Formation and Reactions of Lithium Ester Silenolates: Silicon Analogues of Lithium Ester Enolates

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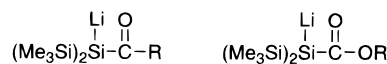
Treatment of cyclohexyl, adamantyl, and benzyl tris(trimethylsilyl)silanecarboxylates with tris(trimethylsilyl)silyllithium afforded the corresponding lithium ester silenolates by Li– Me₃Si exchange. The lithium ester silenolates thus prepared reacted readily with electrophiles including water, alkyl halides, and chlorosilanes to produce Si-substituted products. Oxidative coupling of the lithium ester silenolates with palladium dichloride gave polysilane-1,2-dicarboxylates. With mesitaldehyde, a lithium ester silenolate produced products arising from addition of the ester silenolate across the carbonyl bond of the aldehyde.

Introduction

There has been current interest in the preparation of functionalized silyllithiums, which are potentially useful for the synthesis of various organosilicon compounds.[1,2] In the course of our studies concerning the chemical behavior of acylpolysilanes toward organolithium reagents,[3] we have demonstrated that the reactions of acyltris(trimethylsilyl)silanes with tris-(trimethylsilyl)silyllithium give the corresponding lithium silenolates (**1**, Chart 1) by replacement of a trimethyl-silyl group with lithium, if the acylpolysilane has no enolizable protons and contains a sterically bulky group on the carbonyl carbon atom.[4] Lithium silenolates **1** are silicon analogues of lithium enolates and react readily with electrophiles such as water, alkyl halides, and chlorosilanes to give substitution products.[4,5] They react also with dienes[6] and carbonyl compounds[7] to give the addition products. Oxidative coupling of **1** with palladium dichloride leads to the formation of bis(acyl)-polysilanes as the first example of polysilanes with two Si–acyl bonds in a molecule.[8]

Recently, we have reported that the reaction of methyl tris(trimethylsilyl)silanecarboxylate, (Me₃Si)₃SiCO₂Me, with tris(trimethylsilyl)silyllithium gives tetrakis(tri-

Chart 1

$$\text{(Me}_3\text{Si)}_2\overset{\overset{\text{Li}}{|}}{\text{Si}}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{R} \qquad \text{(Me}_3\text{Si)}_2\overset{\overset{\text{Li}}{|}}{\text{Si}}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{OR}$$

1 R = alkyl or aryl   **2**

methylsilyl)silane in 63% yield as the sole volatile product, indicating that abstraction of a trimethylsilyl group occurs.[9] However, all attempts to trap the lithium ester silenolate (**2**, Chart 1, R = Me), which must be produced simultaneously with tetrakis(trimethylsilyl)-silane, with chlorosilanes, water, and methyl iodide have been unsuccessful. This is probably due to oligo-merization of **2** (R = Me), giving nonvolatile products under the reaction conditions.

In this paper, we report the successful synthesis of silicon analogues of lithium ester enolates with a bulkier alkyl group on the ester oxygen of **2** (R = Cy, Ad, CH₂-Ph). The enolates **2** are moderately stable in solution and can be detected by NMR spectroscopy and trapping experiments.

Results and Discussion

Synthesis of Lithium Ester Silenolates. The starting tris(trimethylsilyl)silanecarboxylates (**3a–c**) were prepared as shown in Scheme 1. Thus, the reaction of tris(trimethylsilyl)silanecarboxylic acid and cyclohexanol afforded cyclohexyl tris(trimethylsilyl)silanecarboxylate (**3a**), while adamantyl and benzyl tris(trimethylsilyl)silanecarboxylate (**3b,c**) were obtained by the reactions of tris(trimethylsilyl)silyllithium with the respective haloformates. Attempted preparation of compound **3c** by esterification of tris(trimethylsilyl)silanecarboxylic acid with benzyl alcohol was unsuccessful. In this reaction, benzyl tris(trimethylsilyl)silyl ether, which would arise from decarbonylation of **3c** under the reaction conditions, was obtained as the sole volatile product.

The reactions of **3a–c** with 1 molar equiv of tris-(trimethylsilyl)silyllithium in THF at −80 °C, followed

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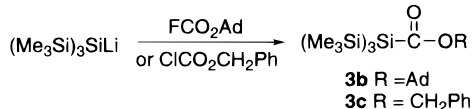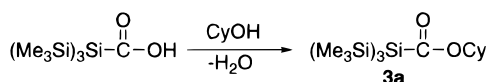
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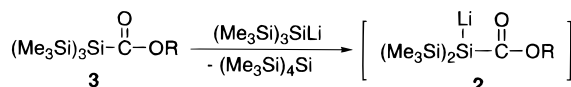
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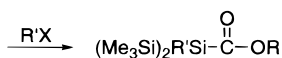
Scheme 1

Scheme 2

by addition of triethylchlorosilane, gave the corresponding (triethylsilyl)bis(trimethylsilyl)silanecarboxylates (**4a**−**c**) in 77−82% isolated yield, along with an almost quantitative yield of tetrakis(trimethylsilyl)silane. The formation of these products suggested that the lithium ester silenolates **2a**−**c** had been formed initially (Scheme 2).

Results of the reactions of **2a**−**c** with other electrophiles are summarized in Table 1. The isolated yields of the products were lower than those determined by GLC analysis of the reaction mixtures, which may be ascribed to decomposition of the products during purification. All reactions gave Si-substituted products in high yields, and no O-substituted products were detected by either GLC or spectrometric analysis of the reaction mixtures. Previously we have demonstrated that lithium silenolates **1** react with triethylchlorosilane to give products arising from Si- or O-substitution exclusively, depending on the nature of the substituent on the carbonyl carbon atom (Scheme 3). As shown in Scheme 3, lithium silenolates **1** having an aryl group on the carbonyl carbon afford O-silylation products, while silenolates **1** with an alkyl substituent give Si-silylation products. On the other hand, in the present reactions of **2a**−**c**, no O-silylation, which would give silicon analogues of ketene silyl acetal, was involved even with sterically bulky chlorosilanes, such as *tert*-butyldimethylchlorosilane and triphenylchlorosilane. We also carried out the reaction of **2a** with tributyltin chloride, again in the hope of obtaining O-substitution products. However, this reaction gave a complex mixture from which no major products could be isolated.

Lithium ester silenolates **2a**−**c** are fairly stable at −80 °C, but slowly decompose to give nonvolatile products even at this temperature. Of these, **2b** was most stable, probably due to kinetic stabilization by the sterically bulky adamantyl group. It could be characterized by ^{13}C and ^{29}Si NMR spectroscopy (see Experimental Section). As shown in Table 2, the NMR signal of the central silicon atom is high-field shifted by about 35 ppm from the starting carboxylate **3b**. This is in

Table 1. Reactions of Lithium Ester Silenolates with Electrophiles

ester (silenolate)	electrophile	product	yield/%[a]
3a (**2a**)	Et$_3$SiCl	**4a**	78 (92)
	t-BuMe$_2$SiCl	**5a**	81 (96)
	Ph$_3$SiCl	**6a**	55
	H$_2$O	**7a**	52 (95)
	MeI	**8a**	86 (97)
	i-BuBr	**9a**	83 (90)
3b (**2b**)	Et$_3$SiCl	**1b**	82 (90)
	H$_2$O	**7b**	56 (95)
	MeI	**8b**	73 (98)
3c (**2c**)	Et$_3$SiCl	**4c**	77 (96)

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

Scheme 3

Table 2. ^{29}Si NMR Spectral Data for the Central Silicon Atom of 2b, 3b, and Related Compounds in THF

compound	δ	compound	δ
2b	−118.0	**3b**	−82.6
1[a]		(Me$_3$Si)$_3$SiCOR[a]	
R = Mes	−59.9		−75.3
R = Ad	−70.5		−79.0
R = t-Bu	−70.3		−79.6
(Me$_3$Si)$_3$SiLi[b,c]	−185.4	(Me$_3$Si)$_4$Si[b,c]	−135.5
(Me$_3$Si)$_2$MeSiLi[b]	−133.5	(Me$_3$Si)$_3$MeSi[b]	−88.1

[a] See ref 4. [b] See ref 1b. [c] In benzene.

contrast to lithium silenolates **1**, whose central silicon signals appear at slightly lower fields than those of the respective acylpolysilanes, (Me$_3$Si)$_3$SiCOR.[4] Presumably, the anionic charge in **2b** is more localized on the silicon atom relative to **1**, compatible to the fact that no O-substitution products were produced on treatment of **2a**−**c** with electrophiles. However, the high-field shift is smaller than those of permethyloligosilanyllithiums from the respective oligosilanes shown in Table 2; that is, replacement of a trimethylsilyl group of the oligosilanes with a lithium atom leads to large high-field shifts of 45−50 ppm.[1b] This suggests that the central Si−C bond of **2b** still possesses sp^2 character to some extent.

Oxidative Coupling of Lithium Ester Silenolates 2a,b. When **2a** was treated with 0.5 equiv of palladium dichloride in THF at −80 °C, polysilanedicarboxylate **10a** and polysilanemonocarboxylate **11a** were obtained in 12% and 7% isolated yield, respectively, as shown in Scheme 4. Similarly, treatment of **2b** with palladium dichloride gave **10b** and **11b** in 17% and 8% isolated yield, respectively. Rather low isolated yields of products **10a,b** may be ascribed to decomposition of the products during purification, especially on treating them with preparative GPC. In fact, the ^{1}H NMR spectrum of the reaction mixture of **2a** and palladium dichloride showed that product **10a** had been formed in 57% yield. Monoesters **11a,b** may be produced by oxidative coupling of **2a,b** with an excess of the tris(trimethylsilyl)silyllithium used for the preparation of **2a,b** from **3a,b**.
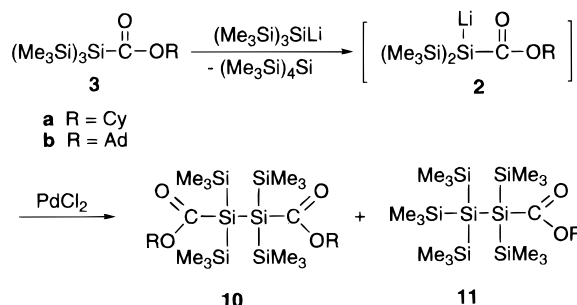
Scheme 4

Table 3. Crystal Data, Experimental Conditions, and Summary of Structural Refinement for 10a,b

	10a	10b
mol formula	$C_{26}H_{58}O_4Si_6$	$C_{34}H_{66}O_4Si_6$
mol wt	603.25	707.41
space group	$P\bar{1}$	$P\bar{1}$
cell dimens		
a, Å	13.583(2)	12.620(3)
b, Å	14.166(3)	15.919(4)
c, Å	9.7811(9)	11.680(2)
α, deg	95.98(1)	108.22(2)
β, deg	96.05(1)	109.65(2)
γ, deg	98.95(1)	88.83(2)
V, Å^3	1834.8(5)	2089.8(9)
Z	2	2
D_{cacld}, Mg/m^3	1.092	1.124
F_{000}	660.00	772.00
cryst size, mm^3	$0.5 \times 0.4 \times 0.2$	$0.5 \times 0.3 \times 0.1$
cryst color	colorless	colorless
μ, mm^{-1}	2.335	2.119
diffractometer	Rigaku AFC-6S	Rigaku AFC-6S
temp, K	233	213
wavelength, Å	1.5418 (Cu Kα)	1.5418 (Cu Kα)
monochromator	graphite cryst	graphite cryst
scan type	$\omega-2\theta$	$\omega-2\theta$
scan speed, deg/min	4	4
scan width, deg	$6 \leq 2\theta \leq 125.8$	$6 \leq 2\theta \leq 125.7$
h, k, l range		
h	$0 \leq h \leq 16$	$-15 \leq h \leq 15$
k	$-16 \leq k \leq 16$	$-18 \leq k \leq 0$
l	$-11 \leq l \leq 11$	$-14 \leq l \leq 14$
no. of unique reflns	5535	6156
no. of obsd reflns ($I \geq 3\sigma(I)$)	3575	3590
corrections	Lorentz−polarization absorption (trans. factors: 0.3065−0.9986)	Lorentz−polarization absorption (trans. factors: 0.6254−1.0000)
R	0.049	0.065
$R_w{}^a$	0.057	0.078

^{a} Weighting scheme is $(\sigma(F_o)^2 + 0.0004|F_o|^2)^{-1}$.

The crystal structures of compounds **10a,b** were determined by single-crystal X-ray diffraction studies. Cell dimensions, data collection and refinement parameters, and selected bond lengths and angles are summarized in Tables 3 and 4. Figures 1−3 depict ORTEP views of compounds **10a,b**. As shown in Figure 3, the structures have a slightly distorted anti conformation with respect to the disilanylene bridge, having two ester groups located in a trans fashion with torsion angles of C1−Si1−Si2−C2 = 167(2)° for **10a** and 166.7(4)° for **10b**. All Si−Si bond lengths in **10a,b** are in the normal range (2.33−2.37 Å),[10] in contrast to the crystal struc-

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Table 4. Selected Distances (Å) and Angles (deg) for Compound 10a,b with Their Esd's in Parentheses

10a					
Si1−Si2	2.346(2)	Si1−Si3	2.362(2)	Si1−Si4	2.353(2)
Si1−C1	1.927(5)	Si2−Si5	2.351(2)	Si2−Si6	2.364(2)
Si2−C2	1.932(5)	O1−C1	1.186(6)	O2−C1	1.311(6)
O2−C3	1.505(7)	O3−C2	1.206(6)	O4−C2	1.342(6)
O4−C9	1.487(6)				
Si2−Si1−Si3	113.18(8)	Si2−Si1−Si4	117.10(8)		
Si2−Si1−C1	101.7(2)	Si3−Si1−Si4	109.83(8)		
Si3−Si1−C1	108.8(2)	Si4−Si1−C1	105.3(2)		
Si1−Si2−Si5	117.74(8)	Si1−Si2−Si6	113.45(7)		
Si1−Si2−C2	101.4(2)	Si5−Si2−Si6	108.62(8)		
Si5−Si2−C2	103.9(2)	Si6−Si2−C2	111.0(2)		
C1−O2−C3	118.8(4)	C2−O4−C9	118.1(4)		
Si1−C1−O1	123.8(4)	Si1−C1−O2	115.1(4)		
O1−C1−O2	121.1(5)	Si2−C2−O3	124.3(4)		
Si2−C2−O4	113.1(3)	O3−C2−O4	122.5(5)		

| 10b					
Si1−Si2	2.345(3)	Si1−Si3	2.356(3)	Si1−Si4	2.366(3)
Si1−C1	1.936(8)	Si2−Si5	2.359(3)	Si2−Si6	2.371(3)
Si2−C2	1.936(8)	O1−C1	1.201(9)	O2−C1	1.342(9)
O2−C3	1.475(8)	O3−C2	1.205(9)	O4−C2	1.318(9)
O4−C13	1.470(8)				
Si2−Si1−Si3	114.5(1)	Si2−Si1−Si4	116.8(1)		
Si2−Si1−C1	102.2(2)	Si3−Si1−Si4	108.1(1)		
Si3−Si1−C1	99.8(3)	Si4−Si1−C1	114.3(3)		
Si1−Si2−Si5	119.8(1)	Si1−Si2−Si6	110.3(1)		
Si1−Si2−C2	102.0(3)	Si5−Si2−Si6	111.2(1)		
Si5−Si2−C2	107.9(3)	Si6−Si2−C2	104.1(3)		
C1−O2−C3	122.0(5)	C2−O4−C13	123.1(6)		
Si1−C1−O1	123.5(6)	Si1−C1−O2	111.1(5)		
O1−C1−O2	125.2(7)	Si2−C2−O3	124.6(6)		
Si2−C2−O4	112.1(6)	O3−C2−O4	123.1(7)		
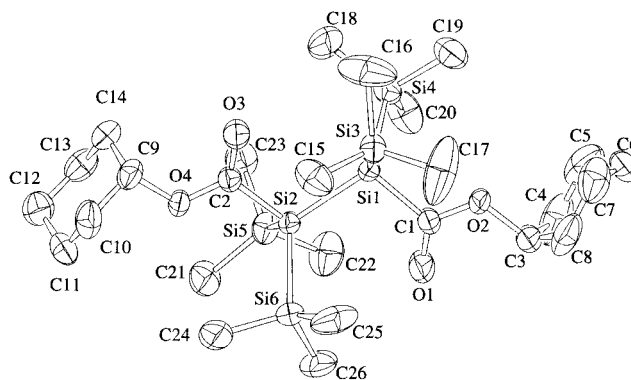
Figure 1. ORTEP drawing of compound **10a** with an atomic numbering scheme. Protons are omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

ture of 1,2-diadamantoyl-1,1,2,2-tetrakis(trimethylsilyl)-disilane reported previously, in which the central Si−Si bond (2.399 Å) is a little longer than the normal value.[7] Presumably steric repulsion between the substituents is reduced by introduction of the ether bonds in **10a,b**. However, smaller Si−Si(central)−C(carbonyl) angles (101.6° (av) for **10a**, 102.1° (av) for **10b**) than Si−Si(central)−Si angles (115.4° (av) for **10a**, 115.6° (av) for **10b**) seem to indicate that steric repulsion between trimethylsilyl groups still remains in **10a,b** to some extent.

The UV spectra of **10a,b** in THF show an absorption at 209 and 210 nm, respectively, at almost the same wavelengths as those of **3a,b** (209 and 209 nm), indicating that no unambiguous orbital interaction between the ester groups through the Si−Si bond takes place in
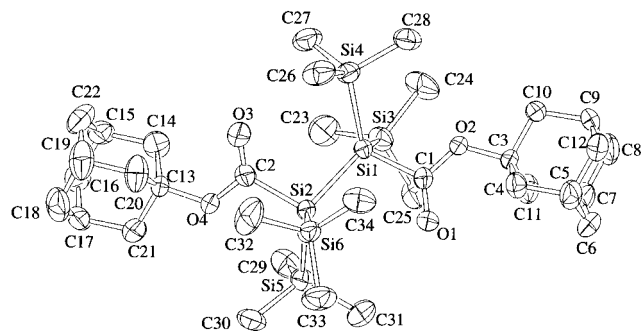
Figure 2. ORTEP drawing of compound **10b** with an atomic numbering scheme. Protons are omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

these molecules, similar to bis(acyl)polysilanes reported previously.[7]

Reaction of Lithium Ester Silenolate 2a with Mesitaldehyde. Treatment of **2a** and 1.5 equiv of mesitaldehyde in THF at −100 °C followed by trapping of the resulting anion with triethylchlorosilane and methyl iodide gave products **12a** and **13a** in 22% and 31% yields, respectively (Scheme 5). The reaction of **2b** with mesitaldehyde did not proceed even at −50 °C, and mesitaldehyde was recovered unchanged. Similar reactions of **2a** and **2b** with benzaldehyde gave complex mixtures. The structures of **12a** and **13a** were verified by spectral and elemental analysis. Thus, the ^{29}Si NMR spectrum of **12a** shows signals due to Si−O at 20.56 ppm and a trisilane unit at −36.98, −13.99, and −11.89 ppm, of which the signals at −13.99 and −11.89 ppm couple with the trimethylsilyl proton signals at −0.33 and 0.20 ppm, respectively, in the long-range Si−H COSY spectrum, indicating the presence of a Si(SiMe$_3$)$_2$ fragment in the molecule. For **13a**, the ^{29}Si NMR spectrum displays a signal at 17.60 ppm due to an Si−O silicon in addition to signals of the disilane unit, consistent with the proposed structure.

The formation of **12a** and **13a** can be explained by a series of reactions, including addition of lithium ester silenolate **2a** to the C=O double bond of mesitaldehyde, to produce a lithium alkoxide (**A**) as the initial step, as shown in Scheme 5. Lithium alkoxide **A** then reacts with triethylchlorosilanes, leading to product **12a**, whereas, for **13a**, intermediate **A** would undergo a Peterson-type elimination of lithium trimethylsilanolate, producing a silene intermediate (**B**).[11] Addition of lithium trimethylsilanolate to the resulting silene **B** then gives a lithium ester silenolate intermediate (**C**). Subsequetly, **C** reacts with methyl iodide to give **13a**. The formation of intermediate **C** from **A** may be understood also by a 1,3-silyl shift from silicon to oxygen without assuming intermediate **B**. The reaction course from **2a** to intermediate **C** is quite similar to that proposed for the reactions of lithium silenolates (**1**) with aldehydes, in which intermediates analogous to **C** react further with the aldehyde to give 1:2 adducts.[6]

Conclusions

We have synthesized lithium ester silenolates **2a**−**c** by the reactions of the respective tris(trimethylsilyl)-

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(11) Peterson-type olefination leading to the formation of silenes has been reported previously (refs 3 and 12).

silanecarboxylates **3a**−**c** with tris(trimethylsilyl)silyllithium as the first example of silicon analogues of lithium ester enolates. The NMR spectra of **2b** indicated that the negative charge is mostly localized on the central silicon atom, which is compatible with the chemical behavior of **2a**−**c** toward electrophiles, which always afforded Si-substituted products. With palladium dichloride, **2a**−**c** underwent oxidative coupling leading to the formation of polysilanedicarboxylates. To our knowledge, this is the first synthesis of compounds in which two carboxylates are linked by a two-silicon bridge. The reactions of **2a** with mesitaldehyde gave products arising from addition of the central silicon atom of **2a** to the carbonyl bond. Further studies concerning the chemical behavior of lithium ester silenolates are in progress.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of purified argon. Usual workup mentioned in the following experimental procedures includes hydrolysis of the reaction mixture with water, separation of the organic layer, extraction of the aqueous layer with hexane, drying the combined organic layer and extracts with anhydrous magnesium sulfate, and then evaporation of the solvent to give a mixture of organic products. Yields of products from the reactions of **2a**−**c** are based on the respective tris(trimethylsilyl)silanecarboxylates used. Mass spectra were measured on a Hitachi M-80B spectrometer. NMR spectra were recorded on a JEOL Lambda-400 spectrometer using tetramethylsilane as an internal standard. IR spectra were measured on a Perkin-Elmer FT1600 spectrophotometer. UV spectra were measured with a Hitachi U-3210 spectrophotometer.

Materials. THF was dried over sodium−potassium alloy and distilled just before use. Tris(trimethylsilyl)silanecarboxylic acid was prepared as reported in the literature.[13] Tris(trimethylsilyl)silyllithium was prepared by the reaction of tetrakis(trimethylsilyl)silane and methyllithium as reported in the literature and used without purification.[14]

Preparation of 3a. A mixture of 5.00 g (0.0171 mol) of tris(trimethylsilyl)silanecarboxylic acid, 12.0 g (0.12 mol) of cyclohexanol, and a catalytic amount of *p*-toluenesulfonic acid in 100 mL of benzene was heated at reflux for 3h with continuous removal of the resulting water from the mixture by using a Dean−Stark apparatus. After the usual workup, the resulting mixture was chromatographed on a silica gel column, eluting with hexane to give crude **3a**. The crude product was subjected to preparative GPC, eluting with benzene, to give 3.99 g (62% yield) of analytically pure **3a** as a colorless oil: MS *m/z* 374 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.21 (s, 27H, Me$_3$Si), 1.20−1.81 (m, 10H, H$_2$C), 4.88 (q, 1H, HC, J = 4.12 Hz); ^{13}C NMR (δ in CDCl$_3$) 0.71 (Me$_3$Si), 23.96, 25.45, 32.31, 70.28 (Cy), 186.94 (C=O); ^{29}Si NMR (δ in CDCl$_3$) −81.03 (center Si), −11.52 (SiMe$_3$); IR 1658 cm^{-1} (C=O); UV λ_{max} (in THF) 209 nm. Anal. Calcd for C$_{16}$H$_{38}$Si$_4$O$_2$: C, 51.27; H, 10.22. Found: C, 51.26; H, 10.33.

Preparation of 3b,c. To a suspension of 5.00 g (0.0252 mol) of 1-adamantyl fluoroformate in 30.0 mL of THF was added

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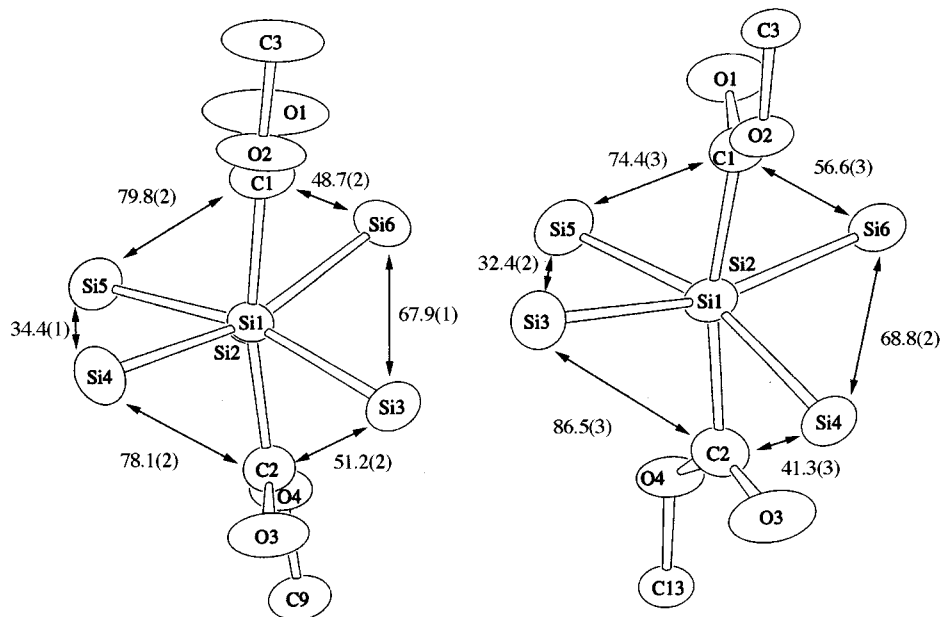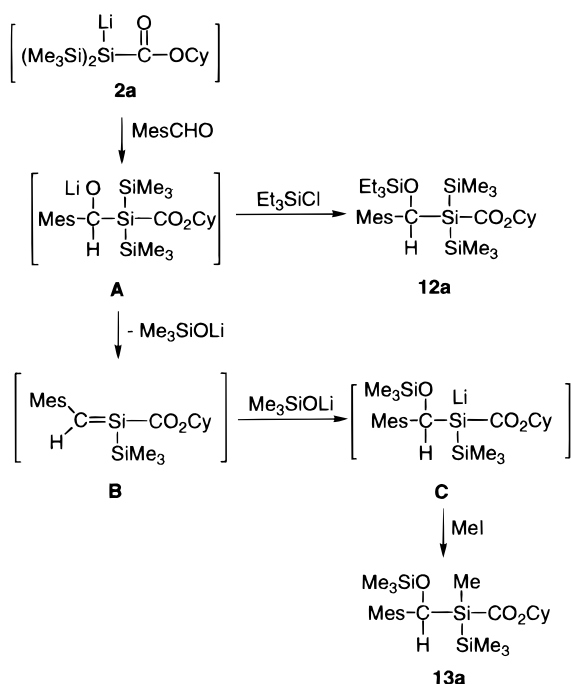
Figure 3. ORTEP drawing along the Si1−Si2 vector with torsion angles, for (left) compound **10a** and (right) compound **10b**. Alkyl groups are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Scheme 5

dropwise a solution of tris(trimethylsilyl)silyllithium in 25 mL of THF at −80 °C. The resulting mixture was allowed to warm to room temperature over a period of 5 h. After the usual workup, the resulting mixture was chromatographed on a silica gel column, eluting with 10:1 hexane/ethyl acetate to give crude **3b**. Recrystallization of the crude product from hexane gave 3.82 g (35% yield) of analytically pure **3b** as colorless crystals: mp 91.0−93.8 °C; MS m/z 426 (M⁺); ¹H NMR (δ in CDCl₃) 0.22 (s, 27H, Me₃Si), 1.64 (br s, 6H, Ad), 2.12 (br s, 9H, Ad); ¹³C NMR (δ in CDCl₃) 0.71 (Me₃Si), 30.89, 36.30, 42.36, 80.92 (Ad), 197.52 (C=O); ²⁹Si NMR (δ in CDCl₃) −79.15 (center Si), −11.67 (SiMe₃); IR 1656 cm⁻¹ (C=O); UV λ_{max} (in THF) 209 nm. Anal. Calcd for C₂₀H₄₂Si₄O₂: C, 56.27; H, 9.92. Found: C, 56.29; H, 10.22.

Compound **3c** was prepared by the reaction of benzyl chloroformate with tris(trimethylsilyl)silyllithium in a fashion similar to the synthesis of **3b**. Compound **3c** was purified by

preparative GPC eluting with benzene: 65% yield; colorless oil; MS m/z 382 (M⁺); ¹H NMR (δ in CDCl₃) 0.14 (s, 27H, Me₃-Si), 5.02 (s, 2H, *H₂C*Ph), 7.19−7.26 (m, 5H, Ph); ¹³C NMR (δ in CDCl₃) 0.71 (Me₃Si), 64.04 (*C*H₂Ph), 127.76, 128.32, 128.43, 136.97 (Ph), 187.41 (C=O); ²⁹Si NMR (δ in CDCl₃) −79.15 (center Si), −11.30 (SiMe₃); IR 1658 cm⁻¹ (C=O). Anal. Calcd for C₁₇H₃₄Si₄O₂: C, 53.34; H, 8.95. Found: C, 53.30; H, 9.00.

Reaction of 3a−c with Tris(trimethylsilyl)silyllithium, Followed by Treatment with Electrophiles. To a solution of 168 mg (0.449 mmol) of **3a** in 0.5 mL of THF was added an equimolar amount of tris(trimethylsilyl)silyllithium in 0.5 mL of THF at −80 °C, and the mixture was stirred for 1 h at this temperature. Triethylchlorosilane (0.1 mL, 0.60 mmol) was added to the mixture at −80 °C, and the mixture was allowed to warm to room temperature. After the usual workup, the resulting mixture was analyzed by GLC, using 80 mg (0.283 mmol) of *n*-eicosane as an internal standard, as being **4a** (90% yield) and tetrakis(trimethylsilyl)silane (98% yield). The mixture was chromatographed on a silica gel column, eluting with 10:1 hexane/ethyl acetate to give 153 mg (82% isolated yield) of analytically pure **4a**: MS m/z 416 (M⁺); ¹H NMR (δ in CDCl₃) 0.23 (s, 18H, Me₃Si), 0.77 (q, 6H, H₃C*H₂*CSi, J = 7.86 Hz), 0.98 (t, 9H, *H₃*CH₂CSi, J = 7.86 Hz), 1.24−1.83 (br m, 10H, H₂C of Cy), 4.87 (q, 1H, HC of Cy, J = 4.16 Hz); ¹³C NMR (δ in CDCl₃) 1.04 (Me₃Si), 5.38 (H₃CH₂*C*Si), 8.42 (H₃*C*H₂CSi), 24.14, 25.46, 32.34, 70.52 (Cy), 187.69 (C=O); ²⁹Si NMR (δ in CDCl₃) −81.72 (center Si), −11.35 (SiMe₃), 0.64 (SiEt₃); IR 1655 cm⁻¹ (C=O). Anal. Calcd for C₁₉H₄₄Si₄O₂: C, 54.74; H, 10.64. Found: C, 54.72; H, 10.58.

The syntheses of lithium ester silenolates **2a−c** and their reactions with electrophiles were performed in a fashion similar to that above, and the results are summarized in Table 1.

Data for **5a**: MS m/z 416 (M⁺); ¹H NMR (δ in CDCl₃) 0.18 (s, 6H, Me₂Si) 0.24 (s, 18H, Me₃Si), 0.94 (s, 9H, t-Bu), 1.17−1.84 (br m, 10H, H₂C of Cy), 4.88 (q, 1H, HC of Cy, J = 4.59 Hz); ¹³C NMR (δ in CDCl₃) −2.99 (Me₂Si), 1.15 (Me₃Si), 18.28 (*C*Me₃) 24.13, 25.45 (CH₂ of Cy) 27.61 (*Me₃*C) 32.36 (CH₂ of Cy), 70.58 (HC of Cy), 187.64 (C=O); ²⁹Si NMR (δ in CDCl₃) −81.33 (center Si), −11.10 (SiMe₃), 3.89 (SiMe₃); IR 1656 cm⁻¹ (C=O). Exact MS calculated for C₁₉H₄₄Si₄O₂ (M⁺): 416.2416, observed 416.2418.

Data for **6a**: MS m/z 560 (M⁺); ¹H NMR (δ in CDCl₃) 0.07 (s, 18H, Me₃Si) 1.18−1.72 (br m, 10H, H₂C of Cy), 4.86 (q, 1H,

HC of Cy, $J = 4.16$ Hz), 7.31−7.57 (m, 15H, Ph); ^{13}C NMR (δ in CDCl$_3$) 0.92 (Me$_3$Si), 24.04, 25.39, 32.06, 71.14 (Cy), 127.78, 129.20, 135.32, 136.30 (Ph), 186.71 (C=O); ^{29}Si NMR (δ in CDCl$_3$) −79.60 (center Si), −15.47 (SiMe$_3$), −10.83 (SiPh$_3$); IR 1652 cm^{-1} (C=O). Anal. Calcd for C$_{31}$H$_{44}$Si$_4$O$_2$: C, 66.37; H, 7.90. Found: C, 66.18; H, 7.88.

Data for **7a**: MS *m/z* 302 (M$^+$); ^{1}H NMR (δ in C$_6$D$_6$) 0.22 (s, 18H, Me$_3$Si), 1.19−1.81 (br m, 10H, H$_2$C of Cy), 3.43 (s, 1H, H−Si), 4.93 (q, 1H, HC of Cy, $J = 4.47$ Hz); ^{13}C NMR (δ in C$_6$D$_6$) −0.25 (Me$_3$Si), 23.89, 25.43, 32.19, 70.53 (Cy), 185.32 (C=O); ^{29}Si NMR (δ in C$_6$D$_6$) −74.10 (center Si), −15.08 (SiMe$_3$); IR 2103 cm^{-1} (Si−H), 1680 cm^{-1} (C=O). Exact MS calculated for C$_{12}$H$_{27}$Si$_3$O$_2$ (M$^+$ − Me): 287.1317, observed 287.1355.

Data for **8a**: MS *m/z* 316 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.15 (s, 18H, Me$_3$Si), 0.23 (s, 3H, MeSi), 1.24−1.80 (br m, 10H, H$_2$C of Cy), 4.94 (q, 1H, HC of Cy, $J = 4.41$ Hz); ^{13}C NMR (δ in CDCl$_3$) −10.56 (Si−Me), −1.19 (Me$_3$Si) 23.84, 25.46, 32.23, 69.89 (Cy), 187.95 (C=O); ^{29}Si NMR (δ in CDCl$_3$) −49.99 (center Si), −14.81 (SiMe$_3$); IR 1670 cm^{-1} (C=O). Anal. Calcd for C$_{14}$H$_{32}$Si$_3$O$_2$: C, 53.10; H, 10.19. Found: C, 53.10; H, 10.21.

Data for **9a**: MS *m/z* 358 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.18 (s, 18H, Me$_3$Si), 0.94 (d, 6H, *Me*$_2$CH, $J = 6.52$ Hz), 1.29−1.84 (br m, 13H, H$_2$C of Cy, and HC and H$_2$C of i-Bu), 4.93 (q, 1H, HC of Cy, $J = 4.35$ Hz); ^{13}C NMR (δ in CDCl$_3$) −0.43 (Me$_3$Si), 20.11 (CH of i-Bu), 23.94, 25.46 (CH$_2$ of Cy), 26.11 (CH$_2$ of i-Bu), 27.01 (Me of i-Bu), 32.25, 69.98 (Cy), 187.95 (C=O); ^{29}Si NMR (δ in CDCl$_3$) −46.76 (center Si), −14.78 (Me$_3$Si); IR 1666 cm^{-1} (C=O). Anal. Calcd for C$_{17}$H$_{38}$Si$_3$O$_2$: C, 56.92; H, 10.68. Found: C, 56.91; H, 10.69.

Data for **4b**: MS *m/z* 468 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.23 (s, 18H, Me$_3$Si), 0.76 (q, 6H, H$_3$C*H$_2$*CSi, $J = 7.88$ Hz), 0.99 (t, 9H, *H$_3$*CH$_2$CSi $J = 7.88$ Hz), 1.57−1.68 (br m, 6H, Ad), 2.12 (s, 9H, Ad); ^{13}C NMR (δ in CDCl$_3$) 1.04 (Me$_3$Si), 5.36, 8.43 (Et$_3$Si), 30.90, 36.31, 42.25, 80.97 (Ad), 188.05 (C=O); ^{29}Si NMR (δ in CDCl$_3$) −81.21 (center Si), −11.60 (SiMe$_3$), 0.523 (SiEt$_3$); IR 1656 cm^{-1} (C=O). Anal. Calcd for C$_{23}$H$_{48}$Si$_4$O$_2$: C, 58.91; H, 10.32. Found: C, 58.86; H, 10.52.

Data for **7b**: MS *m/z* 354 (M$^+$); ^{1}H NMR (δ in C$_6$D$_6$) 0.33 (s, 18H, Me$_3$Si), 1.97 (br s, 6H, Ad), 2.24−2.27 (br m, 9H, Ad), 3.85 (s, 1H, HSi); ^{13}C NMR (δ in C$_6$D$_6$) −0.01 (Me$_3$Si), 31.22, 36.45, 42.60, 80.90 (Ad), 184.38 (C=O); ^{29}Si NMR (δ in C$_6$D$_6$) −72.57 (center Si), −14.15 (SiMe$_3$); IR 2099 cm^{-1} (Si−H), 1671 cm^{-1} (C=O). Exact MS calculated for C$_{16}$H$_{31}$Si$_3$O$_2$ (M$^+$ − CH$_3$): 339.1632, observed 339.1648; calculated for C$_{14}$H$_{25}$Si$_2$O$_2$ (M$^+$ − SiMe$_3$) 281.1392, observed 281.1397.

Data for **8b**: MS *m/z* 368 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.16 (s, 18H, Me$_3$Si), 0.19 (s, 3H, MeSi), 1.59−1.68 (br m, 6H, Ad), 2.12 (br. s, 9H, Ad); ^{13}C NMR (δ in CDCl$_3$) −10.54 (MeSi), −1.12 (Me$_3$Si), 30.90, 36.32, 42.35, 80.60 (Ad), 188.69 (C=O); ^{29}Si NMR (δ in CDCl$_3$) −50.31 (center Si), −14.81 (SiMe$_3$); IR 1656 cm^{-1} (C=O). Anal. Calcd for C$_{18}$H$_{36}$Si$_3$O$_2$: C, 58.63; H, 9.84. Found: C, 58.58; H, 9.82.

Data for **4c**: MS *m/z* 424 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.14 (s, 18H, Me$_3$Si), 0.68 (q, 6H, H$_3$C*H$_2$*CSi, $J = 7.89$ Hz), 0.88 (t, 9H, *H$_3$*CH$_2$CSi, $J = 7.85$ Hz), 5.00 (s, 2H, H$_2$CPh), 7.20−7.26 (m, 5H, Ph); ^{13}C NMR (δ in CDCl$_3$) 0.98 (Me$_3$Si), 5.34 (H$_3$C*H$_2$C*Si), 8.30 (H$_3$*C*H$_2$CSi), 64.17 (*C*H$_2$Ph), 127.77, 128.26, 128.69, 136.80 (Ph), 187.95 (C=O); ^{29}Si NMR (δ in CDCl$_3$) −81.03 (center Si), −11.24 (SiMe$_3$), 0.82 (SiEt$_3$); IR 1665 cm^{-1} (C=O). Anal. Calcd for C$_{20}$H$_{40}$Si$_4$O$_2$: C, 56.54; H, 9.49. Found: C, 56.77; H, 9.59.

NMR Measurements of 2b. To a solution of **3b** in 0.6 mL of THF-d_8 was added an equimolar amount of tris(trimethylsilyl)silyllithium in 0.6 mL of THF at −80 °C. After stirring the mixture for 1 h at −80 °C, one-half of the mixture was placed in an NMR tube and subjected to NMR measurements at −80 °C: ^{13}C NMR (δ in 50% THF-d_8 + 50% THF) 3.40 (Me$_3$Si), 30.89, 36.50, 42.42, 76.76 (Ad), 215.59 (C=O); ^{29}Si NMR (δ in 50% THF-d_8 + 50% THF) −117.97 (center Si), −7.80 (SiMe$_3$).

Reaction of 2a with Palladium Dichloride. To a suspension of 0.047 g (0.267 mmol) of palladium dichloride in 0.3 mL of THF was added dropwise a solution of **2a** prepared from 0.207 mg (0.535 mmol) of **3a** and an equimolar amount of tris-(trimethylsilyl)silyllithium in 2 mL of THF, at −80 °C. The resulting mixture was allowed to warm to room temperature over a period of 4 h. After the usual workup, the resulting mixture was chromatographed (preparative GPC, eluting with benzene) to give crude **10a** and **11a**. The crude products were recrystallized from hexane to give 15 mg (12% yield) of **10a** and 9 mg (7% yield) of **11a** as colorless crystals. Data for **10a**: mp 149.8−150.7 °C; MS *m/z* 602 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.27 (s, 36H, Me$_3$Si), 1.25−1.84 (br m, 20H, H$_2$C of Cy), 4.85 (q, 2H, HC of Cy, $J = 4.53$ Hz); ^{13}C NMR (δ in CDCl$_3$) 1.20 (Me$_3$Si), 24.26, 25.45, 32.43, 71.21 (Cy), 186.82 (C=O); ^{29}Si NMR (δ in CDCl$_3$) −76.85 (center Si), −10.01 (SiMe$_3$); IR 1647 cm^{-1} (C=O); UV λ_{max} (in THF) 209, 228 (shoulder). Anal. Calcd for C$_{26}$H$_{58}$Si$_6$O$_4$: C, 51.77; H, 9.69. Found: C, 51.78; H, 9.62. Data for **11a**: mp 125.7−127.2 °C; MS *m/z* 548 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.15 (s, 27H, Me$_3$Si), 0.17 (s, 18H, Me$_3$Si), 1.09−1.77 (br m, 10H, H$_2$C of Cy), 4.74 (q, 1H, HC of Cy, $J = 4.53$ Hz); ^{13}C NMR (δ in CDCl$_3$) 2.21, 3.32 (Me$_3$Si), 24.33, 25.44, 32.45, 71.20 (Cy), 187.89 (C=O); IR 1655 cm^{-1} (C=O). Anal. Calcd for C$_{22}$H$_{56}$Si$_7$O$_2$: C, 48.11; H, 10.28. Found: C, 48.12; H, 10.34.

The reaction of **2b** with palladium dichloride was carried out in a fashion similar to that of **2a**. Data for **10b**: 17% yield, colorless crystals; mp 251.3−252.9 °C; MS *m/z* 706 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.27 (s, 36H, Me$_3$Si), 1.61 (br d, 6H, H$_2$C of Ad, $J = 12.44$ Hz), 1.66 (br d, 6H, H$_2$C of Ad, $J = 12.44$ Hz), 2.12 (s, 18H, Ad); ^{13}C NMR (δ in CDCl$_3$) 1.30 (Me$_3$Si), 30.94, 36.29, 42.26, 81.34 (Ad), 186.86 (C=O); ^{29}Si NMR (δ in CDCl$_3$) −76.48 (center Si), −10.19 (SiMe$_3$); IR 1653 cm^{-1} (C=O); UV λ_{max} (in THF) 210, 228 (shoulder). Anal. Calcd for C$_{34}$H$_{66}$Si$_6$O$_4$: C, 57.73; H, 9.40. Found: C, 57.65; H, 9.52. Data for **11b**: 8% yield; colorless crystals; mp 206.8−208.0 °C; MS *m/z* 600 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) 0.25 (s, 27H, Me$_3$Si), 0.26 (s, 18H, Me$_3$Si), 1.61 (br d, 3H, H$_2$C of Ad, $J = 11.96$ Hz), 1.67 (br d, 3H, H$_2$C of Ad, $J = 11.96$ Hz), 2.12 (s, 9H, Ad); ^{13}C NMR (δ in CDCl$_3$) 2.25, 3.37 (Me$_3$Si), 30.93, 36.27, 42.24, 81.28 (Ad), 187.96 (C=O); IR 1657 cm^{-1} (C=O). Anal. Calcd for C$_{26}$H$_{60}$Si$_7$O$_2$: C, 51.93; H, 10.06. Found: C, 51.67; H, 10.20.

Reaction of 2a with Mesitaldehyde, Followed by Quenching with Electrophiles. To a solution of 150 mg (1.2 mmol) of mesitaldehyde in 2 mL of THF was added **2a** prepared from 300 mg (0.8 mmol) of **3a** and an equimolar amount of tris(trimethylsilyl)silyllithium in 2.0 mL of THF at −80 °C. The mixture was stirred at this temperature for 1 h, and 0.1 mL (0.60 mmol) of triethylchlorosilane was added to the resulting mixture. After evaporation of the solvent, the residue was analyzed by GLC as being **12a** (22% yield). Compound **12a** was isolated by silica gel column chromatography, eluting with 10:1 hexane/ethyl acetate: MS *m/z* 564 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) −0.33 (s, 9H, Me$_3$Si), 0.20 (s, 9H, Me$_3$Si), 0.26−0.44 (m, 3H, H$_3$C*H$_2$*CSi), 0.35 (br q, 3H, H$_3$C*H$_2$*-CSi, $J = 7.59$ Hz), 0.70 (br t, 9H, *H$_3$*CH$_2$CSi, $J = 7.75$ Hz), 1.27−1.78 (m, 10H, H$_2$C of Cy), 2.10 (s, 3H, p-Me), 2.22 (s, 3H, o-Me), 2.25 (s, 3H, o-Me), 4.88 (q, 1H, HC of Cy, $J = 4.12$ Hz), 5.71 (s, 1H, *H*C(Mes)O), 6.59 (s, 1H, Mes ring proton), 6.62 (s, 1H, Mes ring proton); ^{13}C NMR (δ in CDCl$_3$) −2.36, −0.90 (Me$_3$Si), 2.95, 5.03 (Et$_3$Si), 18.99, 19.16 (o-Me), 21.13 (p-Me), 22.48, 23.65, 30.68, 69.11 (Cy), 62.64 (H*C*(Mes)O), 126.89, 128.05, 131.35, 133.60, 135.12, 137.01 (Mes), 186.86 (C=O); ^{29}Si NMR (δ in CDCl$_3$) −36.98 (center Si), −13.99, −11.89 (SiMe$_3$), 20.56 (SiEt$_3$); IR 1658 cm^{-1} (C=O). Anal. Calcd for C$_{29}$H$_{56}$Si$_4$O$_3$: C, 61.64; H, 9.99. Found: C, 61.66; H, 10.06.

The reaction of **2a** with mesitaldehyde, followed by quenching with methyl iodide, was carried out in fashion similar to that above. Data for **13a**: 31% yield; MS *m/z* 464 (M$^+$); ^{1}H NMR (δ in CDCl$_3$) −0.19 (s, 9H, Me$_3$Si), −0.03 (s, 9H, Me$_3$Si), 0.46 (s, 3H, MeSi), 1.25−1.82 (m, 10H, H$_2$C of Cy), 2.21 (s,

3H, p-Me), 2.31 (s, 3H, o-Me), 2.33 (s, 3H, o-Me), 4.96 (q, 1H, HC of Cy, J = 4.12 Hz), 5.47 (s, 1H, HC(Mes)O), 6.72 (s, 1H, Mes ring proton), 6.74 (s, 1H, Mes ring proton); ^{13}C NMR (δ in CDCl$_3$) −6.95 (MeSi), −2.20, −0.20 (Me$_3$Si), 20.76, 20.92 (o-Me), 21.66 (p-Me), 23.94, 25.46, 32.17, 70.22 (Cy), 62.52 (HC(Mes)O), 128.67, 130.29, 133.05, 135.30, 137.33, 137.52 (Mes), 187.15 (C=O); ^{29}Si NMR (δ in CDCl$_3$) −20.06 (center Si), −17.58, 17.60 (SiMe$_3$); IR 1665 cm^{-1} (C=O). Anal. Calcd for C$_{24}$H$_{44}$Si$_3$O$_3$: C, 62.01; H, 9.54. Found: C, 62.26; H, 9.78.

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Xray Crystallographic Analysis of 10a,b. The structures were solved by SIR92 direct methods[15] and expanded using DIRDIF94 Fourier techniques.[16] The non-hydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber.[17] Anomalous dispersion effects were included in F_{calc};[18] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[19] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[20] All calculations were performed using the teXsan[21] crystallographic software package of Molecular Structure Corporation.

Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compounds **10a** and **10b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990395Z