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Reaction of Dilithio Reagents with $PhSiH_3$: Formation of Siloles and 3-Silacyclopentenes

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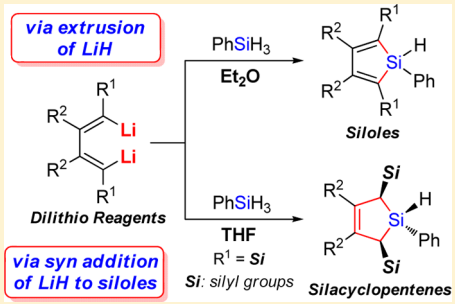
Supporting Information

ABSTRACT: The reaction chemistry between 1,4-dilithio-1,3-butadienes (dilithio reagents for short) and $PhSiH_3$ has been investigated. Direct substitution of two hydride ions from $PhSiH_3$ with the dilithio reagents led to multisubstituted siloles (silacyclopentadienes) in diethyl ether solution, with the concomitant generation of LiH. When THF was used as the solvent, the reaction between $PhSiH_3$ and 1,4-bis(silyl) dilithio reagents afforded *cis*-3-silacyclopentenes stereoselectively. Experimental results demonstrated that reactive LiH was generated in situ in the reaction system. Formal *syn* addition of LiH to silacyclopentadiene intermediates would afford silacyclopentenes, most likely via pentavalent organosilicates.

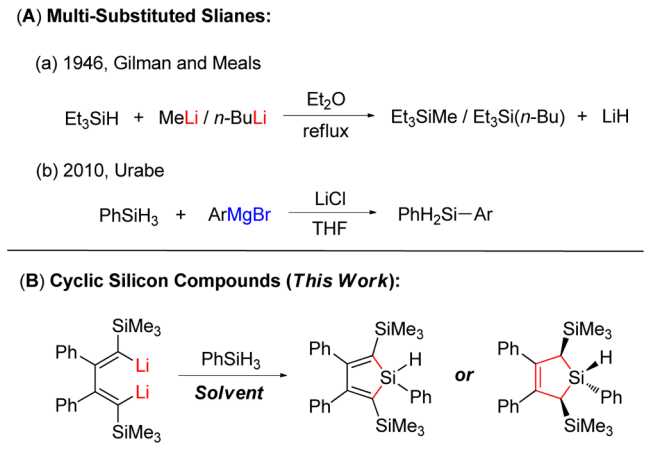


INTRODUCTION

Silanes are useful for the synthesis of organosilicon compounds.[1] Because of the nature of $Si^{\delta+}-H^{\delta-}$ bonds, silanes behave in many cases like alkyl halides.[2] Therefore, the typical nucleophilic substitution reaction can readily occur to silanes (Scheme 1). Gilman[3a] and Meals[3b] reported that triethylsilane reacted with methyl- or *n*-butyllithium reagents to give their corresponding tetrasubstituted silanes and LiH. Further investigation has demonstrated that this is a general reaction between silanes and organolithium compounds or other organometallic reagents.[4,5] However, the method is not practical in synthetic chemistry due to the inefficient substitution of the hydride ion and the difficulty in selective synthesis of silanes with certain number of substituents. A noteworthy progress was made in 2010 by Urabe and co-workers, who demonstrated that the practical and efficient substitution of one hydride ion in silanes could be achieved by Grignard reagents in the presence of either stoichiometric or catalytic amounts of LiCl.[5c] As a consequence, substitution of silanes indeed made available the synthesis of a wide variety of multisubstituted silanes. Nonetheless, the synthetic utility of silanes still remains rather limited, albeit that hydrosilylation represents a reliable method for the synthesis of organosilicon compounds.[6]

Our group has focused on developing 1,4-dilithio-1,3-butadienes as organo-di-lithio reagents for organic and organometallic synthesis.[7] The cooperative effect of these organo-di-metallic reagents has enabled us to synthesize diversified compounds that are not readily accessible by other means.[7] In continuation of our interest in synthetic applications of dilithio reagents and in an endeavor to advance the synthetic utility of silanes, we envisioned that the shortcoming of inefficient substitution of the hydride ion of silanes might be overcome by a double nucleophilic substitution strategy. Herein, we report the facile synthesis of two kinds of silacyclic compounds via a one-pot intermolecular/intramolecular double nucleophilic substitution procedure between dilithio reagents and $PhSiH_3$ (Scheme 1B). Siloles and silacyclopentenes, which have wide applications in materials science,[8−10] were constructed in due conditions, respectively.

Scheme 1. Organosilicon Products via Nucleophilic Substitution Reaction of Silanes



RESULTS AND DISCUSSION

1,4-Dilithio-1,3-butadienes **1** could be readily synthesized by the reported procedures.[11] Initially we performed the reaction of **1a** ($R^1 = R^2 = Et$; Scheme 2) with the commercially available

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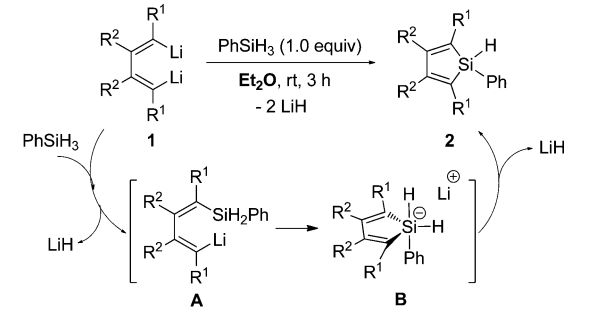
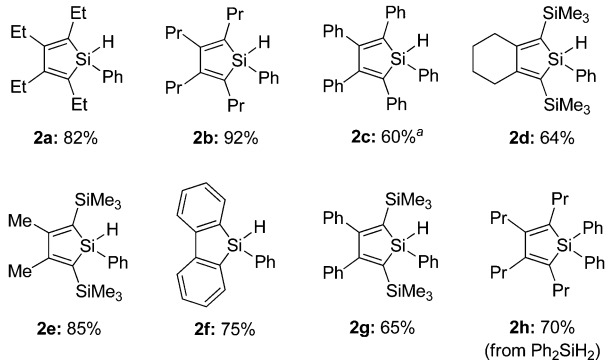
Scheme 2. Formation of Siloles by the Reaction of Dilithio Reagents with $PhSiH_3$ or Ph_2SiH_2



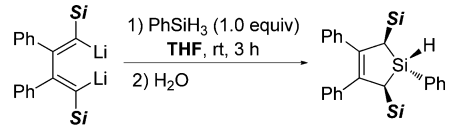


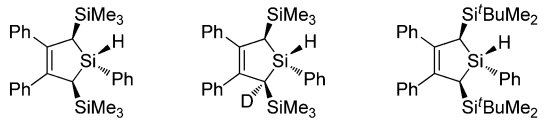
$PhSiH_3$ in hexane at room temperature. However, we failed to obtain noticeable products even with extended reaction time, probably due to the low reactivity of **1a** in the nonpolar solvent. Polar solvent Et_2O was then determined to be a suitable medium to balance the reactivity and stability of **1a**. When **1a** was treated with 1 equiv of $PhSiH_3$ in Et_2O at room temperature for 3 h, a turbid solution was formed, and the silole product **2a** was isolated in 82% yield upon hydrolysis (Scheme 2). It should be noted that compound **2a** was formed in situ without hydrolysis as indicated by NMR spectroscopy. In addition, when an excess (2 equiv or more) of $PhSiH_3$ was used, the product **2a** was still formed exclusively. These experimental results are informative to understand the reaction mechanism. A one-pot intermolecular/intramolecular nucleophilic substitution process would take place leading to the final product (Scheme 2).[12] In this process a pentavalent organosilicate **B** might be involved, which was usually observed only in solution by low-temperature NMR spectroscopy.[13] The intermediate **B** may adopt a trigonal bipyramidal geometry with the silole ring in the equatorial plane, placing the phenyl group and one hydride in the axial position in terms of their repulsion.[13] Computational studies revealed that the axial hydride in pentavalent organosilicates has better leaving ability.[13b] Thus, at room temperature, the heterolytic cleavage of the axial Si−H bond in corresponding intermediate **B** would generate **2a** in this reaction, with the concomitant loss of LiH. The precipitation of LiH in Et_2O may provide some driving force in this transformation.

With this method in hand, as shown in Scheme 2, various multisubstituted siloles **2b−g** could be synthesized in good to excellent yields from their corresponding dilithio compounds and $PhSiH_3$. Silane Ph_2SiH_2 was also tried, giving **2h** in 70% isolated yield. However, all attempts to apply trisubstituted silanes such as $PhMe_2SiH$, Et_3SiH and $(EtO)_3SiH$ in this reaction failed. The reactivity of silanes decreases with the increase of substituents. Thus, the intermolecular substitution process could not proceed smoothly due to the inefficient substitution of the hydride ion of trisubstituted silanes.[14]

Since both the solubility of the generated LiH and the reactivity of Si−H bonds will become enormously greater in more polar solvents,[15] we then turned to investigate the reaction of dilithio reagents with $PhSiH_3$ in THF. Although all other dilithio reagents afforded a mixture of products, the 1,4-bis(silyl)-2,3-diphenyl dilithio reagents **1g** (***Si*** = $SiMe_3$) and **1g′** (***Si*** = Si^tBuMe_2) reacted with $PhSiH_3$ relatively cleanly, affording 3-silacyclopentenes **3a** and **3b** with perfect selectivity in moderate yields, respectively (Scheme 3).[9]

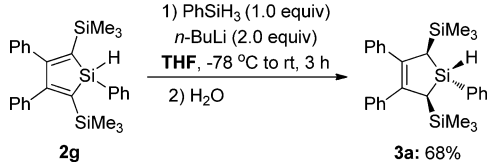
Scheme 3. Formation of 3-Silacyclopentenes by the Reaction of Dilithio Reagents (1g and 1g′) with $PhSiH_3$





The structure of **3a** was confirmed by single-crystal X-ray analysis (see Figure S24). The crystal structure of **3a** shows that the two silyl groups lie on the same face of the five-membered ring, and the phenyl group attached to silicon is oriented to the opposite side. This unexpected stereoselective formation of *cis*-3-silacyclopentenes **3** prompted us to investigate the mechanism. First, a mixed solvent of THF/Et_2O (1:1 in volume) was used. Formation of both **2g** and **3a** was observed from the reaction between **1g** and $PhSiH_3$. Second, the reaction of **1g** with $PhSiH_3$ in THF was quenched with D_2O, which afforded **3a-D** in 63% isolated yield with more than 95% deuterium incorporation at C2-position of the five-membered ring (Scheme 3). These experimental results indicated that the in situ generated LiH in THF solution underwent formal *syn* addition to siloles **2**, which resulted in the formation of *cis*-3-silacyclopentenes **3**. Actually, the reaction of siloles with MH (M = Li, Na, K) has been reported in the literature,[16] which proceeded via pentavalent organosilicates to generate silacyclopentenes. Thus, to make sure the product **3a** can be formed via addition of LiH to the silole **2g**, the experiment shown in Scheme 4 was carried out. In this experiment, LiH was generated in situ from 1 equiv of $PhSiH_3$ and 2 equiv of lithium reagent.[3,17] The compound **3a** could be successfully obtained in 68% yield after hydrolysis.

Scheme 4. Reaction of 2g with LiH Generated in Situ



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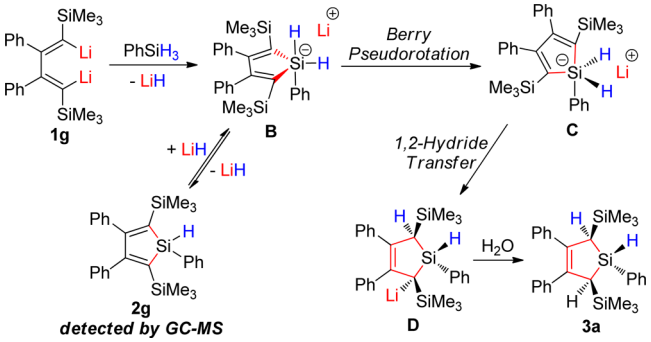
All the above-mentioned experimental results supported the mechanism given in Scheme 5. At first, the aforementioned

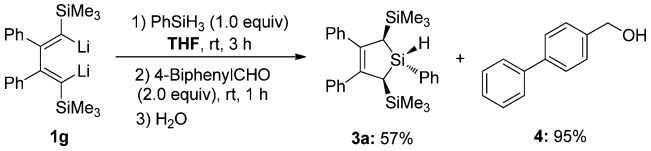
Scheme 5. Mechanism for the Formation of 3a in THF



intermediate **B** was proposed to be formed from **1g**. The observation of **2g** may come from an equilibrium in THF via the loss of LiH from intermediate **B**.[13a] The trigonal bipyramidal geometry of **B** made the C−Si−C angle of the silole ring close to 120°, but the angle in all known siloles is near 90°.[18a] Thus, Berry pseudorotation[18b] will be favored to release the ring strain forming intermediate **C**, in which the silole ring occupies axial and equatorial positions with the C−Si−C angle much closer to 90°. Then, a subsequent and favored 1,2-hydride transfer from silicon to an adjacent ring carbon in intermediate **C** leads to the exclusive isomer **D**.[16c] Hydrolysis of **D** will give *cis*-3-silacyclopentene **3a**. The *trans* arrangement between the $SiMe_3$ groups and the phenyl group attached to silicon in **3a** verifies the pseudorotation process in some degree. In comparison with the transformation in Et_2O, the increased solubility of intermediate **B** in THF may prompt the further pseudorotation process toward the formation of **3a**.

Since 1 equiv of LiH has been proposed to remain in situ in Scheme 5, we then tried to trap it to better understand the reaction mechanism. The experimental procedure is given in Scheme 6. The reduction product **4** was isolated in 95% yield

Scheme 6. Trapping of the Remaining LiH by Isolation of 4



resulting from one remaining equiv of LiH. Because of the steric congestion, the precursor of **3a** (**D**; in Scheme 5) was inefficient to be trapped by 4-biphenylcarboxaldehyde, and **3a** was still obtained in 57% yield.

In summary, we have demonstrated that the reaction of 1,4-dilithio-1,3-butadienes with $PhSiH_3$ is solvent dependent. In diethyl ether solution, the axial Si−H bonds in pentavalent organosilicates would be prone to be heterolytically cleaved. In more polar solvent such as THF, the Berry pseudorotation process may be more favored to promote a subsequent 1,2-hydride transfer. Siloles and 3-silacyclopentenes, which are important compounds in many aspects, are thus prepared.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under a slightly positive pressure of dry and oxygen-free argon by using standard Schlenk line techniques. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by a solvent purification system and dried over fresh Na chips in the glovebox. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) at room temperature. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^1H NMR spectrum as 0.00 ppm. High-resolution mass spectra (HRMS) were recorded on an FT-MS mass spectrometer using ESI (electrospray ionization) or an FT-ICR mass spectrometer using EI (Electron Ionization).

General Procedure for the Synthesis of 2a−g. To a solution of 1,4-dilithio-1,3-butadienes **1a−1g** (0.5 mmol) in Et_2O (5 mL) in a 25 mL Schlenk tube, $PhSiH_3$ (55 mg, 0.50 mmol) dried with molecular sieves was added at room temperature. The reaction mixture became turbid slowly and was stirred at room temperature for 3 h. Then, the reaction mixture was quenched with H_2O at 0 °C. The aqueous layer of the solution was extracted with Et_2O for three times and the combined organic layer was washed with brine. Solvent was evaporated and the residue was purified by column chromatography using hexane as eluent to give products **2a−g**.

2a. Colorless oil, isolated yield 82% (0.41 mmol, 104 mg). ^1H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ 0.96 (t, J = 7.6 Hz, 6H, CH_3), 1.04 (t, J = 7.6 Hz, 6H, CH_3), 2.14−2.23 (m, 2H, CH_2), 2.30−2.42 (m, 6H, CH_2), 4.86 (s, 1H, SiH), 7.29−7.37 (m, 3H, CH), 7.49−7.51 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ 14.6, 16.1, 21.1, 22.1, 128.0, 129.4, 133.4, 135.2, 135.8, 156.7. HRMS (EI, m/z) calcd for $C_{18}H_{26}Si$ $[M]^+$: 270.1804, found 270.1807.

2b. Pale yellow oil, isolated yield 92% (0.46 mmol, 150 mg). ^1H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ 0.82 (t, J = 7.2 Hz, 6H, CH_3), 0.97 (t, J = 7.2 Hz, 6H, CH_3), 1.30−1.47 (m, 8H, CH_2), 2.09−2.16 (m, 2H, CH_2), 2.25−2.33 (m, 6H, CH_2), 4.83 (s, 1H, SiH), 7.27−7.36 (m, 3H, CH), 7.47−7.49 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ 14.4 (4C), 23.3, 24.8, 30.5, 31.7, 128.0, 129.4, 133.6, 134.7, 135.2, 155.7. HRMS (ESI, m/z) calcd for $C_{22}H_{35}Si$ $[M + H]^+$: 327.2502, found 327.2501.

2c. Yellow solid, recrystallized from hexane/ethyl acetate (1/1) mixed solvent in 60% yield (0.30 mmol, 138 mg). ^1H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ 5.49 (s, 1H, SiH), 6.85−6.88 (m, 4H, CH), 6.90−6.92 (m, 4H, CH), 6.97−7.04 (m, 12H, CH), 7.32−7.40 (m, 3H, CH), 7.68 (d, J = 6.8 Hz, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ 125.9, 126.5, 127.6, 127.9, 128.4, 129.3, 129.8, 130.3, 130.6, 135.6, 137.4, 138.7, 156.9.[19a]

2d. Pale yellow oil, isolated yield 64% (0.32 mmol, 114 mg). ^1H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ −0.19 (s, 18H, $SiMe_3$), 1.49−1.52 (m, 4H, CH_2), 2.49−2.52 (m, 4H, CH_2), 4.70 (s, 1H, SiH), 7.05−7.13 (m, 3H, CH), 7.23−7.26 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ 0.4, 23.6, 33.1, 127.8, 129.3, 133.3, 135.2, 136.6, 169.0. HRMS (EI, m/z) calcd for $C_{20}H_{32}Si_3$ $[M]^+$: 356.1812, found 356.1806.

2e. Light yellow oil, isolated yield 85% (0.43 mmol, 140 mg). ^1H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ 0.05 (s, 18H, $SiMe_3$), 2.23 (s, 6H, CH_3), 4.92 (s, 1H, SiH), 7.28−7.38 (m, 3H, CH), 7.48 (dd, J = 7.6 Hz, 1.6 Hz, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ 0.5, 21.0, 127.8, 129.3, 133.2, 135.2, 137.5, 168.2. HRMS (EI, m/z) calcd for $C_{18}H_{30}Si_3$ $[M]^+$: 330.1655, found 330.1660.

2f. White solid, isolated yield 75% (0.38 mmol, 97 mg). ^1H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ 5.37 (s, 1H, SiH), 7.26 (t, J

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= 7.2 Hz, 2H, CH), 7.30−7.34 (m, 2H, CH), 7.37−7.41 (m, 1H, CH), 7.45 (td, J = 7.6 Hz, 1.2 Hz, 2H, CH), 7.59 (dd, J = 8.0 Hz, 1.2 Hz, 2H, CH), 7.68 (d, J = 7.2 Hz, 2H, CH), 7.85 (d, J = 7.6 Hz, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ 121.1, 127.7, 128.2, 130.3, 130.8, 131.6, 134.1, 134.2, 135.3, 149.0.[19b]

2g. Pale yellow solid, isolated yield 65% (0.33 mmol, 147 mg); mp: 125.4−126.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ −0.29 (s, 18H, $SiMe_3$), 5.20 (s, 1H, SiH), 6.92 (dd, J = 7.2 Hz, 1.6 Hz, 4H, CH), 7.03−7.09 (m, 6H, CH), 7.34−7.42 (m, 3H, CH), 7.62 (dd, J = 7.6 Hz, 1.6 Hz, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ 0.6, 126.4, 127.1, 128.1, 128.6, 129.8, 132.3, 135.3, 142.3, 142.4, 171.6. HRMS (ESI, m/z) calcd for $C_{28}H_{35}Si_3$ $[M + H]^+$: 455.2041, found 455.2040.

Synthesis of Compound 2h. To a solution of 1,2,3,4-tetrapropyl-1,4-dilithio-1,3-butadiene **1h** (0.5 mmol) in Et_2O (5 mL) in a 25 mL Schlenk tube, Ph_2SiH_2 (93 mg, 0.50 mmol) dried with molecular sieves was added at room temperature. The reaction mixture became turbid slowly and was stirred at room temperature for 3 h. Then, the reaction mixture was quenched with H_2O at 0 °C. The aqueous layer of the solution was extracted with Et_2O for three times, and the combined organic layer was washed with brine. Solvent was evaporated, and the residue was purified by column chromatography using hexane as eluent to give compound **2h**.

2h. Colorless oil, isolated yield 70% (0.35 mmol, 141 mg). ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ 0.68 (t, J = 7.2 Hz, 6H, CH_3), 0.98 (t, J = 7.2 Hz, 6H, CH_3), 1.13−1.22 (m, 4H, CH_2), 1.41−1.50 (m, 4H, CH_2), 2.29 (q, J = 8.0 Hz, 8H, CH_2), 7.30−7.38 (m, 6H, CH), 7.59 (d, J = 7.6 Hz, 4H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ 14.4, 14.5, 23.4, 24.0, 30.4, 32.2, 127.8, 129.3, 134.2, 135.5, 135.7, 155.6. HRMS (ESI, m/z) calcd for $C_{28}H_{39}Si$ $[M + H]^+$: 403.2816, found 403.2816.

General Procedure for the Synthesis of 3a and 3b. To a solution of 1,4-bis(silyl) 2,3-diphenyl dilithio reagent **1g** or **1g′** (0.5 mmol) in THF (5 mL) in a 25 mL Schlenk tube, $PhSiH_3$ (55 mg, 0.50 mmol) dried with molecular sieves was added at room temperature. The reaction mixture was dark red and was stirred at room temperature for 3 h. Then, the reaction mixture was quenched with H_2O at 0 °C. The aqueous layer of the solution was extracted with Et_2O for three times and the combined organic layer was washed with brine. Solvent was evaporated and the residue was purified by column chromatography using hexane as eluent to give products **3a** and **3b**.

3a. White solid, isolated yield 62% (0.31 mmol, 141 mg); mp: 147.6−148.5 °C. ^{1}H NMR (400 MHz, C_6D_6, $SiMe_4$): δ −0.02 (s, 18H, $SiMe_3$), 1.98 (d, J = 4.0 Hz, 2H, CH), 5.01 (t, J = 4.0 Hz, 1H, SiH), 6.84 (t, J = 7.2 Hz, 2H, CH), 6.96 (t, J = 7.6 Hz, 4H, CH), 7.07−7.09 (m, 4H, CH), 7.24−7.34 (m, 3H, CH), 7.82 (dd, J = 8.0 Hz, 1.6 Hz, 2H, CH); ^{13}C NMR (100 MHz, C_6D_6, $SiMe_4$): δ −0.5, 28.4, 126.2, 127.7, 128.6, 129.5, 130.1, 134.9, 137.2, 140.8, 143.0. HRMS (ESI, m/z) calcd for $C_{28}H_{37}Si_3$ $[M + H]^+$: 457.2198, found 457.2193. Recrystallization of **3a** from hexane at room temperature gave single crystals suitable for X-ray analysis.

3a-D. The title compound was obtained by quenching the reaction mixture with D_2O (0.3 mmol scale). White solid, isolated yield 63% (0.19 mmol, 86 mg). ^{1}H NMR (400 MHz, C_6D_6, $SiMe_4$): δ −0.02 (s, 18H, $SiMe_3$), 1.98 (d, J = 4.0 Hz, 1.03 H, CH), 5.02 (d, J = 4.0 Hz, 1H, SiH), 6.85 (t, J = 7.2 Hz, 2H, CH), 6.96 (t, J = 7.6 Hz, 4H, CH), 7.08 (d, J = 8.0 Hz, 4H, CH), 7.25−7.34 (m, 3H, CH), 7.82 (dd, J = 8.0 Hz, 1.6 Hz, 2H, CH); ^{13}C NMR (100 MHz, C_6D_6, $SiMe_4$): δ −0.53, −0.51, 28.5 (somewhat compressed), 126.3, 128.7, 129.5, 130.2, 134.9, 137.2, 140.8, 140.9, 143.1.

3b. Pale yellow solid, isolated yield 52% (0.26 mmol, 140 mg); mp: 133.2−135.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ −0.35 (s, 6H, CH_3), 0.16 (s, 6H, CH_3), 0.72 (s, 18H, CMe_3), 1.96 (d, J = 1.2 Hz, 2H, CH), 5.15 (t, J = 1.2 Hz, 1H, SiH), 6.95−6.99 (m, 2H, CH), 7.04−7.12 (m, 8H, CH), 7.45 (t, J = 3.2 Hz, 3H, CH), 7.76−7.78 (m, 2H, CH); ^{13}C NMR (100 MHz, $CDCl_3$, $SiMe_4$): δ −4.0, −3.7, 17.9, 25.8, 27.1, 125.8, 127.1, 128.3, 129.5, 129.7, 134.0, 138.8, 140.8, 143.1. HRMS (EI, m/z) calcd for $C_{34}H_{48}Si_3$ $[M]^+$: 540.3064, found 540.3059.

Isolation of 4. To a solution of **1g** (1.0 mmol) in THF (6 mL) in a 25 mL Schlenk tube, $PhSiH_3$ (109 mg, 1.0 mmol) dried with molecular sieves was added at room temperature. The reaction mixture was dark red and was stirred at room temperature for 3 h. Then, 4-biphenylcarboxaldehyde (364 mg, 2.0 mmol) was added at 0 °C. After 1 h, the reaction mixture was quenched with H_2O. The aqueous layer of the solution was extracted with Et_2O for three times, and the combined organic layer was washed with brine. Solvent was evaporated, and the residue was purified by column chromatography using hexane as eluent to isolate **3a** and using hexane/ethyl acetate (5:1) as eluent to give product **4.**

4.[19c] White solid, isolated yield 95% (0.95 mmol, 173 mg). ^{1}H NMR (400 MHz, $CDCl_3$, $SiMe_4$): δ 2.10 (s, 1H, OH), 4.68 (s, 2H, CH_2), 7.33 (t, J = 7.2 Hz, 1H, CH), 7.39−7.44 (m, 4H, CH), 7.56 (d, J = 7.6 Hz, 4H, CH).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01595.

Crystallographic data for **3a**, NMR spectra for all synthesized compounds (PDF)
(CIF)

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Notes

The authors declare no competing financial interest.

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