

Cycloaddition Reactions of Aldehydes to Tetramesityldisilene and Tetramesitylgermasilene: Evidence for a Biradical Intermediate

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Abstract: The mechanism of the addition of aldehydes to disilenes and germasilenes was investigated by examining the reaction between *trans*-(2-phenylcyclopropyl)carboxaldehyde and tetramesityldisilene or tetramesitylgermasilene. [Dimesityl(2-*cis*-4-*trans*-1-oxa-5-phenylpentadienyl)silyl]dimesitylsilane (**1**) and 2,2,3,3-tetramesityl-4-phenyloxa-2,3-disilacyclohept-6-ene (**2**) were formed in the reaction between the aldehyde and the disilene, and the analogous [dimesityl(2-*cis*-4-*trans*-1-oxa-5-phenylpentadienyl)silyl]dimesitylgermane (**4**) and 2,2,3,3-tetramesityl-4-phenyloxa-2,3-silagermacyclohept-6-ene (**5**) were formed in reaction with the germasilene. It is proposed that compounds **1**, **2**, **4**, and **5** are the result of either disproportionation or ring closure of an intermediate biradical derived from initial bond formation between the oxygen atom of the aldehyde and the doubly bonded silicon atom of the dimetallene.

Introduction

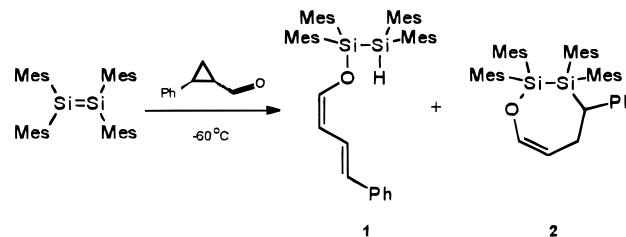
Since their discovery over 15 years ago, much has been, and continues to be, learned about the reactivity of group 14 dimetallenes.¹ However, despite the obvious synthetic potential of these compounds, relatively few mechanistic investigations of the reactions of dimetallenes have been carried out. There have been a few reports concerning the mechanism of the addition of alcohols,^{2–6} and alkenes^{2,7} to disilenes, and recently, we reported our preliminary results on the mechanism of alkene additions to tetramesitylgermasilene and tetramesityldisilene.⁸ In contrast, the mechanism for the addition of carbonyl compounds such as aldehydes and ketones to dimetallenes has not been examined, despite being one of the most extensively investigated synthetic reactions of dimetallenes.⁹

There are numerous mechanistic probes available for exploring the possibility of the intermediacy of radicals in chemical reactions.¹⁰ One class of probes, developed by Newcomb and co-workers, takes advantage of the extremely fast ring opening reaction of phenyl-substituted cyclopropylcarbinyl radicals.¹¹ The intermediacy of a radical center adjacent to the cyclopropyl

ring is often inferred from the isolation of products derived from the opening of the cyclopropyl ring. We realized that the nature of the reactive intermediate involved (if any) in the addition of carbonyl compounds to dimetallenes could be probed by examination of the products from the reaction between *trans*-(2-phenylcyclopropyl)carboxaldehyde (a variation on the probes developed by Newcomb) and a dimetallene, specifically, tetramesityldisilene or -germasilene. The results of our investigations are presented here.

Results

When *trans*-(2-phenylcyclopropyl)carboxaldehyde was allowed to react with tetramesityldisilene at $-60\text{ }^{\circ}\text{C}$ in hexanes, two adducts, **1** and **2**, were produced in approximately a 1:1



mixture as determined by ¹H NMR spectroscopy. The ¹H NMR spectrum of **1** is completely consistent with the assigned

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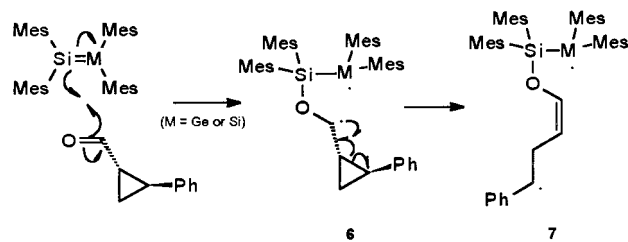
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Scheme 1

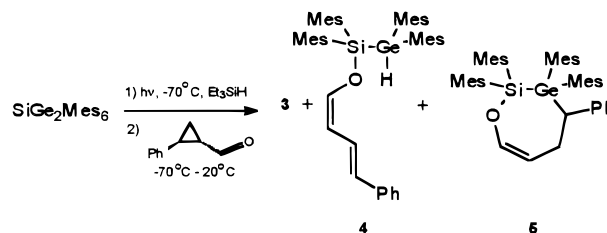


structure. Perhaps the most striking feature in the ^1H NMR spectrum is the presence of resonances entirely consistent with the oxydienic moiety (see the Experimental Section). The chemical shifts of these signals, along with their respective coupling constants, suggest the *cis*–*trans* orientation for the diene substructure in compound **1**. The ^{13}C , ^1H COSY, $^1\text{H}/^{29}\text{Si}$ HSQC, and $^1\text{H}/^{29}\text{Si}$ HMBC NMR spectra all support the assigned structure for compound **1**. For example, the $^1\text{H}/^{29}\text{Si}$ HMBC and $^1\text{H}/^{29}\text{Si}$ HSQC NMR spectra indicated two-bond ($^2J_{\text{Si,H}} = 12.1$ Hz) and one-bond ($^1J_{\text{Si,H}} = 180.9$ Hz) Si–H couplings, respectively, which is in agreement with the structure assigned.

Compound **2** was also identified by NMR spectroscopy. Many of the signals attributed to the mesityl substituents and the hydrogen atoms of the oxadisilacycloheptene ring were broadened in the NMR spectra of this compound, and thus, some spectra were recorded at higher temperatures to sharpen the signals. Central to assigning the structure for compound **2** was confirming the hydrogen and carbon atom coupling interactions that would be expected for the oxadisilacycloheptene ring. The $^1\text{H}/^{13}\text{C}$ HSQC NMR spectrum indicated that the 6.33 and 4.76 ppm signals assigned to the enolic hydrogen atoms in the ^1H dimension correlated with signals found at 140.6 and 111.8 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 and demonstrated that the signal at 4.76 ppm ($=\text{CH}-\text{CHH}$) was coupled to two broad signals at 3.48 ppm ($=\text{CH}-\text{CHH}$) and 2.44 ppm ($=\text{CH}-\text{CHH}$, overlapped by Mes CH_3 signals). The $^1\text{H}/^{13}\text{C}$ HSQC NMR spectrum indicated a correlation between the 3.48 and 2.44 ppm signals in the ^1H dimension with a ^{13}C signal found at 33.0 ppm. Taken together, these coupling interactions support the assignment of the 3.48 and 2.44 ppm signals to the methylene moiety for compound **2**. Finally, the COSY NMR spectrum indicated a correlation between the methylene hydrogen atoms and a signal at 4.02 ppm ($-\text{CHPh}$). The 4.02 ppm signal was also found to correlate with a resonance at 43.5 ppm in the ^{13}C dimension of the $^1\text{H}/^{13}\text{C}$ HSQC NMR spectrum. The NMR spectral data reported here indicate the appropriate coupling interactions for the hydrogen and carbon atoms of the proposed seven-membered ring structure of compound **2**. The $^1\text{H}/^{29}\text{Si}$ HMBC NMR spectrum at 67 °C indicated a correlation between the signal at -0.5 ppm in the ^{29}Si dimension and the ^1H signal at 6.33 ppm ($\text{O}-\text{CH}=\text{CH}$), and thus, this signal is assigned to the silicon of the silyl enol ether moiety. The chemical shift of this signal agrees well with that observed in the analogous compound derived from the germsilene (2.4 ppm; see below) and the silyl enol ether **1** (1.2 ppm). The signal at -8.5 ppm (shifted from -11.9 ppm at 30 °C) correlated to the methine hydrogen atom at 4.03 ppm, and thus was assigned to the silicon atom attached to the carbon atom bearing the phenyl substituent.

Addition of *trans*-(2-phenylcyclopropyl)carboxaldehyde to a solution of tetramesitylgermsilene, produced by photolysis of

hexamesitylsiladigermirane at -70 °C in the presence of Et_3SiH , yielded three products, $(\text{Et}_3\text{Si})\text{GeMes}_2\text{H}$ (**3**),¹² **4**, and **5**, in



a ratio of 2:1:1, respectively, as determined by ^1H NMR spectroscopy. The features of the ^1H NMR spectrum of compound **4** are completely compatible with the assigned structure. The ^1H COSY NMR spectrum confirmed the expected couplings for the diene moiety. The relative chemical shift of the signals, along with their respective coupling constants, suggest the *cis*–*trans* orientation for the diene substructure in compound **4**. The ^{13}C and $^1\text{H}/^{29}\text{Si}$ HMBC NMR spectra all support the assigned structure for compound **4**. For example, the $^1\text{H}/^{29}\text{Si}$ HMBC spectrum shows a two-bond correlation between the signal at 3.75 ppm in the ^{29}Si dimension and the signal assigned as the Ge–H resonance at 5.65 ppm in the ^1H dimension. Compound **5** was also identified by NMR spectroscopy. The spectral features of this compound were very similar to those previously discussed for compound **2**. The $^1\text{H}/^{29}\text{Si}$ HMBC spectrum shows a correlation between the signal at 2.43 ppm in the ^{29}Si dimension and the signal assigned to the $\text{OCH}=\text{CH}$ resonance (6.35 ppm) in the ^1H dimension, supporting the assigned regiochemistry of **5**.

Discussion

The structures of compounds **1**, **2**, **4**, and **5** indicate that the cyclopropyl ring found in the aldehyde has opened during the course of the reaction. We believe the ring opening is the result of the rearrangement of an intermediate biradical (Scheme 1). Initial addition of the carbonyl double bond to the Si–M double bond of germsilene or the disilene would lead to biradical **6**. We expect the cyclopropylcarbinyl radical moiety in **6** to undergo rapid rearrangement to the secondary benzyl/homoallyl radical, **7**. Following rearrangement, **7** can disproportionate to give **1** or **4** or can undergo ring closure to yield compound **2** or **5**.

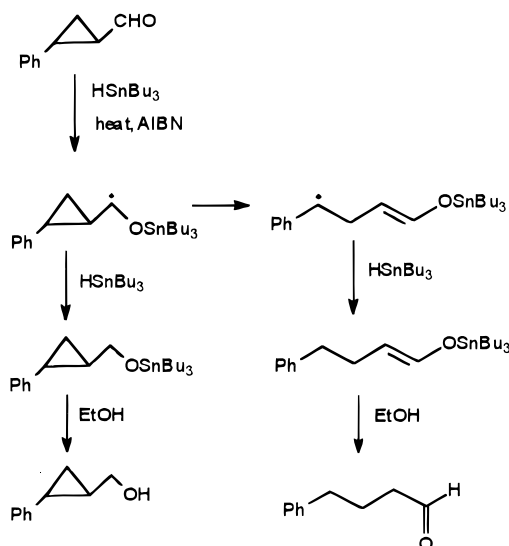
Biradical **6** contains an oxy-substituted cyclopropylcarbinyl radical. Although the rate constant for the ring opening of oxy-substituted cyclopropylcarbinyl radicals is unknown, Newcomb and co-workers have shown that the cyclization rate constant of the 1-methoxy-6,6-diphenyl-5-hexenyl radical is nearly equal to the related radical lacking the methoxy group.¹³ Thus, it is not unreasonable to assume that the oxy-substituted cyclopropylcarbinyl radical will open at a rate similar to that of the unsubstituted analogue. The following two examples give precedents for the rapid ring opening of an oxycyclopropylcarbinyl radical. Thermolysis of *trans*-(2-phenylcyclopropyl)carboxaldehyde and tributyltin hydride in the presence of AIBN gave a 2.5:1 mixture of 4-phenylbutanal and (2-phenylcyclopropyl)carbinol (Scheme 2).¹⁴ The tributyltin radical is believed to add to the carbonyl oxygen of the aldehyde to give the

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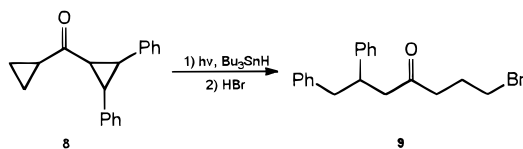
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Scheme 2

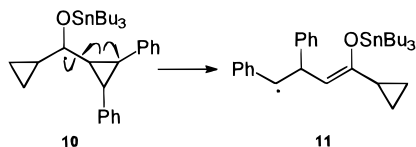


oxycyclopropylcarbinyl radical which either abstracts a hydrogen atom from the tin hydride or undergoes ring opening before hydrogen atom abstraction. The observed products are obtained after solvolysis (ethanol) of the stannyl ethers.

Furthermore, Castellino and Bruce reported that the dicyclopopyl ketone **8** gave, among other products, compound **9**



when irradiated in the presence of Bu_3SnH , followed by addition of HBr to the reaction mixture.¹⁵ Compound **9** is the result of the ring opening rearrangement of the phenyl-substituted cyclopropyl moieties. The rearrangement involves the generation of an oxycyclopropylcarbinyl radical, **10**, which rearranges to the secondary benzyl/homoallyl radical, **11**. The rate of this



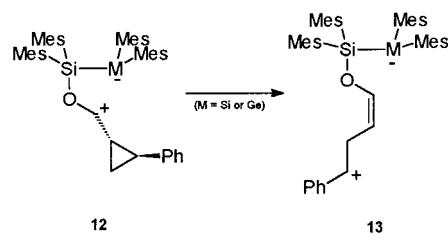
rearrangement was estimated to be at least $2 \times 10^{10} \text{ s}^{-1}$. Given these precedents, as well as the investigations by Newcomb on the rapid ring opening reactions of phenyl-substituted cyclopropylcarbinyl radicals,¹¹ it is reasonable to propose a cyclopropyl pathway for the addition of *trans*-(2-phenylcyclopropyl)carboxaldehyde to tetramesitylgermasilene and -disilene.

Many rearrangements that may occur from a biradical intermediate may also arise from a zwitterionic intermediate, so despite the precedents that favor a radical mechanism, the ionic pathway was also considered.¹⁶ For an ionic mechanism, the first intermediate formed would most reasonably be **12**.¹⁷ To arrive at compound **1**, **2**, **4**, or **5**, rearrangement from the

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Scheme 3



cyclopropylmethyloxonium **12** to the secondary benzyl carbocation **13** is required (Scheme 3). However, a comparison of the relative stabilizing abilities of the groups substituted on the carbocationic center (oxy > phenyl \approx cyclopropyl) suggests that the cyclopropylmethyloxonium intermediate would be the lower energy species relative to the secondary benzyl carbocation. Rearrangement to a higher energy species seems unreasonable. The notion that the three-membered ring in a cyclopropylmethyloxonium ion does not readily open under ionic conditions is also supported by reports that the carbonyl group of *trans*-(2-phenylcyclopropyl)carboxaldehyde can be successfully deprotected under acidic conditions without any evidence for opening of the cyclopropyl ring.^{18,19} Despite the many precedents in support of a biradical (rather than zwitterionic) intermediate, we continue to design and execute experiments which will allow us to distinguish between these two possibilities.

Summary

In summary, the addition of *trans*-(2-phenylcyclopropyl)carboxaldehyde to tetramesitylgermasilene or -disilene yielded products which are consistent with the formation of cyclopropylcarbinyl radical intermediates. The formation of these products suggests that the addition of aldehydes to tetramesitylgermasilene and -disilene proceeds via a biradical intermediate. The results detailed here are interesting in light of a recent report by Bradaric and Leigh on the mechanism of the ene addition of acetone to several 1,1-diphenylsilene derivatives.²⁰ The results of their study are consistent with a mechanism involving initial, reversible formation of a zwitterionic silene–ketone complex which collapses to product by rate-controlling proton transfer. Furthermore, it is suggested that the formal [2 + 2] addition of nonenolizable carbonyl compounds to reactive silenes might also proceed through the intermediacy of silene–carbonyl complexes.^{20,21} Our results, however, indicate that it is unlikely there is an initial dimetallene–carbonyl zwitterionic complex formed in the addition of aldehydes to dimetallenes, but rather, the cycloaddition most likely proceeds through a stepwise, biradical pathway without the involvement of the oxygen lone pair. Once again, it appears that the doubly bonded silicon atom, at least in disilenes, is not as Lewis acidic²² as in silenes²³ and silanimines.²⁴

(17) Nucleophilic addition of the dimetallene to the aldehyde to give a zwitterion with a positive charge at Si (or Ge) and an oxy anion would most probably rapidly close to the dimetallaacetone and not lead to cyclopropyl ring opening.

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Experimental Section

All experiments were carried out in flame-dried glassware under an atmosphere of argon. Toluene, benzene, THF, and Et₂O were freshly distilled from sodium benzophenone ketyl prior to use, whereas pentane, hexanes, and Et₃SiH were distilled from LiAlH₄ prior to use. *trans*-(2-Phenylcyclopropyl)carboxylic acid was obtained from the Aldrich Chemical Co. and used without additional purification. Chromatography was carried out on silica gel plates using a Chromatotron (Harrison Research) or on conventional silica gel preparative plates.

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. NMR spectra were recorded on a Varian Gemini 200, a Varian XL or Gemini 300, or a Bruker Avance DRX-500 using benzene-*d*₆ as a solvent. The standards were as follows: residual C₆D₅H 7.15 ppm for ¹H spectra; C₆D₆ central transition for ¹³C NMR spectra; and Me₄Si as an external standard, 0 ppm for ²⁹Si. IR spectra were recorded (cm^{−1}) as thin films on a Perkin-Elmer System 2000 FT IR spectrometer. A Finnegan MAT model 8230 instrument, with an ionizing voltage of 70 eV, was used to obtain electron impact mass spectra (reported in mass-to-charge units, *m/z*, with ion identity and peak intensities relative to the base peak in parentheses).

Cyclic voltammetry was performed using a PAR 263A potentiostat interfaced to a personal computer using PAR 270 electrochemistry software. The electrochemical cell was maintained at 25 °C and contained 0.1 mol/L tetraethylammonium perchlorate in *N,N*-dimethylformamide purged by argon. Cell *iR* compensation was adjusted to at least 95% of the oscillation value. At the beginning of the experiment, the 3 mm glassy carbon working electrode was freshly polished with 1 μm diamond paste and ultrasonically cleaned in ethanol for 15 min. The counter electrode was a platinum plate and the reference a silver wire immersed in a glass tube containing the solvent and 0.1 mol/L electrolyte with a fine sintered bottom. Ferrocene was used as an internal redox reference, and the reported potential was calibrated against the saturated calomel electrode (SCE).

Dimesitylbis(trimethylsilyl)silane²⁵ and hexamesitylsiladigermirane²⁶ were prepared following the reported procedures. *trans*-(2-Phenylcyclopropyl)carboxylic acid was reduced with lithium aluminum hydride in diethyl ether to give the corresponding alcohol²⁷ which was subsequently oxidized using Swern conditions to *trans*-(2-phenylcyclopropyl)carboxaldehyde.¹⁹

Addition of *trans*-(2-Phenylcyclopropyl)carboxaldehyde to Tetramesityldisilene. Mes₂Si(SiMe₃)₂ (100 mg, 0.24 mmol) was dissolved in hexanes (8 mL) and photolyzed (254 nm) at −60 °C for 12 h. *trans*-(2-Phenylcyclopropyl)carboxaldehyde was added dropwise to this solution until the yellow color of the disilene had faded (approximately 5 drops). Following removal of the solvent, the reaction mixture was purified by preparative thin-layer chromatography (30:70 CH₂Cl₂/hexanes) to yield approximately a 1:1 ratio of compounds **1** and **2**. The mixture was separated by additional preparative thin-layer chromatography (5:95 Et₂O/hexanes) to give compound **1** (23 mg, 28%) and compound **2** (15 mg, 18%) (combined yield 46%).²⁸

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(28) While the isolated yields of the adducts are low, they appear as the major components in the crude reaction mixture, as determined by ¹H NMR spectroscopy. Loss of material appears to occur during the separation and purification of the compounds by chromatography.

[Dimesityl(2-*cis*-4-*trans*-1-oxa-5-phenylpentadienyl)silyl]dimesitylsilane (1): IR (thin film, cm^{−1}) 3020 (m), 2958 (m), 2926 (s), 2859 (m), 2134 (Si–H, m), 1641 (m), 1607 (s), 1497 (m), 1453 (s), 1409 (m), 1279 (m), 1238 (s), 1151 (s), 1063 (s); ¹H NMR (ppm) 7.64 (dd, 1 H, O–CH=CH–CH=CH–Ph, ³*J* = 15.7 Hz, ³*J* = 11.2 Hz), 7.48 (d, 2 H, Ph, ³*J* = 7.4 Hz), 7.26 (t, 2 H, Ph, ³*J* = 7.7 Hz), 7.07 (t, 1 H, Ph, ³*J* = 7.4 Hz), 6.75 (s, 4 H, Mes CH), 6.66 (s, 4 H, Mes CH), 6.39 (d, 1 H, O–CH=CH–CH=CH–Ph, ³*J* = 16.0 Hz), 6.23 (d, 1 H, O–CH=CH–CH=CH–Ph, ³*J* = 5.7 Hz), 5.66 (s, 1 H, Si–H), 5.38 (dd, 1 H, O–CH=CH–CH=CH–Ph, ³*J* = 5.8 Hz, ³*J* = 10.9 Hz), 2.33 (br s, 24 H, Mes *o*-CH₃), 2.14 (s, 6 H, Mes *p*-CH₃), 2.07 (s, 6 H, Mes *p*-CH₃); ¹³C NMR (ppm) 145.51, 144.96 (Mes C and Ph C), 141.62 (O–CH=CH–CH=CH–Ph), 139.75, 138.99, 131.52, 130.48 (Mes C and Ph C), 129.81, 129.11 (Mes CH), 128.0 (O–CH=CH–CH=CH–Ph), 128.92, 127.02, 126.47 (Ph CH), 124.20 (O–CH=CH–CH=CH–Ph), 110.82 (O–CH=CH–CH=CH–Ph), 24.46 (br s), 23.94 (br s), 21.11, 20.99 (Mes CH₃); ²⁹Si NMR (ppm) −56.5 (Si–H, ¹*J*_{Si–H} = 180.9 Hz, ²*J*_{Si–H} = 12.1 Hz), 1.2 (Si–O); MS (*m/z*) 678 (M⁺, 0.3), 559 (M⁺ – Mes, 0.5), 533 (Mes₂Si – SiHMe₂, 1.4), 430 (Mes₃SiO – SiHMe₂, 29), 411 (Mes₂SiOC₄H₄Ph, 100), 291 (MesSiOC₄H₃Ph, 19); high-resolution MS calcd for C₄₆H₅₄Si₂O 678.3713, found 678.3686.

2,2,3,3-Tetramesityl-4-phenyloxa-2,3-disilacyclohept-6-ene (2): IR (thin film, cm^{−1}) 3024 (m), 2927 (s), 2860 (m), 1750 (w), 1656 (m), 1611 (s), 1559 (w), 1454 (s), 1413 (m), 1387 (w), 1297 (m), 1136 (m), 1036 (m), 856 (s); ¹H NMR (ppm) 6.89 (s, 5 H, Ph CH), 6.85 (br s, 2 H, Mes CH), 6.70 (s, 2 H, Mes CH), 6.59 (br s, 2 H, Mes CH), 6.39 (br s, 2 H, Mes CH), 6.33 (d, ³*J* = 6.2 Hz, 1 H, O–CH=CH), 4.76 (ddd, ³*J* = 6.2 Hz, ³*J* = 8.1 Hz, ³*J* = 6.2 Hz, 1 H, O–CH=CH), 4.02 (br m, 1 H, CHPh), 3.48 (br m, 1 H, =C–CHH), 2.90 (br s, 6 H, Mes CH₃), 2.60 (br s, 6 H, Mes CH₃), ~2.4 (vbr s, approximately 4 H total, =C–CHH and Mes CH₃), 2.30 (br s, 3 H, Mes CH₃), 2.11 (s), 2.085 (s), 2.079 (s), 2.05 (s, 12 H total, Mes CH₃), 1.76 (vbr s, 3 H, Mes CH₃), 1.59 (br s, 3H, Mes CH₃); ¹H NMR (ppm, 67.5 °C) 6.83–6.93 (m, Ph CH), 6.70 (s, Mes CH), 6.59 (br s, Mes CH), 6.32 (d, ³*J* = 6.3 Hz, O–CH=CH), 4.74 (ddd, ³*J* = 6.3 Hz, ³*J* = 8.1 Hz, ³*J* = 6.3 Hz O–CH=CH), 4.03 (dd, ³*J* = 7.3 Hz, ³*J* = 2.6 Hz, CHPh), 3.36 (ddd, ³*J* = 7.3 Hz, ³*J* = 8.1 Hz, ²*J* = −14.1 Hz, =C–CHH), 2.48 (ddd, ³*J* = 2.6 Hz, ³*J* = 6.3 Hz, ²*J* = −14.1 Hz, =C–CHH), 2.56 (s), 2.10–2.45 (vbr s), 2.10 (s), 2.08 (s), 2.05 (s, =C–CHH and Mes CH₃); ¹³C NMR (ppm) 146.04, 145.37 (Mes C and Ph C), 140.63 (O–CH=CH), 138.75, 138.64, 138.31, 137.76 (Mes C and Ph C), 131.06 (Ph CH), 130.28, 129.56, 128.83 (Mes CH), 127.01, 125.07 (Ph CH), 111.76 (O–CH=CH), 43.51 (CHPh), 33.03 (br s, CHH), 28.03 (br s), 26.88 (br s), 26.20 (br s), 25.85 (br s), 23.52 (br s), 20.88, 20.69 (Mes CH₃); ²⁹Si NMR (ppm) −0.53 (Si–CHR), −11.83 (Si–O); MS (*m/z*) 678 (M⁺, 14), 549 (Mes₄Si₂O, 14), 439 (Mes₂SiOC₄H₄Ph, 28), 267 (Mes₂Si + H, 100), 147 (MesSi, 100); high-resolution MS calcd for C₄₆H₅₄Si₂O 678.3713, found 678.3602.

Addition of *trans*-(2-Phenylcyclopropyl)carboxaldehyde to Tetramesitylgermasilene. SiGe₂Mes₆ (50 mg, 0.058 mmol) and Et₃SiH (0.5 mL, excess) were dissolved in toluene (4 mL) and photolyzed (350 nm) at −70 °C for 12 h. To this solution was added *trans*-(2-phenylcyclopropyl)carboxaldehyde dropwise until the yellow color of the germasilene had faded (approximately 5 drops). The yellow color did not entirely fade upon addition of the aldehyde, so the reaction mixture was allowed to warm to 22 °C and stand for an additional 2 h. After this time, there was no further change in color. Following removal of the solvent, the reaction mixture was separated by preparative thin-layer chromatography (30:70 CH₂Cl₂/hexanes) to give compounds **4** and **5** as a 1:1 mixture. This 1:1 mixture was separated by additional preparative thin-layer chromatography (5:95 Et₂O/hexanes) to give compound **4** (13 mg, 31%) and compound **5** (8 mg, 19%) (combined yield 50%).²⁸

[Dimesityl(2-*cis*-4-*trans*-1-oxa-5-phenylpentadienyl)silyl]dimesitylgermane (4): IR (thin film, cm^{−1}) 3022 (m), 2967 (s), 2912 (s), 2857 (m), 2028 (Ge–H, w), 1732 (w), 1691 (w), 1609 (s), 1443 (s), 1061 (m), 1028 (m), 978 (m), 853 (m); ¹H NMR (ppm) 7.64 (dd, 1 H, O–CH=CH–CH=CH–Ph, ³*J* = 15.9 Hz, ³*J* = 11.1 Hz), 7.48 (d, 2 H, Ph, ³*J* = 7.4 Hz), 7.26 (t, 2 H, Ph, ³*J* = 7.7 Hz), 7.07 (t, 1 H, Ph, ³*J* = 7.4 Hz), 6.77 (s, 4 H, Mes CH), 6.65 (s, 4 H, Mes CH), 6.39 (d, 1 H, O–CH=CH–CH=CH–Ph, ³*J* = 16.1 Hz), 6.22 (d, 1 H, O–

$\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{Ph}$, $^3J = 5.6$ Hz), 5.65 (s, 1 H, Ge-H), 5.38 (dd, 1 H, $\text{O}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{Ph}$, $^3J = 5.7$ Hz, $^3J = 10.9$ Hz), 2.36 (br s, Mes *o*-CH₃), 2.34 (br s, Mes *o*-CH₃) (24 H total), 2.15 (s, 6 H, Mes *p*-CH₃), 2.06 (s, 6 H, Mes *p*-CH₃); ^{13}C NMR (ppm) 144.75, 144.19 (Mes C and Ph C), 141.26 ($\text{O}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{Ph}$), 139.98, 138.94, 138.05, 135.24, 131.08 (Mes C and Ph C), 129.93 (Mes CH), 128.96 (Mes CH and Ph CH, coincident peaks), 128.55 ($\text{O}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{Ph}$), 127.78, 126.50 (Ph CH), 123.99 ($\text{O}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{Ph}$), 111.03 ($\text{O}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{Ph}$), 24.79, 23.88, 21.06, 20.99 (Mes CH₃); ^{29}Si NMR (ppm) 3.75 (Si-O); MS (*m/z*) 594 (Mes₂SiO - GeMes₂, 12), 474 (MesSiO - GeMes₂ - H, 11), 411 (Mes₂SiOCHCHCHCHPh, 100), 283 (Mes₂SiO + H, 62).

2,2,3,3-Tetramesityl-4-phenyloxa-2,3-silagermacyclohept-6-ene (5): IR (thin film, cm^{-1}) 3024 (m), 2920 (s), 2867 (m), 1652 (m), 1611 (s), 1559 (w), 1454 (s), 1409 (w), 1383 (w), 1290 (m), 1133 (m), 1036 (m), 856 (m); ^1H NMR (ppm) 6.84–6.97 (m, Ph CH and Mes CH), 6.69 (br s, Mes CH), 6.61 (br s, Mes CH), 6.40 (br s), 6.35 (d, $^3J = 6$ Hz, Mes CH and $\text{O}-\text{CH}=\text{CH}$), 4.79–4.86 (m, $\text{O}-\text{CH}=\text{CH}$),

4.13–4.22 (br m, CHPh), 3.44–3.60 (vbr m, $=\text{C}-\text{CHH}$), 2.86 (br s, Mes CH₃), 2.58 (br s, Mes CH₃), 2.29 (vbr s, Mes CH₃), 2.102 (s), 2.095 (s), 2.07 (s), (Mes CH₃), 1.54 (br s, Mes CH₃); ^{13}C NMR (ppm) 145.60 (br s), 145.52, 144.12, 143.71 (br s), 143.20 (br s), 142.85 (br s), 140.55, 139.02, 138.94, 137.52, 137.05, 135.25 (br s), 130.60, 129.75, 129.31, 128.93, 128.58, 127.06, 125.29, 112.28, 48.66, 33.01, 28.06 (br s), 26.32 (br s), 25.54 (br s), 20.89, 20.74; ^{29}Si NMR (ppm) 2.43; MS (*m/z*) 724 (M^+ , 2), 594 (Mes₂SiOGeMes₂, 19), 474 (MesSiOGeMes₂ - H, 23), 411 (Mes₂SiOC₄H₄Ph, 43), 385 (Mes₃Si, 55), 312 (Mes₂Ge, 90), 267 (Mes₂SiH, 100), 192 (MesGe - H, 94); high-resolution MS calcd for C₄₆H₅₄SiGeO 724.3156, found 724.3556.

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