

Preparation of 1,1-disubstituted silacyclopentadienes

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Abstract

Several new 1,1-disubstituted siloles containing substituents on the ring carbon atoms have been synthesized. The new siloles: 1,1-dihydrido-2,5-bis(trimethylsilyl)-3,4-diphenylsilole (**5**), 1,1-dihydrido-2,5-dimethyl-3,4-diphenylsilole (**6**), 1,1-dimethoxy-2,5-bis(trimethylsilyl)-3,4-diphenylsilole (**7**), 1,1-bis(4-methoxyphenyl)-2,5-bis(trimethylsilyl)-3,4-diphenylsilole (**8**), 1,1-dipropoxy-2,5-bis(trimethylsilyl)-3,4-diphenylsilole (**9**), and 1,1-dibromo-2,5-bis(trimethylsilyl)-3,4-diphenylsilole (**13**) were prepared from reactions originating from the previously reported, 1,1-bis(diethylamino)-2,5-bis(trimethylsilyl)-3,4-diphenylsilole (**1**) or 1,1-bis(diethylamino)-2,5-dimethyl-3,4-diphenylsilole (**2**). In addition, three other new organosilane byproducts were observed and isolated during the current study, bis(4-methoxyphenyl)bis(phenylethynyl)silane (**11**), bis(4-methoxyphenyl)di(propoxy)silane (**12**) and 1-bromo-4-bromodi(methoxy)silyl-1,4-bis(trimethylsilyl)-3,4-diphenyl-1,3-butadiene (**14**). Compounds **13** and **14** were characterized by X-ray crystallography and **14** is the first 1,1-dibromosilole whose solid state structure has been determined.

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1. Introduction

The study of silacyclopentadienes, also known as siloles, has recently received substantial attention due to the unique aspects of their synthesis and reaction chemistry as well as the novel photophysical and electronic properties exhibited by this class of compounds [1–4]. Siloles possess a low-energy LUMO due to the $\sigma^*-\pi^*$ conjugation involving the σ^* orbital of the exocyclic substituents on Si and the π^* orbitals of the butadiene unit in the ring that result in high electron affinity properties for siloles [5,6]. Silole-containing π -conjugated systems generally exhibit long wavelength absorptions in the UV–Vis region [7,8], and many have been found to display high photoluminescent quantum efficiency, especially in the solid state [9]. These novel properties make siloles ideal candidates for components in light-emitting devices [10]. Siloles have also been recognized as chemical sensors for nitroaromatic and other types of explosives [11].

The first reported syntheses of a silole by Braye and Hübel [12] and Leavitt and coworkers [13] occurred nearly 50 years ago. To date, several methods have been utilized for the preparation of siloles [4] but there are two routes that appear to be the most versatile and most widely used. One involves the salt metathesis reaction between an active 1,4-metalla-1,3-butadiene with a dihalosilane (or related precursor) to form two new Si–C bonds upon ring closure. The other route involves preparation of a silane containing two alkynyl substituents, then effecting ring closure through formation of a new C–C bond by reductive coupling. The most challenging aspect of the first method involves construction of the required 1,4-dihalo-1,3-butadiene precursor. However, a convenient one-pot synthesis of such compounds has been reported that involves the preparation of a titanacyclopentadiene intermediate as a precursor to the substituted 1,4-dihalo-1,3-butadienes via halogenolysis [14]. The second method utilizes a reductive cyclization reaction of bis(phenylethynyl)silanes [7] for a multi-step preparation of 2,5-difunctionalized siloles. The latter method has been limited primarily to phenylethynylsilanes but the reductive cyclization has also been success-

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ful with 4-*N*-indolylphenyl- and 4-*N*-7-azaindolylphenylethynylsilanes [10b].

We report here the synthesis of six new 2,5-bis(trimethylsilyl)-3,4-diphenyl- and 2,5-dimethyl-3,4-diphenyl-substituted siloles in addition to other organosilyl-containing products that have been obtained during the preparation of synthetically useful silole compounds. The new siloles were prepared by modifications of procedures reported by Tamao and coworkers for the reductive cyclization employing a bis(phenylethynyl)diethylaminosilane precursor [15]. The aim of our study was to prepare new siloles in which there were different substituents on the ring carbon atoms and functional groups on silicon that may be used as precursors to build more complex silole derivatives.

2. Results and discussion

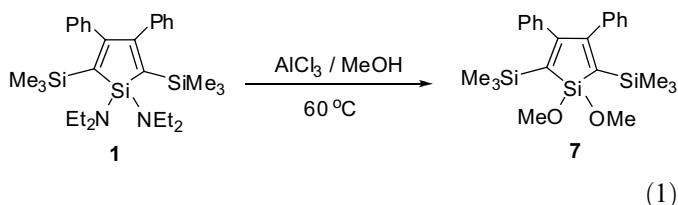
2.1. Preparation and characterization of new compounds

Siloles **1** and **2** have been prepared previously starting from bis(diethylamino)-bis(phenylethynyl)silane [3,15]. Siloles **1** and **2** were chosen as the starting silole reagents since they are easily prepared and have been reported to produce the corresponding 1,1-dichlorosiloles **3** and **4** in ca. 80% yield upon treatment with dry HCl [15]. The latter could then serve as convenient precursors for the preparation of a variety of new siloles functionalized at silicon. Two of the six new siloles, **5** and **6**, reported here contain hydrogen substituents on the silicon atom (Scheme 1). The obvious route to **5** and **6** starting from $\text{H}_2\text{Si}(\text{C}\equiv\text{CPh})_2$ [16] was unsuccessful.

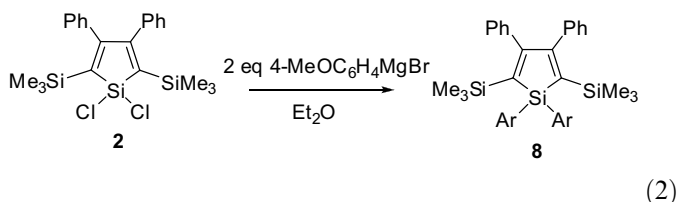
The 1,1-dihydrosiloles **5** and **6** were isolated as air and/or moisture sensitive light yellow or white solids in yields of 50% and 80%, respectively. Exposure of hexane solutions of either **5** or **6** resulted in the formation of an unidentified white solid after a few minutes. Only a few 1,1-dihydrosiloles have been previously reported [17]. In contrast to **5** and **6**, siloles that have phenyl substituents at the 2,5-positions [18–20] are stable to air and moisture but 1-hydro-1-methyl-2,5-diphenylsilole was found to decompose slowly

at room temperature [20]. Thus, the relative stability of siloles is probably related to the presence of groups at the ring carbon atoms [8,21].

The 1,1-diethylaminosilole **1** was converted to 1,1-dimethoxysilole (**7**) by treatment with methanol in the presence of AlCl_3 (Eq. (1)), by analogy to the related and previously prepared 1,1-diethoxysilole [15]. However, it was found that an excess amount of AlCl_3 and a temperature of 60 °C were required to obtain a 81% yield of **7** (see Table 1).



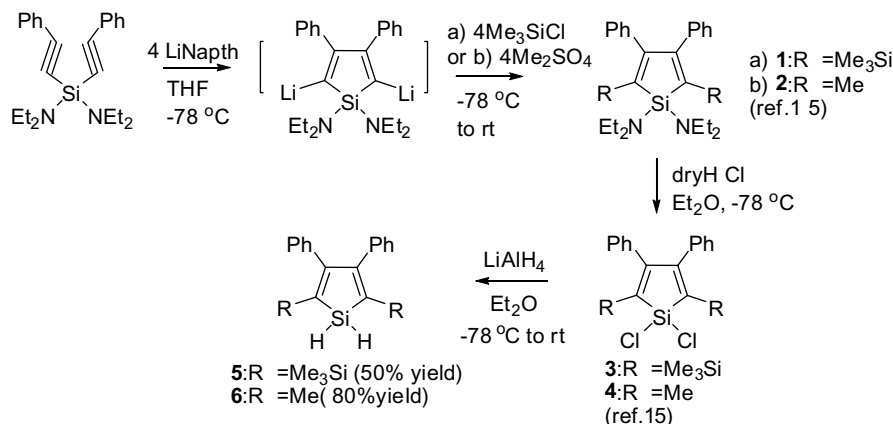
Treatment of 1,1-dichlorosilole **2** in diethyl ether with (4-MeOC₆H₄)MgBr [22] prepared from 4-bromoanisole afforded the 1,1-diarylsilole **8** in 82% yield (Eq. (2)). However, changing the solvent from Et₂O to THF using either an ArLi or ArMgBr



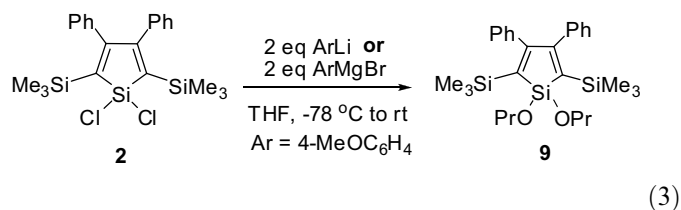
reagent did not lead to the formation of **8** but instead gave the 1,1-dipropoxysilole **9** as illustrated in Eq. (3). The pres-

Table 1
Synthesis of 1,1-dimethoxy-2,5-bis(trimethylsilyl)-3,4-diphenylsilole **7**

Reaction run	1	2	3	4	5
AlCl_3 (equiv.)	25	25	50	50	55
Temperature (°C)	25	60	60	60	60
Time (h)	20	20	20	48	48
Yield (%)	15	34	66	78	81

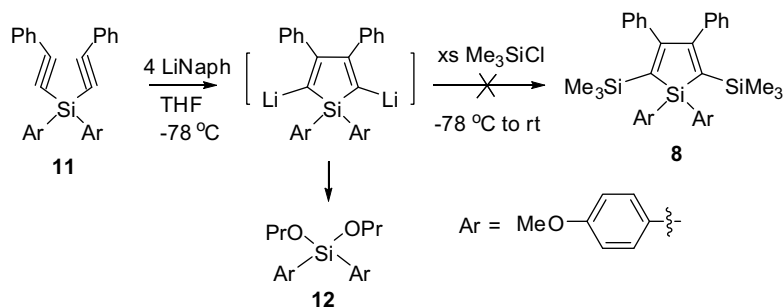


ence of the propoxy groups in **9** resulting from the attempted coupling reaction in THF was an unexpected result. The origin of the propoxy groups in **9** is not certain but clearly occurs when THF is used as the solvent. It is known that active organometallic reagents can promote ring cleavage of THF to produce ethylene and the enolate salt of acetaldehyde both of which are two carbon fragments [23]. The enolate can be trapped, for example, with chlorotrimethylsilane [24], however, no such related product was identified in the reaction mixtures from **8** and Ar–M (M = Li and MgBr) as determined by GC–MS. Since no reaction was observed when 1,1-dichlorosilole (**2**) was dissolved in pure THF after two days under an inert atmosphere the organometallic reagents must be implicated in this unusual result. To the best of our knowledge, the generation of a three carbon unit from the cleavage of THF has not been previously established. It should be noted that the coupling of either an organolithium or Grignard reagent with 1-chloro-1-phenyl-2,3,4,5-tetraphenylsilole in THF was successful [9f]. As was the coupling of 2 equiv. of HC≡CMgBr with 1,1-dichloro-2,3,4,5-tetraphenylsilole in THF [25].

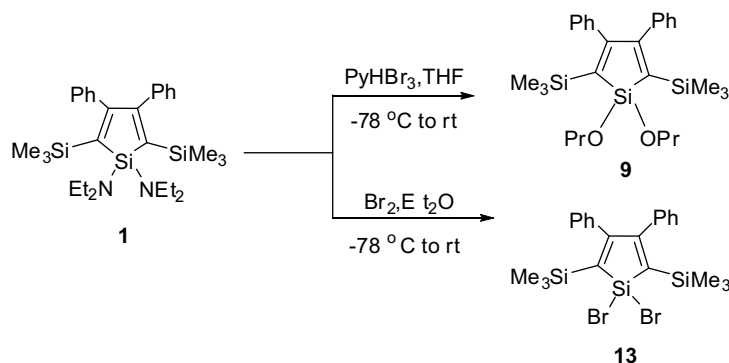


In a separate attempt to prepare 1,1-diarylsiloles, bis(phenylethynyl)bis(4-methoxyphenyl)silane (**11**) was synthesized as a potential precursor for a 1,1-diaryl-substituted silole via a reductive cyclization route. Reaction of the aryl-Grignard, 4-methoxyphenylmagnesium bromide [22] with silicon tetrachloride produced dichloro-bis(4-methoxyphenyl)silane [26] **10** which was then treated with phenylethyneyllithium to afford product **11** in 76% yield (from **10**). Unfortunately, the attempted reductive cyclization of **11** did not produce the desired silole **8**. Instead, bis(4-methoxyphenyl)dipropoxysilane **12** was isolated as the major product in 42% yield (Scheme 2). As with compound **9**, the origin of the propoxy groups is believed to come from THF but the mechanism by which it is incorporated into the product is not known.

Ring-functionalized 2,5-disubstituted siloles have been prepared via halodesilylation of 2,5-disilyl-substituted siloles. Tamao and coworkers have reported the halodesilylation of 1,1-dialkyl-2,5-bis(trimethylsilyl)-3,4-diphenylsiloles (Me, Et, or *i*-Pr) with pyridinium bromide perbromide, PyHBr₃ [27]. Complex reaction mixtures were obtained with the less bulky methyl and ethyl substituents on silicon (probably due to competing reactions from attack at the ring silicon atom). But with the bulkier *i*-Pr groups the halogenolysis was successful, producing the corresponding 2,5-dibromosilole in 40% yield. The authors found that the reactivity of the siloles was dependent on the nature of the substituents in the 3,4-positions of the silole ring [27]. Cleaner reactions were observed with 3,4-dialkyl vs.



Scheme 2.



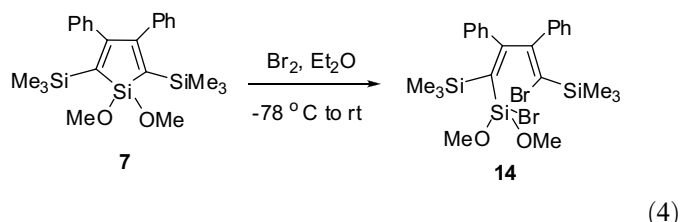
Scheme 3.

3,4-diphenylsiloles. A related reaction involving halodesilylation using Br_2 with a dithienothiasiline ring system has been reported to remove a silyl group from the thiophene rings [28]. With molecular halogens, the most common reaction of siloles, germoles, and stannoles appears to be cleavage of one or both of the endocyclic Group 14 element-carbon bonds with subsequent complicating reactions [1a]. In a related study, replacement of the two exocyclic phenyl substituents in hexaphenylstannole by treatment with X_2 ($\text{X} = \text{Br}, \text{I}$) while preserving the metallole core was originally reported [29]. However, a later study showed that the actual product was the ring-opened compound, 1-bromo-4-bromodiphenylstannyl-1,2,3,4-tetraphenyl-1,3-butadiene [30].

The brominating reagents PyHBr_3 and Br_2 produced different results. Reaction of 1,1-diethylaminosilole **1** with PyHBr_3 in THF did not result in the halodesilylation of the SiMe_3 groups by bromine. Instead, the unexpected and previously observed product, **9** was formed in 25% yield (Scheme 3).

The reaction of **1** with Br_2 in Et_2O replaced the NEt_2 groups instead of cleaving the trimethylsilyl groups. Colorless crystals of 1,1-dibromosilole **13** were obtained in 52% yield (Scheme 3). The structure of **13** was confirmed by X-ray crystallography. However, more rigorous conditions were used to prepare a related silole, 1,1-dibromo-2,3,4,5-tetramethylsilole in 28% yield from the reaction of the 1,1-bis(cyclopentadienyl)-2,3,4,5-tetramethylzirconacyclopentadiene with SiBr_4 for two days at 150°C [31].

In contrast when 1,1-dimethoxysilole **7** was reacted with Br_2 the ring-opened product **14** was obtained from attack at the ring silicon atom (Eq. (4)). White crystals of **14** were obtained in 77% yield and the structure confirmed by X-ray crystallography



The unsymmetrical environment in **14** was confirmed by ^1H and ^{13}C NMR spectroscopy where two sets of resonances were observed for the SiMe_3 and OMe groups. The ^1H NMR spectrum exhibited two signals at 0.48 and -0.07 ppm for the two distinct SiMe_3 groups as well as two separate resonances for the OMe groups at 3.71 and 3.65 ppm. The presence of two $\text{Si}(\text{OMe})_2$ signals can be attributed to the two diastereotopic OMe groups.

Table 2

Crystal data and structure refinement details for compounds **13** and **14**

	13	14
Empirical formula	$\text{C}_{22}\text{H}_{28}\text{Br}_2\text{Si}_3$	$\text{C}_{24}\text{H}_{34}\text{Br}_2\text{O}_2\text{Si}_3$
M_r	536.53	598.60
T (K)	100(2)	100(2)
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a (Å)	20.3293(6)	14.4929(6)
b (Å)	10.3868(3)	10.8030(4)
c (Å)	11.5102(3)	18.5479(8)
α (°)	90	90
β (°)	98.168(2)	109.920(2)
γ (°)	90	90
V (Å ³)	2405.80(12)	2730.24(19)
Z	4	4
D_c (Mg m ⁻³)	1.481	1.456
μ (mm ⁻¹)	3.525	3.119
F_{000}	1088	1224
Crystal size (mm)	0.26 × 0.21 × 0.18	0.21 × 0.17 × 0.11
θ Range (°)	2.02–33.33	1.49–25.00
Index ranges	$-31 \leq h \leq 31,$ $-16 \leq k \leq 15,$ $-17 \leq l \leq 17$	$-16 \leq h \leq 17,$ $-12 \leq k \leq 12,$ $-22 \leq l \leq 22$
Number of reflections collected	41 123	49 358
Number of independent reflections (R_{int})	4659 (0.040)	4810 (0.1042)
Completeness to θ , % (°)	100.0 (25.00)	100 (33.33)
Absorption correlation	Numerical	Numerical
Maximum/minimum transmission	0.608/0.471	0.7663/0.6432
Number of data/restraints/parameters	4659/0/179	4810/1/316
Goodness-of-fit on F^2	1.041	1.122
R_1 [$I > 2\sigma(I)$]	0.0238	0.0454
wR_2 (all data)	0.0510	0.1022
Maximum, minimum peaks (e/Å ³)	0.506, -0.315	0.701, -0.595

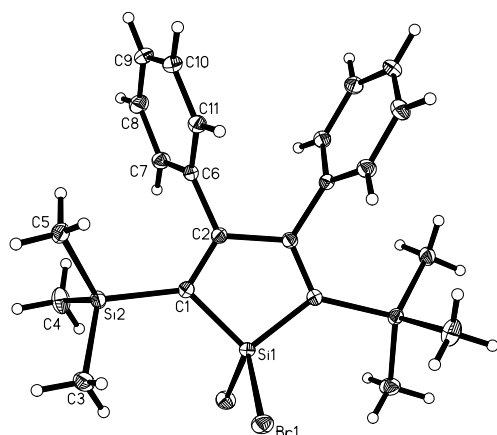


Fig. 1. Molecular structure of 1,1-dibromo-2,5-bis(trimethylsilyl)-3,4-diphenylsilole **13**. Selected bond distances (Å) and angles (°): Si(1)–Br(1), 2.2161(3); Si(1)–C(1), 1.8502(12); Si(1)–C(1)#1, 1.8501(12); Si(2)–C(1), 1.8774(12); C(1)–C(2), 1.3578(17); C(2)–C(2)#1, 1.526(2); Br(1)#1–Si(1)–Br(1), 106.47(2); C(1)#1–Si(1)–C(1), 98.10(8); C(1)–C(2)–C(2)#1, 117.74(7); C(1)–Si(1)–Br(1), 115.69(4); C(1)–Si(1)–Br(1)#1, 110.55(4).

2.2. X-ray crystallographic studies

The molecular structure of **13** is shown in Fig. 1 along with selected bond distances and angles. The crystal data and structure refinement details for compounds **13** and **14** are listed in Table 2. The ring silicon center in **13** exhibits a distorted tetrahedral geometry with an endocyclic C–Si–C angle of 98.1° due to the constraints imposed by the 5-membered silole ring whereas the Br–Si–Br angle was larger at 106.5°. Typical endocyclic C–Si–C angles for siloles fall in the range of 90.5–97° [32]. Placement of electronegative groups in the 2,5-positions of the silole ring results in a decrease of the C–Si–C ring angle [32]. The planar silole ring exhibits endocyclic C=C double bonds and a C–C single bond within the expected range [10c]. The Si–Br bond distance of 2.216(3) Å found in **13** is comparable to other structurally characterized four-coordinate organobromosilanes [33]. The structural environment in **13** is similar to the related 1,1-dichloro-2,3,4,5-tetraphenylsilole but with shorter distances found in the expected Si–Cl distances but also with the Si–C bond lengths [34].

The molecular structure of the unsymmetrical compound **14** was also confirmed by X-ray crystallography (Fig. 2). The C=C (1.34–1.37 Å) and C–C (1.49 Å) bond distances in the butadiene unit are within the expected range and are similar to those found in the related tin system, 1-bromo-4-bromodiphenylstannyl-1,2,3,4-tetraphenyl-1,3-butadiene [30]. Other bond distances and angles found in **14** fall within the anticipated range.

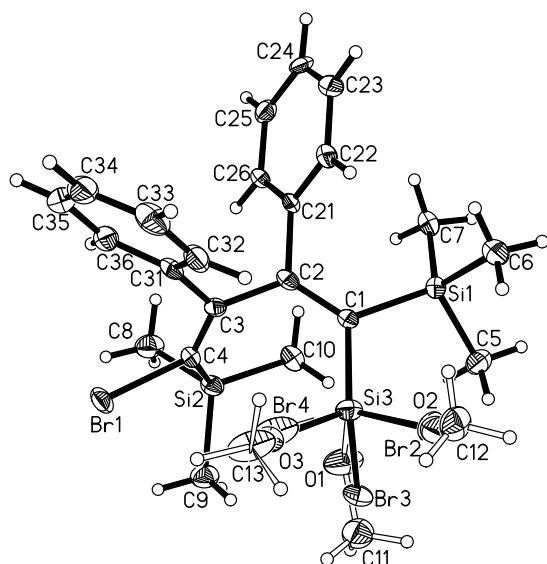


Fig. 2. Molecular structure of 1-bromo-4-bromodimethoxysilyl-1,4-bis(trimethylsilyl)-3,4-diphenyl-1,3-butadiene (**14**). Selected bond distances (Å) and angles (°): Si(1)–C(1), 1.903(5); Si(2)–C(4), 1.890(5); Si(3)–C(1), 1.850(4); C(1)–C(2), 1.375(6); C(2)–C(3), 1.494(6); C(3)–C(4), 1.343(6); C(4)–Br(1), 1.945(5); Si(3)–Br(2), 2.100(5); Si(3)–Br(3), 2.042(10); Si(3)–Br(4), 2.2163(18); C(2)–C(1)–Si(3), 122.1(4); C(4)–C(3)–C(2), 121.0(4); C(1)–C(2)–C(3), 124.6(4); C(2)–C(1)–Si(1), 123.8(3); C(3)–C(4)–Si(2), 134.8(4); C(3)–C(4)–Br(1), 116.6(4).

3. Conclusion

The current study involves the preparation of several new 1,1-disubstituted-2,5-bis(trimethylsilyl)-3,4-diphenylsiloles using the modified literature procedures [7,15]. Two new compounds were structurally characterized by X-ray crystallography, 1,1-dibromosilole (**13**) and the ring-opened bromosilyl-butadiene compound **14**. The results from this study have shown that the chemistry involved in the preparation and reactivity of siloles continues to be complex and unusual. However, unexpected results may be obtained in THF as reported in this study. We are continuing to prepare novel silole systems with functionality at silicon.

4. Experimental

4.1. General

All reactions were performed in flame- or oven-dried glassware under dry nitrogen or argon on a dual-manifold Schlenk line or in an inert atmosphere box. Tetrahydrofuran and diethyl ether were distilled from sodium/9-Fluorenone under nitrogen [35]. Hexane, pentane, and methylene chloride solvents were distilled from calcium hydride under nitrogen. Other commercial reagents including phenylacetylene and 4-bromoanisole were also dried and distilled from calcium hydride under nitrogen. The chlorosilanes, HSiCl₃, SiCl₄ and Me₃SiCl were freshly distilled before use from potassium carbonate under argon. Diethylamine was distilled after refluxing for 3 h over barium oxide. Methanol was dried and distilled from magnesium under nitrogen. Naphthalene was dried in vacuo at room temperature for 2 h before use. Aluminum trichloride was sublimed at atmospheric pressure under argon with heating. Hydrochloric acid solutions in diethyl ether were prepared by reaction of ammonium chloride with concentrated sulfuric acid or purchased as a 2 N solution from Aldrich Chemical Co. Other commercially available chemicals were used as received. The siloles, 1,1-diethylamino-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (**1**), 1,1-dichloro-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (**3**), 1,1-diethylamino-2,5-dimethyl-3,4-diphenyl-1-silacyclopentadiene (**2**), and 1,1-dichloro-2,5-dimethyl-3,4-diphenyl-1-silacyclopentadiene (**4**) were prepared according to the literature procedures [3,15]. NMR solvents were obtained from Cambridge Isotopes Inc. and dried over activated molecular sieves. The ¹H, ¹³C, and ²⁹Si NMR spectra were recorded on a Bruker ARX-500 spectrometer at 500 MHz for ¹H, 125 MHz for ¹³C, and 99 MHz for ²⁹Si at ambient temperature. Proton chemical shifts (δ) are reported relative to residual protonated solvent, CD₂Cl₂ (5.32 ppm) and CDCl₃ (7.27 ppm). Carbon chemical shifts (δ) are reported relative to the NMR solvent, CD₂Cl₂ (54.00 ppm) and CDCl₃ (77.23 ppm). Silicon chemical shifts (δ) are reported relative to external TMS (0 ppm). Chemical shifts are given in ppm and coupling

constants in Hz. Melting point determinations were obtained on a Mel-Temp capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Thermo-Nicolet Avatar 360 ESP FT-IR spectrometer. Mass spectral analyses were determined on a Hewlett-Packard GC–MS System Model 5988A (EI) or a JEOL MStation JMS-700 mass spectrometer and peaks >15% of the base peak are listed as well as selected smaller parent ion peaks in some cases. The X-ray crystal structure determinations were performed on a Bruker SMART 1K diffractometer equipped with a CCD area detector at 100 K. Elemental analysis determinations were obtained from Atlantic Microlabs, Inc, Norcross, GA.

4.2. Syntheses of compounds 5–14

4.2.1. 1,1-Dihydro-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (5)

Dry HCl gas, generated from NH_4Cl (0.53 mg, 10 mmol) and concentrated H_2SO_4 (0.59 mL, 11 mmol) at room temperature, was bubbled through a diethyl ether solution (30 mL) containing 1,1-bis(diethylamino)-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (**1**) [15] (0.52 g, 1.0 mmol) at -78°C over 1 h. The resulting mixture was concentrated *in vacuo* followed by addition of dry hexane (3×20 mL). After filtration under argon, the filtrate was concentrated under reduced pressure to obtain 1,1-dichloro-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (**3**) which was used without isolation for the preparation of **5** [15]. Freshly distilled diethyl ether (30 mL) was added to dichlorosilole **3**, the solution was cooled to -78°C , followed by addition of solid LiAlH_4 (38 mg, 1.0 mmol) from a bent glass tube. The mixture was allowed to gradually warm to ambient temperature and stirred for 3 h. The ether was removed under reduced pressure and dry hexane (3×20 mL) was added by syringe. After filtration, the resulting filtrate was concentrated under vacuum to give a pale yellow viscous oil (0.19 mg, 41% of **3** by GC). Recrystallization from pentane at -50°C in an inert atmosphere box provided pale yellow crystals of 1,1-dihydrido-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (**5**) (0.056 g, 15%). M.p. $83\text{--}87^\circ\text{C}$. ^1H NMR (CD_2Cl_2): δ 7.09–7.07 (m, 6 H, ArH), 6.91–6.89 (m, 4H, ArH), 4.56 (s, 2H, $^1J_{\text{Si-H}} = 196$, SiH_2), -0.12 (s, 18 H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 172.4, 143.1, 140.8, 129.2, 127.6, 126.9, -2.1 . $^{29}\text{Si}\{^1\text{H}\}$ NMR: (DEPT, CDCl_3): δ -7.9 (s, SiMe_3), -26.9 (s, SiH_2). IR (solid, cm^{-1}): $\nu_{\text{Si-H}}$ 2125. EI-MS: m/z (relative abundance, %) 378 (M^+ , 5), 376 ($\text{M}^+ - 2$, 19), 159 (17), 145 (25), 135 (17), 73 (100).

4.2.2. 1,1-Dihydro-2,5-dimethyl-3,4-diphenyl-1-silacyclopentadiene (6)

An HCl solution (2 N in ether, 4 mL), was added dropwise to a diethyl ether (30 mL) solution of 1,1-bis(diethylamino)-2,5-dimethyl-3,4-diphenyl-1-silacyclopentadiene (**2**) [15] (0.40 g, 1.0 mmol) at -78°C over 50 min and the mixture was stirred at low temperature for another 2 h.

The resulting mixture was concentrated *in vacuo* then dry hexane (3×15 mL) was added. After filtration the filtrate was condensed under reduced pressure to give 1,1-dichloro-2,5-dimethyl-3,4-diphenyl-1-silacyclopentadiene (**5**) which was used without isolation for the preparation of **6** [15]. Dry diethyl ether (25 mL) was added to dichlorosilole **4**, the resulting solution cooled to -78°C , and solid LiAlH_4 (38 mg, 1.0 mmol) was added to the solution via a bent tube. The mixture was allowed to gradually warm to ambient temperature and stirred for an additional 2.5 h. The ether was removed under reduced pressure and dry hexane (3×15 mL) was added to the residue. After filtration, the filtrate was condensed under vacuum to provide a white solid and a small amount of viscous oil. The white solid was purified by recrystallization from pentane at -50°C to give 1,1-dihydrido-2,5-dimethyl-3,4-diphenyl-1-silacyclopentadiene (**6**) in 80% yield (0.21 g, 93% purity by GC). M.p. $103\text{--}109^\circ\text{C}$. ^1H NMR (CD_2Cl_2): δ 7.17–7.08 (m, 6H, ArH), 6.89–6.86 (m, 4H, ArH), 4.40 (s, 2 H, $^1J_{\text{Si-H}} = 196$, SiH_2), 1.90 (s, 6H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 158.2, 139.4, 129.7, 129.5, 127.9, 126.7, 15.7. $^{29}\text{Si}\{^1\text{H}\}$ NMR (DEPT, CD_2Cl_2): δ -34.4 (s). IR (solid, cm^{-1}): ν_{SiH} 2151, 2130. EI-MS: m/z (relative abundance, %) 262 (M^+ , 74), 247 (56), 145 (47), 143 (23), 131 (19), 129 (21), 121 (42), 115 (34), 105 (100), 77 (16), 67 (18), 53 (22).

4.2.3. 1,1-Dimethoxy-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (7)

Table 1 lists various reaction conditions that were examined for the formation of **7**. Reaction run 5 is described in the following experiment. 1,1-Bis(diethylamino)-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (**1**) [15] (0.26 g, 0.50 mmol) and AlCl_3 (0.037 g, 0.28 mmol) were placed in a two-necked round bottomed flask with a condenser inside the dry box then transferred to a Schlenk line under argon. Dry methanol (15 mL) was added to the mixture by syringe with vigorous stirring. The mixture was warmed to 60°C and kept at that temperature for 2 days before removing the methanol under reduced pressure. The residue was washed with hexane (3×15 mL) and filtered through silica gel. The crude product was purified by flash column chromatography using silica gel (ethyl acetate:hexane, 3:400). The eluted product was recrystallized from hexane at -40°C to give colorless crystals of 1,1-dimethoxy-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (**7**) in 81% yield (0.18 g). M.p. $90\text{--}92^\circ\text{C}$.

^1H NMR (CDCl_3): δ 7.07–7.03 (m, 6 H, ArH), 6.85–6.81 (m, 4H, ArH), 3.65 (s, 6H, OCH_3), -0.11 (s, 18H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 171.0, 142.6, 134.3, 128.5, 127.3, 126.6, 50.5, 0.2. $^{29}\text{Si}\{^1\text{H}\}$ NMR (DEPT, CDCl_3): δ -5.8 (SiMe_3), -9.6 (SiOCH_3). EI-MS: m/z (relative abundance, %) 438 (M^+ , 18), 423 (26), 406 (22), 391 (46), 365 (22), 319 (15), 249 (64), 219 (45), 159 (72), 145 (29), 131 (25), 129 (25), 115 (82), 105 (31), 89 (33), 73 (100), 59 (63). Anal. Calc. for $\text{C}_{24}\text{H}_{34}\text{O}_2\text{Si}_3$: C, 65.69; H, 7.81. Found: C, 65.87; H, 7.75%.

4.2.4. 1,1-Bis(4-methoxyphenyl)-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (**8**)

A solution of 4-methoxyphenylmagnesium bromide [22] was prepared by treatment of 4-bromoanisole (0.37 g, 2.0 mmol) in 35 mL diethyl ether with magnesium turnings (0.062 g, 2.6 mmol). The Grignard reagent was filtered to remove any unreacted Mg metal. A solution containing 1,1-dichloro-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (**2**) [15] (0.45 g, 1.0 mmol in 20 mL of diethyl ether) was added dropwise to the Grignard solution which had been cooled to -78°C . The mixture was warmed to ambient temperature after 2 h, then stirred overnight. The resulting reaction mixture was washed with water (2×50 mL) and the organic layer was dried over anhydrous MgSO_4 for 30 min then filtered. The filtrate was concentrated and the residue was purified by flash column chromatography using silica gel (dichloromethane:hexane, ratio = 1:7). The solid product obtained was recrystallized from a dichloromethane–diethyl ether–pentane mixture at 2°C to obtain colorless crystals of 1,1-bis(4-methoxyphenyl)-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (**8**) in 82% yield. M.p. $204.5\text{--}206^{\circ}\text{C}$.

^1H NMR (CDCl_3): δ 7.75 (m, 4H, ArH), 7.09–7.04 (m, 6H, PhH), 7.00 (m, 4H, ArH), 6.95–6.92 (m, 4H, PhH), 3.88 (s, 6 H, OCH_3), -0.38 (s, 18H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 171.4, 161.2, 144.2, 142.9, 137.4, 129.0, 127.2, 126.3, 123.7, 113.9, 55.2, 1.0. $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl_3): δ 8.14 (SiAr_2), -9.0 (SiMe_3). HR-MS (FAB, NBA): calcd for $\text{C}_{36}\text{H}_{43}\text{O}_2\text{Si}_3$, 591.2572. Found: 591.2582. EI-MS: m/z (relative abundance, %) 482 ($[\text{M}-\text{C}_7\text{H}_8\text{O}]^+$, 23), 467 (7), 409 (4), 343 (28), 257 (17), 207 (64), 165 (48), 159 (15), 135 (33), 73 (100), 59 (26). Anal. Calc. for $\text{C}_{36}\text{H}_{42}\text{O}_2\text{Si}_3$: C, 73.16; H, 7.16. Found: C, 73.19; H, 7.09%.

4.2.5. 1,1-Dipropoxy-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (**9**)

4.2.5.1. Method A. A solution of *n*-BuLi (2.5 M in hexane, 0.4 mL, 1.0 mmol) was added to 4-bromoanisole (0.19 g, 1.0 mmol) in THF (10 mL) at -78°C and stirred for an additional 1.5 h [22]. In a separate flask, the dichlorosilole **2** [15] (0.45 g, 1.0 mmol) was dissolved in THF (20 mL) and added to the cooled solution containing 4-methoxyphenyllithium and then allowed to warm to room temperature. The THF was removed under vacuum and the residue was dissolved in dichloromethane (40 mL) and washed with water (2×30 mL). The organic layer was dried over MgSO_4 and filtered. After removal of the solvent the crude product **9** was purified by flash column chromatography using silica gel (dichloromethane:hexane, 1:7) to give a colorless oil (0.47 g) in 95% yield.

4.2.5.2. Method B. 4-Methoxyphenylmagnesium bromide (1.0 mmol) was prepared in THF (10 mL) and reacted with the dichlorosilole **2** [15] (0.45 g, 1.0 mmol) at -78°C . Compound **9** was obtained in 13% yield after the same workup procedure as described in Method A.

4.2.5.3. Method C. Pyridinium tribromide, PyHBr_3 (0.34 g, 1.05 mmol) was dissolved in THF (8 mL) and added dropwise to a solution of **1** [15] (0.26 g, 0.5 mmol in 25 mL of THF) over 5 min at -78°C . The mixture was stirred at low temperature for 30 min and gradually warmed to ambient temperature over 8 h. The THF was removed under vacuum and the residue was dissolved in diethyl ether (30 mL), washed with water and brine (20 mL), dried over MgSO_4 , filtered, and condensed. The crude product **9** was purified as described in Method A to give a colorless oil (0.049 g) in 25% yield.

^1H NMR (CDCl_3): δ 7.07–7.03 (m, 6H, ArH), 6.84–6.81 (m, 4 H, ArH), 3.79 (t, $J = 6.8$ Hz, 4 H, CH_2), 1.71 (sextet, 4H, CH_2), 1.00 (t, $J = 7.4$ Hz, 6H, CH_3), -0.11 (s, 18H, SiMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 170.6, 142.3, 135.2, 128.6, 127.2, 126.5, 64.9, 26.1, 10.7, 0.5. $^{29}\text{Si}\{^1\text{H}\}$ NMR ($\text{DEPT}, \text{CDCl}_3$): δ -8.7 (SiOPr), -9.9 (SiMe_3). EI-MS: m/z (relative abundance, %) 494 (M^+ , 3), 393 (27), 235 (23), 219 (24), 163 (17), 159 (33), 135 (21), 133 (85), 75 (15), 73 (100). Anal. Calc. for $\text{C}_{28}\text{H}_{42}\text{O}_2\text{Si}_3$: C, 67.95; H, 8.55. Found: C, 68.14; H, 8.76%.

4.2.6. Bis(4-methoxyphenyl)bis(phenylethynyl)silane (**11**)

4-Methoxyphenylmagnesium bromide was prepared by treatment of 4-bromoanisole (3.40 g, 18.2 mmol) with magnesium (0.57 g, 24 mmol) in THF (30 mL) and filtered [22]. The filtrate was added to a silicon tetrachloride (1.39 g, 8.18 mmol) solution in hexane (35 mL). The mixture was kept at ca. 40°C during the addition and then heated at reflux overnight. Most of the solvent was removed under reduced pressure and the residue was washed with hexane (3×20 mL), the resulting slurry was filtered through celite. The filtrate was concentrated and subjected to a Kugelrohr distillation (180°C , 0.5 mmHg) to give bis(4-methoxyphenyl)dichlorosilane **10** (0.85 g, 2.7 mmol) in 33% yield as a colorless oil [26].

In a separate flask, phenylacetylene (0.55 g, 5.4 mmol) was diluted with diethyl ether (10 mL) and cooled to 0°C followed by dropwise addition of *n*-BuLi (2.5 M in hexane, 2.16 mL, 5.4 mmol) with vigorous stirring. After 1 h, the brown mixture was cooled to -78°C and the previously prepared diaryldichlorosilane **10** (0.85 g, 2.7 mmol) was dissolved in diethyl ether (10 mL) and added dropwise to the chilled solution (-78°C) containing the phenylethynyllithium. The mixture was gradually warmed to ambient temperature and stirred overnight. The solvent was removed under vacuum and the mixture was dissolved in dichloromethane (50 mL) and washed with water, then brine (35 mL). The organic layer was dried over MgSO_4 , filtered, and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (dichloromethane:hexane, 1:4) to afford bis(4-methoxyphenyl)bis(phenylethynyl)silane **11** in 76% yield (0.91 g) as a white solid. M.p. $142\text{--}143^{\circ}\text{C}$, which was recrystallized from dichloromethane–diethyl ether–pentane. ^1H NMR (CDCl_3): δ 7.83–7.80 (m, 4H, ArH), 7.62–7.59 (m, 4H, PhH), 7.39–7.33 (m, 6H, PhH), 7.01–

6.99 (m, 4 H, ArH), 3.85 (s, 6H, OCH₃). ¹³C{¹H} NMR (CDCl₃): δ 161.6, 136.7, 132.5, 129.3, 128.5, 124.4, 122.8, 114.1, 108.5, 88.6, 55.3. ²⁹Si{¹H} NMR (CDCl₃): δ -48.4. EI-MS: *m/z* (relative abundance, %) 444 (M⁺, 22), 208 (25), 207 (100), 191 (17), 129 (33), 73 (30), 59 (47). Anal. Calc. for C₃₀H₂₄O₂Si: C, 81.04; H, 5.44. Found: C, 80.82; H, 5.47%.

4.2.7. Attempted preparation of 1,1-bis(4-methoxyphenyl)-2,5-bis(trimethylsilyl)-3,4-diphenylsilacyclopentadiene: isolation of bis(4-methoxyphenyl)dipropoxysilane (**12**)

Lithium naphthalenide was prepared by stirring a mixture of lithium (28 mg, 4.0 mmol) and naphthalene (0.53 g, 4.1 mmol) in THF (8 mL) at room temperature for 6 h. A THF solution (10 mL) of **11** (0.44 g, 1.0 mmol) was added dropwise to the solution of lithium naphthalenide at -78 °C. The mixture was stirred for 1.5 h then trimethylchlorosilane (0.56 mL, 4.4 mmol) was added. After stirring at -78 °C for 10 min, the mixture was allowed to gradually warm to room temperature and stirred overnight. The volatiles were removed under vacuum then dry hexane (3 × 20 mL) was added to dissolve the product and the lithium salts were removed by filtration. After evaporation of hexane, the residue was condensed and subjected to Kugelrohr distillation (70 °C/0.1 mmHg) to remove naphthalene and other low boiling point components. The crude yellow product was subjected to flash column chromatography column using silica gel (dichloromethane:hexane, 1:10) to give a colorless oil of bis(4-methoxyphenyl)dipropoxysilane (**12**) in 42% yield (0.15 g). ¹H NMR (CDCl₃): δ 7.64–7.61 (m, 4H, ArH), 6.96–6.93 (m, 4H, ArH), 3.84 (s, 6H, OCH₃), 3.76 (t, 4 H, *J* = 6.5 Hz, OCH₂), 1.65 (m, 4H, OCH₂CH₂), 0.96 (t, *J* = 7.5 Hz, CH₂CH₃). ¹³C{¹H} NMR (CDCl₃): δ 161.4, 136.7, 113.9, 113.7, 64.9, 55.2, 25.9, 10.5. ²⁹Si{¹H} NMR (CDCl₃): δ -31.3. EI-MS: *m/z* (relative abundance, %) 360 (M⁺, 28), 301 (42), 259 (35), 253 (16), 244 (17), 243 (64), 223 (18), 211 (18), 197 (40), 195 (17), 193 (18), 169 (76), 168 (18), 153 (31), 152 (17), 149 (40), 148 (100), 139 (17), 121 (24), 108 (51), 77 (17). HR-MS (FAB, NBA+NaI): calcd for C₂₀H₂₈O₄Si, 360.1757. Found: M + Na = 383.1657.

4.2.8. 1,1-Dibromo-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (**13**)

A sample of 1,1-bis(diethylamino)-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (**1**) [15] (0.26 g, 0.50 mmol) was dissolved in 20 mL of dry diethyl ether and cooled to -78 °C. Bromine (51.4 μL, 1.0 mmol) was diluted with 5 mL of dry diethyl ether and added to the silole solution dropwise over 5 min. The resulting red solution was kept at low temperature for 10 min during which time the color of the solution became yellow and a white solid precipitated. The mixture was stirred at ambient temperature for another 30 min. The ether was removed under vacuum and the residue was dissolved in dry pentane (3 × 15 mL) and filtered. The solution was stored in the

refrigerator (-40 °C) for several days. Colorless crystals of 1,1-dibromo-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (**13**) were obtained in 52% yield (0.14 g). M.p. 137–138 °C. The crystals of **13** were suitable for X-ray crystallographic analysis. ¹H NMR (CDCl₃): δ 7.10–7.07 (m, 6 H, ArH), 6.87–6.83 (m, 4H, ArH), -0.01 (s, 18 H, SiMe₃). ¹³C{¹H} NMR (CDCl₃): δ 168.6, 140.1, 137.3, 128.5, 127.5, 127.3, 0.6. ²⁹Si{¹H} NMR (CDCl₃): δ: 4.9 (SiBr₂), -7.6 (SiMe₃). EI-MS: *m/z* (relative abundance, %) 523 (M⁺-15, 2), 521 (M⁺-15, 3), 519 (M⁺-15, 1), 456 (15), 454 (12), 441 (12), 439 (10), 245 (13), 159 (100), 129 (27), 73 (50). Anal. Calc. for C₂₂H₂₈Br₂Si₃: C, 49.25; H, 5.26. Found: C, 49.15; H, 5.36%.

4.2.9. 1-Bromo-4-bromodimethoxysilyl-1,4-bis(trimethylsilyl)-3,4-diphenyl-1,3-butadiene (**14**)

To a diethyl ether (35 mL) solution containing 1,1-dimethoxy-2,5-bis(trimethylsilyl)-3,4-diphenyl-1-silacyclopentadiene (**7**) (0.44 g, 1.0 mmol) was added a diethyl ether (5 mL) solution of bromine (51.4 μL, 1.0 mmol) at -78 °C. The resulting solution was kept at low temperature for 10 min. Then the mixture was stirred at ambient temperature for another 30 min. The ether was removed under vacuum and the residue was dissolved in dry pentane (3 × 20 mL) and the solution was filtered. The product, bromodimethoxy[4-bromo-2,3-diphenyl-1,4-bis(trimethylsilyl)butadienyl]silane (**14**) was isolated after cooling the pentane solution to -40 °C as a white crystalline solid suitable for X-ray crystallographic analysis in 77% yield (0.46 g). M.p. 105–109 °C. ¹H NMR (CDCl₃): δ 7.15–7.12 (m, 8H, ArH), 6.98–6.96 (m, 2H, ArH), 3.71 (s, 3H, OMe), 3.65 (s, 3H, OMe), 0.48 (s, 9H, SiMe₃), -0.073 (s, 9H, SiMe₃). ¹³C{¹H} NMR (CDCl₃): δ 169.8, 158.8, 142.8, 141.6, 138.2, 131.7, 130.0, 129.0, 128.3, 127.9, 127.6, 127.4, 52.8, 52.1, 2.3, 1.6. ²⁹Si{¹H} NMR (DEPT, CDCl₃): δ -0.4 (SiMe₃), -4.3 (SiMe₃), -44.7 (Si(O-Me)₂Br). HR-MS (EI): calcd for C₂₄H₃₄⁷⁹Br₂O₂Si₃, 596.0304. Found, 596.0240. EI-MS: *m/z* (relative abundance, %) 600 (M⁺, 11), 598 (M⁺, 19), 596 (M⁺, 9), 520 (18), 519 (45), 518 (21), 517 (37), 455 (27), 446 (21), 444 (19), 431 (31), 429 (28), 367 (19), 365 (100), 351 (19), 349 (17), 335 (23), 333 (18), 319 (30), 318 (15), 317 (34), 292 (27), 291 (19), 265 (15), 262 (15), 261 (55), 245 (30), 217 (18), 202 (40), 191 (75), 179 (24), 178 (15), 175 (16), 161 (19), 159 (70), 149 (19), 115 (21), 73 (95), 69 (17). Anal. Calc. for C₂₄H₃₄Br₂O₂Si₃: C, 48.16; H, 5.73. Found: C, 48.34; H, 5.78%.

4.2.10. X-ray structure determination of **13** and **14**

Crystals of appropriate dimension were obtained from pentane at -40 °C. Crystals for data collection were mounted on glass fibers in random orientations. Preliminary examination and data collection were performed using a Bruker Kappa Apex II Charge Coupled Device (CCD) Detector system single crystal X-Ray diffractometer equipped with an Oxford Cryostream LT device. All data were collected using graphite monochromated Mo K α radi-

ation ($\lambda = 0.71073 \text{ \AA}$) from a fine focus sealed tube X-ray source. Preliminary unit cell constants were determined with a set of 36 narrow frame scans. Typical data sets consist of combinations of ϖ and ϕ scan frames with typical scan width of 0.5° and counting time of 15–30 seconds/frame at a crystal to detector distance of 4.0 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. APEX II and SAINT software packages (Bruker Analytical X-Ray, Madison, WI, 2006) were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of xyz centroids harvested from the complete data set. Collected data were corrected for systematic errors using SADABS [36] based on the Laue symmetry using equivalent reflections.

Crystal data and intensity data collection parameters are listed in Table 2. Structure solution and refinement were carried out using the SHELXTL-PLUS software package [37]. The structures were solved by direct methods and refined successfully in the space groups, $C2/c$ and $P2_1/c$, respectively. Full matrix least-squares refinement was carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. All hydrogens were located and refined freely for **13** whereas all hydrogen atoms were treated using appropriate riding model (AFIX m3) for **14**. The $(\text{OMe})_2\text{SiBr}$ group found in compound **14** exhibits rotational disorder. The disorder was modeled using partial occupancies.

Crystal data and intensity data collection parameters, final residual values and structure refinement parameters, complete listings of positional and isotropic displacement coefficients for hydrogen atoms, and anisotropic displacement coefficients for the non-hydrogen atoms are listed as supplementary material. Tables of calculated and observed structure factors are available in electronic format in supplementary information.

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Appendix A. Supplementary material

CCDC 671353 and 671354 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.01.017](https://doi.org/10.1016/j.jorganchem.2008.01.017).

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