

Article

Synthesis of Thiophene-Fused Siloles through Rhodium-Catalyzed *Trans*-Bis-Silylation

 Akinobu Naka ^{1,*} , Maho Inoue ¹, Haruna Kawabe ¹ and Hisayoshi Kobayashi ^{2,*}
¹ Department of Life Science, Kurashiki University of Science and the Arts, Nishinoura, Tsurajima-cho, Kurashiki, Okayama 712-8505, Japan; s25b005@kusa.ac.jp (M.I.); s26b010@kusa.ac.jp (H.K.)

² Kyoto Institute of Technology, Matsugasaki, Kyoto 606-8585, Japan

* Correspondence: anaka@chem.kusa.ac.jp (A.N.); hisabbit@yahoo.co.jp (H.K.)

Abstract: Rhodium-catalyzed reactions of 3-ethynyl-2-pentamethyldisilanylthiophene derivatives (**1a–1c**) have been reported. At 110 °C, compounds **1a–1c** reacted in the presence of a rhodium complex catalyst, yielding thiophene-fused siloles (**2a–2c**) through intramolecular *trans*-bis-silylation. To understand the production of **2a** from **1a**, the mechanism was investigated using density functional theory (DFT) calculations.

Keywords: rhodium-catalyzed reaction; *trans*-bis-silylation; silole; DFT calculation; 3-ethynyl-2-pentamethyldisilanylthiophene; cyclic silicon compound; Sonogashira coupling; palladium-catalyzed reaction; energy diagram

1. Introduction

Organosilicon compounds have been frequently utilized in various fields, including organic synthesis, materials, and pharmaceuticals, owing to their unique physical and chemical properties [1–5]. Among the synthetic methods for organosilicon compounds, a bis-silylation reaction has emerged, enabling the simultaneous formation of two silicon-carbon bonds. In most bis-silylation reactions, *cis*-adducts are stereoselectively formed [6–20]; however, *trans*-adduct formation reactions have been recently reported. In 2012, Matsuda et al. demonstrated the possibility of *trans*-selective bis-silylation of a C-C triple bond via intramolecular cyclization using a Rh(I) catalyst with (2-alkynylphenyl)disilanes [21]. In 2022, we reported the first intramolecular *trans*-bis-silylation reaction in the presence of PdCl₂(PPh₃)₂-CuI as the catalyst [22]. In 2023, we discovered the synthesis of siloles with condensed pyridine rings through intramolecular *trans*-bis-silylation reactions in the presence of a rhodium complex catalyst [23]. Silole derivatives have also attracted attention as novel functional materials with excellent electronic and photophysical properties for various applications such as organic light-emitting diodes (OLEDs), photovoltaic devices, and semiconductors [24–29].

Zhao et al. reported the intermolecular *trans*-bis-silylation of terminal alkynes using a Pd catalyst and 8-(2-substituted-1,1,2,2-tetramethyldisilanyl)quinoline (TMDQ) to selectively form *trans*-bis-silylated alkenes [30], as well as the divergent bis-silylation of alkynoates using TMDQ in a synergistic Pd/Lewis acid catalytic system [31].



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Furthermore, much attention has been paid to the synthesis of thiophene-based materials, which display potential for use in electrochromic devices, field-effect transistors, OLEDs, and organic photovoltaics [32]. Therefore, investigating the synthesis of siloles using thiophenes is of considerable interest. In this paper, we report the synthesis of siloles with condensed thiophene rings using a rhodium complex catalyst in an intramolecular *trans*-bis-silylation reaction. Furthermore, we elucidated the reaction mechanism through computational calculations using density functional theory (DFT). This paper represents the first report of synthesizing thiophene-fused siloles via transition-metal-catalyzed bis-silylation reactions.

2. Materials and Methods

2.1. General Procedure

All experiments were conducted in an inert atmosphere using dry nitrogen. Nuclear magnetic resonance (NMR) spectra were acquired utilizing a JMN-ECS400 spectrometer (^1H NMR (400 MHz), ^{13}C NMR (100.6 Hz), ^{29}Si NMR (79.5 MHz)). Low-resolution mass spectrometry was executed via a JEOL JMS-700 mass spectrometer, while high-resolution mass spectrometry (HR-MS) was conducted using the same instrument. Gas chromatographic separations were accomplished with a 3 m \times 10 mm column packed with 30% silicone on chromosorb W AM DMCS 80/100. Gel permeation chromatography was carried out utilizing an LC-908 Recycling Preparative HPLC system from Japan Analytical Industry Co., Ltd., Tokyo, Japan. Column chromatography was performed on a silica gel column (Wakogel C-300; Wako Pure Chemical Industries, Osaka, Japan). Chemicals such as bis(triphenylphosphine)palladium(II) dichloride [$\text{PdCl}_2(\text{PPh}_3)_2$], copper(I) iodide (CuI), Di- μ -chloro-tetracarbonyldirrhodium(I) [$\text{RhCl}(\text{CO})_2$] $_2$, Bis(norbornadiene- μ -chlororhodium) [$\text{RhCl}(\text{nbd})$] $_2$, and tris(triphenylphosphine)rhodium(I) chloride [$\text{RhCl}(\text{PPh}_3)_3$] were procured from Sigma-Aldrich, St. Louis, MO, USA. Tetrahydrofuran (THF), triethylamine, and toluene were purchased from Tokyo Kasei Kogyo (Tokyo, Japan). Triethylamine underwent distillation over KOH under nitrogen immediately before use, while THF and toluene were distilled from sodium benzophenone ketyl under nitrogen immediately before use.

2.2. Procedures

Preparation of 3-Iodo-2-(1,1,2,2,2-Pentamethyldisilanyl)thiophene: 2,3-Diiodothiophene (9.646 g, 28.7 mmol) was added to 30 mL of dry THF in a 200-mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel. Thereafter, a THF solution comprising 18 mL (36.0 mmol) of 2.0 M ethyl magnesium chloride was added dropwise at room temperature. The mixture was stirred for 1.5 h at room temperature and 5.885 g (35.3 mmol) of chloropentamethyldisilane was added. The resulting mixture was stirred for 6 h and then treated with distilled water. 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 and eluted with hexane to obtain 7.268 g (70% yield) of 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene. HR-MS: calcd. for $\text{C}_9\text{H}_{17}\text{Si}_2\text{I}$: (M^+):340.1806, found: 340.1800. MS m/z 340 (M^+); ^1H NMR $\delta(\text{CDCl}_3)$ 0.16 (s, 9H, Me_3Si), 0.48 (s, 6H, Me_2Si), 7.22 (d, 1H, thienyl ring proton, $J = 4.4$ Hz), 7.38 (d, 1H, thienyl ring proton, $J = 4.4$ Hz); ^{13}C NMR $\delta(\text{CDCl}_3)$ -2.6 (Me_2Si), -1.4 (Me_3Si), 86.4, 131.5, 138.1, 139.3 (thienyl ring carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ -20.3 , -17.9 .

Synthesis of Compound 1a: In a 100-mL three-necked flask equipped with a stirrer, reflux condenser, and dropping funnel, 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene (1.751 g, 5.14 mmol), bis(triphenylphosphine)dichloropalladium (0.181 g, 0.258 mmol), and copper(I) iodide (0.049 g, 0.257 mmol) were combined with 15 mL of dry triethylamine. Following this, ethynylbenzene (1.063 g, 10.4 mmol) was slowly added to the mixture at room temperature via dropwise addition. The resulting mixture was refluxed for 12 h. Afterward, distilled water was added to the mixture, and the organic layer was isolated, washed with water, and dried using anhydrous magnesium sulfate. Evapora-

tion of the solvent followed, and the remaining residue was subjected to chromatography on a silica gel column, eluting with hexane–ethyl acetate (50:1). This process yielded 0.702 g (43% yield) of compound **1a**: HR-MS: calcd. for $C_{17}H_{22}Si_2S$ (M^+): 314.0981, found: 314.0980. MS m/z 314 (M^+); 1H NMR δ ($CDCl_3$) 0.11 (s, 9H, Me_3Si), 0.51 (s, 6H, Me_2Si), 7.29 (d, 1H, thienyl ring proton, $J = 4.8$ Hz), 7.33–7.35 (m, 3H, phenyl ring protons), 7.48 (d, 1H, thienyl ring proton, $J = 4.8$ Hz), 7.49–7.51 (m, 2H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) –3.1 (Me_2Si), –1.9 (Me_3Si), 86.9, 90.3 (sp carbons), 123.6, 128.0, 128.4, 128.6, 129.3, 131.2, 132.5, 142.7 (thienyl and phenyl ring carbons); ^{29}Si NMR δ ($CDCl_3$) –22.7, –17.4.

Synthesis of Compound 1b: A total of 1.028 g (3.02 mmol) of 3-Iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene, 0.106 g (0.151 mmol) of bis(triphenylphosphine) dichloropalladium, and 0.029 g (0.152 mmol) of copper(I) iodide were combined with 10 mL of dry triethylamine in a 100-mL three-necked flask equipped with a stirrer, reflux condenser, and dropping funnel. While at room temperature, 0.701 g (6.04 mmol) of 4-ethynyltoluene was slowly added dropwise to this mixture. The resulting mixture was then heated under reflux for 12 h. Afterward, distilled water was added to the mixture, and the organic layer was isolated, washed with water, and dried using anhydrous magnesium sulfate. Subsequently, the solvent was evaporated, and the remaining residue was subjected to chromatography on a silica gel column using a hexane–ethyl acetate (50:1) elution system, yielding 0.324 g (33% yield) of compound **1b**: HR-MS: calcd. for $C_{18}H_{24}Si_2S$ (M^+): 328.1137, found: 328.1135. MS m/z 328 (M^+); 1H NMR δ ($CDCl_3$) 0.11 (s, 9H, Me_3Si), 0.50 (s, 6H, Me_2Si), 2.37 (s, 3H, CH_3), 7.15 (d, 2H, phenylene ring protons, $J = 8.0$ Hz), 7.28 (d, 1H, thienyl ring proton, $J = 4.8$ Hz), 7.39 (d, 2H, phenylene ring protons, $J = 8.0$ Hz), 7.47 (d, 1H, thienyl ring proton, $J = 4.8$ Hz); ^{13}C NMR δ ($CDCl_3$) –3.2 (Me_2Si), –2.0 (Me_3Si), 21.5 (CH_3), 86.2, 90.4 (sp carbons), 120.5, 128.8, 129.1, 129.3, 131.1, 132.4, 138.1, 142.3 (thienyl and phenylene ring carbons); ^{29}Si NMR δ ($CDCl_3$) –22.7, –17.5.

Synthesis of Compound 1c: In a 100 mL three-necked flask equipped with a stirrer, reflux condenser, and dropping funnel, 1.007 g (2.96 mmol) of 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene, along with 0.104 g (0.148 mmol) of bis(triphenylphosphine)dichloropalladium and 0.029 g (0.152 mmol) of copper(I) iodide, were combined with 10 mL of dry triethylamine. To this mixture, 0.679 g (5.85 mmol) of 3-ethynyltoluene was slowly added dropwise at room temperature. The resulting mixture was then refluxed for 12 h. Following this, distilled water was added to the mixture, and the separated organic layer was washed with water and dried using anhydrous magnesium sulfate. After evaporating the solvent, the remaining residue was subjected to chromatography on a silica gel column employing a hexane–ethyl acetate (50:1) elution system, yielding 0.501 g (52% yield) of compound **1c**: HR-MS: calcd. for $C_{18}H_{24}Si_2S$ (M^+): 328.1137, found: 328.1130. MS m/z 328 (M^+); 1H NMR δ ($CDCl_3$) 0.11 (s, 9H, Me_3Si), 0.51 (s, 6H, Me_2Si), 2.32 (s, 3H, CH_3), 7.14 (d, 1H, phenylene ring proton, $J = 7.6$ Hz), 7.23 (t, 1H, phenylene ring proton, $J = 7.6$ Hz), 7.28 (d, 1H, thienyl ring proton, $J = 4.4$ Hz), 7.31 (d, 1H, phenylene ring proton, $J = 7.6$ Hz), 7.32 (s, 1H, phenylene ring proton), 7.47 (d, 1H, thienyl ring proton, $J = 4.4$ Hz); ^{13}C NMR δ ($CDCl_3$) –3.1 (Me_2Si), –2.0 (Me_3Si), 21.3 (CH_3), 86.5, 90.4 (sp carbons), 123.4, 128.2, 128.3, 128.7, 128.9, 129.3, 131.8, 132.5, 138.0, 142.6 (thienyl and phenylene ring carbons); ^{29}Si NMR δ ($CDCl_3$) –22.7, –17.5.

Reaction of Compound 1a in the Presence of $[RhCl(CO)_2]_2$ Catalyst: Compound **1a** (0.234 g, 0.745 mmol) and 0.029 g (0.0746 mmol) of $[RhCl(CO)_2]_2$ were added to dry toluene (1.5 mL) in a 30 mL two-necked flask fitted with a reflux condenser. Subsequently, the mixture underwent reflux for 12 h. Following this, distilled water was added to the mixture, leading to the isolation of the organic layer, which was washed with water and desiccated using anhydrous magnesium sulfate. The solvent was evaporated, and the resulting residue underwent chromatography on a silica gel column, eluting with hexane–ethyl acetate (50:1). Ultimately, the initial compound **1a** was retrieved.

Reaction of Compound 1a in the Presence of $[RhCl(nbd)]_2$ Catalyst: In a 30 mL two-necked flask equipped with a reflux condenser, dry toluene (1.5 mL), compound **1a**

(0.103 g, 0.327 mmol), and $[\text{RhCl}(\text{nbd})]_2$ (0.015 g, 0.0325 mmol) were combined. The mixture was refluxed for 1 h. Subsequently, distilled water was added to the mixture, leading to the isolation of the organic layer, which was washed with water and dried using anhydrous magnesium sulfate. After evaporating the solvent, chromatography on a silica gel column was performed, eluting with hexane, resulting in the yield of 0.044 g (43%) of compound **2a**: HR-MS: calcd. for $\text{C}_{17}\text{H}_{22}\text{Si}_2\text{S}$ (M^+): 314.0981, found: 314.0979. MS m/z 314 (M^+); ^1H NMR $\delta(\text{CDCl}_3)$ 0.01 (s, 9H, Me_3Si), 0.31 (s, 6H, Me_2Si), 7.04 (dd, 2H, phenyl ring protons, $J = 8.2$ Hz, 1.6 Hz), 7.22 (tt, 1H, phenyl ring proton, $J = 8.2$ Hz, 1.6 Hz), 7.30 (t, 2H, phenyl ring protons, $J = 8.2$ Hz), 7.31 (d, 1H, thienyl ring proton, $J = 4.8$ Hz), 7.64 (d, 1H, thienyl ring proton, $J = 4.8$ Hz); ^{13}C NMR $\delta(\text{CDCl}_3)$ -4.1 (Me_2Si), 0.8 (Me_3Si), 125.2, 125.8, 127.1, 127.9, 132.5, 133.6, 143.0, 150.1, 160.8, 162.4 (thienyl, phenyl ring and olefinic carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ -6.8 , 0.1.

Reaction of Compound 1a in the Presence of $\text{RhCl}(\text{PPh}_3)_3$ Catalyst: A total of 0.222 g (0.707 mmol) of compound **1a** and 0.065 g (0.0703 mmol) of $\text{RhCl}(\text{PPh}_3)_3$ were combined with dry toluene (1.5 mL) in a 30 mL two-necked flask equipped with a reflux condenser. The mixture underwent reflux heating for 12 h. Afterward, distilled water was added to the mixture, followed by separation of the organic layer, washing with water, and drying using anhydrous magnesium sulfate. The solvent was then evaporated, resulting in a residue that underwent chromatography on a silica gel column. Elution was performed using hexane–ethyl acetate (50:1) as the solvent, ultimately leading to the recovery of the initial compound **1a**.

Reaction of Compound 1b in the Presence of $[\text{RhCl}(\text{nbd})]_2$ Catalyst: In a 30 mL two-necked flask equipped with a reflux condenser, dry toluene (1.5 mL) was combined with compound **1b** (0.108 g, 0.329 mmol) and $[\text{RhCl}(\text{nbd})]_2$ (0.015 g, 0.0325 mmol). The resulting mixture was refluxed for 1 h. Post-reflux, distilled water was added to the mixture, followed by separation of the organic layer, which was then washed with water and dried using anhydrous magnesium sulfate. The solvent was evaporated, and the remaining residue was subjected to chromatography on a silica gel column, eluting with hexane, yielding 0.032 g (30% yield) of compound **2b**: HR-MS: calcd. for $\text{C}_{18}\text{H}_{24}\text{Si}_2\text{S}$ (M^+): 328.1137, found: 328.1135. MS m/z 328 (M^+); ^1H NMR $\delta(\text{CDCl}_3)$ 0.02 (s, 9H, Me_3Si), 0.30 (s, 6H, Me_2Si), 2.36 (s, 3H, CH_3), 6.93 (d, 2H, phenylene ring protons, $J = 8.0$ Hz), 7.10 (d, 2H, phenylene ring protons, $J = 8.0$ Hz), 7.30 (d, 1H, thienyl ring proton, $J = 4.8$ Hz), 7.63 (d, 1H, thienyl ring proton, $J = 4.8$ Hz); ^{13}C NMR $\delta(\text{CDCl}_3)$ -4.1 (Me_2Si), 0.9 (Me_3Si), 21.2 (CH_3), 125.2, 127.0, 128.6, 132.4, 133.5, 135.3, 139.9, 149.9, 160.9, 162.5 (thienyl, phenylene ring, and olefinic carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ -7.0 , -0.3 .

Reaction of Compound 1c in the Presence of $[\text{RhCl}(\text{nbd})]_2$ Catalyst: In a 30 mL two-necked flask with a reflux condenser, compound **1c** (0.305 g, 0.928 mmol) and $[\text{RhCl}(\text{nbd})]_2$ (0.043 g, 0.0932 mmol) dissolved in 1.5 mL were introduced into dry toluene. The resulting mixture underwent reflux for 1 h. Afterward, distilled water was added to the mixture, leading to the separation of the organic layer, which was subsequently washed with water and dried using anhydrous magnesium sulfate. Evaporation of the solvent followed, and the residue underwent chromatography on a silica gel column, being eluted with hexane, resulting in 0.050 g (16% yield) of compound **2c**: HR-MS: calcd. for $\text{C}_{18}\text{H}_{24}\text{Si}_2\text{S}$ (M^+): 328.1137, found: 328.1133. MS m/z 328 (M^+); ^1H NMR $\delta(\text{CDCl}_3)$ 0.01 (s, 9H, Me_3Si), 0.31 (s, 6H, Me_2Si), 2.39 (s, 3H, CH_3), 6.84 (d, 1H, phenylene ring protons, $J = 7.6$ Hz), 6.85 (s, 1H, phenylene ring proton), 7.02 (d, 1H, phenylene ring proton, $J = 7.6$ Hz), 7.18 (t, 1H, phenylene ring proton, $J = 7.6$ Hz), 7.31 (d, 1H, thienyl ring proton, $J = 4.8$ Hz), 7.63 (d, 1H, thienyl ring proton, $J = 4.8$ Hz); ^{13}C NMR $\delta(\text{CDCl}_3)$ -4.0 (Me_2Si), 0.9 (Me_3Si), 21.5 (CH_3), 124.2, 125.2, 126.5, 127.8, 127.9, 132.5, 133.5, 137.3, 142.9, 149.9, 160.9, 162.5 (thienyl, phenylene ring and olefinic carbons); ^{29}Si NMR $\delta(\text{CDCl}_3)$ -7.0 , -0.1 .

Synthesis of Compound 3: 3-Iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene (0.479 g, 1.41 mmol), bis(triphenylphosphine)dichloropalladium (0.049 g, 0.070 mmol), and copper(I) iodide (0.013 g, 0.070 mmol) were added to 10 mL of dry triethylamine in a 100-mL three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel. 3,3-

Dimethyl-1-butyne (0.372 g, 4.53 mmol) was then added dropwise to this mixture at room temperature. The mixture was then heated at reflux for 12 h. Distilled water was added to the mixture 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 and eluted with hexane–ethyl acetate (50:1) to obtain 0.065 g (16% yield) of compound **3**: HR-MS, calculated for $C_{15}H_{26}Si_2S$ (M^+): 294.1294, found: 294.1290. MS m/z 294 (M^+); 1H NMR $\delta(CDCl_3)$ 0.10 (s, 9H, Me_3Si), 0.46 (s, 6H, Me_2Si), 1.31 (s, 9H, $t-Bu$), 7.15 (d, 1H, thienyl ring proton, $J = 3.6$ Hz), 7.40 (d, 1H, thienyl ring proton, $J = 3.6$ Hz); ^{13}C NMR $\delta(CDCl_3)$ -3.2 (Me_2Si), -1.9 (Me_3Si), 28.0 (CMe_3), 31.0 (Me_3C), 76.3, 98.9 (sp carbons), 128.9, 129.6, 132.9, 140.3 (thienyl ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ -23.0 , -17.4 .

Reaction of Compound 3 in the Presence of $[RhCl(nbd)_2]_2$ Catalyst: Dry toluene (1.5 mL), along with compound **3** (0.065 g, 0.221 mmol) and $[RhCl(nbd)_2]_2$ (0.010 g, 0.0217 mmol), were combined in a 30 mL two-necked flask equipped with a reflux condenser. The mixture was refluxed for 12 h. Following this, the addition of distilled water to the mixture led to the isolation of the organic layer, which was washed with water and dried using anhydrous magnesium sulfate. Evaporation of the solvent was performed, and the remaining residue underwent chromatography on a silica gel column, eluting with hexane. As a result, compound **3** was obtained once again.

Synthesis of Compound 4: In a 100-mL three-necked flask equipped with a stirrer, reflux condenser, and dropping funnel, 1.019 g (2.99 mmol) of 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene, 0.105 g (0.150 mmol) of bis(triphenylphosphine) dichloropalladium, and 0.029 g (0.152 mmol) of copper(I) iodide were combined with 10 mL of dry triethylamine. Subsequently, ethynyltrimethylsilane (0.648 g, 6.60 mmol) was added dropwise at room temperature. The resulting mixture was heated at reflux for 12 h. Following this, distilled water was added to the mixture, and the organic layer was separated, washed with water, and dried using anhydrous magnesium sulfate. Evaporation of the solvent followed, and the remaining residue was subjected to chromatography on a silica gel column, eluting with hexane–ethyl acetate (50:1), yielding 0.213 g (23% yield) of compound **4**: HR-MS: calcd. for $C_{14}H_{26}Si_3S$ (M^+): 310.1063, found: 310.1066. MS m/z 310 (M^+); 1H NMR $\delta(CDCl_3)$ 0.10 (s, 9H, Me_3Si), 0.23 (s, 9H, Me_3Si), 0.46 (s, 6H, Me_2Si), 7.21 (d, 1H, thienyl ring proton, $J = 4.4$ Hz), 7.40 (d, 1H, thienyl ring proton, $J = 4.4$ Hz); ^{13}C NMR $\delta(CDCl_3)$ -3.3 (Me_2Si), -1.9 , -0.1 (Me_3Si), 95.2, 102.3 (sp carbons), 128.7, 129.1, 132.7, 143.7 (thienyl ring carbons); ^{29}Si NMR $\delta(CDCl_3)$ -22.6 , -17.8 , -17.1 .

Reaction of Compound 4 in the Presence of $[RhCl(nbd)_2]_2$ Catalyst: In a 30 mL two-necked flask equipped with a reflux condenser, compound **4** (0.101 g, 0.325 mmol) and 0.015 g (0.0325 mmol) of $[RhCl(nbd)_2]_2$ were introduced into dry toluene (1.5 mL). The resulting mixture was then subjected to reflux for 12 h. Afterward, distilled water was added to the mixture, leading to the separation of the organic layer, which was subsequently washed with water and dried using anhydrous magnesium sulfate. Evaporation of the solvent followed, and the residue underwent chromatography on a silica gel column, being eluted with hexane. Ultimately, the initial compound **4** was recovered.

Synthesis of Compound 5: In a 100-mL three-necked flask equipped with a stirrer, reflux condenser, and dropping funnel, 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene (1.007 g, 2.96 mmol), bis(triphenylphosphine)dichloropalladium (0.104 g, 0.148 mmol), and copper(I) iodide (0.029 g, 0.152 mmol) were combined with 10 mL of dry triethylamine. Gradually, 3-phenyl-1-propyne (0.722 g, 6.21 mmol) was added dropwise to this mixture at room temperature. The resulting solution was refluxed for 12 h. Post-reflux, distilled water was added to the mixture, leading to the separation of the organic layer, which was subsequently washed with water and desiccated using anhydrous magnesium sulfate. Evaporation of the solvent ensued, and the remaining residue underwent chromatography on a silica gel column, eluting with hexane–ethyl acetate (50:1). The resulting yield was 0.070 g (7%) of compound **5**: HR-MS, calculated for $C_{18}H_{24}Si_2S$ (M^+): 328.1137, found: 328.1130. MS m/z 328 (M^+); 1H NMR $\delta(CDCl_3)$ 0.07 (s, 9H, Me_3Si), 0.41 (s, 6H, Me_2Si), 3.81

(s, 2H, CH₂), 7.20 (d, 1H, thienyl ring proton, *J* = 4.4 Hz), 7.24 (t, 1H, phenyl ring proton, *J* = 8.0 Hz), 7.33 (t, 2H, phenyl ring protons, *J* = 8.0 Hz), 7.39 (d, 2H, phenyl ring protons, *J* = 8.0 Hz), 7.42 (d, 1H, thienyl ring proton, *J* = 4.4 Hz); ¹³C NMR δ(CDCl₃) −3.2 (Me₂Si), −2.0 (Me₃Si), 26.0 (CH₂), 79.8, 88.4 (sp carbons), 126.6, 128.1, 128.5, 129.0, 129.1, 132.6, 136.6, 141.8 (phenyl and thienyl ring carbons); ²⁹Si NMR δ(CDCl₃) −23.1, −17.6.

Reaction of Compound 5 in the Presence of [RhCl(nbd)₂]₂ Catalyst: In a 30 mL two-necked flask equipped with a reflux condenser, dry toluene (1.5 mL), compound 5 (0.101 g, 0.307 mmol), and [RhCl(nbd)₂]₂ (0.015 g, 0.0325 mmol) were combined and refluxed for 1 h. Afterward, distilled water was added to the mixture, leading to the isolation of the organic layer, which was washed with water and dried using anhydrous magnesium sulfate. Evaporation of the solvent followed by chromatography on a silica gel column, eluting with hexane, revealed consumption of the initial compound 5. However, upon analysis using gas–liquid chromatography (GLC) and gel permeation chromatography (GPC), numerous products were detected in the reaction mixture. No thiophene-fused silole derivatives were found in the reaction mixture.

Synthesis of Compound 6: In a 100 mL two-necked flask equipped with a reflux condenser, 1.007 g (2.96 mmol) of 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene, 0.104 g (0.148 mmol) of bis(triphenylphosphine)dichloropalladium, and 0.029 g (0.152 mmol) of copper(I) iodide were combined with 10 mL of dry triethylamine. To this mixture, 1-ethynylcyclohexene (0.628 g, 5.92 mmol) was slowly added dropwise at room temperature, followed by heating at reflux for 12 h. After the reflux, distilled water was added to the mixture, and the resulting organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. Evaporation of the solvent ensued, and the remaining residue was subjected to chromatography on a silica gel column, eluting with hexane–ethyl acetate (50:1), yielding 0.598 g (63% yield) of compound 6: HR-MS, calculated for C₁₇H₂₆Si₂S (M⁺): 318.1294, found: 328.1291. MS *m/z* 318 (M⁺); ¹H NMR δ(CDCl₃) 0.10 (s, 9H, Me₃Si), 0.45 (s, 6H, Me₂Si), 1.58–1.70 (m, 4H, CH₂), 2.11–2.22 (m, 4H, CH₂), 6.13–6.16 (m, 1H, olefinic proton), 7.18 (d, 1H, thienyl ring proton, *J* = 4.4 Hz), 7.41 (d, 1H, thienyl ring proton, *J* = 4.4 Hz); ¹³C NMR δ(CDCl₃) −3.2 (Me₂Si), −2.0 (Me₃Si), 21.5, 22.3, 25.7, 29.1 (CH₂), 84.1, 92.2 (sp carbons), 120.9, 129.1, 129.2, 132.4, 134.3, 141.4 (thienyl ring and olefinic carbons); ²⁹Si NMR δ(CDCl₃) −23.0, −17.6.

Reaction of Compound 6 in the Presence of [RhCl(nbd)₂]₂ Catalyst: In a 30 mL two-necked flask equipped with a reflux condenser, compound 6 (0.110 g, 0.345 mmol) and 0.016 g (0.0347 mmol) of [RhCl(nbd)₂]₂ were introduced into dry toluene (1.5 mL). The resulting mixture was heated under reflux for 1 h. Post-reflux, distilled water was added to the mixture, leading to the separation of the organic layer, which was subsequently washed with water and dried using anhydrous magnesium sulfate. Evaporation of the solvent followed, and the remaining residue underwent chromatography on a silica gel column, being eluted with hexane. Compound 6 was consumed in the reaction; however, multiple products were detected in the reaction mixture via gas–liquid chromatography (GLC) and gel permeation chromatography (GPC). No derivatives of thiophene-fused silole were identified in the reaction mixture.

Reaction of 3-Iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene with 1-Hexyne in the Presence of Palladium and Copper Catalysts: In a 100 mL two-necked flask equipped with a reflux condenser, 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene (1.003 g, 2.95 mmol), bis(triphenylphosphine)dichloropalladium (0.104 g, 0.148 mmol), and copper(I) iodide (0.028 g, 0.147 mmol) were combined with 10 mL of dry triethylamine. Gradual addition of 1-hexyne (0.487 g, 5.93 mmol) to this mixture at room temperature was followed by refluxing for 12 h. Analysis via GLC and GPC revealed the presence of numerous products in the reaction mixture. Subsequently, the addition of distilled water to the mixture led to the separation of the organic layer, which underwent washing with water and drying using anhydrous magnesium sulfate. Evaporation of the solvent and chromatography on a silica gel column, eluting with hexane–ethyl acetate (10:1), were performed. Surprisingly, 3-(hex-1-yn-1-yl)-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene, an expected product from the

Sonogashira coupling reaction between 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene and 1-hexyne akin to compounds **1a–1c**, was not detected in the mixture. All efforts to isolate this compound were unsuccessful.

Reaction of 3-Iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene with 1-Octyne in the Presence of Palladium and Copper Catalysts: In a 100 mL two-necked flask equipped with a reflux condenser, 1.005 g (2.95 mmol) of 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene, 0.104 g (0.148 mmol) of bis(triphenylphosphine)dichloropalladium, and 0.028 g (0.147 mmol) of copper(I) iodide were combined with 10 mL of dry triethylamine. Gradually, 1-octyne (0.651 g, 5.91 mmol) was added dropwise to this mixture at room temperature, and the resulting mixture was heated at reflux for 12 h. Multiple products were identified in the reaction mixture via GLC and GPC. Afterward, distilled water was added to the mixture, and the organic layer was separated, washed with water, and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed, and the remaining residue was subjected to chromatography on a silica gel column, eluting with hexane–ethyl acetate (10:1). Interestingly, the expected 3-(oct-1-yn-1-yl)-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene, anticipated from the Sonogashira coupling reaction of 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene and 1-octyne, similar to compounds **1a–1c**, was not detected.

Reaction of 3-Iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene with ethynylcyclohexane in the presence of palladium and copper catalysts: In a 100 mL two-necked flask equipped with a reflux condenser, 1.001 g (2.94 mmol) of 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene, 0.104 g (0.148 mmol) of bis(triphenylphosphine)dichloropalladium, and 0.029 g (0.152 mmol) of copper(I) iodide were combined with 10 mL of dry triethylamine. Following this, ethynylcyclohexane (0.641 g, 5.93 mmol) was added dropwise to this mixture at room temperature, and the resulting mixture was heated at reflux for 12 h. Multiple products were identified in the reaction mixture through GLC and GPC. Post-reaction, distilled water was added to the mixture, leading to the separation of the organic layer, which was subsequently washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent ensued, and the remaining residue underwent chromatography on a silica gel column, being eluted with hexane–ethyl acetate (10:1). Surprisingly, the anticipated 3-(cyclohexylethynyl)-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene, expected from the Sonogashira coupling reaction of 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene and ethynylcyclohexane, akin to compounds **1a–1c**, was not produced.

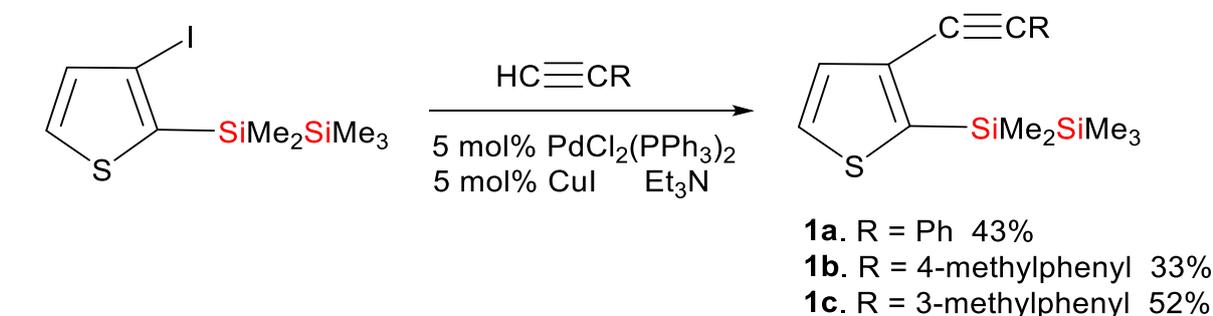
3. Results and Discussion

3.1. Synthesis and Reactions

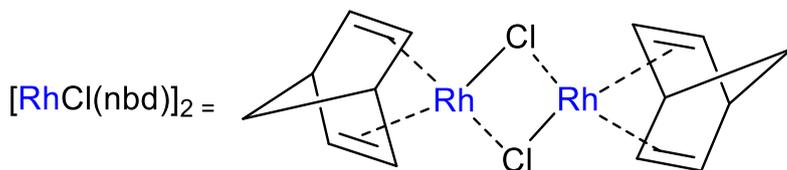
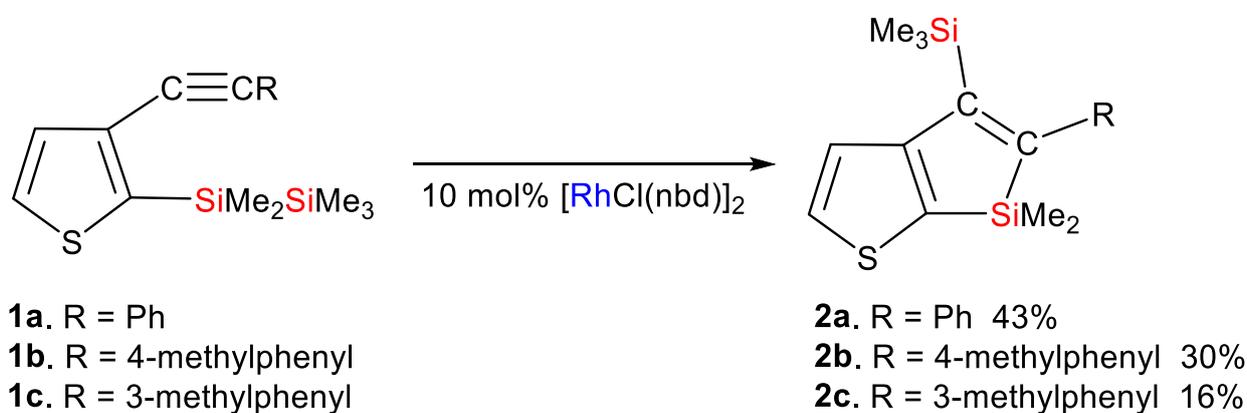
The starting compound, 2-(1,1,2,2,2-pentamethyldisilanyl)-3-(phenylethynyl)thiophene (**1a**), was prepared in 43% yield via the Sonogashira coupling of 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene with ethynylbenzene in triethylamine (Scheme 1). Similarly, the starting compounds **1b** and **1c** were synthesized in 33% and 52% yields, respectively (Scheme 1). In the current reactions, the disilane in starting compounds **1a–1c** is located on the carbon adjacent to a sulfur atom. The synthesis of compounds **1a–1c** could not be achieved from 2,3-dibromothiophene; instead, it necessitated the use of 2,3-diiodothiophene.

We first examined the reaction of **1a** in the presence of the dicarbonyl(chloro)rhodium(I) dimer $[\text{RhCl}(\text{CO})_2]_2$ [23]. The treatment of **1a** in the presence of a catalytic amount of $[\text{RhCl}(\text{CO})_2]_2$ in refluxing toluene produced no products within 12 h. Starting compound **1a** was recovered quantitatively. Next, we performed the reaction of **1a** with $[\text{RhCl}(\text{ncd})]_2$ (ncd = norborna-2,5-diene). When **1a** was heated to reflux in toluene in the presence of $[\text{RhCl}(\text{ncd})]_2$, 6,6-dimethyl-5-phenyl-4-(trimethylsilyl)-6H-silolo[2,3-*b*]thiophene (**2a**) was obtained in 43% yield (Scheme 2). Compound **2a** was obtained via the intramolecular *trans*-bis-silylation of compound **1a**. The structure of **2a** was verified using spectroscopic analysis. The mass spectrum for **2a** shows parent ions at m/z 314,

which correspond to the calculated molecular weight of $C_{17}H_{22}Si_2S$. The 1H NMR spectrum for **2a** shows signals at 0.01 and 0.31 ppm due to the methyl protons on the silicon atoms, and two doublets of doublet signals at 7.31 and 7.64 ppm due to the thienyl ring protons and phenyl ring protons. The ^{29}Si NMR spectrum for **2a** shows signals at -6.8 and 0.1 ppm.



Scheme 1. Synthesis of compounds **1a–1c**.



Scheme 2. Reactions of **1a–1c** with Rh complexes.

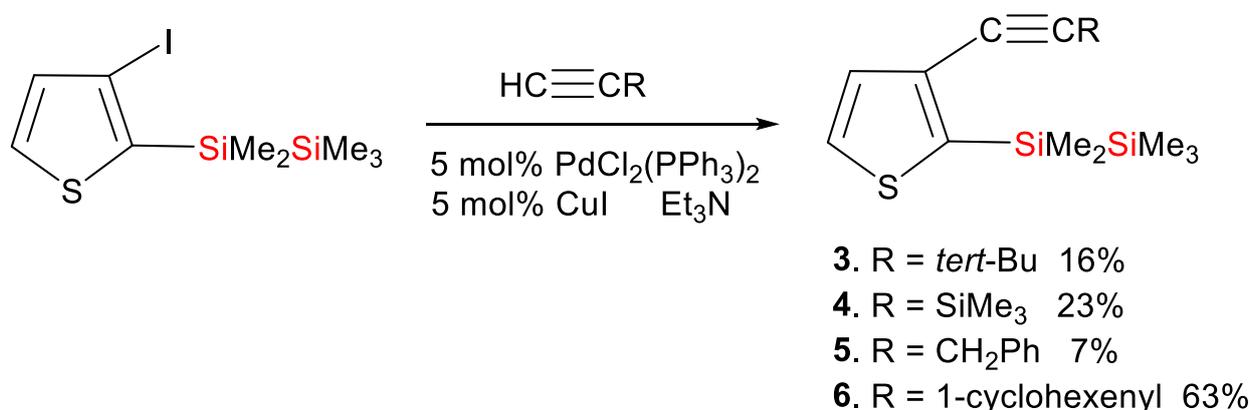
A similar reaction of **1a** in the presence of $RhCl(PPh_3)_3$ did not yield **2a**. Starting compound **1a** was recovered quantitatively.

The reaction of 2-(1,1,2,2,2-pentamethyldisilanyl)-3-(*p*-tolylethynyl)thiophene (**1b**) in the presence of a catalytic amount of $[RhCl(nbd)]_2$ afforded 6,6-dimethyl-5-(*p*-tolyl)-4-(trimethylsilyl)-6*H*-silolo[2,3-*b*]thiophene (**2b**) in 30% yield.

Compound **1c**, 2-(1,1,2,2,2-pentamethyldisilanyl)-3-(*m*-tolylethynyl)thiophene, underwent a reaction using the $[RhCl(nbd)]_2$ catalyst, resulting in the production of 6,6-dimethyl-5-(*m*-tolyl)-4-(trimethylsilyl)-6*H*-silolo[2,3-*b*]thiophene (**2c**) with an isolated yield of 16%. NMR and MS analyses revealed the existence of the bis-silylation product **2c**. Many unidentified products were detected in the reaction mixture by GLC and GPC.

Next, 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene was reacted with 3,3-dimethyl-1-butyne and ethynyltrimethylsilane in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$ -CuI. When 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene and 3,3-dimethyl-1-butyne were stirred under reflux for 12 h in triethylamine in the presence of a catalytic amount of the Pd complex, 3-(*tert*-butylethynyl)-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene (**3**) was obtained in 16% isolated yield (Scheme 3). A similar reaction between 3-iodo-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene and ethynyltrimethylsilane affords 2-(1,1,2,2,2-

pentamethyldisilanyl-3-(trimethylsilylethynyl)thiophene (**4**) in 23% yield. Many unidentified products were detected in the reaction mixture by GLC and GPC.



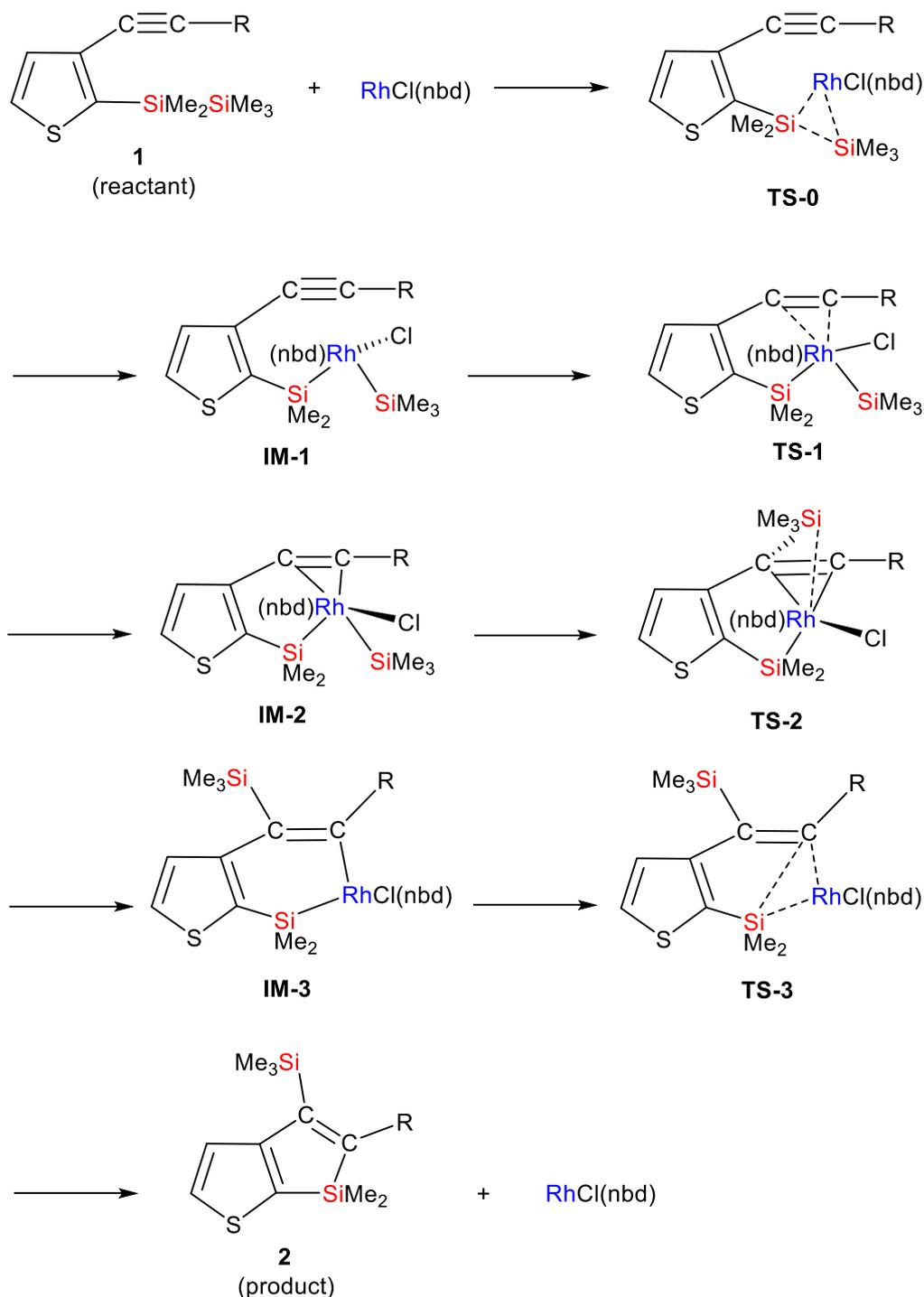
Scheme 3. Synthesis of compounds **3–6**.

The reactions of **3** and **4** in the presence of [RhCl(nbd)]₂ did not afford 6,6-dimethyl-4-(trimethylsilyl)-6*H*-silolo[2,3-*b*]thiophene derivatives. The starting compounds, **3** and **4**, were recovered. This may be caused by the presence of bulky substituents such as *tert*-butyl and trimethylsilyl that would prevent the formation of silole derivatives via intramolecular *trans*-bis-silylation.

The Sonogashira coupling of 3-iodo-2-(1,1,2,2-pentamethyldisilanyl)thiophene with 3-phenyl-1-propyne and 1-ethynylcyclohexene in triethylamine produced 1,1,1,2,2-pentamethyl-2-(3-(3-phenylprop-1-yn-1-yl)thiophen-2-yl)disilane (**5**) and 1,1,1,2,2-pentamethyl-2-(3-((1-methyl-1λ⁵-cyclohex-1-en-1-yl)ethynyl)thiophen-2-yl)disilane (**6**) in 7% and 63% yields, respectively (Scheme 3). The [RhCl(nbd)]₂ catalyzed reactions of **5** and **6** did not afford *trans*-bis-silylation adducts. The starting compound was consumed; however, many unidentified products were detected in the reaction mixture by GLC and GPC.

Following the reaction of 3-iodo-2-(1,1,2,2-pentamethyldisilanyl)thiophene with 1-hexyne using the PdCl₂(PPh₃)₂-CuI catalyst, numerous products were observed in the reaction mixture via GLC and GPC. Efforts to isolate 3-(hex-1-yn-1-yl)-2-(1,1,2,2-pentamethyldisilanyl)thiophene, similar to compounds **1a–1c**, were unsuccessful. Similarly, the reactions of 3-iodo-2-(1,1,2,2-pentamethyldisilanyl)thiophene with 1-octyne and ethynylcyclohexane did not yield 2-ethynyl-3-(1,1,2,2-pentamethyldisilanyl)thiophene derivatives. Analysis by GLC and GPC again revealed the presence of multiple products in the reaction mixture.

Scheme 4 illustrates a possible mechanistic interpretation of the reaction. The formation of **2** can be best explained by its reaction with rhodacyclopentene. The reaction of compound **1** with RhCl(nbd) activates the Si-Si bond to produce intermediate-1 (**IM-1**) via transition state-0 (**TS-0**) (rhodacyclopentene). A structural change from **IM-1** to **IM-2** is due to a migration of the spectator Cl anion, and **TS-1** exists between the two local minima (LMs). During this change, the Rh-C (in C≡C) bond distances were decreased from 4.75 Å and 4.28 Å to 2.40 Å and 2.54 Å. (See Figures S44 and S46 in Supplementary Materials). The trimethylsilyl group on the rhodium atom then migrates to the carbon atom bonded to the thiophene ring through **TS-2**, and **IM-3** is formed. Finally, the dimethylsilyl group bonds to the carbon atom adjacent to R (via **TS-3**), and elimination of the rhodium species affords **2**.



Scheme 4. Proposed mechanism for production of 2.

3.2. Theoretical Study

DFT calculations were conducted to clarify the transformation mechanism from reactant 1 to product 2, as illustrated in Scheme 4. The computational analysis utilized the Gaussian09 software package [33] employing Becke's three-parameter Lee–Yang–Parr hybrid functional [34]. Los Alamos effective core potentials [35] in combination with Dunning–Huzinaga full double-basis sets [36] were applied for the Rhodium atom augmented by single 4f function, while the H, C, N, O, Si, and Cl atoms were treated with the 6-31+G(d,p) basis sets.

First, the transition states were identified and characterized. Subsequently, the intrinsic reaction coordinate (IRC) [37] was examined for both the reactant and product directions corresponding to each TS. At the end of the IRC, normal optimization procedures were applied until two LMs were achieved.

RhCl(nbd) was considered the active catalyst species formed by the decomposition of $[\text{RhCl}(\text{nbd})]_2$. The sum of the energies of **1** and RhCl(nbd) was adopted as the reference energy. The reaction proceeds in the following order: $[\mathbf{1} + \text{RhCl}(\text{nbd})] \rightarrow \text{TS-0} \rightarrow \text{IM-1} \rightarrow \text{TS-1} \rightarrow \text{IM-2} \rightarrow \text{TS-2} \rightarrow \text{IM-3} \rightarrow \text{TS-3} \rightarrow [\mathbf{2} + \text{RhCl}(\text{nbd})]$. All optimized structures are shown in the Supplementary Materials (Figures S41–S50). For all TSs and IMs, the Gibbs free energies were evaluated at 383.15 K. Figure 1 shows the SCF energy and the free energy changes along the reaction coordinate referring to the reference energy. Both energies change in parallel, and the free energy lies on the higher potential energy surface. The rate-determining step was TS-2, and the activation energies measured from the lowest LM were 159 kJ mol^{-1} and 176 kJ mol^{-1} for the SCF and free energies, respectively. Thus, the conversion of **1** into **2** was demonstrated using DFT calculations.

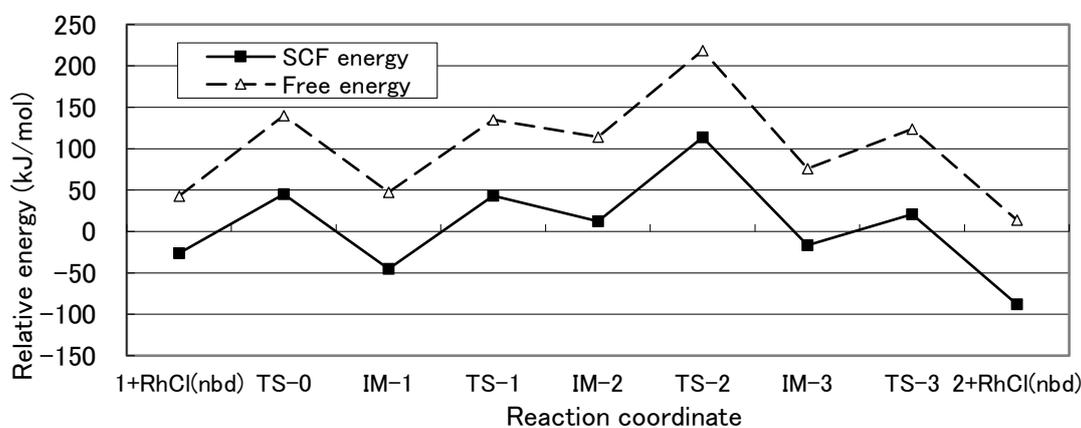


Figure 1. Energy changes along reaction coordinate.

4. Conclusions

Herein, we describe the rhodium-catalyzed reaction of 3-(ethynyl)-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene derivatives. The reaction of 3-(ethynyl)-2-(1,1,2,2,2-pentamethyldisilanyl)thiophene derivatives (**1**) in the presence of a catalytic amount of rhodium complexes afforded thiophene-fused silole 6,6-dimethyl-4-(trimethylsilyl)-6*H*-silolo[2,3-*b*]thiophene derivatives (**2**). DFT calculations were conducted to provide an explanation for the generation of compound **2** through the intramolecular *trans*-bis-silylation process involving compound **1**. Similar reactions with 3-(alkylethynyl)-2-(1,1,2,2,2-pentamethyldisilanyl)thiophenes were unsuccessful. This paper reports a new method for the synthesis of thiophene-fused siloles. Furthermore, the $[\text{RhCl}(\text{nbd})]_2$ used in the catalyzed reactions differs from the rhodium complex used in the synthesis of pyridine-condensed siloles reported previously [23], providing new insights into the reaction mechanism in computational chemistry.

Supplementary Materials: The following supporting information can be downloaded from <https://www.mdpi.com/article/10.3390/appliedchem4010003/s1>: NMR spectra (Figure S1–Figure S40), optimized structures for all local minima (LMs), transition states (TSs) (Figure S41–Figure S50).

Author Contributions: Conceptualization, A.N.; methodology, A.N.; software, A.N and H.K. (Hisayoshi Kobayashi); validation, A.N. and H.K. (Hisayoshi Kobayashi); formal analysis, A.N.; investigation, A.N., M.I., H.K. (Haruna Kawabe) and H.K. (Hisayoshi Kobayashi); writing—original draft preparation, A.N. and H.K. (Hisayoshi Kobayashi); writing—review and editing, A.N. and H.K.

(Hisayoshi Kobayashi); supervision, A.N.; project administration, A.N.; funding acquisition, A.N. All authors have read and agreed to the published version of the manuscript.

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