Articles

Mechanistic Studies of the Addition of Carbonyl Compounds to Tetramesityldisilene and Tetramesitylgermasilene

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The mechanism for the addition of carbonyl compounds to disilenes and germasilenes was investigated by examination of the structure of the products obtained from the reaction of the modified mechanistic probe, *trans*,*trans*-2-methoxy-3-phenylcyclopropane carbaldehyde, with tetramesityldisilene and tetramesitylgermasilene. The aldehyde was found to undergo characteristic ring-opening reactions depending on whether a radical or a cation develops at the carbinyl carbon. Thus, reaction of the mechanistic probe under ionic conditions (*p*-TsOH) yielded a mixture of *cis*- and *trans*-2-methoxy-3-phenyl-2,3-dihydrofuran (**6**) from ring-opening toward the methoxy substituent. In contrast, reaction of the mechanistic probe under radical conditions ($HSi(SiMe_3)_3$, AIBN) yielded a mixture of *cis*- and *trans*-3-methoxy-4-phenyl-1-[tris(trimethylsilyl)siloxy]but-1-ene (**7**) from regioselective ring-opening toward the phenyl substituent. 2,2,3,3-Tetramesityl-4-phenyl-5-methoxyoxa-2,3-disilacycloheptene (**8**) was formed from the reaction between the aldehyde and tetramesityldisilene, and a mixture of three isomers of 2,2,3,3-tetramesityl(phenyl)(methoxy)oxagermasilacycloheptene (**10a**−**c**) and [dimesityl(1-oxa-4-methoxy-5-phenylpentadienyl)silyl]germane (**10d**) was formed in the reaction of the aldehyde with tetramesitylgermasilene. The formation of **8**, **10a**, **10b**, and **10d** provides unequivocal evidence for the presence of radical intermediates in the addition of carbonyl compounds to the disilene and germasilene.

Introduction

In a single volume of *Advances in Organometallic Chemistry* (1996), the authors of three different chapters[1] independently noted that although many syntheses and reactions of group 14 doubly bonded compounds are well-known, little is known about the reaction mechanisms. In general, mechanistic studies of this class of compounds have been hampered by the inherent kinetic instability of these derivatives as well as the difficulty associated with the syntheses of appropriate substrates to study. While two chapters have recently appeared that summarize the progress made in this area,[2] the kinetics and mechanisms of the reactions of dimetallenes, in particular, still remain relatively unexplored. Since a detailed understanding of the reaction chemistry is essential for further development of the field, the need for mechanistic studies remains.[3]

In recent years, our focus[4] has been on the mechanism of the addition of aldehydes and ketones to disilenes and germasilenes, one of the most well-studied reactions of these compounds.[5,6] The reaction between carbonyl compounds and disilenes and germasilenes generally gives the corresponding dimetallaoxetanes, although recently, the formation of an ene-type product was observed.[7] The addition of carbonyl compounds continues to be an important reaction of dimetallenes.[7,8] Our approach in the investigation of the mechanism of carbonyl addition to disilenes and germasilenes employs the use of a mechanistic probe to investigate the nature

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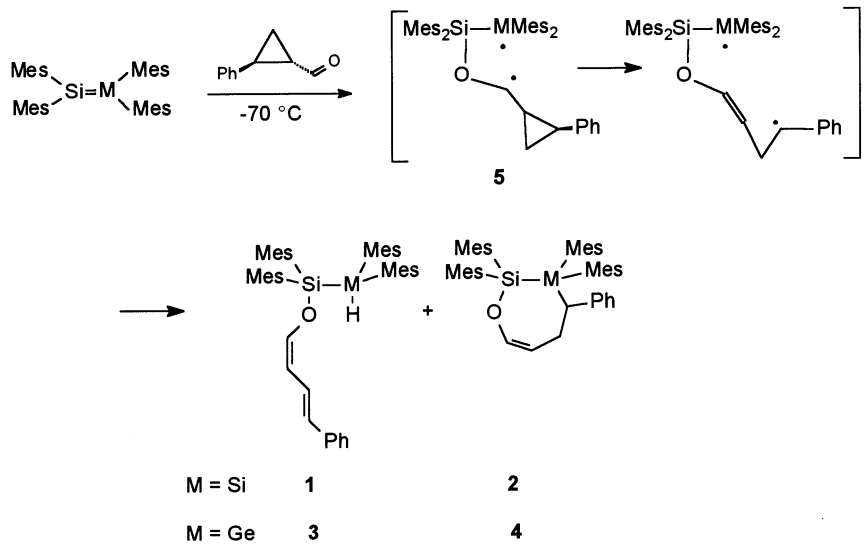
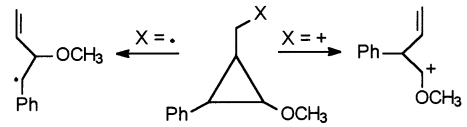
Scheme 1



of any reactive intermediates formed. The initial probe design was based upon the rapid ring-opening of the phenyl-substituted cyclopropylcarbinyl radical.[9,10] We have reported the use of *trans*-2-phenylcyclopropane carbaldehyde as a mechanistic probe in the examination of the mechanism of the addition of carbonyl compounds to disilenes and germasilenes.[4] When tetramesityldisilene and tetramesitylgermasilene were allowed to react with *trans*-2-phenylcyclopropane carbaldehyde, a 1:1 mixture of the oxapentadienylsilylmetallanes **1** (M = Si) and **3** (M = Ge) and the oxasilametallacycloheptenes **2** (M = Si) and **4** (M = Ge) was obtained (Scheme 1). We argued that the formation of compounds **1**−**4** is best explained by the initial formation of a biradical intermediate **5**, which undergoes rapid ring-opening to give the benzylic radical, which then undergoes disproportionation to give **1/3** or ring-closure to give **2/4**. The alternative explanation that compounds **1**−**4** are the result of ring-opening of a zwitterionic intermediate resulting from nucleophilic addition of the aldehyde to the dimetallene was discounted on the basis of the evidence that *trans*-2-phenylcyclopropane carbaldehyde has been reported to be stable (i.e., not undergo ring-opening) under acidic conditions[11] and the argument that the oxonium ion is more stable than the benzyl cation and, thus, was unlikely to rearrange. Our results were particularly interesting in light of the fact that the accumulated evidence is in favor of a zwitterionic intermediate in the addition of carbonyl compounds to silenes.[2a]

Scheme 2



The novelty of our findings prompted us to continue to gather more evidence in support of a biradical intermediate in the addition of aldehydes to disilenes and germasilenes. Thus, the mechanism for the addition of carbonyl compounds to both group 14 dimetallenes and metallenes was examined using density functional and multiconfigurational perturbation theory.[12] In agreement with our experimental findings, the most energetically favorable reaction pathway for the addition of formaldehyde to the parent disilene or germasilene in the gas phase was found to involve the formation of a biradical intermediate.

Although we have argued that an intermediate cyclopropylcarbinyl cation (oxonium ion) is not likely to undergo ring-opening, the fact remains that many of the characteristic radical rearrangement products of mechanistic probes may also be the result of a cationic rearrangement.[13,14] To distinguish between the two possible types of intermediates, Newcomb and coworkers have developed a class of hypersensitive probes with the (alkoxy)(phenyl)cyclopropylmethyl framework (see Scheme 2), which has demonstrated a high level of discrimination between radical and cationic intermediates.[13] The discrimination relies on the ability of a phenyl group to stabilize a radical center more strongly than an alkoxy group and the ability of an alkoxy group to stabilize a cation to a greater extent. Thus, the cyclopropylcarbinyl radical (X = •) opens regioselectively toward the phenyl group to give a 2° benzylic/homoallylic radical, whereas the cyclopropylmethyl carbocation

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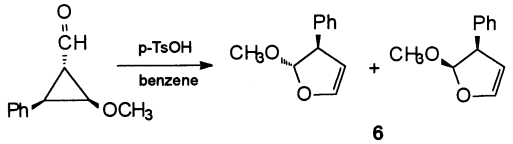
(X = +) opens regioselectively toward the alkoxy group to give the alkoxonium ion.

To further substantiate our previous conclusions that carbonyl compounds add to disilenes and germasilenes to give a biradical intermediate and to remove any ambiguity that may result from the possibility of indistinguishable radical/cationic rearrangement products, we have further refined the structure of our probe. We now report on the use of *trans*,*trans*-2-methoxy-3-phenylcyclopropane carbaldehyde as a mechanistic probe. On the basis of the characteristic rearrangements of this molecule, we believe we have been able to determine unequivocally the nature of the intermediates formed during the addition of aldehydes to disilenes and germasilenes.

The results contained herein will also be of interest in surface silicon chemistry. The addition of carbonyl compounds to Si(111)−H,[15] Si(100),[16] and porous silicon[17] surfaces has recently been investigated.[18] The reactions of molecular disilenes may provide some insight into these surface reactions, particularly those of reconstructed Si(100)-2×1, which is composed of silicon dimers on the surface. The nature of the reconstructed Si(100) surface is a matter of some debate. A doubly bonded structure, a diradical, and a twisted zwitterion have been proposed. Our probe may be able to provide some insight into the nature of the dimer on the reconstructed Si(100) surface. It has been recognized that mechanistic probes, such as *trans*,*trans*-2-methoxy-3-phenylcyclopropane carbaldehyde, may play an important role in the study of the reaction mechanisms at all types of silicon surfaces.[18b]

Results

Treatment of *trans*,*trans*-2-methoxy-3-phenylcyclopropane carbaldehyde with a catalytic amount of *p*-toluenesulfonic acid in benzene yielded *cis*- (major product) and *trans*-2-methoxy-3-phenyl-2,3-dihydrofuran (*cis*-**6** and *trans*-**6**). Other unidentified products, presumably from further hydrolysis of the acetal, were also formed. *trans*-**6** was readily identified by comparison of the ^{1}H and ^{13}C NMR spectral data to the literature values.[19] The ^{1}H and ^{13}C NMR spectral data of *cis*-**6** were similar to that of the *trans* isomer. The regiochemistry of the methoxy and phenyl groups was unequivocally established by analysis of the chemical shifts of the saturated ring carbon atoms (assigned from a ^{13}C− ^{1}H HSQC spectrum). The chemical shifts of the saturated ring carbon atoms of the *cis* isomer are dramatically different (107 and 52 ppm). These data are consistent only with the 2-methoxy-3-phenyl isomer since one carbon has two oxygen substituents and the other has two sp^2-hybridized carbon substituents. Since the saturated ring carbon atoms of the 3-methoxy-2-phenyl isomer have virtually identical substituents, one would expect the chemical shifts of the two ring carbons to be similar.[20] This was not observed. The chemical shifts of the ring ^{1}H's followed the same trend. The *cis* orientation of the two substituents was confirmed by the larger coupling constant (8 Hz versus 3 Hz) of the CH(OMe)CHPh hydrogens as expected based on the Karplus equation and as has been observed in other substituted dihydrofurans.[21]



(1)

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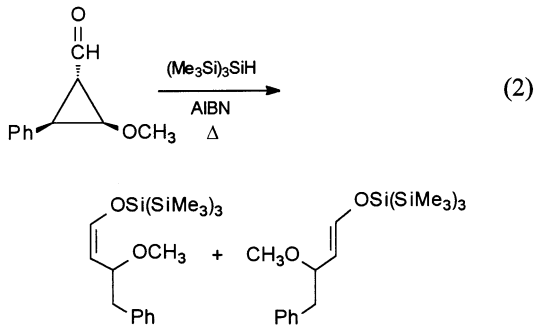
Thermolysis of *trans*,*trans*-2-methoxy-3-phenylcyclopropane carbaldehyde in the presence of tris(trimethylsilyl)silane and AIBN yielded a 2:1 mixture of *cis*-**7** and *trans*-**7**, as determined by ^{1}H NMR spectroscopy. *cis*-**7** and *trans*-**7** could not be separated cleanly from one another. The features of the ^{13}C, ^{1}H COSY, DEPT, ^{1}H−^{13}C HSQC, and ^{1}H−^{29}Si HMBC NMR spectra of the mixture are completely compatible with the assigned structures. For each isomer, there is a single upfield



(2)

7

resonance assigned to the tris(trimethylsilyl)silyl moiety, a signal that can be assigned to the methoxy group and a multiplet that can be assigned to the ^{1}H's of the phenyl group. The chemical shifts and the coupling constants identified the OCH=CH−CH(X)−CH$_2$Y spin system. The enol hydrogens resonated at 6.21 ppm (dd, J = 6 Hz, J = 1 Hz, OC*H*=CH) and 4.43 ppm (dd, J = 9 Hz, J = 6 Hz, OCH=C*H*) for *cis*-**7**, and 6.32 ppm (d, J = 12 Hz, OC*H*=CH) and 4.98 ppm (dd, J = 12 Hz, J = 9 Hz, OCH=C*H*) for *trans*-**7**. *cis*-**7** shows a long-range four-bond coupling between the OCH of the enol and the signal at 4.62 ppm (dtd, J = 9 Hz, J = 7 Hz, J = 1 Hz) assigned to the hydrogen atom geminal to the X group. This long-range coupling was not observed in the

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(20) The chemical shifts of the ring carbon atoms of 3-methoxy-2-phenyl-2,3-dihydrofuran were calculated to be 85.6 and 86.2 ppm using the ACD, Inc./I-lab service. For comparison, the chemical shifts of the corresponding carbon atoms in 2-methoxy-3-phenyl-2,3-dihydrofuran were calculated to be 110.0 and 51.9 ppm.

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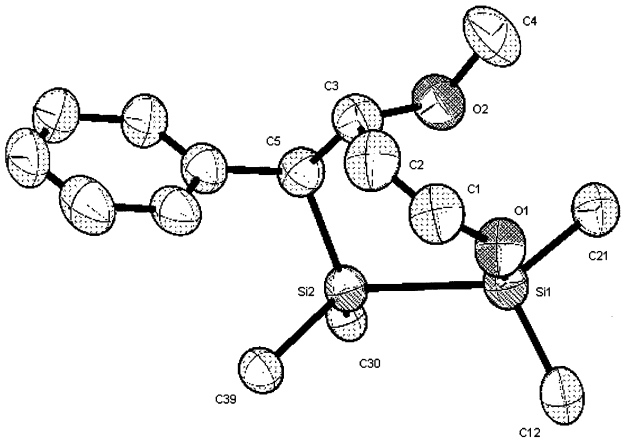
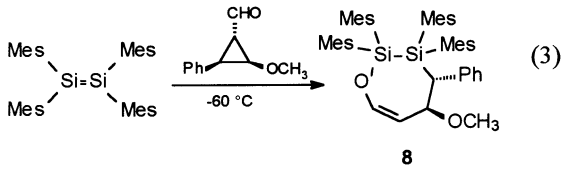


Figure 1. Molecular structure of **8**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and the carbons of the mesityl substituents have been omitted for clarity.

^{1}H NMR spectrum of *trans*-**7** (CHX: 3.61 ppm, dt $J = 9$ Hz, $J = 6$ Hz). The ^{1}H NMR spectrum of **7** also shows the presence of four doublets of doublets: at 2.89 ppm ($J = 14$ Hz, $J = 6$ Hz, CYH_a) and 3.08 ppm ($J = 14$ Hz, $J = 7$ Hz, CYH_b) for *cis*-**7** and 2.79 ppm ($J = 14$ Hz, $J = 6$ Hz, CYH_a) and 3.02 ppm ($J = 14$ Hz, $J = 7$ Hz, CYH_b) for *trans*-**7**, consistent with two pairs of diastereotopic hydrogen atoms. The ^{13}C DEPT and gHSQC spectra reveal that the ^{13}C signals at 42.88 and 43.85 ppm are due to methylene carbon atoms and the ^{13}C signals at 75.10 and 80.86 ppm are due to methine carbon atoms. Given the chemical shifts of these signals, the phenyl group must be attached to the methylene carbon and the methoxy group must be attached to the methine carbon. The regiochemistry is thus established. The ^{1}H−^{29}Si HMBC spectrum indicates a correlation between the signal at 6.21 ppm and the resonance at 7.6 ppm in the ^{29}Si dimension for *cis*-**7** and a correlation between the signal at 6.32 ppm and a resonance at 5.5 ppm in the ^{29}Si dimension for *trans*-**7**. The ^{1}H−^{29}Si HMBC NMR spectrum indicates that the ^{29}Si chemical shifts of the trimethylsilyl groups of both isomers are accidentally coincident at −14.8 ppm.

Addition of *trans*,*trans*-2-methoxy-3-phenylcyclopropane carbaldehyde dissolved in toluene to a solution of tetramesityldisilene at −60 °C in hexanes yielded a white solid after removal of the solvent. Compound **8** precipitated out of the crude product mixture upon addition of a 1:1 acetone/benzene solution. No other products could be isolated or identified from the crude product mixture.



(3)

8

Compound **8** was identified by a single-crystal X-ray structure determination. The molecular structure of the molecule is presented in Figure 1. The crystal data and selected structure refinement parameters are given in Table 1. Selected interatomic distances and angles are listed in Table 2. Perhaps the most striking feature about the structure of **8** is the Si−Si bond length of 2.559(2) Å, significantly longer than the average Si−Si bond length of 2.35 Å. The longer bond length is probably due to the high steric congestion of the bulky mesityl groups.

Table 1. Crystal Data and Structure Refinement Parameters for 8

empirical formula	$C_{47}H_{56}O_2Si_2$
fw	709.10
temp	294(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P2(1)/n$
unit cell dimens	$a = 12.250(3)$ Å, $\alpha = 90°$ $b = 22.862(5)$ Å, $\beta = 105.37(3)°$ $c = 14.938(3)$ Å, $\gamma = 90°$
vol, Z	4033.7(14) Å^3, 4
density (calcd)	1.168 Mg/m^3
abs coeff	0.125 mm^{-1}
$F(000)$	1528
cryst size	0.7 × 0.12 × 0.03 mm^3
θ range for data collection	2.62−23.26°
index ranges	$-13 \le h \le 13$, $-25 \le k \le 25$, $-16 \le l \le 16$
no. of reflns coll	13 872
no. of indep reflns	5779 [R(int) = 0.0512]
completeness to $\theta = 25.00°$	99.7%
abs corr	integration
max. and min. transmn	0.9963 and 0.9791
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	5779/0/450
goodness-of-fit on F^2	1.099
final R indices [$I>2\sigma(I)$]	R1 = 0.0707, wR2 = 0.1822
R indices (all data)	R1 = 0.1120, wR2 = 0.2400
extinction coeff	0.0040(13)
largest diff peak and hole	0.397 and −0.476 e A^{-3}

Table 2. Selected Bond Distances (Å) and angles (deg) for 8

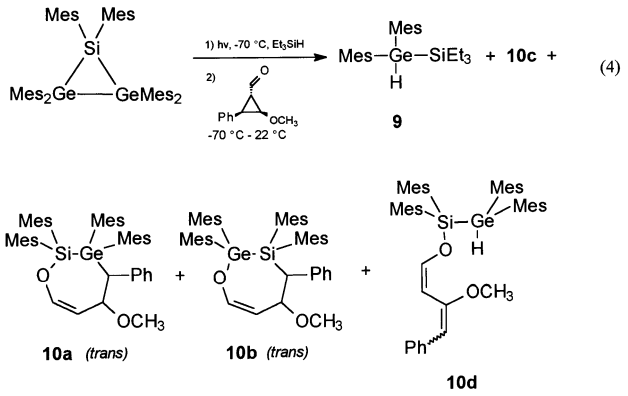
Si(1)−O(1)	1.671(3)	O(1)−Si(1)−Si(2)	104.99(13)
Si(1)−C(12)	1.916(5)	C(5)−Si(2)−Si(1)	103.28(15)
Si(1)−C(21)	1.922(5)	C(1)−O(1)−Si(1)	135.2(3)
Si(1)−Si(2)	2.5588(18)	C(2)−C(1)−O(1)	127.8(5)
Si(2)−C(39)	1.927(5)	C(1)−C(2)−C(3)	127.4(5)
Si(2)−C(30)	1.930(5)	C(2)−C(3)−C(5)	116.7(4)
Si(2)−C(5)	1.967(5)	C(3)−C(5)−Si(2)	115.6(3)
O(1)−C(1)	1.352(6)		
O(2)−C(3)	1.429(6)		
C(1)−C(2)	1.321(7)		
C(2)−C(3)	1.501(7)		
C(3)−C(5)	1.529(7)		
C(5)−C(6)	1.540(5)		

The spectroscopic data contributed very little to the elucidation of the structure of **8**. The ^{1}H NMR spectrum of **8** was very difficult to interpret due to broadening of the signals arising from the mesityl substituents and the hydrogen atoms of the seven-membered ring. Perhaps the most unusual feature of the ^{1}H NMR spectrum at room temperature was the apparent lack of signals that could be attributed to the methoxy group or the enolic hydrogen atoms. High-temperature (96 °C) ^{1}H NMR spectroscopy succeeded in sharpening some of the signals; however, several broad signals still remained. In contrast, all signals in the ^{1}H NMR spectrum of compound **8** at −68 °C are sharp. The number of signals indicates the presence of two conformations. Consistently, the signals assigned to the OC*H*═ (d at 6.39 ppm and d at 6.30 ppm) and OC═C*H* (t at 4.40 ppm and t at 4.67 ppm) hydrogen atoms of the two conformations of **8** at −68 °C coalesce to a single set of signals (d at 6.33 ppm and t at 4.61 ppm) at 96 °C. Furthermore, only two signals were observed in the ^{1}H−^{29}Si HMBC

spectrum of **8** at −68 °C (vide infra), also suggesting that only one compound is present.

The ^{1}H, ^{13}C, ^{1}H COSY, ^{1}H−^{29}Si HMBC, and ^{1}H−^{13}C HSQC NMR spectroscopic data at −68 °C were entirely consistent with the crystallographically determined structure. Although the structure of compound **8** was established by X-ray crystallography, a discussion of the details of the NMR spectroscopic data of **8** is worthwhile since it will aid in the interpretation of the spectroscopic data of the compounds isolated from the reaction of the aldehydic probe with tetramesitylgermasilene. Consistent with the structure assigned for **8** is the appearance of ^{1}H resonances at −68 °C at 6.39 ppm (d, J = 7 Hz, OC*H*=CH, partially overlapped by a Mes CH signal) and 4.40 ppm (t, J = 6 Hz, OCH=C*H*) for conformation 1 and 6.30 ppm (d, J = 6 Hz, OC*H*=CH, partially overlapped by a Mes CH signal) and 4.67 ppm (t, J = 6 Hz, OCH=C*H*) for conformation 2, which are in the expected chemical shift range for enolic hydrogen atoms. The ^{1}H−^{13}C HSQC NMR spectrum indicated that the 6.30, 6.39, 4.67, and 4.40 ppm signals in the ^{1}H dimension correlated with signals found at 138.4, 141.8, 113.6, and 107.6 ppm in the ^{13}C dimension, respectively. These ^{13}C NMR resonances are in the expected chemical shift range for oxygen-substituted vinylic carbon atoms. The COSY NMR spectrum showed the expected coupling interactions for these hydrogen atoms. The COSY NMR spectrum also showed that the signal at 4.40 ppm (=C*H*CH) was coupled to a signal at 3.66 ppm (=CHC*H*) for conformation 1 and the signal at 4.67 ppm (=C*H*CH) was coupled to a signal at 4.29 ppm (=CHC*H*) for conformation 2. The ^{1}H−^{13}C HSQC NMR spectrum indicated that the 3.66 and 4.29 ppm signals in the ^{1}H dimension correlated with signals found at 82.3 and 78.1 ppm in the ^{13}C dimension, respectively. These ^{13}C NMR resonances are in the expected chemical shift range for carbon atoms with both an oxygen and vinyl substituent. The COSY NMR spectrum also showed a correlation between the signal at 3.66 ppm (=CHC*H*OCH$_3$) and a signal at 4.64 ppm (C*H*Ph) for conformation 1 and the signal at 4.29 ppm (=CHC*H*OCH$_3$) with a signal at 4.74 ppm (C*H*Ph) for conformation 2. The 4.64 and 4.74 ppm signals were also found to correlate with the resonances at 51.1 and 44.0 ppm, respectively, in the ^{13}C dimension of the ^{1}H−^{13}C HSQC NMR spectrum, which are typical chemical shifts for phenyl-substituted carbon atoms. The ^{1}H−^{13}C HSQC NMR spectrum also showed a correlation between the signals at 2.42 ppm (OCH_3) and 3.00 ppm (OCH_3) in the ^{1}H dimension and resonances at 54.0 and 50.1 ppm, respectively, in the ^{13}C dimension. The ^{13}C NMR resonances are in the expected chemical shift range for methoxy carbon atoms. The ^{1}H−^{29}Si HMBC spectrum showed a correlation of the doublets at 6.30 (OC*H*=) and 4.64 (C*H*Ph) ppm to the signals at −4.5 and −10.1 ppm, respectively, in the ^{29}Si dimension. These correlations allowed for assignment of the signal at −4.5 ppm as *Si*−O and the signal at −10.1 as *Si*−CHPh. The ^{29}Si NMR chemical shifts of **8** agree well with the ^{29}Si shifts reported for compound **2** (−0.5 ppm for *Si*−O and −11.9 ppm for *Si*−CHPh).[4a]

Addition of *trans*,*trans*-2-methoxy-3-phenylcyclopropane carbaldehyde to a solution of tetramesitylgermasilene, produced by photolysis of hexamesitylsiladigermirane at −70 °C in the presence of Et_3SiH, yielded (Et_3Si)$GeMes_2H$ (**9**) and a white solid (**10a**−**d**; 34%). Compound **9** was readily identified by comparison of its ^{1}H NMR data with the known literature values.[22] Compounds **10a**−**d** were identified by NMR spectroscopy and mass spectrometry.



When potassium (K^+) ionization of desorbed species (K^+IDS) was used as a mild ionization technique[23] in the mass analysis of **10**, the presence of an ion at 793.6 amu which can be attributed to an adduct between the germasilene and the aldehyde (+39 amu) was evident. The NMR spectra of **10** at RT were very difficult to interpret due to broadening of the signals arising from the mesityl substituents and the seven-membered ring. However, the NMR spectra of compound **10** at −68 °C showed this compound to be a mixture of four isomers, **10a**, **10b**, **10c**, and **10d**, in a ratio of approximately 3:1:1:1. Furthermore, there are four different ^{29}Si signals in the ^{1}H−^{29}Si HMBC spectrum, consistent with four different compounds.

The ^{1}H−^{1}H COSY spectrum of **10** at −68 °C showed correlations between four distinct spin systems: **10a** [4.02 ppm (dd, J = 5 Hz, J = 12 Hz), 4.33 ppm (d, J = 12 Hz), 4.63 ppm (t, J = 6 Hz), 6.30 ppm (d, J = 6 Hz)]; **10b** [3.84 ppm (dd, J = 6 Hz, J = 12 Hz), 4.27 ppm (d, J = 12 Hz), 4.59 ppm (t, J = 6 Hz), 6.62 ppm (d, J = 8 Hz)]; **10c** [3.48 ppm (d, J = 12 Hz), 4.07 ppm (t, J = 7 Hz), 5.40 ppm (dd, J = 7 Hz, 12 Hz), 6.42 (d, J = 6 Hz)]; **10d** [4.55 ppm (d, J = 6 Hz), 6.35 ppm (d, J = 6 Hz)]. The multiplicities and chemical shifts of the ^{1}H signals for **10a**, **10b**, and **10c** are consistent with an OCH=CHCHCH spin system present in an oxadimetallacycloheptene ring, whereas the chemical shifts and multiplicities of the ^{1}H signals of **10d** are consistent with a CH=CH spin system present in an (oxapentadienyl)-dimetallane structure.

The ^{1}H−^{13}C HSQC NMR spectrum at −68 °C showed a correlation between the doublet at 4.27 ppm (**10b**) and a signal at 45.8 ppm in the ^{13}C dimension. The signal at 45.8 ppm was assigned to *C*HPh on the basis of a comparison with the chemical shift of the analogous carbon signals in **8** (44.0−50.1 ppm) and in **4** (48.7 ppm).[4a] Since a correlation between this carbon signal and a doublet was observed, the phenyl substituent must be at the end of the OCH=CHCHCH spin system. From this, the regiochemistry of the butenyl moiety of

(22) Baines, K. M.; Cooke, J. A. Vittal, J. J. *J. Chem Soc., Chem. Commun.* **1992**, 1484−1485.
(23) Simonsick, W., Jr. *J. Appl. Polym. Sci. Appl. Polym. Symp.* **1989**, *43*, 257−274.

the seven-membered ring of **10b** was assigned to M−CHPh−CH(OCH$_3$) and not M−CH(OCH$_3$)−CHPh, where M = Si or Ge. The ^{1}H−^{13}C HSQC NMR spectrum did not show a correlation of the doublets at 4.33 ppm (**10a**) or 3.47 ppm (**10c**) to any signals in the ^{13}C dimension. The chemical shifts and multiplicities of the ^{1}H's in the seven-membered ring of **10a** are very similar to the chemical shifts, the multiplicities, and the coupling constants of the ^{1}H's in the seven-membered ring of **10b** (±0.3 ppm). Thus, we believe that **10a** and **10b** have the same regiochemistry and stereochemistry of the CH=CHCHCH moiety in the seven-membered ring. Since the magnitude of the CHPh−CHOMe coupling constant is the same as was observed in **8** (a *trans* isomer), we have tentatively assigned the stereochemistry in both **10a** and **10b** as *trans*. The ^{1}H−^{29}Si HMBC spectrum of **10** contained four signals. The signal at −16.7 ppm in the ^{29}Si dimension was shown to correlate only to the doublet at 4.27 ppm (**10b**). Thus, the regiochemistry of the OMM′ portion of the seven-membered ring was tentatively assigned to the oxa-2-germa-3-silacycloheptene structure for **10b**. Furthermore, the ^{29}Si NMR chemical shift (−16.7 ppm) agrees well with the Si−*Si*CHR ^{29}Si shift observed in compounds **8** (−10.1 ppm) and **2** (−11.8 ppm).[4a] The signal at 10.2 ppm in the ^{29}Si dimension of the ^{1}H−^{29}Si HMBC spectrum of **10** was shown to correlate to the triplet at 4.63 ppm, to the doublet of doublets at 4.02 ppm, and weakly to the doublet at 6.30 ppm in the ^{1}H dimension and, thus, was assigned to **10a**. Since ^{29}Si shifts of O*Si* groups are typically observed downfield from OSi*Si* signals in the seven-membered rings, the regiochemistry of the dimetallane **10a** has tentatively been assigned to OSiGe. In support of this assignment, the ^{29}Si chemical shift of 10.2 ppm is in the same range as the chemical shift of the silicon atom in **4** (2.4 ppm).[4a] The 10.2 ppm signal was also found to correlate to signals at 2.14, 2.33, 2.43, and 2.80 ppm, which are presumably due to the mesityl *o*-methyl groups and also found to correlate to signals at 6.17, 6.30, and 6.79 ppm, which are presumably due to the aryl hydrogen of the mesityl groups.

The chemical shifts of the ^{1}H's of the seven-membered ring in **10c** are quite different from those of **10a** and **10b**; a doublet is observed at 3.48 ppm and a doublet of doublets at 5.40 ppm (compared to 4.33 and 4.02 ppm for the analogous signals in **10a**). The signal at 6.0 ppm in the ^{29}Si dimension of the ^{1}H−^{29}Si HMBC spectrum was shown to correlate to the doublet at 3.48 ppm and the obscured doublet at 6.42 ppm of **10c**. Since the ^{29}Si chemical shift of 6.0 ppm is comparable to that in **10a**, the oxa-2-sila-3-germacycloheptene regiochemistry is tentatively assigned to **10c**. The doublets assigned to the CHPh group in dimetallacycloheptenes **8** and **10a,b** resonate downfield from the doublet of doublets assigned to the CH(OMe) moiety. The same trend is observed for the analogous signals in dimetallacycloheptenes **2** and **4**. In **10c**, however, this trend is reversed; the doublet of doublets resonates downfield from the doublet. Due to the different chemical shifts of the H's attached to the butenyl moiety, it is possible that the regiochemistry of the substituents has changed (i.e., OCH=CHCH(Ph)CH(OMe)). Alternatively, **10c** may be the *cis* isomer or a conformation of **10a**. At this point, it is difficult to assign even a tentative structure for **10c**.

The remaining signals in the 3.4−5.5 ppm region of the ^{1}H NMR spectrum of **10** appear to be a singlet at 3.82 ppm and a doublet at 4.55 ppm. The doublet at 4.55 ppm correlates to a doublet at 6.35 ppm in the COSY spectrum. The chemical shifts, the multiplicities, and the coupling constant are consistent with the X−CH=C(Y)−*cis*-CH=CHOM moiety. Furthermore, the chemical shift of 3.82 ppm for the singlet implies that X = Ph and Y = MeO. The remaining ^{29}Si signal at −1.6 ppm in the ^{1}H−^{29}Si HMBC spectrum of **10** was shown to correlate to a signal at approximately 6.4 ppm in the ^{1}H dimension. We have tentatively assigned this ^{29}Si signal to **10d**. The ^{29}Si NMR chemical shift of −1.6 ppm compares well to the ^{29}Si shifts of compounds **1** (1.2 ppm) and **3** (3.8 ppm), and thus, the regiochemistry is most likely OSiGe. Furthermore, the ^{29}Si shift in **10d** is not consistent with an Si−H functionality (Compare OSi*Si*H, −56.5 ppm, to O*Si*SiH, 1.2 ppm, in **1**).[4a]

The ^{1}H−^{13}C HSQC and HMBC spectra were quite complex and difficult to interpret; only the following assignments could be made. The ^{1}H−^{13}C HSQC spectrum of **10** showed correlations of signals at 2.25, 2.86, and 3.16 ppm to signals at 53.80, 49.29, and 55.65 ppm, respectively. Consistent with the chemical shifts, these signals were assigned to methoxy groups. The ^{1}H−^{13}C HSQC spectrum also showed correlations of ^{1}H signals at 4.62 and 6.30 ppm to ^{13}C signals at 113.10 and 142.22 ppm, respectively. These signals were assigned to a O*C*H=CH and a OCH=*C*H, respectively. The ^{1}H−^{13}C HMBC spectrum showed a correlation of ^{1}H signals at 2.86 and 4.32 ppm to a signal at 77.62 ppm in the ^{13}C dimension. Thus, the signal at 2.86 ppm was assigned to the methoxy group of **10a**. A correlation was also observed between the ^{1}H signal at 3.16 ppm and the ^{13}C signal at 74.20 ppm in the ^{1}H−^{13}C HMBC spectrum.

Discussion

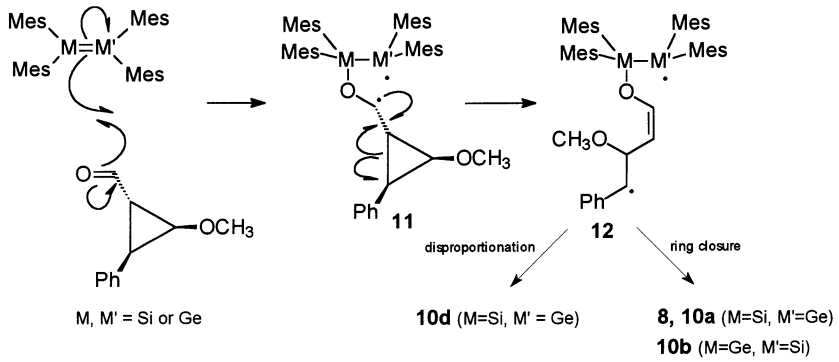
Although *trans*,*trans*-2-methoxy-3-phenylcyclopropane carbaldehyde has the same (alkoxy)(phenyl)cyclopropyl framework as the hypersensitive probes developed by Newcomb,[13] there is one important structural difference: the putative radical or cation[24] has an oxygen substituent. The rate constant for the ring-opening of an oxy-substituted cyclopropylcarbinyl radical is unknown; however, Newcomb and co-workers have shown in other radical reactions that oxygen substituents do not dramatically alter the rates of rearrangement.[25] The rate of the ring-opening of the cyclopropylmethyl cation is also not known; however, undoubtedly it would be slower with an oxygen substituent. Given the structural change to the probe, it was first necessary to confirm that the regioselectivity of the ring-opening remained the same under either radical or cationic conditions.

Under acidic conditions, the cyclopropyl carbaldehyde was found to rearrange to the *cis*- and *trans*-2-methoxy-3-phenyl-2,3-dihydrofurans (**6**). The formation of the

(24) We believe the formation of a zwitterion with a cationic charge at the cyclopropyl methyl is more likely.

(25) Johnson, C. C.; Horner, J. H.; Tronche, C.; Newcomb, M. *J. Am. Chem. Soc.* **1995**, *117*, 1684−1687.

Scheme 3



dihydrofurans is readily explained by ring-opening of the protonated aldehyde regioselectively toward the methoxy group followed by cyclization and deprotonation to the dihydrofuran. The difference in reactivity between the methoxy- and the unsubstituted phenylcyclopropane carbaldehydes is striking. Whereas *trans*-2-phenylcyclopropane carbaldehyde showed no evidence for ring-opening under acidic conditions,[11] the methoxy-substituted derivative readily undergoes ring-opening to give the dihydrofuran derivatives, **6**. On the other hand, treatment of *trans*,*trans*-2-methoxy-3-phenylcyclopropane carbaldehyde with tris(trimethylsilyl)silane under radical conditions led to the formation of **7**. The formation of **7** can readily be explained by the addition of the tris(trimethylsilyl)silyl radical to the oxygen atom of the carbonyl group to give the oxy-substituted carbinyl radical. Ring-opening of the cyclopropyl ring regioselectively toward the phenyl group followed by abstraction of a hydrogen atom would give **7**. Given the ability of a phenyl group to stabilize a radical more strongly than an alkoxy group, it is not surprising that the methoxy-substituted phenylcyclopropane carbaldehyde undergoes ring-opening toward the phenyl substituent under radical conditions. The preceding results indicate that *trans*,*trans*-2-methoxy-3-phenylcyclopropane carbaldehyde can indeed serve as a mechanistic probe with the *added capability* of being able to distinguish between *ring-opened* radical or ionic intermediates. As with *trans*-2-phenylcyclopropane carbaldehyde, this probe can distinguish between the formation of a cation or a radical at the cyclopropylmethyl carbon: it will undergo ring-opening toward the phenyl substituent if a radical is formed at this center and, depending on the kinetics, it may or may not if a cation is formed. However, this probe now offers a distinct reaction pathway in the event that the cationic intermediate does undergo rearrangement: ring-opening toward the methoxy substituent. As such, *trans*,*trans*-2-methoxy-3-phenylcyclopropane carbaldehyde can be utilized to provide more definitive evidence either for or against a biradical intermediate.

Addition of the probe to tetramesityldisilene or tetramesitylgermasilene gave compound **8** or **10a**−**d**, respectively, as the only isolated adducts. Clearly, compounds **8**, **10a**, **10b**, and **10d** arise from ring closure (**8**, **10a**,**b**) or from disproportionation (**10d**) of the 2*E*-benzyl/homoallyl biradical, **12**. Biradical **12** must be derived from the regioselective ring-opening of the phenylmethoxy-substituted cyclopropylcarbinyl radical, **11**, toward the phenyl substituent (see Scheme 3). This provides unequivocal evidence that the addition of the carbonyl group to the Si−Si double bond of the disilene proceeds via a biradical intermediate. Although the uncertainty in the structure of **10c** precludes an unambiguous statement, we can conclude that the major reaction pathway for the addition of aldehydes to germasilenes is also via a biradical intermediate.

We continue to investigate the use of mechanistic probes to determine the nature of any reactive intermediates formed during the addition reactions of doubly bonded group 14 derivatives.

Experimental Section

All experiments were carried out in flame-dried glassware under an inert atmosphere of argon using standard Schlenk line techniques. THF was freshly distilled from sodium benzophenone ketyl prior to use. Toluene, benzene, hexanes, and Et_3SiH were distilled from $LiAlH_4$ prior to use. Tris(trimethylsilyl)silane was obtained from Gelest Inc. and azoisobutyronitrile (AIBN) and *p*-toluenesulfonic acid were obtained from BDH Co. Chromatography was carried out on silica gel plates using a Chromatotron (Harrison Research), on conventional silica gel preparative plates, or by conventional column chromatography. Silica gel and silica gel preparative plates were obtained from BDH Co.

Photolyses were carried out using a Rayonet photochemical reactor. Low-temperature photolyses were carried out by cooling the sample using an Endocal model ULT-70 low-temperature external bath circulator to force cold (−60 or −70 °C) methanol through a vacuum-jacketed quartz (254 nm) or Pyrex (350 nm) immersion well. Melting points were measured using a Gallencamp metal block apparatus and are uncorrected. NMR spectra were recorded on a Varian Gemini 200, a Varian XL or Gemini 300, a Varian Inova 400, or a Bruker Avance DRX-500 using benzene-d_6 as a solvent, unless otherwise noted. The standards used were as follows: residual C_6D_5H 7.15 ppm, residual $C_6D_5CD_2H$ 2.03 ppm (central transition), residual $CDHCl_2$ 5.32 ppm for ^1H spectra; C_6D_6 central transition 128.00 ppm, CD_2Cl_2 central transition 53.80 ppm for ^{13}C NMR spectra; and Me_4Si as an external standard, 0 ppm for ^{29}Si. Literature ^1H NMR chemical shifts agreed to ±0.01 ppm. IR spectra were recorded (cm^{-1}) as thin films on a Perkin-Elmer System 2000 FT-IR spectrometer. DRIFTS IR samples were analyzed as neat powders on a Bruker ISS5S FT-IR using a diffuse reflectance infrared FT spectroscopy (DRIFTS) accessory manufactured by Spectratech. A Finnigan MAT model 8200 instrument, with an ionizing voltage of 70 eV, was used to obtain electron impact mass spectra, and a Finnigan 4615B GC/MS quadrupole mass spectrometer (San Jose, CA) was used to obtain potassium (K^+) ionization of desorbed species (K^+IDS) spectra (reported in mass-to-charge units, *m*/*z*, with ion identity and peak intensities relative to the base peak in parentheses).

2,2-Dimesitylhexamethyltrisilane,[26] hexamesitylsiladigermirane,[27] and *trans*,*trans*-2-methoxy-3-phenylcyclopropane carbaldehyde[13c] were prepared following the published procedures.

Reaction of *trans*,*trans*-2-Methoxy-3-phenylcyclopropane Carbaldehyde with *p*-Toluenesulfonic Acid. *trans*,*trans*-2-Methoxy-3-phenylcyclopropane carbaldehyde (50 mg, 0.28 mmol) and *p*-toluenesulfonic acid (1.9 mg, 0.01 mmol) were dissolved in benzene (3 mL) and stirred at 22 °C for 2 h. The solvent was removed under vacuum to yield an orange oil. The oil was determined to be a 1:8 mixture of *trans*-**6** and *cis*-**6** in addition to minor amounts of other unidentified products.

***trans*-2-Methoxy-3-phenyl-2,3-dihydrofuran (*trans*-6).** ^{1}H NMR (ppm): 7.05−7.25 (m, 5H, Ph C*H*), 6.29 (dd, 1H, OC*H*=C, J = 3 Hz, J = 2 Hz), 5.13 (d, 1H, C*H*OCH$_3$, J = 3 Hz), 4.89 (dd, 1H, C*H*=CHO, J = 3 Hz, J = 3 Hz), 3.94 (ddd, 1H, C*H*Ph, J = 2 Hz, J = 2 Hz, J = 2 Hz), 3.20 (s, 3H, OC*H*$_3$). ^{13}C NMR (ppm): 144.95 (O*C*H=C) 137.59 (Ph *C*), 129.85, 129.25, 127.01 (Ph *C*H), 113.18, 103.33 (*C*HOCH$_3$, OCH=*C*H), 55.36, 52.42 (O*C*H$_3$, *C*HPh).

***cis*-2-Methoxy-3-phenyl-2,3-dihydrofuran (*cis*-6).** ^{1}H NMR (ppm): 7.05−7.25 (m, 5H, Ph C*H*), 6.32 (dd, 1H, OC*H*=C, J = 3 Hz, J = 3 Hz), 5.18 (d, 1H, C*H*OCH$_3$, J = 8 Hz), 4.85 (dd, 1H, C*H*=CHO, J = 3 Hz, J = 2 Hz), 3.98 (ddd, 1H, C*H*Ph, J = 8 Hz, J = 2 Hz, J = 2 Hz), 3.01 (s, 3H, OC*H*$_3$). ^{13}C NMR (ppm): 145.26 (O*C*H=C) 137.59 (Ph *C*), 128.91, 128.29, 127.25 (Ph *C*H), 107.04 (*C*HOCH$_3$), 104.49 (OCH=*C*H), 55.94 (O*C*H$_3$), 52.29 (*C*HPh).

Thermolysis of *trans*,*trans*-2-Methoxy-3-phenylcyclopropane Carbaldehyde in the Presence of Tris(trimethylsilyl)silane. *trans*,*trans*-2-Methoxy-3-phenylcyclopropane carbaldehyde (100 mg, 0.56 mmol), tris(trimethylsilyl)silane (0.2 mL, 0.60 mmol), and AIBN (20 mg, 0.12 mmol) were dissolved in toluene (5 mL) and heated to 80 °C for 3 h. The solvent was removed in vacuo to yield an oily orange residue. The products were separated by preparative thin-layer chromatography (20:80 ethyl acetate/hexanes) to give a 2:1 mixture of *cis*-**7** and *trans*-**7** (42.5 mg, 18%) as a clear, colorless oil. *cis*-**7** (11.3 mg, 5%) could be separated from *trans*-**7** by preparative thin-layer chromatography (20:80 ethyl acetate/hexanes) but contained traces of an unidentified compound. *trans*-**7** was not isolated in pure form. The IR and MS data are of the mixture of *cis*-**7** and *trans*-**7**, and the ^{1}H, ^{13}C, and ^{29}Si NMR data were extracted from spectra of the mixture.

Mixture of *cis*-3-Methoxy-4-phenyl-1-[tris(trimethylsilyl)siloxy]but-1-ene (*cis*-7) and *trans*-3-Methoxy-4-phenyl-1-[tris(trimethylsilyl)siloxy]-but-1-ene (*trans*-7). IR (thin film, cm^{-1}): 2960 (m), 1653 (w), 1261 (s), 1077 (s), 840 (s), 803 (m), 755 (w), 698 (w). MS (*m*/*z*): 351 (M$^+$ − Si(CH$_3$)$_3$, 21), 333 (M$^+$ − OSi(CH$_3$)$_3$, 13), 263 (OSi(Si(CH$_3$)$_3$)$_3$, 18), 247 (Si(Si(CH$_3$)$_3$)$_3$, 21), 221 (27), 205 (SiOCH=CH(OCH$_3$)CH$_2$-Ph, 53), 173 (Si(Si(CH$_3$)$_3$)$_3$ − HSi(CH$_3$)$_3$, 24), 117 (OSiSi(CH$_3$)$_3$, 25), 73 (Si(CH$_3$)$_3$, 100). K$^+$IDS MS (*m*/*z*): 463 (M$^+$ + 39, 100).

***cis*-3-Methoxy-4-phenyl-1-[tris(trimethylsilyl)siloxy]-but-1-ene (*cis*-7).** ^{1}H NMR (ppm): 7.05−7.09 (m, 1H, Ph C*H*), 7.12−7.20 (m, 3H, Ph C*H*), 7.29−7.31 (m, 1H, Ph C*H*), 6.21 (dd, 1H, SiOC*H*=CH, J = 6 Hz, J = 1 Hz), 4.62 (dtd, 1H, C*H*OCH$_3$, J = 7 Hz, J = 9 Hz, J = 1 Hz), 4.43 (dd, 1H, SiOCH=C*H*, J = 6 Hz, J = 9 Hz), 3.30 (s, 3H, OC*H*$_3$), 3.07 (dd, 1H, CH$_a$H$_b$Ph, J = 14 Hz, J = 7 Hz), 2.88 (dd, 1H, CH$_a$*H*$_b$Ph, J = 14 Hz, J = 6 Hz), 0.18 (s, 27H, Si(C*H*$_3$)$_3$. ^{13}C NMR (ppm): 145.66 (SiO*C*H=C), 139.51 (Ph *C*), 130.01, 128.26, 126.18 (Ph *C*H), 110.40 (SiOCH=*C*H), 75.08 (*C*HOCH$_3$), 56.02 (O*C*H$_3$), 42.86 (*C*H$_2$Ph), 0.03 (Si(*C*H$_3$)$_3$). ^{29}Si NMR (ppm): 7.6 (O*Si*(Si(CH$_3$)$_3$), −14.8 (*Si*(CH$_3$)$_3$).

***trans*-3-Methoxy-4-phenyl-1-[tris(trimethylsilyl)siloxy]-but-1-ene (*trans*-7).** ^{1}H NMR (ppm): 7.05−7.09 (m, 1H, Ph C*H*), 7.12−7.20 (m, 3H, Ph C*H*), 7.29−7.31 (m, 1H, Ph C*H*), 6.32 (d, 1H, SiOC*H*=CH, J = 12 Hz), 4.98 (dd, 1H, SiOCH=C*H*, J = 12 Hz, J = 9 Hz), 3.61 (dt, 1H, C*H*OCH$_3$, J = 6 Hz, J = 9 Hz), 3.13 (s, 3H, OC*H*$_3$), 3.01 (dd, 1H, CH$_a$H$_b$Ph, J = 14 Hz, J = 7 Hz), 2.79 (dd, 1H, CH$_a$*H*$_b$Ph, J = 14 Hz, J = 6 Hz), 0.23 (s, 27H, Si(C*H*$_3$)$_3$). ^{13}C NMR (ppm): 148.16 (SiO*C*H=C), 139.29 (Ph *C*), 130.01, 128.26, 126.26 (Ph *C*H), 110.00 (SiOCH=*C*H), 80.84 (*C*HOCH$_3$), 55.40 (O*C*H$_3$), 43.83 (*C*H$_2$Ph), 0.23 (Si(*C*H$_3$)$_3$). ^{29}Si NMR (ppm): 5.5 (O*Si*(Si(CH$_3$)$_3$), −14.8 (*Si*(CH$_3$)$_3$).

Addition of *trans*,*trans*-2-Methoxy-3-phenylcyclopropane Carbaldehyde to Tetramesityldisilene. Mes$_2$Si(SiMe$_3$)$_2$ (100 mg, 0.24 mmol) was dissolved in hexanes (8 mL) and photolyzed (254 nm) at −60 °C for 16 h. After irradiation for 16 h, the reaction mixture appeared clear and bright yellow in color. *trans*,*trans*-2-Methoxy-3-phenylcyclopropane carbaldehyde (86 mg, 0.49 mmol) dissolved in dried, degassed toluene (4 mL) was added to the reaction mixture via cannula. Upon addition, the bright yellow color immediately faded to clear and colorless. The solvent was removed under vacuum to yield an oily yellow residue. The residue was recrystallized from 1:1 acetone/benzene to afford **8** as white crystals (34.9 mg, 41%). No other products were isolated or identified.

2,2,3,3-Tetramesityl-4-phenyl-5-methoxyoxa-2,3-disilacyclohept-6-ene (8). Mp: 218−219 °C. IR (DRIFTS, cm^{-1}): 3022 (m), 2967 (s), 2925 (s), 2856 (m), 2822 (w), 1713 (w), 1644 (s), 1602 (s), 1444 (s), 1292 (s), 1258 (m), 1127 (s), 1093 (s), 1037 (s), 844 (s), 796 (m), 714 (s), 596 (s). ^{1}H NMR (C$_7$D$_8$, −68 °C, ppm): 7.41 (d, J = 7 Hz, Ph C*H*), 7.31 (s, Ph C*H*). 7.26 (d, J = 8 Hz, Ph C*H*), 6.87−7.20 (m, Ph C*H*), 6.85, 6.84, 6.74, 6.73, 6.71, 6.60, 6.58, 6.51 (all s, all Mes C*H*), 6.39 (d, 1H, OC*H*=C, J = 7 Hz, conformation 1), 6.38 (s, Mes C*H*), 6.30 (d, 1H, OC*H*=C, J = 6 Hz, conformation 2), 6.29, 6.20, 6.11 (all s, all Mes C*H*), 4.74 (d, 1H, C*H*Ph, J = 12 Hz, conformation 2), 4.67 (t, 1H, OCH=C*H*, J = 6 Hz, conformation 2), 4.64 (d, 1H, C*H*Ph, J = 4 Hz, conformation 1), 4.40 (t, 1H, OCH=C*H*, J = 6 Hz, conformation 1), 4.29 (dd, 1H, C*H*OCH$_3$, J = 6 Hz, J = 12 Hz, conformation 2), 3.66 (t, 1H, C*H*OCH$_3$, J = 5 Hz, conformation 1), 3.24, 3.06, 3.04 (all s, all Mes C*H*$_3$), 3.00 (s, 3H, OC*H*$_3$, conformation 2), 2.97, 2.94, 2.66, 2.64, 2.60, 2.57 (all s, all Mes C*H*$_3$), 2.42 (s, 3H, OC*H*$_3$, conformation 1), 2.21, 2.17, 2.16, 2.15, 2.13, 1.97, 1.93, 1.81, 1.65, 1.47, 1.15, (all s, all Mes C*H*$_3$). ^{13}C NMR (C$_7$D$_8$, −68 °C, ppm): 146.14, 145.34, 145.00, 144.83, 144.52, 143.95, 143.62, 143.44, 143.13, 142.88, 142.32 (Mes *C* and Ph *C*), 141.81 (O*C*H=C, conformation 1), 141.59, 139.87, 139.14, 138.97 (Mes *C*), 138.35 (O*C*H=C, conformation 2), 136.41 (Mes *C*), 130.86, 130.72, 130.47, 129.95, 129.82 129.00, 128.00 (Mes *C*H), 126.88, 126.48, (Ph *C*H), 113.60 (OCH=*C*H, conformation 2), 107.64 (OCH=*C*H, conformation 1), 82.29 (*C*HOCH$_3$, conformation 1), 78.13 (*C*HOCH$_3$, conformation 2), 54.02 (O*C*H$_3$, conformation 1), 51.07 (*C*HPh, conformation 1), 50.08 (O*C*H$_3$, conformation 2), 44.02 (*C*HPh, conformation 2), 31.06, 30.55, 29.88, 29.50, 29.07, 28.74, 27.99, 27.66, 26.97, 25.97, 25.57, 25.09, 24.50, 24.30, 23.86, 23.39, 23.08, 22.61 (Mes *C*H$_3$). ^{29}Si NMR (C$_7$D$_8$, −68 °C, ppm): −4.5 (*Si*−O), −10.1 (*Si*−CHR). MS (*m*/*z*), CI:isobutane: 709 (M$^+$+ H, 4), 677 (M$^+$ − OCH$_3$, 14), 589 (M$^+$ − Mes, 29), 559 (MH$^+$ − Mes − OCH$_3$, 13), 411 (M$^+$ − SiMes$_2$ −OCH$_3$, 53), 297 (Mes$_2$SiOCH$_3$, 70), 121 (MesH + H, 80), 101 (100). K$^+$IDS MS (*m*/*z*): 747 (M$^+$ + 39, 20). High-resolution MS: calc for C$_{47}$H$_{56}$Si$_2$O$_2$+H: 709.3897, found 709.3865.

Crystals of C$_{47}$H$_{56}$O$_2$Si$_2$ were grown from a 1:1 solution of benzene/acetone. A colorless block was mounted on a glass fiber. Data were collected at room temperature (21 °C) on a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1997) software. Crystal cell refinement and data reduction was carried out using the Nonius DENZO package. The crystal data and refinement parameters for **8** are listed in Table 1. The unit cell parameters were calculated and refined from the full data set. Selected interatomic distances and angles are

(26) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1983**, *3*, 793−800.
(27) Baines, K. M.; Cooke, J. A. *Organometallics* **1991**, *10*, 3419−3421.

listed in Table 2. Complete details are given in the Supporting Information.

Addition of *trans,trans*-2-Methoxy-3-phenylcyclopropane Carbaldehyde to Tetramesitylgermasilene. $SiGe_2Mes_6$ (100 mg, 0.113 mmol) and Et_3SiH (0.10 mL, excess) were dissolved in toluene (8 mL) and photolyzed (350 nm) at −70 °C for 16 h. After irradiation for 16 h, the reaction mixture appeared clear and bright yellow. *trans,trans*-2-Methoxy-3-phenylcyclopropane carbaldehyde (86 mg, 0.49 mmol) dissolved in dried, degassed toluene (4 mL) was added to the reaction mixture via cannula. The bright yellow color did not fade upon addition of the aldehyde. The reaction mixture was warmed to 22 °C. By the time the temperature had reached 22 °C (∼30 min), the bright yellow color faded to a pale yellow. The reaction mixture was allowed to stand for an additional 2 h; there was no further change in the color of the solution. The solvent was evaporated to yield an oily yellow residue. The residue was recrystallized from 1:1 acetone/benzene to afford **10a**−**d** as a fine white powder (29.2 mg, 34%). The crystals were removed by filtration from the solution, and the remaining products were separated by preparative thin-layer chromatography (50:50 CH_2Cl_2/hexanes) to give **9**[22] (27 mg). No other products were isolated or identified.

2,2,3,3-Tetramesityl(phenyl)(methoxy)oxagermasilacyclohept-6-ene (10a−c) and [Dimesityl(1-oxa-4-methoxy-5-phenylpentadienyl)silyl]dimesitylgermane (10d). Mp: 133−134 °C (dec). IR (cm^{-1}): 3413 (m), 2963 (s), 2921 (s), 1724 (w), 1604 (s), 1553 (w), 1449 (s), 1413 (m), 1378 (m), 1261 (s), 1079 (s), 1034 (s), 847 (m), 803 (s), 699 (m), 678 (m), 633 (m). ^{1}H NMR (CD_2Cl_2, −68 °C, ppm): 7.00−7.40 (m, Ph C*H*), 6.93, 6.83, 6.79, 6.78, 6.77, 6.76, 6.74, 6.70, 6.68, 6.67, 6.63 (all s, all Mes C*H*), 6.62 (d, OC*H*═C, J = 8 Hz, **10b**), 6.57, 6.52, 6.48, 6.45 (all s, all Mes C*H*), 6.42 (d, 1H, OC*H*═C, J = 6 Hz, **10c**), 6.35 (d, OC*H*═C, J = 6 Hz, **10d**), 6.33 (s, Mes C*H*), 6.30 (s, OC*H*═C, J = 6 Hz, **10a**), 6.20, 6.17, 6.15, 6.03 (all s, all Mes C*H*), 5.40 (dd, J = 7 Hz, J = 12 Hz, **10c**), 4.63 (t, OCH═C*H*, J = 6 Hz, **10a**), 4.59 (t, OCH═C*H*, J = 6 Hz, **10b**), 4.55 (d, OCH═C*H*, J = 6 Hz, **10d**), 4.33 (d, C*H*Ph, J = 12 Hz, **10a**), 4.27 (d, C*H*Ph, J = 12 Hz, **10b**), 4.07 (t, OCH═C*H*, J = 7 Hz, **10c**), 4.02 (dd, C*H*OCH$_3$, J = 5 Hz, J = 12 Hz, **10a**), 3.84 (dd, C*H*OCH$_3$, J = 6 Hz, J = 12 Hz, **10b**), 3.82 (s, PhC*H*═C, **10d**), 3.48 (d, J = 12 Hz, **10c**), 3.40, 3.36, 3.24 (all s, all Mes CH_3), 3.16 (s, OCH_3), 2.92 (s, Mes CH_3), 2.86 (s, OCH_3), 2.84, 2.82, 2.75, 2.71, 2.67, 2.59, 2.49, 2.46, 2.459, 2.457, 2.41, 2.39, 2.35, 2.34, 2.33, 2.31, 2.30 (all s, all Mes CH_3), 2.25 (s, OCH_3), 2.23, 2.22, 2.20, 2.19, 2.15, 2.14, 2.12, 2.11, 2.10, 2.07, 2.03, 2.02, 2.00, 1.87, 1.78, 1.77, 1.75, 1.58, 1.57, 1.51, 1.50, 1.25, 1.22, 1.16 (all s, all Mes CH_3). ^{13}C NMR (CD_2Cl_2, −68 °C, ppm): 145.08, 144.75, 143.94, 143.20 (Mes and Ph *C*), 142.22 (O*C*H═C), 141.85, 139.49, 137.47, 136.35 (Mes and Ph *C*), 130.06, 129.69, 129.18, 128.72, 128.15 (Mes *C*H), 127.75, 126.67, 124.67 (Ph C*H*), 113.1[28] (OCH═*C*H), 77.62 (*C*HOCH$_3$), 74.2[29] (*C*HOCH$_3$), 55.65 (O*C*H$_3$), 53.8[28] (O*C*H$_3$), 49.29 (O*C*H$_3$), 45.80 (*C*HPh, **10b**), 30.36, 28.16, 27.24, 26.52, 25.66, 25.06, 23.94, 22.58, 21.99, 20.62 (Mes *C*H$_3$). ^{29}Si NMR (*C*D_2Cl_2, −70 °C, ppm): 10.2 (**10a**), 6.0 (**10c**), −1.6 (**10d**), −16.7 (**10b**). MS (*m*/*z*): 491 (M^+ − Mes_2Si, 31), 444 (M^+ − Mes_2Ge) 428 (Mes_2GeCHPhCHCH, 31), 370 (M^+ − Mes, Mes_2Si, 42), 325 (Mes_2GeCH, 72), 311 (Mes_2Ge − H, 27), 219 (MesGeCHCH, 21), 192 (MesGe − H, 23), 119 (Mes, 56). K^+IDS MS (*m*/*z*): 793.6 (M^+ + 39, 100).

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Supporting Information Available: Full crystallographic data, bond lengths, and bond angles for **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Chemical shift estimated from the ^{1}H−^{13}C HSQC spectrum.
(29) Chemical shift estimated from the ^{1}H−^{13}C HMBC spectrum.