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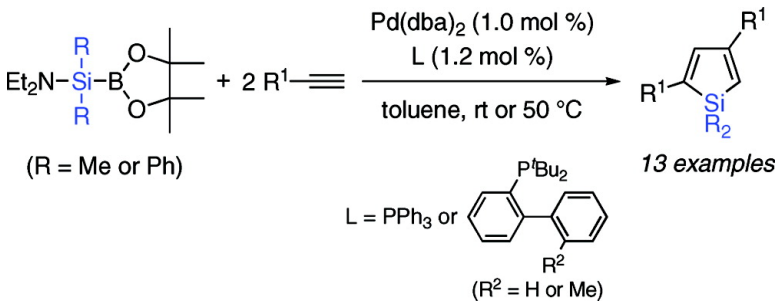

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Silylboranes Bearing Dialkylamino Groups on Silicon as Silylene Equivalents: Palladium-Catalyzed Regioselective Synthesis of 2,4-Disubstituted Siloles

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Siloles have received much attention in materials sciences because of their unique electronic properties, arising mainly from their low-lying LUMO.[1] Particular interest has been focused on the application of π-conjugated siloles to light-emitting materials.[2] As the properties of siloles largely depend upon the substituents on the silole ring, much effort has been devoted to the development of new methods for their efficient and selective synthesis.[2,3]

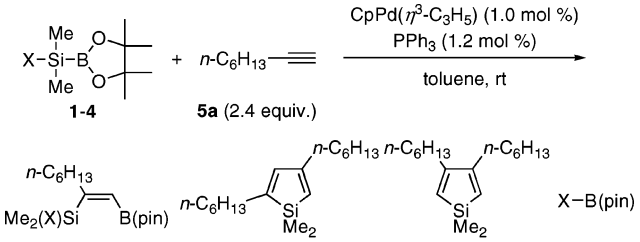
Transition-metal-catalyzed [2 + 2 + 1] cyclization of an alkyne (2 equiv) with a silylene equivalent is one of the most attractive routes to substituted siloles. Nickel- and palladium-catalyzed reactions have been developed with exploration of organosilicon reagents such as hydrodisilane,[4] alkynyldisilane,[5] trisilacyclopropane,[6] (hydrosilyl)stannane,[7] silacyclopropene,[8] and silacyclopropane.[9] These reaction systems allowed synthesis of 2,3,4,5-tetrasubstituted, 2,3,4-trisubstituted, and 3,4-disubstituted siloles, which had been difficult to synthesize.

As part of our study of silylborane,[10] we recently established synthetic access to silylboranes that are functionalized on the silicon atom.[11] By using this method, silylboranes bearing chloro, alkoxy, and dialkylamino groups on silicon are easily prepared on a practical scale. Our interest was then focused on the reactivity of these novel silylboranes in transition-metal-catalyzed silaboration of unsaturated organic molecules. In this paper, we disclose our unexpected finding on the efficient use of amino-substituted silylboronic esters as a silylene equivalent and selective formation of 2,4-disubstituted siloles, for which no efficient synthetic access has so far been established.[12]

Reactions of 1-octyne (**5a**) with silylboranes **1**−**4**,[11] bearing phenyl, chloro, methoxy, and dialkylamino groups on silicon, were carried out in the presence of 1.0 mol % of CpPd(η^3-C_3H_5) and 1.2 mol % of PPh_3 (Table 1).[13] Addition of Ph-substituted silylborane **1** to **5a** took place slowly at room temperature (70 h for full conversion), giving 1-boryl-2-silyl-1-alkene **6** with a quantitative yield (entry 1). Large rate acceleration was observed when the reaction was carried out with Cl-substituted silylborane **2**, resulting in efficient formation of alkene **7** within 15 min (entry 2). Moderate rate acceleration was also observed in the addition of MeO-substituted silylborane **3** (entry 3). These results suggest that the reaction rate of the silaboration critically depends upon the electronic nature of the substituents on the silicon.

Diethylamino-substituted silylborane **4a**[11] was then reacted with **5a** under the same reaction conditions (entry 4). The starting **4a** was completely consumed for 80 min at room temperature, but no silaboration products, such as **9a**, were found in the reaction mixture. We found that 2,4-disubstituted silole **10a** and 3,4-silole **10a′** were formed in good total yield (79%, **10a**:**10a′** = 77:23). The formation of silole was accompanied by the formation of (diethylamino)pinacolborane (**11a**), which suggests the involvement of Pd−silylene species in the catalytic system.[14] This silole formation was found to be general for amino-substituted silylboranes having dimethylamino and pyrrolidino groups on the silicon atom (entries 5 and 6).

Table 1. Palladium-Catalyzed Reaction of Silylboranes **1**−**4** with **5a**[a]



entry	silylborane	time (h)	yield (%)[b] 6–9	10 (10a:10a′)[c]	11
1	**1** (X = Ph)	70	99[d] (**6**)	0	0
2	**2** (X = Cl)	0.2	92 (**7**)	0	0
3	**3** (X = OMe)	4	80 (**8**)	0	0
4	**4a** (X = NEt_2)	1.3	0 (**9a**)	79 (77:23)	56 (**11a**)
5[e]	**4b** (X = NMe_2)	1.5	0 (**9b**)	55[f] (69:31)	77[f] (**11b**)
6[e]	**4c** (X = pyrrolidino)	1.5	0 (**9c**)	69[f] (75:25)	82[f] (**11c**)

[a] **1**−**4** (0.40 mmol), **5a** (0.96 mmol), CpPd(η^3-C_3H_5) (4.0 μmol), and PPh_3 (4.8 μmol) were stirred in toluene (0.2 mL) at room temperature unless otherwise noted. [b] Isolated yield based on silylborane. [c] Determined by ^{1}H NMR analysis. [d] GC yield. [e] Carried out in C_6D_6. [f] ^{1}H NMR yield.

To improve regioselectivity (**10a**:**10a′**), we tested various tertiary phosphine ligands in the reactions of **4a** with **5a**.[15] We found that the highest regioselectivity was attained with sterically hindered P(*t*-Bu)$_2$(2-biphenyl) (**12**), which afforded **10a** and **10a′** with the ratio of 90:10, although the reaction was slower than the original reaction conditions using PPh_3 (entry 1 in Table 2).

Various terminal alkynes were subjected to reaction with **4a** in the presence of palladium catalysts (Table 2). It was found that easily available Pd(dba)$_2$ could be used for this reaction.[16] In the presence of 1.0 mol % of Pd(dba)$_2$ with 1.2 mol % of either **12** or the analogous bulky phosphine P(*t*-Bu)$_2$[2-(2′-methylbiphenyl)] (**13**), reactions of functionalized or unfunctionalized aliphatic alkynes **5a**−**d** gave the corresponding siloles **10a**−**d** in good yields with high regioselectivities (**10**:**10′** = 90:10−96:4, entries 1−4). Reactions of aromatic alkynes were carried out with the Pd/PPh_3 catalyst (entries 5−12). Phenylacetylene (**5e**) and alkynes **5f**−**h** bearing electron-donating groups yielded **10e**−**h** in yields of 80−96% with high regioisomeric ratios (entries 5−8), whereas the reaction of CF_3-substituted **5i** gave a lower yield with good regioselectivity (94:6, entry 9). Sterically demanding arylacetylenes **5j**−**l** reacted with **4a** with no drop in reaction rate to give **10j**−**l** with higher regioselectivities (95:5−99:1, entries 10−12).

We then carried out the reaction of **5e** with $(Et_2N)Ph_2Si$−B(pin) (**14**)[11] in the presence of the Pd/PPh_3 catalyst (eq 1). Although the

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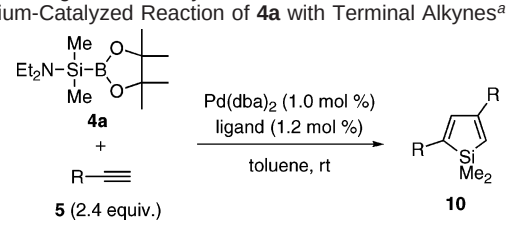
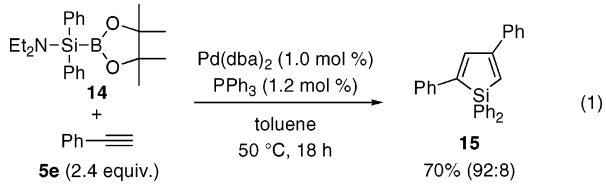
Table 2. Regioselective Synthesis of 2,4-Disubstituted Siloles via Palladium-Catalyzed Reaction of **4a** with Terminal Alkynes[a]



entry	alkyne	ligand[b]	product	yield (%)[c]	ratio[d]
1	**5a** (R = *n*-C_6H_{13})	**12**	**10a**	74	90:10
2	**5b** (R = *n*-C_8H_{17})	**12**	**10b**	71	96:4
3	**5c** [R = $(CH_2)_2$OTBDMS]	**12**	**10c**	83	93:7
4	**5d** [R = $(CH_2)_3$Cl]	**13**	**10d**	78	91:9
5	**5e** (R = Ph)	PPh_3	**10e**	92	95:5
6	**5f** (R = 4-MeC_6H_4)	PPh_3	**10f**	96	95:5
7	**5g** (R = 4-$MeOC_6H_4$)	PPh_3	**10g**	96	96:4
8	**5h** (R = 4-$Me_2NC_6H_4$)	PPh_3	**10h**	80[e]	88:12
9	**5i** (R = 4-$CF_3C_6H_4$)	PPh_3	**10i**	73	94:6
10	**5j** (R = 2-MeC_6H_4)	PPh_3	**10j**	78	95:5
11	**5k** (R = 2,4,6-$Me_3C_6H_2$)	PPh_3	**10k**	80	97:3
12	**5l** (R = 1-naphthyl)	PPh_3	**10l**	75	99:1

[a] **4a** (0.40 mmol), **5** (0.96 mmol), $Pd(dba)_2$ (4.0 μmol), and ligand (4.8 μmol) were stirred in toluene (0.2 mL) at room temperature unless otherwise noted. [b] P(*t*-Bu)$_2$(2-biphenyl) (**12**); P(*t*-Bu)$_2$[2-(2′-methylbiphenyl)] (**13**). [c] Isolated yield. [d] Ratio of 2,4-disubstituted and 3,4-disubstituted siloles, which was determined by ^{1}H NMR analysis of the crude reaction mixture. [e] ^{1}H NMR yield.

reaction was slower than that of **4a**, diphenylsilyl-derived silole **15** was isolated in 70% yield with high regioselectivity (92:8).

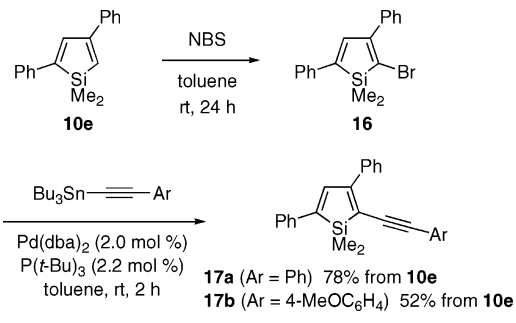


(1)

Conversion of the 2,4-disubstituted silole **10e** to novel π-conjugated 2,3,5-trisubstituted siloles was demonstrated (Scheme 1). Site-selective bromination of **10e** was achieved by treatment with *N*-bromosuccinimide (NBS) at room temperature, giving 2-bromo-1,1-dimethyl-3,5-diphenylsilole (**16**). Migita−Kosugi−Stille coupling of **16** with alkynyltributylstannanes under Fu's conditions[17] afforded **17a** and **17b** in 78 and 52% yields from **10e**, respectively.[18]

In conclusion, we have established new synthetic access to 2,4-disubstituted siloles via Pd-catalyzed reaction of terminal alkynes with (dialkylaminosilyl)pinacolboranes, which serve as new silylene equivalents. Mechanism of the reaction is currently under investigation. The elimination of (dialkylamino)borane seems to be the key driving force for the reaction as recently demonstrated in the Ru-catalyzed reaction system.[19]

Scheme 1. Site-Selective Functionalization of **10e**



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Supporting Information Available: Experimental details and characterization data of the products. This material is available free of charge via Internet at http://pubs.acs.org.

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(14) In the absence of alkyne, silylborane **4a** slowly reacted at room temperature in the presence of the Pd/PPh_3 complex (10 mol %), resulting in the formation of **11a** (84% yield after 48 h) with organosilicon compounds, which exhibited ^{1}H NMR signals in the region of −1.0 to 0.6 ppm. Although they were hardly identifiable, dodecamethylcyclohexasilane was detected by ^{1}H NMR and GCMS analysis as a very minor (<1%) component.
(15) **10a**:**10a′** (PR_3): 80:20 ($PCyPh_2$); 82:18 (PCy_2Ph); 77:23 (PCy_3); 68:32 [P(*t*-Bu)$_3$]; 86:14 [PPh_2(2-biphenyl)]; 88:12 [PCy_2(2-biphenyl)]; 90:10 [P(*t*-Bu)$_2$(2-biphenyl)].
(16) $Pd(OAc)_2$ and $PdCl_2(CH_3CN)_2$ were also effective as catalyst precursors of the reaction, although prolonged reaction time was needed because of longer induction period than $Pd(dba)_2$.
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(18) **10e**: UV/vis λ_{max} 338 nm (ϵ 2.0 × 10^3); FL λ_{max} 452 nm, Φ_f 0.13. **17a**: UV/vis λ_{max} 403 nm (ϵ 2.5 × 10^3); FL λ_{max} 456 nm, Φ_f 0.069. **17b**: UV/vis λ_{max} 420 nm (ϵ 2.2 × 10^4); FL λ_{max} 516 nm, Φ_f 0.015. The photophysical data were measured in $CHCl_3$. Quantum yields (Φ_f) were determined with reference to quinine sulfate in 0.1 M H_2SO_4 (excited at 366 nm).
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