ABSTRACT: Silole derivatives are attracting significant attention as new functional materials with excellent electronic and photophysical properties. Thus, the development of synthesis methods to afford such derivatives is highly desirable. Herein, the synthesis of pyridine-fused siloles under the conditions of the Sonogashira coupling reaction is described. The reactions of 2-bromo-3-(pentamethyldisilanyl)pyridine (1) with ethynylbenzene derivatives in the presence of PdCl₂(PPh₃)₂-CuI as a catalyst afforded the corresponding pyridine-fused siloles (2a−2c) through intramolecular trans-bis-silylation. DFT calculations were also performed to understand the reaction mechanism. This paper is the first to report on the successful use of palladium catalysts in the trans-bis-silylation of alkynes with disilanes.

INTRODUCTION

Silicon-containing compounds are used in various fields ranging from synthetic organic chemistry to functional materials and pharmaceutical synthesis. Thus, new synthetic methods for such compounds have been developed.⁵⁻¹⁵ Many articles have reported on the transition metal-catalyzed bis-silylation of alkynes with disilane.⁶⁻¹³ Some examples of cis-bis-silylation of internal alkynes with acyclic disilanes have also been reported (Scheme 1). For example, Ozawa et al. reported the bis-silylation of Me₃SiSiF₂Ph with internal alkynes using a Pd catalyst.¹⁸ Spencer et al. investigated the intermolecular bis-silylation of internal alkynes with hexamethyldisilane using the [(NHC)₂Pd(SiMe₃)₂] (NHC: N-heterocyclic carbene) complex as a precatalyst.¹⁵ Zhao et al. reported nickel-catalyzed bis-silylation of internal alkynes with an unsymmetrical coordinat-
RESULTS AND DISCUSSION

The reaction of 2,3-dibromopyridine with i-PrMgCl at room temperature followed by quenching with chloropentamethyldisilane afforded 2-bromo-3-(pentamethyldisilanyl)pyridine (1) in 70% yield. To obtain 2-phenylethynyl-3-(pentamethyldisilanyl)pyridine, 1 was reacted with phenylacetylene under the Sonogashira coupling reaction conditions. When a mixture of 1 and ethynylbenzene in the presence of a PdCl$_2$(PPh$_3$)$_2$-CuI catalyst was heated to reflux in triethylamine, an unexpected product, 1,1-dimethyl-2-phenyl-3-(trimethylsilyl)-1H-silolo(3,2-b)pyridine (2a), was obtained in 15% isolated yield, along with intermolecular bis-silylation product 3a (8% yield) from the reaction of 2-phenylethynyl-3-(pentamethyldisilanyl)pyridine with phenylacetylene (Scheme 3). Compound 2a was produced via intramolecular trans-bis-silylation. Many unidentified products were also detected in the reaction mixture by gas liquid chromatography (GLC) and gel permeation chromatography (GPC). Song et al. reported an unsymmetrical disilane by attaching a coordinating group to one of the two silicon atoms, which was successfully applied to the Pd-catalyzed bis-silylation of terminal alkynes. Compound 2a was isolated by column chromatography, and its structure was verified by spectrometric analyses. The mass spectrum for 2a shows a parent ion at m/z 309 corresponding to the calculated molecular weight of C$_{18}$H$_{23}$Si$_2$N. The $^1$H NMR spectrum for 2a shows singlets at 0.04 and 0.29 ppm, representing methyl protons on the silicon atoms, three doublets of doublet signals at 7.00, 7.76, and 8.49 ppm, ascribed to the pyridyl protons, and signals corresponding to the phenyl protons. The $^{29}$Si NMR spectrum for 2a shows signals at −6.2 and 3.7 ppm.

We carried out the Pd(PPh$_3$)$_2$Cl$_2$-catalyzed reaction of 1 with ethynylbenzene in the absence of CuI. Although many unidentified products were detected in the reaction mixture by GLC and GPC, compound 2a was not detected in the reaction mixture. We believe that a copper catalyst is necessary for coupling reactions.

A similar reaction of 1 with 4-ethynyltoluene under the same conditions afforded 1,1-dimethyl-2-(p-tolyl)-3-(trimethylsilyl)-1H-silolo(3,2-b)pyridine (2b) in 21% yield, in addition to compound 3b (7% yield), which is analogous to 3a. Many unidentified products were also detected in the reaction mixture by GLC and GPC. The structures of 2b and 3b were verified by NMR spectroscopy and mass spectrometry. 3-Ethynyltoluene was also reacted with 1 in the presence of the PdCl$_2$(PPh$_3$)$_2$-CuI catalyst to obtain 1,1-dimethyl-2-(m-tolyl)-3-(trimethylsilyl)-1H-silolo(3,2-b)pyridine (2c) in 16% isolated yield. NMR and MS analyses showed the existence of bis-silylation product 3c (3% yield) obtained from the reaction of 3-pentamethyldisilanyl-2-(m-tolylenethyl)pyridine with 3-ethynyltoluene.
When 1 was heated with 1-chloro-4-ethynylbenzene and 2-ethynyl-1,3,5-trimethylbenzene under the same conditions, neither 1H-silolo(3,2-b)pyridine derivatives such as 2a−2c nor the products analogous to 3a−3c were detected by NMR spectroscopy. However, many unidentified products were detected in the reaction mixture by GLC and GPC.

In the proposed reaction mechanism to obtain 2, cyclic products were formed with the catalyst, as shown in Scheme 4. First, compound A is produced by the Sonogashira coupling reaction of 1 with ethynylbenzene derivatives, followed by oxidative addition of Si−Si bonds to produce Pd complex B. Complex B further undergoes Si−C bond formation to deliver intermediate C. Complex C then undergoes ring expansion to the five-membered cyclic complex D, followed by reductive elimination to afford bis-silylated product 2 and regenerate the Pd catalyst.

Next, we carried out a similar reaction of 1 with ethynyltrimethylsilane in the presence of a catalytic amount of Pd catalyst. When compound 1 was stirred under reflux for 12 h in triethylamine in the presence of a catalytic amount of the Pd complex, 3-(1,1,2,2,2-pentamethyldisilanyl)-2-(phenylethynyl)pyridine (4) was obtained in 17% isolated yield (Scheme 5). No 1,1-dimethyl-2,3-bis-(trimethylsilyl)-1H-silolo(3,2-b)pyridine (2d) analogous to 2a−2c was detected in the reaction mixture. A similar reaction of 1 with 3,3-dimethyl-1-butyne afforded 2-(3,3-dimethylbut-1-yn-1-yl)-3-(1,1,2,2,2-pentamethyldisilanyl)pyridine (5) in 5% yield. Many unidentified products were detected in the reaction mixture by GLC and GPC. Bulky substituents, which prevented the formation of 4 and 5, explain their low yields.25

### THEORETICAL STUDY

DFT calculations were performed to investigate the energy and structural changes in the synthesis route from 3-(1,1,2,2,2-pentamethyldisilanyl)-2-(phenylethynyl)pyridine (6) to trans-adduct 2a through cis-adduct (Z)-7,7-dimethyl-8-(phenyl(trimethylsilyl)methylene)-2-aza-7-silabicyclo[4.2.0]octa-1,3,5-triene (7, Scheme 6). The Gaussian 09 program package29 was employed along with Becke’s three-parameter Lee–Yang–Parr hybrid functional.30 The Los Alamos effective core potentials31 and the Dunning/Huzinaga full double zeta basis sets32 were used for the Pd atom, while the 6-311G(d) basis sets were used for the H, C, N, Si, and P atoms.

The Pd catalyst was modeled using the Pd(PPh3)3 complex, which formed when three PPh3 ligands detach from Pd(PPh3)3, owing to steric hindrance. Two reaction mechanisms were expected: (1) a parallel mechanism from 6 to cis-adduct 7 and trans-adduct 2a and (2) a sequential mechanism in which cis-adduct 7 is first formed from 6, and then 7 is converted to 2a. However, only the latter reaction route could be determined by the DFT calculations. Figure 1 shows the energy change along the reaction coordinate which consists of seven transition states (TSs) and eight local minima (LMs). LM0 is 6, LM4 is cis-adduct 7, and LM7 is trans-adduct 2a. Individual structures are shown in the Supporting Information.

The formation of TS6 is the rate-determining step with an activation energy of 215.3 kJ mol⁻¹. Although the activation energy was higher for cis-to-trans conversion than that for the formation of cis-adduct 7, trans-adduct 2a was more stable by 91.4 kJ mol⁻¹. If the activation energy of 161 kJ mol⁻¹ was not a significant barrier under the present reaction conditions, the difference between the stability would be the driving force for the formation of 2a.

We also carried out DFT calculations for the production of trans-adducts 2a in the absence of a ligand on the palladium atom. The results revealed that the TS was the rate-determining step with an activation energy of 215.3 kJ mol⁻¹.
CONCLUSIONS

We investigated the reactions of 2-bromo-3-(pentamethyldisilanyl)pyridine (1) with terminal alkynes in the presence of PdCl$_2$(PPh$_3$)$_2$-CuI as a catalyst. The reactions of 1 with ethynylbenzene derivatives provided the corresponding ring compounds (2a−2c) via intramolecular bis-silylation. Similar reactions of 1 with ethynyltrimethylsilane and 3,3-dimethyl-1-butyne afforded 2-ethynyl-3-(pentamethyldisilanyl)pyridine derivatives 4 and 5, respectively. DFT calculations were performed to rationalize the formation of 1,1-dimethyl-2-phenyl-3-(trimethylsilyl)-1$H$-silolo(3,2-b)pyridine 2a via cis-bis-silylation adduct 7. These reactions comprise the palladium-catalyzed trans-bis-silylation of internal alkynes. To the best of our knowledge, this is the first report on the use of palladium-containing catalysts in such reactions.

METHODS

General Procedure. All reactions of 1 were carried out under an inert atmosphere using dry nitrogen. NMR spectra were recorded on a JMN-ECS400 spectrometer. Low-resolution mass spectrometry (HR-MS) was performed on a JEOL JMS-700 mass spectrometer. High-resolution mass spectrometry (HR-MS) was performed on a JEOL JMS-700 mass spectrometer and a Thermo Scientific LTQ Orbitrap XL hybrid Fourier-transform mass spectrometer using electrospray ionization. Column chromatography was performed using a silica gel column (Wakogel C-300; Wako Pure Chemical Industries).

Preparation of 2-Bromo-3-(1,1,2,2,2-Pentamethyldisilanyl)Pyridine (1). In a 300 mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel, 10.008 g (42.2 mmol) of 2,3-dibromopyridine was added to 100 mL of dry tetrahydrofuran (THF). Next, a THF solution comprising 21.1 mL (42.2 mmol) of 2.0 M isopropyl magnesium chloride was added dropwise at room temperature. The mixture was then stirred for 1 h at room temperature, and 7.047 g (42.2 mmol) of chloropentamethylsilane was added. The resulting mixture was stirred for 6 h. It was then hydrolyzed, after which the organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was chromatographed on a silica gel column eluting with hexane to obtain 8.474 g (70% yield) of 2-bromo-3-(1,1,2,2,2-pentamethyldisilanyl)pyridine 1: HR-MS: calcd for C$_{10}$H$_{19}$NSi$_2$Br: (M + H$^+$): 288.02339, found: 288.02411. MS m/z 287 (M$^+$) ；$^1$H NMR $\delta$(CDCl$_3$) 0.13 (s, 9H, Me$_3$Si), 0.43 (s, 6H, Me$_2$Si), 7.22 (dd, 1H, pyridyl-ring proton, $J$ = 7.2, 5.2 Hz), 7.65 (dd, 1H, pyridyl-ring proton, $J$ = 7.2, 2.4 Hz), 8.29 (dd, 1H, pyridyl-ring proton, $J$ = 5.2, 2.4 Hz); $^{29}$Si NMR $\delta$(CDCl$_3$) −18.1, −17.8.

Palladium-Catalyzed Reaction of 1 with Ethynylbenzene. In a 100 mL two-necked flask fitted with a reflux condenser, 1 (2.014 g, 6.99 mmol), bis(triphenylphosphine)-dichloropalladium (0.244 g, 0.348 mmol), and copper(I) iodide (0.067 g, 0.352 mmol) were added to 25 mL of dry triethylamine. To this mixture, ethynylbenzene (1.491 g, 13.9
mmol) was added dropwise at room temperature, after which the mixture was heated to reflux for 12 h. The solvent was then evaporated, and the residue was chromatographed on a silica gel column eluting with hexane-ethyl acetate (5:1) to obtain 0.303 g (15% yield) of 2a and 0.241 g (8% yield) of 3a. For 2a: HR-MS: calcd for C_{16}H_{12}N_{2}S_{2} (M + H)^{+}: 310.1448; found: 310.14465. MS m/z 309 (M^+); ^1H NMR δ(CDCl_{3}) 0.04 (s, 9H, MeSi), 0.29 (s, 6H, MeSi), 7.00 (dd, 1H, pyridyl-ring proton, J = 6.8 Hz, 5.2 Hz), 7.05 (dd, 2H, phenyl-ring protons, J = 7.2 Hz, 1.6 Hz), 7.23 (tt, 1H, phenyl-ring proton, J = 7.2 Hz, 1.6 Hz), 7.32 (t, 2H, phenyl-ring protons, J = 7.2 Hz), 7.76 (dd, 1H, pyridyl-ring proton, J = 6.8 Hz, 2.0 Hz), 8.49 (dd, 1H, pyridyl-ring proton, J = 5.2 Hz, 2.0 Hz); ^13C NMR δ(CDCl_{3}) −4.9 (MeSi), 0.9 (MeSi), 120.2, 125.9, 126.6, 127.9, 131.3, 138.7, 142.8, 149.5, 158.9, 165.9, 171.7 (phenyl, pyridyl-ring and olefinic carbons); ^31Si NMR δ(CDCl_{3}) = −6.2, 3.7. For 3a: HR-MS: calcd for C_{35}H_{30}N_{15}S_{3} (M + H)^{+}, 412.1911; found, 412.1911MS. MS m/z 411 (M^+) ; ^1H NMR δ(CDCl_{3}) −0.11 (s, 3H, MeSi), 0.19 (s, 9H, MeSi), 0.28 (s, 3H, MeSi), 6.79−8.83 (m, 2H, phenyl-ring protons), 6.89 (s, 1H, HC=C), 7.06−7.08 (m, 3H, phenyl-ring protons), 7.17 (dd, 1H, pyridyl-ring proton, J = 7.4, 4.8 Hz), 7.29−7.31 (m, 3H, phenyl-ring protons), 7.41−7.44 (m, 2H, phenyl-ring protons), 8.12 (dd, 1H, pyridyl-ring protons, J = 7.4 Hz, 2.0 Hz), 8.70 (dd, 1H, pyridyl-ring proton, J = 4.8 Hz, 2.0 Hz); ^13C NMR δ(CDCl_{3}) −1.1 (MeSi), 0.1, 0.5 (MeSi), 93.7, 106.7 (sp carbons), 120.2, 123.0, 127.5, 128.0, 128.2, 128.5, 128.6, 129.5, 131.9, 137.2, 138.7, 144.8, 148.2, 150.2, 166.5 (phenyl, pyridyl-ring, and olefinic carbons); ^31Si NMR δ(CDCl_{3}) = −20.6, −1.2.

**Palladium-Catalyzed Reaction of 1 with 4-Ethenylotenue.** In a 100 mL two-necked flask fitted with a reflux condenser, 1 (2.145 g, 7.44 mmol), bis(triphenylphosphine)-dichloropalladium (0.263 g, 0.375 mmol), and copper(I) iodide (0.069 g, 0.362 mmol) were added to 25 mL of dry triethylamine. To this mixture, 3-ethylotene (1.677 g, 14.4 mmol) was added dropwise at room temperature. The mixture was heated to reflux for 12 h. The solvent was then evaporated, and the residue was chromatographed on a silica gel column eluting with hexane-ethyl acetate (20:1) to obtain 0.420 g (16% yield) of 2c and 0.107 g (3% yield) of 3c. For 2c: HR-MS: calcd for C_{35}H_{29}N_{15}S_{3} (M + H)^{+}, 439.1525; found, 439.1519. MS m/z 439 (M^{+}); ^1H NMR δ(CDCl_{3}) −0.14 (s, 3H, MeSi), 0.19 (s, 9H, MeSi), 0.29 (s, 3H, MeSi), 2.10 (s, 3H, Me), 2.32 (s, 3H, Me), 6.59 (s, 1H, phenylene-ring proton), 6.60 (d, 1H, phenylene-ring proton, J = 8.0 Hz), 6.85 (s, 1H, HC = C), 6.89 (d, 1H, phenylene-ring proton, J = 8.0 Hz), 6.96 (t, 1H, phenylene-ring proton, J = 8.0 Hz), 7.13 (d, 1H, phenylene-ring proton, J = 8.0 Hz), 7.17 (dd, 1H, phenylene-ring proton, J = 7.4, 5.2 Hz), 7.18 (t, 1H, phenylene-ring proton), 7.24 (d, 1H, phenylene-ring proton, J = 8.0 Hz), 7.25 (s, 1H, phenylene-ring proton), 8.13 (dd, 1H, phenylene-ring protons, J = 7.4 Hz, 2.0 Hz), 8.70 (dd, 1H, phenylene-ring proton, J = 5.2 Hz, 2.0 Hz); ^13C NMR δ(CDCl_{3}) −1.1 (MeSi), 0.1, 0.5 (MeSi), 21.16, 21.23 (Me), 92.7, 106.8 (sp carbons), 120.1, 122.7, 126.5, 127.8, 128.1, 128.2, 128.6, 128.9, 129.5, 130.3, 132.4, 137.0, 137.3, 137.8, 138.9, 144.8, 147.8, 150.1, 166.6 (phenyl, pyridyl-ring, and olefinic carbons); ^31Si NMR δ(CDCl_{3}) = −20.6, −1.3.

**Preparation of 3-(1,1,2,2,2-Pentamethyldisilanyl)-2-(Trimethylsilylthethyl)pyridine (4).** In a 300 mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel, 1 (2.007 g, 6.96 mmol), bis(triphenylphosphine)dichloropalladium (0.246 g, 0.351 mmol), and copper(I) iodide (0.067 g, 0.352 mmol) were added to 25 mL of dry triethylamine. To this mixture, ethynyltrimethylsilane (0.784 g, 7.98 mmol) was added dropwise at room temperature. The mixture was heated to reflux for 12 h. The solution was then hydrolyzed, and the organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. The solvent was then evaporated, and the residue was chromatographed on a silica gel column eluting with hexane-ethyl acetate (10:1) to obtain 0.326 g (17% yield) of 4: HR-MS: calcd for C_{35}H_{30}N_{15}S_{3} (M + H)^{+}, 506.15241; found, 506.15237. MS m/z 305 (M^{+}); ^1H NMR δ(CDCl_{3}) 0.09 (s, 9H, MeSi), 0.27 (s, 9H, MeSi), 0.45 (s, 6H, MeSi), 7.17 (dd, 1H, pyridyl-ring proton, J = 7.6, 5.2 Hz), 7.70 (dd, 1H, pyridyl-ring proton, J = 7.6, 2.0 Hz), 8.51 (dd, 1H, pyridyl-ring proton, J = 5.2, 2.0 Hz); ^13C NMR


\[ \delta(CDCl_3) = -3.7 \text{ (Me}_2\text{Si),} -1.5, -0.3 \text{ (Me}_2\text{Si),} 96.6, 106.1 \text{ (sp carbons),} 122.4, 137.3, 142.0, 147.4, 149.4 \text{ (pyridyl-ring carbons).} \]

\[ ^{29}\text{Si NMR } \delta(CDCl_3) = -20.7, -17.2, -16.6. \]

**Preparation of 2-(3,3-Dimethylbutyl-1-yn-1-yl)-3-(1,1,2,2,2-Pentamethyldisilanyl)pyridine (5).** In a 300 mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel, 1 (2.061 g, 7.15 mmol), bis-(triphenylphosphine)dichloropalladium (0.246 g, 0.351 mmol), and copper(I)iodide (0.068 g, 0.357 mmol) were added to 50 mL of dry triethylamine. To this mixture, 3,3-(triphenylphosphine)dichloropalladium (0.246 g, 0.351 mmol), and copper(I)iodide (0.068 g, 0.357 mmol) were added to 50 mL of dry triethylamine. The mixture was heated to reflux for 12 h. The solvent was then hydrolyzed, and the organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. The solvent was then evaporated, and the residue was chromatographed on a silica gel column eluting with hexane-ethyl acetate (10:1) to obtain 0.101 g (5% yield).

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c03637

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The authors declare no competing financial interest.

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