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Articles

Reactions of Lithium Silenolates with Acetylenes. Formation and Characterization of 2-Siladienes

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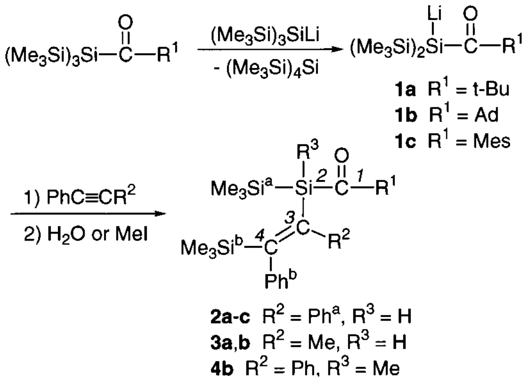
Treatment of lithium silenolates, $(Me_3Si)_2Si{=}C(OLi)R^1$ (**1**; R^1 = t-Bu, Ad, Mes), with phenyl-substituted acetylenes, $PhC{\equiv}CR^2$ (R^2 = Ph, Me), produced lithium ethenylsilenolates, $Ph(Me_3Si)C{=}CR^2(Me_3Si)Si{=}C(OLi)R^1$, cleanly. The ethenylsilenolates thus produced reacted readily with H_2O and MeI to give Si-substitution products in good yield. In contrast, they underwent O-silylation with Et_3SiCl to give 2-siladiene derivatives which were characterized by their NMR spectra.

There has been current interest in the chemistry of functionalized silyllithiums, whose reactions provide a direct method for the synthesis of functionalized organosilicon compounds.[1] In particular, the preparation and chemical behavior of α-heteroatom-substituted silyllithiums, including (alkoxysilyl)-,[2a,b] (aminosilyl)-,[2c−e] (hydrosilyl)-,[2f] and (trichlorosilyl)lithium,[2g] have been extensively studied.

Recently, we have demonstrated that the reactions of acyltris(trimethylsilyl)silanes with (tris(trimethylsilyl)silyl)lithium produce the corresponding lithium silenolates (**1** in Scheme 1) by replacement of a trimethylsilyl group by a lithium atom.[3] Lithium silenolates **1** are silicon analogues of lithium enolates and allow numerous transformations by interaction with electrophiles, leading to interesting organic silicon compounds, including silenes.[3,4] In this paper, we describe the reactions of lithium silenolates with phenyl-substituted acetylenes which produced lithium ethenylsilenolates by the addition of **1** across the acetylene triple bond, followed by a 1,3-trimethylsilyl shift. The formation of 2-siladienes from the reactions of the ethenylsilenolates with Et_3SiCl and their characterization by their NMR spectra are also described.

Scheme 1



Results and Discussion

Formation of Lithium Ethenylsilenolates. When lithium silenolates **1a**−**c** prepared as shown in Scheme 1 were treated with $PhC{\equiv}CPh$, and the resulting anionic species were hydrolyzed with water, acyl(ethenyl)hydrosilanes **2a**−**c** were obtained in good yield (Scheme 1 and Table 1). Similar reactions of **1a**,**b** with $PhC{\equiv}CMe$, followed by hydrolysis, produced products **3a**,**b**, respectively. Quenching the anionic species obtained from **1b** and $PhC{\equiv}CPh$ with MeI gave a methylated product (**4b**). These reactions proceeded with high stereoselectivity to give the *Z* isomer almost exclusively, except for **2b**, which was obtained as a mixture of the geometrical isomers with the ratio of *Z*/*E* = 88/12. With $PhC{\equiv}CMe$, regioselective addition of **1a**,**b** occurred and no products bearing the methyl group at the C4 position were detected in the reaction mixtures by both GLC and NMR spectrometric analysis.

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10.1021/om000851f CCC: $20.00

Table 1. Reactions of Lithium Silenolates with Acetylenes, Followed by Quenching with Electrophiles

silenolate (R^1)	R^2	electrophile	product	yield/%[a]
1a (t-Bu)	Ph	H_2O	**2a**	71 (82)
	Me	H_2O	**3a**	60 (78)
	H	H_2O	**7a**	45 (77)
	Ph	Et_3SiCl	**8a**	(71)
1b (Ad)	Ph	H_2O	**2b**	67 (71)
	Me	H_2O	**3b**	48 (90)
	Ph	MeI	**4b**	82 (85)
	Ph	Et_3SiCl	**8b**	(82)
1c (Mes)	Ph	H_2O	**2c**	43 (49)

[a] Isolated yield. Numbers in parentheses indicate the yields determined by the NMR analysis of the reaction mixture.

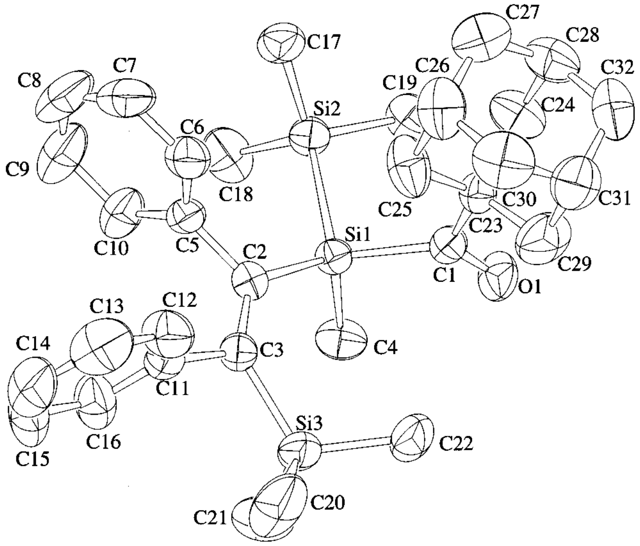


Figure 1. ORTEP drawing of a molecular fragment of compound **4b**. Protons are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Crystal Data, Experimental Conditions, and Summary of Structural Refinement for 4b

mol formula	$C_{32}H_{46}OSi_3$
mol wt	530.97
space group	$P2_1/c$
cell dimens	
a, Å	18.737(3)
b, Å	11.082(3)
c, Å	31.591(1)
β, deg	101.510(7)
V, Å^3	6428(1)
Z	8
D_{calcd}, Mg/m^3	1.097
F_{000}	2304.00
cryst size, mm^3	0.6 × 0.5 × 0.2
cryst color	light yellow
μ(Cu Kα), cm^{-1}	15.09
diffractometer	Rigaku AFC-6S
temp, K	298
wavelength, Å	1.5418 (Cu Kα)
monochromator	graphite cryst
scan type	$\omega-2\theta$
scan speed, deg/min	4
scan width, deg	$6 \le 2\theta \le 126.2$
no. of unique rflns	10 034
no. of obsd rflns ($I > 3\sigma(I)$)	5635
rfln/param ratio	8.7
R	0.062
R_w[a]	0.069

[a] The weighting scheme is $(\sigma(F_o)^2 + 0.0004|F_o|^2)^{-1}$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 4b, with Esd's in Parentheses

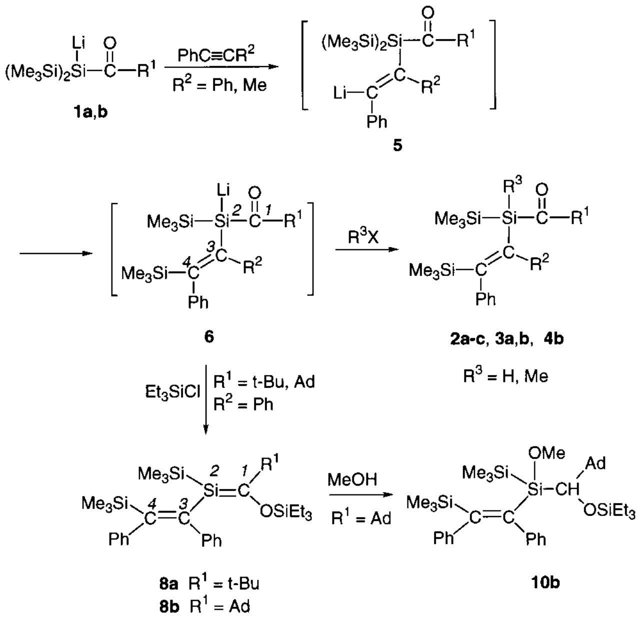
Si1−Si2	2.371(2)	Si3−C3	1.894(6)
Si1−C4	1.876(7)	C2−C3	1.358(7)
C1−C23	1.513(8)	Si1−C2	1.921(6)
C3−C11	1.506(8)	O1−C1	1.214(6)
Si1−C1	1.963(6)	C2−C5	1.488(8)
Si2−Si1−C1	104.0(2)	Si1−C2−C5	113.6(4)
C1−Si1−C2	119.1(2)	Si3−C3−C11	110.2(4)
Si1−C1−O1	113.8(5)	Si2−Si1−C4	104.2(2)
Si1−C2−C3	126.9(4)	C2−Si1−C4	111.1(3)
Si3−C3−C2	131.2(4)	O1−C1−C23	119.7(6)
Si2−Si1−C2	114.2(2)	C3−C2−C5	119.0(5)
C1−Si1−C4	102.7(3)	C2−C3−C11	118.5(5)
Si1−C1−C23	126.1(4)		

The structures of products **2**−**4** were verified mainly by their NMR spectra. For example, the sp^2 carbon signals of (*Z*)-**2b** appear at 150.7 and 163.0 ppm and at 243.3 ppm, which are at lower field than those of standard olefin and carbonyl carbons, respectively, and are characteristic of the silyl-substituted ones. The H−Si proton of (*Z*)-**2b** at 5.40 ppm couples with two silicon signals at −53.5 and −15.4 ppm in the $^{29}Si-^{1}H$ long-range COSY NMR spectrum, the latter of which couples also with a Me_3Si^a proton signal at 0.22 ppm in the same spectrum, indicating the existence of a Me_3Si^a-SiH unit in the molecule. In the $^1H-^1H$ NOESY spectrum, a cross-peak due to the coupling between the Me_3Si^b protons at 0.35 ppm and the H−Si proton is observed, in addition to those of $Me_3Si^a-Ph^a$ and $Me_3Si^b-Ph^b$, indicating that the ethenyl unit must have a *Z* geometry. On the other hand, one of the Me_3Si signals of (*E*)-**2b** at −0.12 ppm couples with both ortho protons of two phenyl groups in the NOESY spectrum, agreeing with the *E* geometry of the ethenyl unit. Furthermore, the crystal structure of **4b** was determined by an X-ray diffraction study. The asymmetric unit contains two crystallographically independent and essentially identical molecules. An ORTEP drawing of one of them is depicted in Figure 1. Cell dimensions, data collection and refinement parameters, and selected bond distances and angles for the molecular fragment are given in Tables 2 and 3. The structure has a highly crowded diphenyldisilylethene unit which is slightly twisted, as demonstrated by the torsion angles of Si1−C2−C3−Si3 = 2.9(9)° and C5−C2−C3−C11 = −4.5(9)°. The larger angles of Si1−C2−C3 (126.9(4)°) and Si3−C3−C2 (131.2(4)°) compared to those of C3−C2−C5 (119.0(5)°) and C2−C3−C11 (118.5(5)°) seem to result from the steric repulsion between two silyl groups. Rather long Si1−C1 (1.963(6) Å) and Si1−C2 (1.921(6) Å) bonds, relative to the standard Si−C bond length (e.g. Si1−C4 = 1.876(7) Å), would also reflect the steric repulsion between the substituents attached to the Si1 atom.

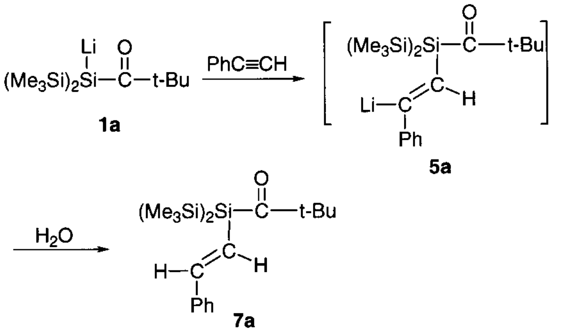
The formation of the products can be best explained as shown in Scheme 2, including the addition of silenolates **1** to acetylenes, giving ethenyllithium intermediates **5** which undergo a 1,3-silyl shift to produce ethenylsilenolates **6**. Presumably, delocalization of the anionic charge over the Si−C═O fragment in ethenylsilenolates **6** (vide infra) and reduction of the steric repulsion between the sterically bulky acylbis(trimethylsilyl)silyl unit and the R^2 group provide the driving force for the 1,3-silyl shift, leading to the formation of intermediates **6** from **5**.

The reaction of **1a** with PhC≡CH under the same conditions, followed by hydrolysis, gave compound **7a**

Scheme 2



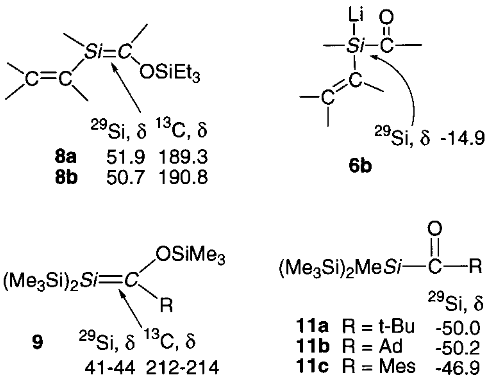
Scheme 3



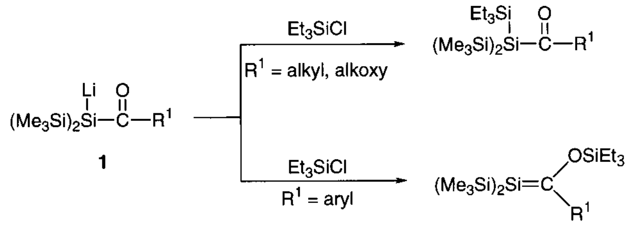
(Scheme 3). No product analogous to **2a** and **3a** was found to be formed by ^{1}H NMR analysis of the reaction mixture. In this reaction, the steric repulsion in the intermediate **5a** would be too small to promote the 1,3-silyl shift, leading to the formation of an intermediate analogous to **6**. The formation of **7** again proceeded regio- and stereoselectively, and only one isomer was obtained. The geometry of the ethenyl unit in **7a** was confirmed by the coupling constant of 14.9 Hz for the trans olefin protons. Lithium silenolates **1** did not react with 4-octyne.

Formation of 2-Siladienes. Ethenylsilenolates **6a**,**b** reacted readily with Et$_3$SiCl to give 2-siladienes (**8a**,**b**) by O-silylation, as shown in Scheme 2. The yields of **8** were estimated on the basis of the intensity ratios in the ^{13}C NMR signals of the reaction mixtures as listed in Table 1. The ^{29}Si NMR spectra of **8** show the silene silicon signals around 50 ppm, which is slightly low-field-shifted from those reported for Brook type silenes **9** (Chart 1) (41−44 ppm).[5] The silene carbon signals appeared at approximately 20 ppm higher field than those of **9** (212−214 ppm).[5] However, the chemical shifts of the ethenyl carbons of **8** are almost the same values as those of ethenylsilane derivatives **2**−**4**, indicating the $\pi-\pi$ conjugation in the present 2-siladiene system does not take place to a significant extent. The steric repulsion between the bulky substituents seems to prevent the siladiene system from retaining high coplanarity.

Chart 1



Scheme 4



The formation of **8** proceeded with complete stereoselectivity, and 2-siladienes **8** were obtained as the single isomer. Saturation of methylene protons of the Et$_3$SiO unit in the NOE-FID experiment of **8b** led to strong enhancement of both of two doublets due to the ortho protons of the phenyl groups at 6.88 and 7.11 ppm, clearly indicating the *E* geometry of the silene unit. The formation of **8b** was confirmed also by a trapping experiment with methanol, giving **10b** in 46% isolated yield (Scheme 2).

Previously, we have demonstrated that lithium silenolates **1** react with Et$_3$SiCl to give products arising from Si or O substitution exclusively, depending on the nature of the substituent on the carbonyl carbon atom (Scheme 4). As shown in Scheme 4, lithium silenolates **1** having an aryl group on the carbonyl carbon afford O-silylation products,[3a,b] while silenolates **1** with an alkyl[3b] or alkoxy[3c] substituent give Si-silylation products. In the present reactions, however, **6a**,**b** gave O-silylation products with Et$_3$SiCl, despite the fact that the carbonyl carbon is substituted with an alkyl group.

NMR Spectroscopic Studies of Ethenylsilenolate 6b. Ethenylsilenolate **6b** (R^1 = Ad, R^2 = Ph) obtained from the reaction of **1b** and PhC≡CPh could be directly analyzed by the NMR spectra of the reaction mixture. Generally, replacement of a methyl group in permethyloligosilanes with a lithium atom leads to an approximately 100 ppm high-field shift of the adjacent silicon signal.[1b] In contrast, the center silicon signal of **6b** appears at −14.9 ppm, about 15 ppm to lower field from that of the methylated compound **4b** (−29.7 ppm), indicating high sp^2 character of this silicon atom that arises from delocalization of the anionic charge over the Si−C−O fragment, due to a hybrid of resonance structures **6b-1** and **6b-2** (Scheme 5). Similar delocalization of the anionic charge has been observed for silenolates **1a**−**c**. However, the center silicon signals of **1a**−**c** resonate at −70,3, −70.5, and −59.9 ppm, respectively,

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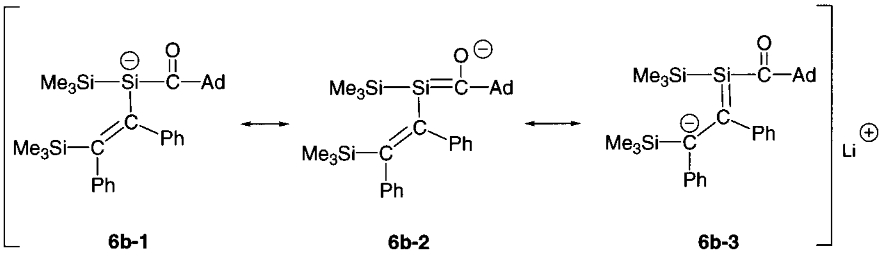
[5] Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, *39*, 71.

Scheme 5



which are shifted to high field from the methylated compounds (**11a**−**c** in Chart 1) by about 20 ppm for **1a**,**b** and 13 ppm for **1c**, in marked contrast to **6b**. These results clearly indicate the higher sp^2 character of the center silicon in **6b** than in **1a**−**c**, and hence, the anionic charge of **6b** seems to be more localized on the oxygen atom than in **1a**,**b**, in accordance with the different chemical behavior of **6a**,**b** toward Et_3SiCl from that of **1a**,**b**, as described above.

The ^{13}C signals of the ethenyl carbons in **6b** were low-field-shifted from those of **4b** only slightly (see Experimental Section), suggesting that the resonance structure of **6b-3** contributes little to the electronic state of **6b**. This may be due to the lack of coplanarity between the ethenyl and silenolate units, as described for 2-siladienes **8a**,**b**.

Interestingly, the NMR spectra reveal only one set of signals due to the single stereoisomer of **6b**. No changes in the NMR spectra depending on the temperature were observed in the temperature range of −80 to 25 °C. This may be explained by either free rotation around the C1−Si2 bond in the temperature range or the absence of rotation of this bond on the NMR time scale giving the single stereoisomer. Previously, we have demonstrated that the temperature-dependent NMR spectra of silenolates **1a**,**b** having an alkyl group on the carbonyl carbon exhibit free rotation around the center Si−C(=O) bond in the NMR time scale even at −80 °C, while those of **1c** with a mesityl group indicate the restricted rotation of this bond, and the two Me_3Si proton signals of **1c** which appear separately at low temperature coalesce around room temperature.[3b] The rotation barrier was calculated to be $\Delta G^{\ddagger}_{TC} = 14.3$ kcal/mol on the basis of the temperature-dependent ^1H NMR spectra. When the higher sp^2 character of the center silicon in **6b** relative to those of **1a**−**c**, indicated by the lower-field shifted center silicon signal of **6b**, is taken into account, it is most likely that the absence of temperature dependence of the NMR profile of **6b** can be ascribed to the frozen rotation of the C1−Si2 bond on the NMR time scale, due to the contribution of resonance structure **6b-2**, although we have not yet obtained any evidence to confirm the stereochemistry of **6b**. The stereoselective formation of 2-siladienes **8b** from the reactions of **6b** seems to also support the absence of rotation with respect to the C1−Si2 bond at the reaction temperature (−80 °C).

In conclusion, the chemistry described above indicates that the reactions of lithium silenolates with phenyl-substituted acetylenes lead to the clean formation of lithium ethenylsilenolates. The ethenylsilenolates reacted readily with electrophiles to give ethenyl-substituted acylpolysilanes and 2-siladienes. Although linear siladienes have received much attention as the simplest conjugated silenes,[5−7] this is the first synthesis of 2-siladienes that have been wholly characterized by the NMR spectra.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of purified argon. Mass spectra were measured on a Hitachi M-80B spectrometer. NMR spectra were recorded on JEOL EX-270 and Lambda-400 spectrometers using tetramethylsilane as an internal standard. IR spectra were measured on a Perkin-Elmer FT1600 spectrophotometer.

Materials. THF was dried over sodium−potassium alloy and distilled just before use. Lithium silenolates **1** were prepared as described previously and used without purification.[3b] (Tris(trimethylsilyl)silyl)lithium was prepared by the reaction of tetrakis(trimethylsilyl)silane and methyllithium as reported in the literature and used without purification.[8]

Reactions of 1a−c with Acetylenes Followed by Quenching with H_2O or MeI. A sample procedure is as follows. To a solution of **1a** prepared from 0.198 g (0.60 mmol) of pivaloyltris(trimethylsilyl)silane and an equimolar amount of (tris(trimethylsilyl)silyl)lithium in 1.3 mL of THF was added 0.107 g (0.60 mmol) of diphenylacetylene at −40 °C. The mixture was stirred overnight at this temperature and hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was analyzed directly by the NMR spectra as being **2a** (82% yield). Product **2a** was separated from the mixture by silica gel chromatography with hexane/ethyl acetate (50/1) as eluent, followed by submitting the resulting crude compound to preparative GPC, with benzene as eluent (71% isolated yield): MS *m*/*z* 353 (M^+ − t-BuCO); ^1H NMR (δ in C_6D_6) 0.21 (s, 9H, Me_3Si), 0.33 (s, 9H, Me_3Si), 1.14 (s, 9H, t-Bu), 5.36 (s, 1H, SiH), 6.78−7.12 (m, 10H, Ph); ^{13}C NMR (δ in C_6D_6) −0.4 (Me_3Si), 1.9 (Me_3Si), 25.2, 49.8 (t-Bu), 125.1, 125.8, 127.7, 128.0, 128.3, 129.1, 144.6, 146.0 (Ph), 150.7, 163.1 (C=C), 243.0 (C=O); ^{29}Si NMR (δ in C_6D_6) −53.9 (center Si), −15.9, −6.6 (Me_3Si); IR ν_{Si-H} 2133 cm^{-1}, $\nu_{C=O}$ 1632 cm^{-1}. Anal. Calcd for $C_{25}H_{38}OSi_3$: C, 68.42; H, 8.73. Found: C, 68.39; H, 8.77.

The other reactions of **1a**−**c** with acetylenes were carried out in a fashion similar to that above, and the results are summarized in Table 1. The NMR yields were determined on

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the basis of integration ratios of trimethylsilyl protons of the products and those of tetrakis(trimethylsilyl)silane which was quantitatively formed from the reactions of acylpolysilanes with (tris(trimethylsilyl)silyl)lithium for the preparation of **1a**−**c**.

Data for **3a**: MS *m*/*z* 361 ($M^+ - Me$); ^1H NMR (δ in C_6D_6) 0.23 (s, 9H, Me_3Si), 0.30 (s, 9H, Me_3Si), 1.13 (s, 9H, t-Bu), 1.92 (s, 3H, Me), 5.24 (s, 1H, SiH), 6.80 (dd, 2H, $J = 7.78$, 0.09 Hz, *o*-Ph), 7.06 (br t, 1H, $J = 7.25$, *p*-Ph), 7.16−7.24 (m, 2H, *m*-Ph); ^{13}C NMR (δ in C_6D_6) −0.7 (Me_3Si), 1.8 (Me_3Si), 22.3 (Me), 24.9, 50.1 (t -Bu), 125.5, 126.8, 128.6, 143.9 (Ph), 146.8, 160.8 (C=C), 244.2 (C=O); ^{29}Si NMR (δ in C_6D_6) −55.7 (center Si), −16.4, −8.2 (Me_3Si); IR ν_{Si-H} 2142 cm^{-1}, $\nu_{C=O}$ 1633 cm^{-1}. Anal. Calcd for $C_{20}H_{36}OSi_3$: C, 63.75; H, 9.63. Found: C, 63.79; H, 9.64.

Data for **7a**: exact MS calculated for $C_{19}H_{34}OSi_3$ (M^+) 362.1915, observed 362.1915; ^1H NMR (δ in C_6D_6) 0.19 (s, 18H, Me_3Si), 1.08 (s. 9H, t-Bu), 6.26, 7.29 (d, total 2H, $J = 14.9$ Hz, olefin), 6.99−7.28 (m, 5H, Ph); ^{13}C NMR (δ in C_6D_6) 0.43 (Me_3Si), 25.5, 49.7 (t-Bu), 125.2, 128.2, 128.5, 128.7 (Ph), 140.0, 146.6 (C=C), 248.3 (C=O); ^{29}Si NMR (δ in C_6D_6) −52.6 (center Si), −12.6 (Me_3Si); IR $\nu_{C=O}$ 1620 cm^{-1}.

Data for (*Z*)-**2b**: exact MS calculated for $C_{31}H_{44}SiO_3$ (M^+) 516.2697, observed 516.2697 (as the *Z*/*E* mixture); ^1H NMR (δ in C_6D_6) 0.22 (s, 9H, Me_3Si), 0.35 (s, 9H, Me_3Si), 1.62−1.69 (m, 9H, Ad), 1.79 (br d, 3H, $J = 7.5$ Hz, Ad), 2.00 (s, 3H, Ad), 5.40 (s, 1H, SiH), 6.63 (d, 2H, $J = 7.5$ Hz, *o*-Ph[a]), 6.68 (dd, 2H, $J = 7.7$, 1.4 Hz, *o*-Ph[b]), 6.79−6.91 (m, 6H, Ph); ^{13}C NMR (δ in C_6D_6) −0.3 (Me_3Si), 2.0 (Me_3Si), 28.2, 36.9, 37.6, 52.6 (Ad), 124.5, 125.1, 127.0, 127.5, 128.2, 128.6, 144.0, 145.6 (Ph), 150.7, 163.0 (C=C), 243.3 (C=O); ^{29}Si NMR (δ in C_6D_6) −54.5 (center Si), −15.4, −6.1 (Me_3Si); IR ν_{Si-H} 2129 cm^{-1}, $\nu_{C=O}$ 1633 cm^{-1} (as the *Z*/*E* mixture). Anal. Calcd for $C_{31}H_{44}OSi_3$: C, 72.03; H, 8.58. Found: C, 72.07; H, 8.58 (as the *Z*/*E* mixture). Data for (*E*)-**2b**: ^1H NMR (δ in C_6D_6) −0.12 (s, 9H, Me_3Si), 0.05 (s, 9H, Me_3Si), 4.54 (s, 1H, SiH), Ad and Ph signals overlap with those of the *Z* isomer; ^{13}C NMR (δ in C_6D_6) −0.5 (Me_3Si), 0.6 (Me_3Si), 28.2, 36.9, 37.8, 52.3 (Ad), 126.2, 126.8, 127.7−129.2, 145.7, 146.9 (Ph), 152.3, 163.5 (C=C), 245.0 (C=O); ^{29}Si NMR (δ in C_6D_6) −61.2 (center Si), −16.0, −6.1 (Me_3Si).

Data for **3b**: exact MS calculated for $C_{25}H_{39}OSi_3$ ($M^+ - Me$) 439.2306, observed 439.2283; ^1H NMR (δ in C_6D_6) 0.25 (s, 9H, Me_3Si), 0.33 (s, 9H, Me_3Si), 1.62−1.69 (m, 5H, Ad), 1.85−1.98 (m, 10H, Ad), 1.89 (s, 3H, Me), 5.29 (s, 1H, SiH), 6.81 (t, 2H, $J = 8.0$ Hz, Ph), 7.07 (t, 1H, $J = 7.4$ Hz, Ph), 7.17−7.23 (m, 2H, Ph); ^{13}C NMR (δ in C_6D_6) −0.5 (Me_3Si), 1.9 (Me_3Si), 22.5 (Me), 28.4, 37.0, 37.3, 52.9 (Ad), 125.5, 126.8, 128.6, 144.2 (Ph), 146.8, 160.5 (C=C), 244.3 (C=O); ^{29}Si NMR (δ in C_6D_6) −57.1 (center Si), −16.4, −8.2 (Me_3Si); IR ν_{Si-H} 2143 cm^{-1}, $\nu_{C=O}$ 1622 cm^{-1}. Anal. Calcd for $C_{26}H_{42}OSi_3$: C, 68.65; H, 9.31. Found: C, 68.67; H, 9.33.

Data for **4b**: colorless crystals; mp 107 °C; MS *m*/*z* 530 (M^+); ^1H NMR (δ in C_6D_6) 0.03 (s, 9H, Me_3Si), 0.23 (s, 9H, Me_3Si), 0.68 (s, 3H, Me), 1.71 (s, 6H, Ad), 2.03−2.15 (m, 9H, Ad), 6.73−6.81 (m, 5H, Ph), 6.91−6.97 (m, 5H, Ph); ^{13}C NMR (δ in C_6D_6) −0.6 (Me_3Si), −0.2 (Me), 1.4 (Me_3Si), 28.6, 37.1, 39.1, 52.2 (Ad), 125.0, 125.1, 127.3, 127.7, 128.3, 128.5, 145.5, 147.3 (Ph), 153.9, 162.2 (C=C), 247.1 (C=O); ^{29}Si NMR (δ in C_6D_6) −29.7 (center Si), −15.9, −6.4 (Me_3Si); IR $\nu_{C=O}$ 1627 cm^{-1}. Anal. Calcd for $C_{32}H_{46}OSi_3$: C, 72.39; H, 8.73. Found: C, 72.27; H, 8.95.

Data for **2c**: MS *m*/*z* 500 (M^+); ^1H NMR (δ in C_6D_6) 0.16 (s, 9H, Me_3Si), 0.32 (s, 9H, Me_3Si), 2.07 (s, 3H, Mes), 2.17 (s, 6H, Mes), 5.34 (s, 1H, SiH), 6.58 (s, 2H, Mes ring H), 6.73−6.97 (m, 10H, Ph); ^{13}C NMR (δ in C_6D_6) −0.8 (Me_3Si), 1.9 (Me_3Si), 19.6, 20.9 (Mes), 125.2, 125.7, 127.9, 128.1, 128.6, 128.7, 129.0, 132.4, 138.2, 144.7, 145.4, 145.8 (Ph and Mes), 149.8, 164.5 (C=C), 244.3 (C=O); ^{29}Si NMR (δ in C_6D_6) −47.3 (center Si), −15.2, −6.0 (Me_3Si); IR ν_{Si-H} 2129 cm^{-1}, $\nu_{C=O}$ 1605 cm^{-1}. Anal. Calcd for $C_{30}H_{40}OSi_3$: C, 71.94; H, 8.05. Found: C, 72.01; H, 8.20.

Reactions of 1a,b with $PhC\equiv CPh$ Followed by Quenching with Et_3SiCl. To a solution of **1a** prepared from 0.300 g (0.90 mmol) of pivaloyltris(trimethylsilyl)silane and an equimolar amount of (tris(trimethylsilyl)silyl)lithium in 2 mL of THF-d_8 was added 0.180 g (1.01 mmol) of $PhC\equiv CPh$ at −40 °C. The mixture was stirred overnight at this temperature. Then to it was added 0.179 g (1.2 mmol) of Et_3SiCl at −40 °C. The mixture was stirred at room temperature and analyzed directly by the ^1H NMR spectra as being **8a** (71% yield). Data for **8a**: ^1H NMR (δ in 20% THF + 80% THF-d_8) −0.05−0.03 (Me_3Si), 0.44−0.81 (Et_3Si), 6.79−7.48 (Ph), t-Bu signal overlaps with those of excess Et_3SiCl; ^{13}C NMR (δ in 20% THF + 80% THF-d_8) 2.0 (Me_3Si), 2.5 (Me_3Si), 7.3, 7.9 (Et_3Si), 30.5, 41.6 (t-Bu), 125.9, 127.5, 128.4, 129.1, 131.5, 132.2, 145.6, 146.6 (Ph), 151.8, 161.7 (C=C), 189.3 (Si=C); ^{29}Si NMR (δ in 20% THF + 80% THF-d_8) −11.0, −5.7 (Me_3Si), 14.6 ($OSiEt_3$), 51.9 (Si=C).

The preparation of **8b** was carried out in a fashion similar to that above. Data for **8b**: ^1H NMR (δ in THF-d_8) 0.23, 0.26 (Me_3Si), 0.79 (q, $J = 7.7$ Hz, H_2CSi), 1.01−1.11 (m, H_3C-Et), 1.64−2.00 (Ad), 6.88 (d, $J = 7.3$ Hz, o-Ph), 7.11 (d, $J = 6.9$ Hz, o-Ph), 6.83−7.48 (Ph); ^{13}C NMR (δ in THF-d_8) 2.0, 2.4 (Me_3Si), 6.9, 7.8 ($SiEt_3$), 29.7, 37.8, 42.8, 43.7 (Ad), 125.7, 127.4, 128.3, 128.8, 131.4, 145.7, 146.5 (Ph), 151.9, 161.6 (C=C), 190.8 (Si=C); ^{29}Si NMR (δ in THF-d_8) −13.7, −7.7 (Me_3Si), 12.71 ($OSiEt_3$), 50.7 (Si=C).

^1H NMR spectra of **8a**,**b** reveal broad signals overlapping with the resulting $(Me_3Si)_4Si$ and excess $PhC\equiv CPh$ and Et_3SiCl. We, therefore, could not determine reliable integration ratios of the signals. However, the approximate ratios are in agreement with the proposed structures. The NMR yields were determined on the basis of intensity ratios of trimethylsilyl carbons of the siladienes and those of tetrakis(trimethylsilyl)silane which was quantitatively formed from the reactions of acylpolysilanes with (tris(trimethylsilyl)silyl)lithium for the preparation of **1a**,**b**.

For the methanolysis of **8b**, to the mixture containing **8b** was added 2.0 mL of methanol at −40 °C. The mixture was warmed to room temperature. After hydrolysis with water, the organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on GPC with benzene as eluent to give product **10b** in 46% yield in pure form. Data for **10b**: MS *m*/*z* 662 (M^+); ^1H NMR (δ in C_6D_6) 0.27 (s, 9H, Me_3Si), 0.37 (s, 9H, Me_3Si), 0.86 (q, 6H, $J = 7.5$ Hz, H_2CSi), 1.10 (t, 9H, $J = 7.7$ Hz, H_3C Et), 1.75−2.00 (m, 12H, Ad), 2.11, (s, 3H, Ad), 3.55 (s, 3H, MeO), 3.82 (s, 1H, $HCOSiEt_3$), 6.80 (t, 1H, $J = 7.4$ Hz, Ph), 6.96 (t, 2H, $J = 7.2$ Hz, Ph), 7.17 (d, 2H, $J = 8.0$ Hz, Ph), 6.75−7.03 (m, 5H, Ph); ^{13}C NMR (δ in C_6D_6) 1.6, 2.7 (Me_3Si), 6.6, 7.7 ($SiEt_3$), 29.2, 37.4, 39.4, 40.6 (Ad), 52.2, (MeO), 80.6, ($CHOSiEt_3$), 124.8, 125.6, 127.3, 130.9, 143.9, 147.3 (Ph, 2 carbons are overlapping), 156.1, 160.0 (C=C); ^{29}Si NMR (δ in C_6D_6) −20.3, −6.9 (Me_3Si), 2.0 (SiOMe), 17.7 ($OSiEt_3$); IR ν_{Si-O} 1094 cm^{-1}. Anal. Calcd for $C_{38}H_{62}O_2Si_4$: C, 68.82; H, 9.42. Found: C, 68.52; H, 9.57.

NMR Measurement of 6b. To a solution of **1b** prepared from 0.501 g (1.22 mmol) of adamantoyltris(trimethylsilyl)silane and an equimolar amount of (tris(trimethylsilyl)silyl)lithium in 2 mL of THF-d_8 was added 0.217 g (1.22 mmol) of $PhC\equiv CPh$ at −40 °C. The mixture was stirred overnight at this temperature. Data for **6b**: ^1H NMR (δ in THF-d_8) 0.11, 0.19 (Me_3Si), 1.75−2.10 (Ad), 6.33−7.48 (Ph); ^{13}C NMR (δ in THF-d_8) 3.7 (Me_3Si), 3.9 (Me_3Si), 30.1, 38.4, 41.2, 48.4 (Ad), 123.4, 124.1, 127.3, 128.9, 129.6, 148.8, 152.3 (Ph), 155.6, 167.9 (C=C), 256.6 (C=O); ^{29}Si NMR (δ in THF-d_8) −14.9 (center Si), −10.7, −1.2 (Me_3Si).

X-ray Crystallographic Analysis of 4b. The structure was solved by SIR92 direct methods.[9] The non-hydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber.[10] Anomalous dispersion effects were included in F_c;[11] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[12] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[13] All calculations were performed using the teXsan[14] crystallographic software package of Molecular Structure Corp. Neither absorption nor decay correction was applied.

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Supporting Information Available: A full ORTEP drawing and tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compound **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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