Lewis basic functionality and copper-catalyzed silylations.

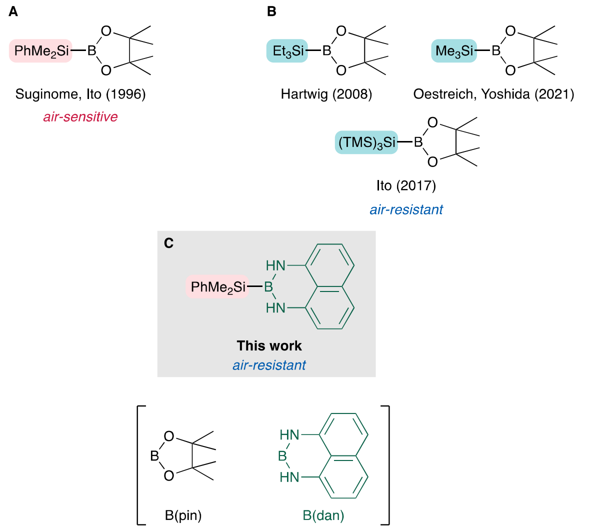

Fig. 1 Various silylboranes.

The target silylborane was found to be readily accessible by a ligand exchange reaction of a known compound, PhMe$_2$Si–B(Ni-Pr$_2$)$_2$,[13,14] with 1,8-diaminonaphthalene to form PhMe$_2$Si–B(dan) (**1**) in 80% yield (Scheme 1). It should be noted that the resulting silylborane can be isolated by silica gel column chromatography under ambient conditions with enough stability toward air, regardless of the presence of the phenyl substituent on the silicon center: **1** fully remained after 30 h upon treatment with dry air in C$_6$D$_6$ at room temperature (Fig. 2),[15] demonstrating that diminishing boron-Lewis acidity is highly effective for blocking the interaction with oxygen. In stark contrast, 75% of

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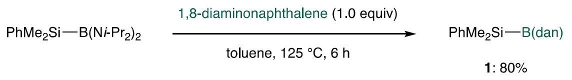


Scheme 1 Synthesis of a dan-substituted silylborane.

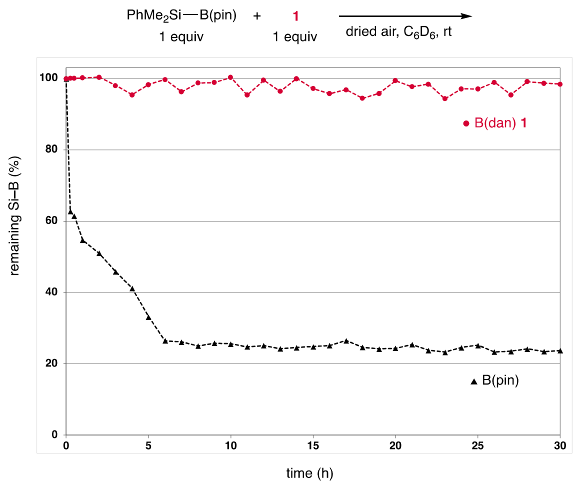


Fig. 2 Stability of silylboranes under dried air conditions. The amount of remaining silylboranes was determined by ^{1}H NMR.

$PhMe_2Si$–B(pin) was decomposed after 6 h under the same conditions.[16]

X-ray crystal structure analysis of the silylborane showed that the six-membered rings of the B(dan) moiety hold a planar configuration as judged by their dihedral angles (0.1–1.9°) with the N1–B1–N2 bond angle of 115.26°, which unambiguously represents the boron centers have a nearly ideal B(sp^2) hybridized orbital (Fig. 3). In addition to the molecular geometry around the boron center, effective electron-donation from lone pairs on the neighboring nitrogen atoms to the vacant p-orbital leads to strong diminishment of the boron-Lewis acidity, which brings about the air-resistant property of **1**.

Synthetic application of robust silylborane **1** to catalytic silylboration of alkynes was next investigated: the reaction with 1-octyne (**2a**) was found to proceed smoothly in 1,2-diethoxyethane (DEE) at 110 °C in the presence of Pt(PPh$_3$)$_4$[3a] to afford *syn*-*vic*-boryl(silyl)alkene (**3a**) having the B(dan) moiety at the terminal carbon in regio- and stereoselective manners (entry 1, Table 1). A palladium catalyst with *t*-OctNC[3a] (entry 3) or a cyclic phosphite (ETPO)[17] (entry 4) as a ligand also promoted the silylboration, albeit at the cost of the yield, whereas the reaction with a triphenylphosphine-coordinated palladium catalyst[18] was inefficient (entry 5).

The characteristic feature of the Pt-catalyzed silylboration with the Lewis acidity-diminished silylborane was well-demonstrated by the reaction with alkynes bearing a Lewis basic (LB) functionality. As depicted in Scheme 2, treatment of **1** with *N*,*N*-diethylpropargyl amine (**2b**) regio- and stereoselectively provided an 86% yield of the silylborated products (**3b** and **3'b**),[19] whereas a similar reaction with Lewis acidic $PhMe_2Si$–B(pin) became sluggish, probably owing to Lewis acid [B(pin)]–base (NEt$_2$) interaction,[20] which may cause decomposition of the silylborane.[21] The difference in the reaction efficiency was also observed with *N*-(2-propynyl)piperidine (**2c**) and phenyl propargyl sulfide (**2d**), resulting in superior yields of the desired products with **1**. The stereochemical outcome in the reaction of **2d**, especially with

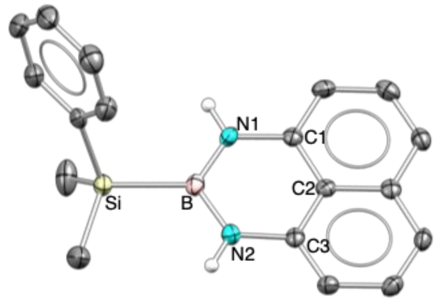
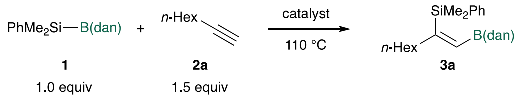


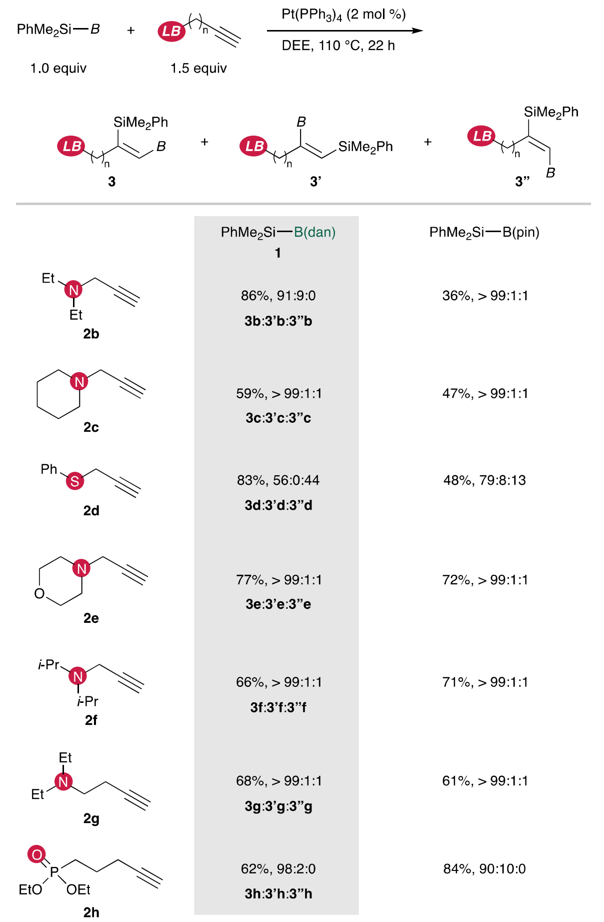
Fig. 3 Solid-state structure of $PhMe_2Si$–B(dan) (**1**) with 50% probability ellipsoids. Most of the hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Si–B 2.023, B–N1 1.421, B–N2 1.416, N1–B–N2 115.26, B–N2–C3 124.50, N2–C3–C2 117.30, C3–C2–C1 121.31, C2–C1–N1 117.78, C2–N1–B 123.81.

Table 1 Catalyst screening for silylboration[a]



entry	catalyst	solvent	time (h)/yield (%)[b]
1	Pt(PPh$_3$)$_4$ (2 mol %)	DEE	22/73
2	Pt(PPh$_3$)$_4$ (2 mol %)	toluene	17/71
3	Pd(OAc)$_2$ (2 mol %) *t*-OcNC (30 mol %)	toluene	1/62
4	Pd$_2$(dba)$_3$ (2.5 mol %) ETPO[c] (10 mol %)	toluene	1/62
5[d]	(η^3-C$_3$H$_5$)Pd(PPh$_3$)Cl (1 mol %)	toluene	3/39

[a] Conditions: **1** (0.250 mmol), **2a** (0.375 mmol), catalyst, 110 °C. [b] Isolated yield. [c] ETPO = 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane. [d] **2a**: 1.2 equiv.

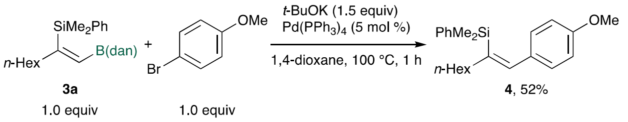


	PhMe$_2$Si—B(dan) **1**	PhMe$_2$Si—B(pin)
2b	86%, 91:9:0 **3b:3'b:3"b**	36%, > 99:1:1
2c	59%, > 99:1:1 **3c:3'c:3"c**	47%, > 99:1:1
2d	83%, 56:0:44 **3d:3'd:3"d**	48%, 79:8:13
2e	77%, > 99:1:1 **3e:3'e:3"e**	72%, > 99:1:1
2f	66%, > 99:1:1 **3f:3'f:3"f**	71%, > 99:1:1
2g	68%, > 99:1:1 **3g:3'g:3"g**	61%, > 99:1:1
2h	62%, 98:2:0 **3h:3'h:3"h**	84%, 90:10:0

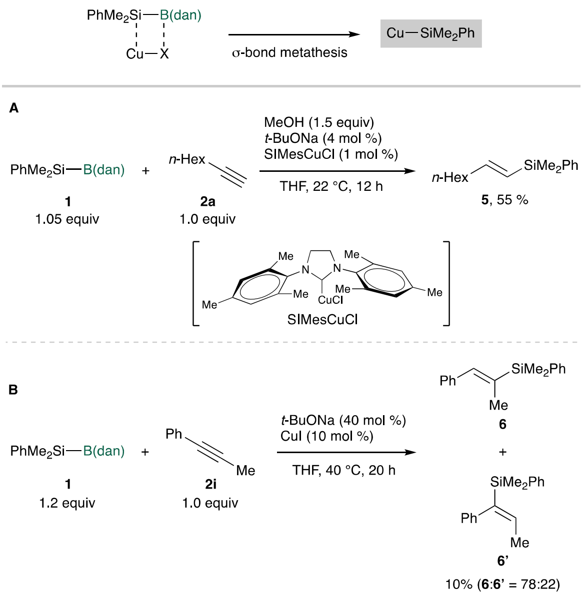
Scheme 2 Pt-catalyzed silylboration of alkynes bearing a Lewis basic functionality.

1, is worth of note: almost half of the B(dan)-containing products was obtained as an *anti*-isomer (**3"d**),[22,23] and the *anti*-addition across a carbon–carbon triple bond took place only in the cases with **2d**, implying a sulfide functional group should be the key to the unique stereoselectivity. On the other hand, there was no appreciable difference in the reactivity between **1** and PhMe$_2$Si–B(pin), when using *N*-(2-propynyl)morpholine (**2e**), *N*,*N*-diisopropylpropargyl amine (**2f**), *N*,*N*-diethylhomopropargyl amine (**2g**) or a terminal alkyne having a phosphonate functional group (**2h**), furnishing the respective silylborated products in good yields. Besides, the alkenyl–B(dan) bond of **3a** was demonstrated to be used for carbon–carbon bond formation without prior deprotection of the dan moiety to afford **4** depending upon our direct cross-coupling reaction (Scheme 3).[10e]

It should be noted that **1** can serve as a silicon donor in the copper-catalyzed silylations that have been gathering attention: treatment of **1** with 1-octyne (**2a**) and methanol in the presence of SIMesCuCl turned out to provide (*E*)-silyloctene (**5**) regio- and stereo-selectively via the formation of a silylcopper species (Scheme 4A).[24,25] On the other hand, we also carried out the reaction of **1** with 1-phenyl-1-propyne (**2i**) under the copper-catalyzed *trans*-selective silylboration conditions[12b] to lead to the unexpected generation of hydrosilylation products (**6** and **6'**), albeit in low yield (Scheme 4B); the NH moieties of B(dan) could act as a proton source for capturing a silyl-substituted alkenylcopper intermediate.[26,27]



Scheme 3 Direct cross-coupling of a silylborated product at its C–B(dan) bond.



Scheme 4 Cu-catalyzed hydrosilylations of alkynes with **1**.

In conclusion, we have demonstrated that diminishing boron-Lewis acidity by the introduction of dan substituent on the boron center significantly stabilizes a dimethyl(phenyl)silylborane toward air with inhibiting the interaction with oxygen. Moreover, the robust silylborane, PhMe$_2$Si–B(dan), has proven to be utilizable for the Pt-catalyzed silylboration of terminal alkynes bearing a Lewis basic functionality and for the Cu-catalyzed silylations. Further studies on synthetic applications of the Lewis acidity-diminished silylborane are in progress.

Author contributions

Y.I. and Y.H. performed the experimental works. K.N., M.N., S.H. and M.A. did the X-ray crystal structure analysis. H.Y. conceptualized and supervised the work, and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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25 B(dan)-installation into **2i** did not occur at all, implying the silylcopper species was exclusively generated through chemoselective σ-bond metathesis between **1** and the Cu(I) catalyst.

26 We have recently reported that NH moieties of an anthranilamide-substituted boron group [B(aam)] act as a proton source for capturing a boryl-substituted alkenylcopper intermediate in copper-catalyzed internal-selective hydroboration of terminal alkynes. See: T. Tsushima, H. Tanaka, K. Nakanishi, M. Nakamoto and H. Yoshida, *ACS Catal.*, 2021, **11**, 14381.

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