Palladium-Catalyzed Intramolecular Hydrosilylation of Alkenylsilanes: Selective Formation of Six-Membered Silicon Heterocycles

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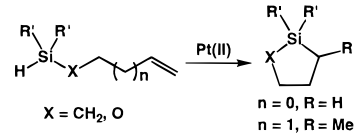
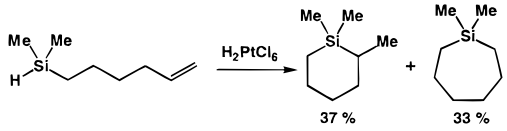
The cationic palladium complex (phen)Pd(Me)(OEt_2)$^+BAr_4^-$ [phen = 1,10-phenanthroline; Ar = 3,5-$C_6H_3(CF_3)_2$] catalyzed the intramolecular hydrosilylation of 4-pentenylsilanes and 5-hexenylsilanes to form silacyclohexanes in 43−87% isolated yield and with excellent regioselectivity (typically ≥ 98:1).

Introduction

Transition metal-catalyzed intramolecular hydrosilylation of alkenylsilanes[1−5] and alkenylsilyl ethers[6−9] has proven an effective means for the regioselective formation of five-membered silicon heterocycles.[10] For example, Pt(II) complexes catalyze the cyclization of 4-pentenylsilanes,[1,2] 5-hexenylsilanes,[1] 2-propenylsilyl ethers,[6−8] and 3-butenylsilyl ethers[6] to form five-membered heterocycles with excellent regioselectivity (eq 1). Oxidation of the C−Si bonds of these silacyclopentanes or 1-sila-2-oxacyclopentanes provides a selective route to the synthesis of 1,4-diols or 1,3-diols, respectively.[11] In contrast, 4-pentenylsilanes or 3-butenylsilyl ethers are converted selectively to six-membered silicon heterocycles only when the internal olefinic carbon atom bears substitution.[12] Furthermore, selective conversion of 5-hexenylsilanes or 4-pentenylsilyl ethers to six-membered silacycles has not been demonstrated.[13] For example, reaction of dimethyl-5-hexenylsilane with chloroplatinic acid forms a ∼1:1 mixture of six- and seven-membered silacycles in 70% yield (eq 2).[1]



eq 1



eq 2

Cationic Pd(II) complexes employed in conjunction with weakly coordinating counterions possess high activity with respect to olefin β-migratory insertion[14] and have been employed as catalysts for the polymerization of α-olefins[15] and for the copolymerization of ethylene and CO.[16] These complexes also cleave Si−H bonds via low-energy σ-bond metathesis pathways and have been employed as olefin hydrosilylation catalysts.[17] We have exploited the insertion/metathesis reactivity of cationic Pd(II) complexes to effect the tandem cyclization/hydrosilylation of 1,6-dienes.[18] For example, reaction of triethylsilane and dimethyl diallylmalonate

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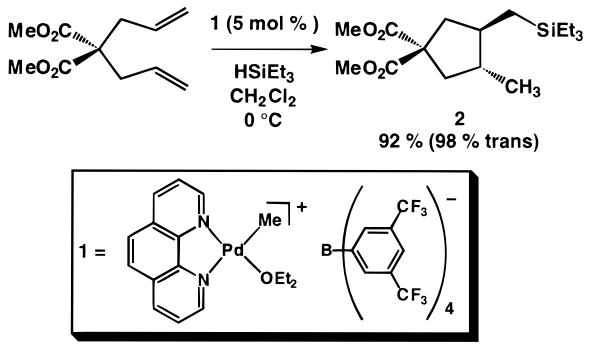
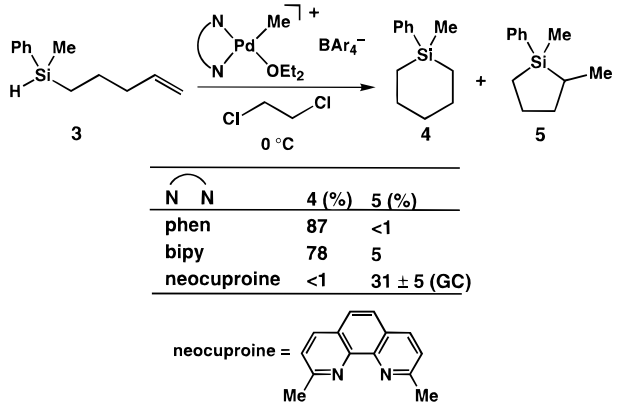
Scheme 1



Scheme 2



N N	4 (%)	5 (%)
phen	87	<1
bipy	78	5
neocuproine	<1	31 ± 5 (GC)

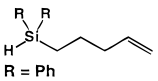
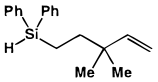
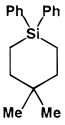
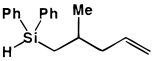
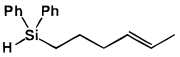
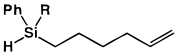
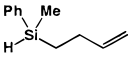
in the presence of (phen)PdMe(OEt_2)$^+BAr_4^-$ [Ar = 3,5-$C_6H_3(CF_3)_2$] (**1**) (5 mol %) at 0 °C for 5 min led to the isolation of the *trans*-silylated cyclopentane **2** in 92% yield as a 54:1 ratio of isomers (Scheme 1).[18] Due to the high activity and good regioselectivity displayed by **1** in the cyclization/hydrosilylation of dienes, we considered that **1** might also serve as an effective, regioselective catalyst for intramolecular hydrosilylation of alkenylsilanes. Here we report that **1** catalyzes the intramolecular hydrosilylation of 4-pentenylsilanes and 5-hexenylsilanes to selectively form silacyclohexanes.

Results and Discussion

When methyl-4-pentenylphenylsilane (**3**) was added to a dichloroethane solution of **1** (0.03 M, 3 mol %) at 0 °C, the pale yellow solution turned dark within 1 min with complete consumption of the starting material as determined by GC analysis. Evaporation of solvent and flash chromatography of the residue gave 1-methyl-1-phenylsilacyclohexane (**4**) in 87% yield (Scheme 2). Significantly, GC, ^{1}H NMR, and ^{13}C NMR analysis of the crude reaction mixture revealed no detectable concentration of 1,2-dimethyl-1-phenylsilacyclopentane (**5**). The 1,1′-bipyridyl complex (bipy)PdMe(OEt_2)^+B-Ar_4^- also catalyzed the cyclization of **3** to form a 16:1 ratio of **4**:**5** in 83% yield (Scheme 2).[19] However, reaction of **3** with the more sterically crowded catalyst (neocuproine)PdMe(OEt_2)$^+BAr_4^-$ at room temperature for 24 h formed exclusively **5** in 31% yield by GC analysis (Scheme 2).[19]

The cyclization protocol tolerated both dialkyl- and diaryl-substituted 4-pentenylsilanes (Table 1, entries 1, 2). However, the efficiency of the cyclization protocol was diminished by the presence of substitution on the alkyl or olefinic carbon atoms of the pentenyl chain. For example, treatment of diphenyl(3,3-dimethyl-4-pentenyl)silane with **1** led to isolation of a 7:1 ratio of 4,4-dimethyl-1,1-diphenylsilacyclohexane and 1,1-diphenyl-2,4,4-trimethylsilacyclopentane in 80% yield (Table 1, entry 3). Cyclization of diphenyl(2-methyl-4-pentenyl)silane led to isolation of 1,1-diphenyl-3-methylsilacyclohexane in 43% yield as a single regioisomer (Table 1, entry 4). This reaction also formed considerable quantities (~50%) of polymeric material; polymerization is a common side reaction in intramolecular hydrosilylation.[1,4] Diphenyl-4-hexenylsilane failed to cyclize in the presence of **1** after 5 h at room temperature (Table 1, entry 5).

Table 1. Hydrosilylation of Alkenylsilanes Catalyzed by 1 (3−5 Mol %) in Dichloroethane at 0 °C

entry	alkenylsilane	silacycle[a]	yield[b]	regioselectivity[c]
1	 R = Ph		86	>98:1
2	R = Me		(104 ± 5)[d]	>98:1
3			80	7:1
4			43	>98:1
5			(0)	
6	 R = Me		68	>98:1[e]
7	R = Ph		56 (64 ± 5)	>98:1
8			(0)	

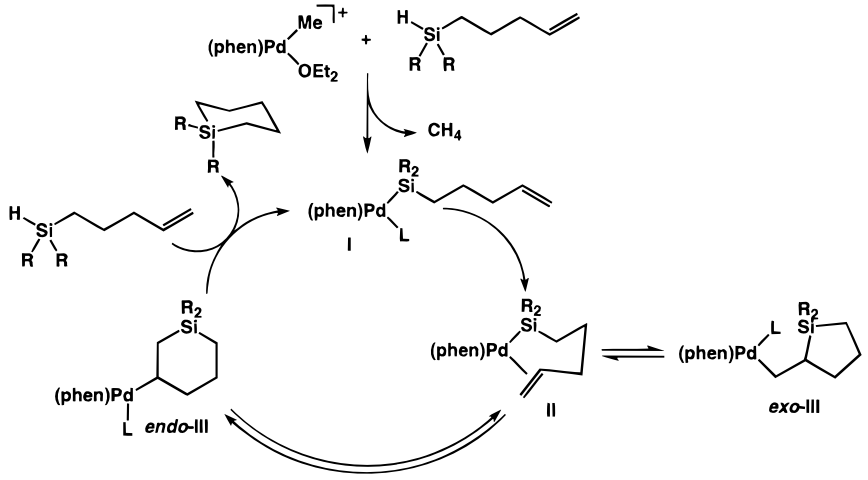
[a] Major isomer shown. [b] Isolated yields; GC yields in parentheses. [c] Determined by capillary GC analysis of crude reaction mixture. [d] Products identified by GCMS and co-injection with authentic sample. [e] Formed as a 1.1:1 mixture of diastereomers.

The cyclization protocol also selectively converted 5-hexenylsilanes to 2-methylsilacyclohexanes. For example, reaction of 5-hexenylmethylphenylsilane with **1** formed 1,2-dimethyl-1-phenylsilacyclohexane in 68% isolated yield as a 1:1.1 mixture of diastereomers (Table 1, entry 6). Similarly, reaction of diphenyl-5-hexenylsilane with **1** led to isolation of 2-methyl-1,1-diphenylsilacyclohexane in 56% yield (64% by GC) as a single regioisomer (Table 1, entry 7). In contrast, cyclization of 3-butenylsilanes was inefficient. Treatment of 3-butenylmethylphenylsilane with **1** led to ~75% conversion after 5 h at room temperature with no detectable formation of 1-methyl-1-phenylsilacyclopentane (Table 1, entry 8).

The mechanism of intermolecular hydrosilylation catalyzed by **1** has been studied by Brookhart.[17,20] This work has shown that **1** reacts with hydrosilanes (presumably via σ-bond metathesis) to form cationic palladium silyl complexes with release of methane. These Pd−Si complexes react with olefins to initially form

(19) Compound **5** formed as a ~2:1 ratio of diastereomers.

Scheme 3



palladium(silyl)olefin complexes which undergo rapid and reversible β-migratory insertion of the coordinated olefin into the Pd−Si bond. Reaction of silane with the resulting palladium alkyl complex completes the catalytic cycle. The final silylation reaction was particularly sensitive to steric effects, and because the palladium alkyl complexes are also prone to reversible β-hydride elimination, silylation of the least sterically hindered isomer was typically observed.[17]

By analogy with intermolecular hydrosilylation, reaction of 4-pentenylsilane with **1** could form the palladium silyl intermediate **I** (Scheme 3). 1,2-β-Migratory insertion of the coordinated olefin into the Pd−Si bond of **II** would generate palladium alkyl intermediate *endo*-**III**. Reaction of *endo*-**III** with silane would then release the silacycle and regenerate the palladium silyl complex **I**. However, formation of *endo*-**III** via kinetic 1,2-insertion appears unusual in light of both Baldwin's rules[21] and related transition metal-catalyzed carbocyclization reactions.[22] Rather, the greater stability of six-membered carbocycles and heterocycles[23] relative to five-membered rings suggests that the observed *endo*-cyclization product forms under thermodynamic conditions. Therefore, we propose that rapid and reversible 1,2- and 2,1-β-migratory insertion of the pendant olefin into the Pd−Si bond of intermediate **II** forms an equilibrium mixture of *exo*-**III** and *endo*-**III**. The observed formation of the six-membered silacycle could result from preferential formation of *endo*-**III** relative to *exo*-**III** and/or selective silylation of *endo*-**III** in preference to *exo*-**III**.

Conclusions

The cationic palladium complex **1** serves as an effective catalyst for the selective conversion of 4-pentenylsilanes or 5-hexenylsilanes to silacyclohexanes. Although the protocol tolerated alkyl and aryl substitution on the silicon atom, the efficiency of cyclization was diminished by substitution on the alkyl and olefinic carbon atoms of the alkenyl chain. The high selectivity for the formation of six-membered silacycles is unusual and may result from formation of silacycles under thermodynamic conditions.

Experimental Section

General Methods. All reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. NMR spectra were obtained on a General Electric QE 300 spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C in $CDCl_3$ unless otherwise noted. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 25 m poly(dimethylsiloxane) capillary column. Flash chromatography was performed employing 200−400 mesh silica gel (EM). Elemental analyses were performed by E+R Microanalytical Laboratories (Parsippany, NJ). THF and ether were distilled from sodium/benzophenone ketyl under nitrogen; CH_2Cl_2 and $C_2H_4Cl_2$ were distilled from CaH_2 under nitrogen. GC yields for cyclization reactions employed naphthalene as an internal standard and are assumed accurate to ±5%.

(Phen)$PdMe_2$, (bipy)$PdMe_2$, and $HB[3,5\text{-}C_6H_3(CF_3)_2]_4\cdot(OEt_2)_2$ were prepared by known procedures and were stored under inert atmosphere at −30 °C.[24,25] 1-Bromo-5-hexene, 1-bromo-4-pentene, 1-bromo-3-butene, methyl 2-methyl-4-pentenoate (Aldrich), diphenylchlorosilane, and phenylmethylchlorosilane (Lancaster) were used as received. 1-Bromo-3,3-dimethyl-4-pentene[26] was formed in two steps ($LiAlH_4/PPh_3Br_2$) from ethyl 3,3-dimethyl-4-pentenoate in 61% yield. 1-Bromo-4-hexene[27] was isolated from reaction of 5-heptene-1-ol and PBr_3 in 33% yield. 1-Bromo-2-methyl-4-pentene[28] was synthesized in two steps ($LiAlH_4/PPh_3Br_2$) from methyl 2-methyl-4-pentenoate in 38% overall yield. Dimethyl-4-pentenylsilane,[29] diphenyl-4-pentenylsilane,[30] and methyl-4-pentenylphenylsilane (**3**)[30] were prepared by known procedures.

An authentic sample of dimethylsilacyclohexane was purchased from Lancaster. Authentic samples of 1-methyl-1-

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phenylsilacyclohexane[31] and 1-methyl-1-phenylsilacyclopentane[32] were generated from reaction of the corresponding di-Grignard reagent with chloromethylphenylsilane. An authentic sample of 1,2-dimethyl-1-phenylsilacyclopentane (**5**) was prepared by reaction of chloroplatinic acid with **3** in refluxing hexane.[30]

3-Butenylmethylphenylsilane. 1-Bromo-3-butene (3.5 g, 26 mmol) was added dropwise to a mixture of magnesium turnings (350 mg, 14.6 mmol) and a crystal of iodine in THF (20 mL) at a rate sufficient to maintain a gentle reflux. The resulting dark supernatant was transferred via cannula to a second flask and cooled to 0 °C. Chloromethylphenylsilane (2.5 g, 16 mmol) was added over 2 min and the resulting solution stirred for 30 min at room temperature. Water (40 mL) and ether (30 mL) were added, and the layers were separated. The aqueous layer was extracted with ether (2 × 40 mL), and the combined organic fractions were washed with brine, dried ($MgSO_4$), and concentrated using a rotary evaporator. Vacuum distillation (0.1 Torr, bp ~50 °C) gave 3-butenylmethylphenylsilane (2.05 g, 74%) as a colorless oil. ^{1}H NMR: δ 7.53 (m, 4 H), 7.35 (m, 6 H), 5.87 (tdd, J = 6.3, 10.3 16.8 Hz, 1 H), 4.99 (dd, J = 1.7, 17.0 Hz, 1 H), 4.90 (dd, J = 1.5, 10.1 Hz, 1 H), 4.37 (sextet, J = 3.6 Hz, 1 H), 2.13 (br q, J = 6.9 Hz, 2 H), 0.94 (ddt, J = 3.6, 4.8, 7.4 Hz, 2 H), 0.35 (d, J = 3.9 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 140.9, 136.4, 134.5, 129.5, 128.1, 113.5, 28.7, 12.8, −5.8. Anal. Calcd (found) for $C_{11}H_{16}$Si: H, 9.15 (9.34); C, 74.93 (75.11).

Diphenyl(3,3-dimethyl-4-pentenyl)silane. Reaction of 3,3-dimethyl-4-pentenylmagnesium bromide (generated from 1.2 g of 1-bromo-3,3-dimethyl-4-pentene) with diphenylchlorosilane (1.0 g, 4.6 mmol) in ether gave diphenyl(3,3-dimethyl-4-pentenyl)silane (200 mg, 16%) as a colorless oil after workup and distillation. ^{1}H NMR: δ 7.54 (m, 4 H), 7.31 (m, 6 H), 5.70 (dd, J = 10.8, 17.6 Hz, 1 H), 4.91 (dd, J = 1.2, 10.8 Hz, 1 H), 4.88 (dd, J = 1.2, 17.6 Hz, 1 H), 4.80 (t, J = 3.6 Hz, 1 H), 1.39 (m, 2 H), 1.02 (m, 2 H), 0.95 (s, 6 H). ^{13}C{^{1}H} NMR: δ 149.0, 136.2, 135.6, 130.6, 129.0, 112.0, 38.8, 38.0, 27.2, 7.6. HRMS (CI) calcd (found) for $C_{19}H_{23}$Si (M^+ − H): 279.1569 (279.1569).

Diphenyl(2-methyl-4-pentenyl)silane. Reaction of 2-methyl-4-pentenylmagnesium bromide (generated from 1.55 g of 1-bromo-2-methyl-pent-4-ene) and diphenylchlorosilane (1.25 g, 8.5 mmol) in ether gave diphenyl(2-methyl-4-pentenyl)-silane (1.47 g, 72%, 90% pure) as a colorless oil after workup and distillation. Chromatography (SiO_2, petroleum ether) provided analytically pure material (560 mg, 27%). ^{1}H NMR: δ 7.55 (m, 4 H), 7.36 (m, 6 H), 5.73 (tdd, J = 7.1, 10.7, 16.4 Hz, 1 H), 5.00 (m, 1 H), 4.94 (m, 2 H), 2.09 (td, J = 6.9, 14.2 Hz, 1 H), 2.01 (td, J = 6.9, 13.7 Hz), 1.76 (m, 1 H), 1.31 (td, J = 5.0, 14.9 Hz, 1 H), 1.03 (ddd, J = 3.4, 8.8, 14.8 Hz, 1 H), 0.96 (d, J = 6.6 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 137.4, 135.3, 135.2, 129.6, 128.1, 116.2, 44.5, 29.8, 22.5, 20.2. Anal. Calcd (found) for $C_{18}H_{22}$Si: H, 8.32 (8.42); C, 81.14 (81.00).

Diphenyl-4-hexenylsilane. Reaction of 4-hexenylmagnesium bromide (generated from 1.0 g of 1-bromo-4-hexene) and diphenylchlorosilane (0.90 g, 4.0 mmol) in ether gave diphenyl-4-hexenylsilane (0.69 g, 64%) as a colorless oil after workup and distillation. ^{1}H NMR: δ 7.55−7.31 (m, 10 H), 5.36 (m, 2 H), 4.82 (t, J = 3.6 Hz, 1 H), 2.02 (M, 2 H), 1.61 (t, J = 4.8 Hz, 3 H), 1.50−1.44 (m, 2 H), 1.14−1.09 (m, 2 H). ^{13}C{^{1}H} NMR: δ 136.2, 135.7, 132.0, 130.6, 129.0, 129.4, 37.0, 25.5, 19.0, 12.8. Anal. Calcd (found) for $C_{18}H_{22}$Si: H, 8.32 (8.97); C, 81.14 (81.41).

Diphenyl-5-hexenylsilane. Reaction of 5-hexenylmagnesium bromide (generated from 2.0 g of 1-bromo-5-hexene) with diphenylchlorosilane (2.25 g, 10.3 mmol) in THF gave diphenyl-5-hexenylsilane (2.13 g, 78%) as a colorless oil after distillation. ^{1}H NMR: δ 7.53 (m, 4 H), 7.35 (m. 6 H), 5.75 (tdd, J = 6.8, 10.4, 17.2 Hz, 1 H), 4.95 (qd, J = 1.6, 17.2 Hz, 1 H), 4.89 (td, J = 1.6, 2.0, 10.0 Hz, 1 H), 4.83 (t, J = 3.6 Hz, 1 H), 2.00 (m, 2 H), 1.45 (m, 2 H), 1.15 (m, 2 H). δ ^{13}C{^{1}H} NMR: δ 140.0, 136.2, 135.6, 130.6, 129.0, 115.3, 34.4, 33.4, 25.0, 13.1. Anal. Calcd (found) for $C_{18}H_{22}$Si: H, 8.32 (8.68); C, 81.14 (81.38).

5-Hexenylmethylphenylsilane. Reaction of 5-hexenylmagnesium bromide (generated from 1.0 g of 1-bromo-5-hexene) with methylphenylchlorosilane (0.75 g, 4.8 mmol) in THF gave diphenyl-5-hexenylsilane (721 mg, 74%) as a colorless oil after chromatography (SiO_2, petroleum ether). ^{1}H NMR: δ 7.66 (m, 2 H), 7.48 (m, 3 H), 5.89 (tdd, J = 6.7, 10.0, 18.8 Hz, 1 H), 5.09 (qd, J = 1.5, 18.8 Hz, 1 H), 5.03 (qd, J = 1.5, 10.5 Hz, 1 H), 4.45 (sextet. J = 3.6 Hz, 1 H), 2.15 (br q, J = 6.7 Hz, 2 H), 1.53 (m, 4 H), 0.96 (m, 2 H), 0.45 (d, J = 3.7 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 140.1, 137.8, 135.5, 130.4, 129.0, 115.5, 34.7, 33.6, 25.1, 14.5, −4.4. HRMS (CI): calcd (found) for $C_{13}H_{19}$Si (M^+ − H): 203.1256 (203.1254). Anal. Calcd (found) for $C_{13}H_{20}$Si: H, 9.85 (10.09); C, 76.40 (76.49).

General Procedure for Hydrosilylation of Alkenylsilanes. Dichloroethane (10 mL) was added to a mixture of (Phen)$PdMe_2$ (8 mg) and $HB[3,5\text{-}C_6H_3(CF_3)_2]_4\cdot(OEt_2)_2$ (24 mg) at 0 °C to give a pale yellow solution of **1** (0.025 mmol, 3 mol %). Alkenylsilane (~150 mg) was added via syringe and the solution was stirred at 0 °C for 2 min, which led to considerable darkening. Solvent was evaporated under vacuum, and the residue was extracted with ether and filtered through a small pad of silica gel. Evaporation of the solvent and flash chromatography (SiO_2/petroleum ether) gave pure silacycle as a colorless oil.

1-Methyl-1-phenylsilacyclohexane.[31] ^{1}H NMR: δ 7.33−7.54 (m, 5 H), 0.79−1.78 (m, 10 H), 0.24 (s, 3 H). ^{13}C{^{1}H} NMR: δ 139.0, 133.7, 128.8, 127.8, 30.1, 24.5, 13.0, −2.89.

1,1-Diphenylsilacyclohexane.[33] ^{1}H NMR: δ 7.24−7.55 (m, 10 H), 1.72−1.78 (m, 4 H), 1.50−1.53 (m, 2 H), 1.18 (t, J = 6.6 Hz, 4 H). ^{13}C{^{1}H} NMR: δ 135.9, 134.5, 129.1, 127.9, 31.0, 25.5, 11.6.

4,4-Dimethyl-1,1-diphenylsilacyclohexane. ^{1}H NMR: δ 7.53 (m, 4 H), 7.35 (m, 6 H), 1.57 (br t, J = 6.6 Hz, 4 H), 1.17 (br t, J = 6.6 Hz, 4 H), 0.92 (s, 6 H). ^{13}C{^{1}H} NMR: δ 136.6 134.5 129.2 127.9 36.4 32.4 28.7 7.1. Anal. Calcd (found) for $C_{19}H_{24}$Si: H, 8.62 (8.88); C, 81.36 (81.69).

1,1-Diphenyl-3-methylsilacyclohexane. ^{1}H NMR: δ 7.65 (m, 2 H), 7.46 (m, 2 H), 7.40 (m, 6 H), 7.32 (m, 6 H), 2.20 (m, 1 H), 1.72 (m, 2 H), 1.50−1.30 (m, 4 H), 1.00 (d, J = 6.4 Hz, 3 H), 0.85 (dt, J = 5.2, 14.3 Hz, 1 H), 0.69 (dd, J = 12.6, 14.6 Hz, 1 H). ^{13}C{^{1}H} NMR: δ 134.7, 134.3, 129.1, 129.0, 127.9, 127.8, 38.3, 31.4, 27.7, 23.7 20.8, 10.6. Anal. Calcd (found) for $C_{18}H_{22}$Si: H, 8.32 (8.68); C, 81.14 (81.18).

1,1-Diphenyl-2-methylsilacyclohexane. ^{1}H NMR: δ 7.65−7.58 (m, 4 H), 7.40 (br, 6 H), 1.0−2.0 (m, 9 H), 1.16 (d, J = 7.7 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 135.7, 134.7, 129.1, 127.8, 127.6, 34.2, 28.3, 24.8, 18.4, 16.7, 11.2. Anal. Calcd (found) for $C_{18}H_{22}$Si: H, 8.32 (8.16); C, 81.14 (81.11).

1,2-Dimethyl-1-phenylsilacyclohexane.[31] ^{1}H NMR: δ 7.53 (m, 2 H), 7.34 (m, 3 H), 2.0−1.65 (m, 3 H), 1.50−1.20 (m, 3 H), 0.92 (m, 3 H), 0.60−0.90 (m, 3 H), [0.25 (s, minor isomer), 0.23 (s, major isomer), 3 H]. ^{13}C{^{1}H} NMR: δ 139.5, 135.0, 130.0, 128.8, 35.8, 30.5, 25.6, 21.2, 17.3, 13.9, −8.0 [major isomer]; 138.5, 135.8, 129.9, 128.7, 35.2, 29.5, 26.0, 20.2, 17.4, 12.9, −3.0 [minor isomer]. HRMS (CI): calcd (found) for $C_{13}H_{20}$Si: 204.1334 (204.1331).

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