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The Addition of Carbonyl Compounds to Tetramesitylgermasilene and Dimesitylgermylene

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ABSTRACT

*Hexamesitylsiladigermirane, **1**, has been photolyzed/thermolyzed in the presence of three representative carbonyl compounds: acetone, pivalaldehyde, and benzaldehyde. In each case, a [2 + 2] adduct between the carbonyl compound and* $Mes_2Ge = SiMes_2$ *was formed regioselectively to give a 2,3-silagermaoxetane. The 2,3-silagermaoxetanes have been fully characterized by IR and NMR (*^1H*,* ^{13}C*, and* ^{29}Si*) spectroscopy and mass spectrometry. In two cases, the structures have been confirmed by X-ray crystallography: 4,4-dimethyl-2,2,3,3-tetramesityl-2,3-silagermaoxetane, **2a**; crystals are triclinic, space group* $P\bar{1}$ *with Z = 2 in a unit cell of dimensions a = 12.318(3) Å, b = 12.436(2) Å, c = 11.884(2) Å, α = 100.13(1)°, β = 103.80(2)°, and γ = 89.97(2)°. The structure was solved by direct methods and refined by least squares on the basis of 2955 observed reflections to* R_I *and* wR_2 *values of 0.0600 and 0.1363, respectively. The structure of 4-tert-butyl-2,2,3,3-tetramesityl-2,3-silagermaoxetane, **2b**, was also determined; crystals are monoclinic, space group Cc with Z = 4 in a unit cell of dimensions a = 11.306(2) Å, b = 21.292(4) Å, c = 16.524(2) Å, and β = 106.83(1)°. The structure was determined by direct methods and refined by full-matrix least squares on the basis of 1817 observed reflections to* R_I *and* wR_2 *values of 0.0621 and 0.1681, respectively. An adduct between dimesitylgermylene and the carbonyl compound was also isolated in each reaction. The structure of the adduct appears to depend upon the steric bulk of the group attached to the carbonyl carbon.*

INTRODUCTION

The chemistry of addition reactions of carbonyl compounds to doubly bonded silicon and germanium compounds is quite diverse, both in the types of compounds that have been added and the types of products formed. Stable (or relatively stable) disilenes and digermenes undergo a formal [2 + 2] cycloaddition reaction with carbonyl compounds to give isolable 2,3-disilaoxetanes or 2,3-digermaoxetanes, respectively. The reaction is quite general: saturated and α,β-unsaturated, enolizable and nonenolizable aldehydes and ketones [1–5] all react in the same manner. In two examples, the reaction of tetra-*tert*-butyldisilene with acetone and with acetophenone, small to modest quantities of products derived from an ene reaction have also been obtained [2]. The addition reactions of other classes of carbonyl compounds have been investigated, with tetramesityldisilene being used as a representative disilene. Tetramesityldisilene is unreactive toward most esters but has been found to react with methyl furoate [5], diphenylketene [6], dimethylketene [6], and heptafluorobutyryl chloride [6] to give 2,3-disilaoxetanes as well. With the 1,2-diketone, benzil, disilenes undergo a formal [2 + 4] cycloaddition with the diketone acting as the four-electron component [7,8]. A [2 + 4] cycloaddition also took place in the reaction between tetramesityldisilene and 3,4,5-trimethoxybenzoyl chloride, with the acid chloride acting as the four-electron component [6].

Stable silenes and germenes react with nonenolizable alkyl or aryl aldehydes and ketones to give the analogous 2-sila- [9,10] or 2-germaoxetanes [11], respectively. Unlike the homonuclear doubly bonded species, compounds derived from a nominal [2 + 4] cycloaddition, where either the silene

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Dedicated to Prof. Adrian Gibbs Brook, a respected mentor and friend, on the occasion of his seventieth birthday.

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or the aromatic ketone acts as the four-electron component, have also been obtained [9,10]. Stable silenes and germenes give only ene-type compounds when the carbonyl compound has enolizable hydrogen atoms [11,12]. With nonaromatic α,β-unsaturated aldehydes, ketones and esters, silenes [13,14] and germenes [15] give the [2 + 4] cycloadduct as the predominant product, although in some cases the [2 + 2] adduct or a CH-insertion product has been isolated [13,14].

We have reported the synthesis of the relatively stable germasilene, tetramesitylgermasilene [16]. We are interested in comparing the chemistry of this heteronuclear group 14 doubly bonded compound with that of homonuclear disilenes and digermenes and heteronuclear silenes and germenes. Herein, we report on the reactions between tetramesitylgermasilene and three representative carbonyl compounds: acetone, pivalaldehyde, and benzaldehyde. As a consequence of the method for generating tetramesitylgermasilene (by the regioselective thermolysis/photolysis of hexamesitylsiladigermirane), we have also had the opportunity to study the reaction between dimesitylgermylene and carbonyl compounds.

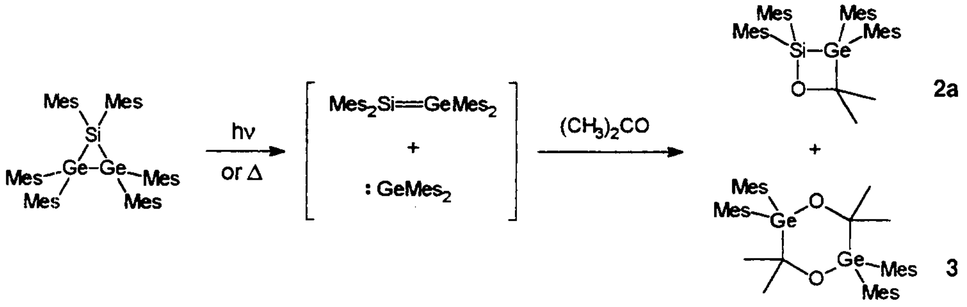
RESULTS

Photolysis or thermolysis of hexamesitylsiladigermirane (**1**) in the presence of acetone cleanly gave two products, **2a** and **3**. Compound **2a** was easily separated and purified by chromatography on silica gel; however, compound **3** could not be isolated. Attempts to isolate compound **3** by chromatography on trimethylsilyl-capped silica gel or Florisil were not successful. Fractional crystallization of the reaction mixture from hexane partially separated the two compounds: **2a** crystallized, whereas **3** remained in the mother liquor. From the IR, ^{1}H, ^{13}C, and ^{29}Si NMR and the mass spectral data, compound **2a** was identified as a [2 + 2] adduct of acetone with $Mes_2Ge{=}SiMes_2$; however, it was impossible to determine from the spectral data which regioisomer had formed. Mass spectrometry did not provide any information, as the fragment corresponding to Mes_4GeSi was the only one of the possible six fragments from a retro [2 + 2] cleavage observed. Fragments corresponding to acetone or a silene and/or a germanone or a germene and/or a silanone were not present. The regiochemistry of the addition also cannot be determined by ^{29}Si NMR spectroscopy: the chemical shifts of the two silicon atoms in the [2 + 2] acetone adduct of $Mes_2Si{=}SiMes_2$ resonate within 3 ppm of each other (17.08, 19.88 [5]) and, thus, are not diagnostic of a silicon atom attached to an oxygen or a carbon in a four-membered ring. However, the regiochemistry of the addition could be determined by X-ray crystallography (see subsequent discussion); compound **2a** is the 2-sila-3-germaoxetane and not the 3-sila-2-germaoxetane. Compound **2a** can also be formed by low-temperature (approximately −70°C) photolysis of the siladigermirane in the presence of triethylsilane to preform the germasilene, followed by addition of acetone and warming to room temperature.

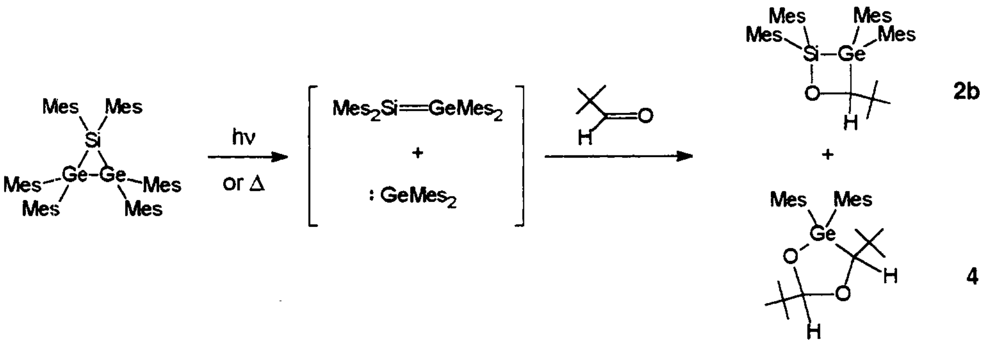
Though compound **3** could not be isolated in pure form, from the ^{1}H NMR spectrum of a mixture containing **2a**, $Mes_2Ge(OH)Mes_2GeH$ [17], and compound **3** in approximately a 32:25:43 ratio, compound **3** was identified as a 1:1 adduct between acetone and Mes_2Ge, with both equivalent methyl and equivalent mesityl groups. We tentatively assign the structure of compound **3** to the six-membered ring adduct shown below, although we acknowledge that other structures do fit the data.

Either photolysis or thermolysis of the siladigermirane, **1**, in the presence of base-washed and freshly distilled pivalaldehyde gave two major compounds **2b** and **4**. Compound **2b** was identified as the [2 + 2] adduct between pivalaldehyde and $Mes_2Ge{=}SiMes_2$ by NMR spectroscopy and mass spectrometry, and the regiochemistry of the addition was again determined by X-ray crystallography (see subsequent discussion). This reaction is also regioselective giving the 2,3-silagermaoxetane and not the isomer with an oxygen bonded to the germanium. The second compound was identified as 3,5-di-*tert*-butyl-2,2-dimesityl-2-germa-1,4-dioxolane, **4**, formed regioselectively and stereoselectively, although which stereoisomer is formed remains unknown. If the pivalaldehyde used was not carefully washed with base, then dried and distilled before thermolysis with **1**, a different germylene trapping product, **5**, was isolated after chromatography on trimethylsilyl-capped silica gel using hexane/CH_2Cl_2 as the eluent. Compound **5** was identified as the germyl ester, $Mes_2GeHOCO$-*tert*-Bu, presumably formed by insertion of Mes_2Ge into the acidic OH bond of the corresponding acid present as an impurity [18]. Typically, a 100-fold excess of the aldehyde was used in the thermolysis experiment. Although we could not detect any acid in the aldehyde by gas chromatography, if we assume the acid was present as an impurity in the amount of approximately 5%, there is a fivefold excess present. On the basis of these assumptions, we suggest that dimesitylgermylene must react with the acid at an extremely fast rate compared to the aldehyde.

Photolysis of **1** in the presence of benzaldehyde also gave a mixture of two major products, **2c** and **6**, which were readily separated by chromatography. The structure of **2c**, the silagermaoxetane, was assigned on the basis of its spectral data. The regiochemistry of the addition is believed to follow the same trend established by the addition of acetone and pivalaldehyde to $Mes_2Ge{=}SiMes_2$, with the oxygen of the carbonyl group becoming bonded



(1)



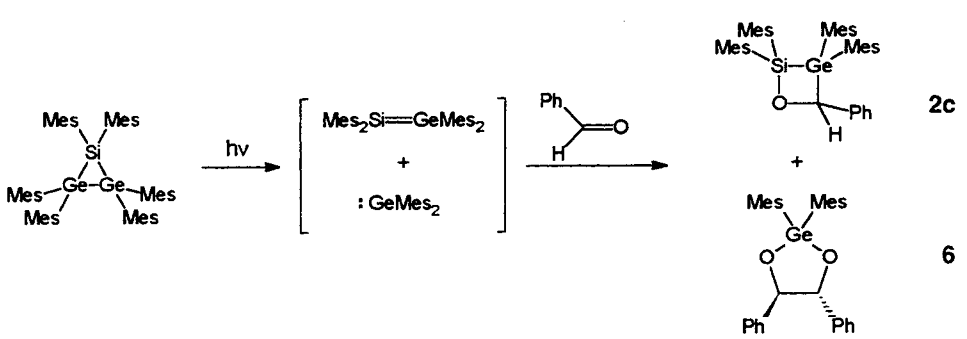
(2)

to the silicon of the germasilene. Compound **2c**, again, can be formed by addition of benzaldehyde to the preformed germasilene. Compound **6** results from the addition of benzaldehyde to Mes_2Ge:. From the integration of the ^1H NMR spectrum, two molecules of the aldehyde have added to the germylene and, from the ^1H NMR and the mass spectra, the structure can be unequivocally assigned as *trans*-2,2-dimesityl-4,5-diphenyl-2-germa-1,3-dioxolane, **6**. The addition is both regioselective and stereoselective.

DISCUSSION

The addition of three representative carbonyl compounds to $Mes_2Ge{=}SiMes_2$ has been studied: acetone, as an example of an enolizable ketone; pivalaldehyde, as an example of an alkyl, nonenolizable aldehyde; and benzaldehyde, as an aromatic aldehyde. In each case, the only product obtained was the [2 + 2] cycloaddition product, the 2,3-silagermaoxetane, formed regioselectively. In the case of acetone, there was no evidence for the formation of an ene-type product, and, in the case of the benzaldehyde, there was no evidence for the formation of a [2 + 4] cycloaddition product where the aldehyde acted as the four-electron component. In every case, the germasilene did not act as the four-electron component in a cycloaddition reaction. From these results, we can conclude that germasilenes react more like disilenes and digermenes, which show the same trend in reactivity, rather than silenes or germenes.

From our system, we have also had the opportunity to study the addition of Mes_2Ge: to carbonyl compounds. Surprisingly, we were unable to find any reports in the literature of germylenes adding to simple aldehydes or ketones; however, the addition of germylenes to α,β-unsaturated aldehydes, ketones, esters, and diketones has been studied [19]. Dimesityl germylene most probably adds to the carbonyl group to give an intermediate germoxirane, similar to the addition of Mes_2Ge: to adamantanethione to give a stable thiagermirane [20]. The germoxirane may then dimerize or add a second equivalent of the carbonyl compound. The reactions we have studied are both regioselective and stereoselective, indicating that the fate of the germoxirane intermediate is very dependent on the steric bulk of the groups attached to the carbon atom of the three-membered ring. When the groups are quite small, as in the case of acetone, i.e., dimethyl, the germoxirane dimerizes to give the six-membered ring. Larger groups, for example, phenyl or *tert*-butyl, preclude the formation of the larger ring, and instead a five-membered ring is formed. With the phenyl substituent, the second carbonyl compound adds to give the thermodynamically fa-



(3)

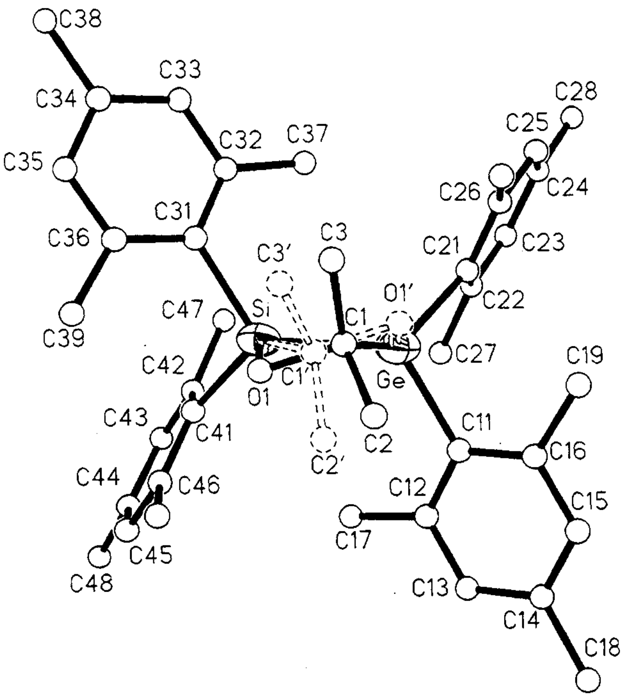


FIGURE 1 A view of the molecule **2a** showing the disorder. The hydrogen atoms are omitted.

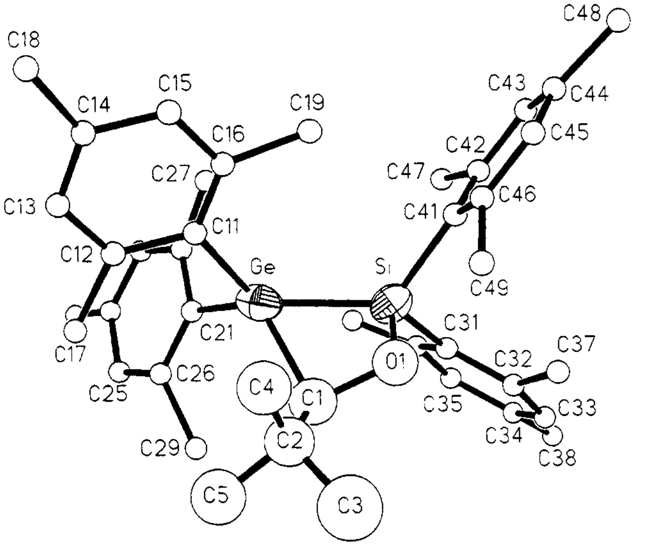


FIGURE 2 A perspective view of the molecule **2b** showing only the major component of the disorder fragment O–Si–Ge–CMe_3.

vored *trans*-4,5-diphenyl-2-germa-1,3-dioxolane ring system; however, with the bulkier *tert*-butyl groups, the 2-germa-1,4-dioxolane ring system is favored. In each case, the stereoselectivity is most probably the result of minimizing the steric interaction between the groups.

Structures of **2a** *and* **2b**. A view of the molecule **2a** is shown in Figure 1 along with the disorder fragment (see subsequent discussion). Figure 2 shows a view of the molecule **2b**, omitting the disorder. Selected bond lengths and angles are presented in Table 1. The accuracy and precision in the bond distances and angles were limited by the severe disorder present in the molecules **2a** and **2b**. Nevertheless, the structures of the molecules have been unequivocally determined. The anomaly in the bond distances (e.g., Si–O) may be attributed to the artifact of disorder; hence, bond lengths and angles are not discussed.

The validity of the models in **2a** and **2b** is supported by the following observations. (1) The total number of electrons obtained for the two sites from the refinements of occupancy factors indicates it is a "Si–Ge" fragment alone and not "Ge_2" or a mixture of "Si–Ge" and "Ge_2." (2) The Si–O bond lengths of model compounds are significantly smaller than the Ge–O bond lengths, whereas the Si–C and Ge–C bond lengths are similar (see Table 2). The bonding distances observed for **2a** and **2b** indicate that the compound is isometrically pure, and there is no mixture of O–Si–Ge–C and C–Si–Ge–O moieties in the crystal. (3) The packing of the molecules in the disordered models is normal, and no unexpected close contacts were observed. The closest nonbonding contacts are between H(18C) . . . H(3A'), 1.920 Å $(1 - x, 1 - y, -z)$ and H(3B') . . . H(3C),

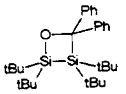
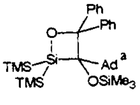
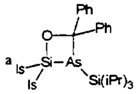
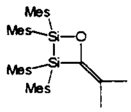
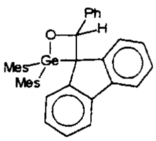
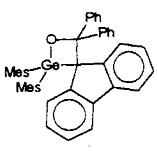
TABLE 1 Selected Bond Distances (Å) and Angles (°)

	2a	**2b**
Ge–Si	2.315(1)	2.298(2)
Ge–C(11)	2.015(3)	1.995(5)
Ge–C(21)	2.033(3)	2.062(7)
Si–C(31)	2.007(3)	1.996(6)
Si–C(41)	1.995(3)	1.990(6)
Ge–C(1)	2.119(11)	2.107(22)
Si–O(1)	1.587(6)	1.504(16)
C(1)–O(1)	1.485(13)	1.572(28)
C(1)–C(2)	1.520(12)	1.536(17)
C(1)–C(3)	1.509(12)	—
C(2)–C(3)	—	1.500(18)
C(2)–C(4)	—	1.517(18)
C(2)–C(5)	—	1.530(18)
Ge′–C(1)′	2.148(17)	2.164(18)
Si′–O(1)′	1.487(9)	1.553(14)
C(1)′–O(1)′	1.497(21)	1.383(28)
C(1)′–C(2)′	1.505(16)	1.542(18)
C(1)′–C(3)′	1.520(16)	—
C(1)–C(1)′	0.499(16)	0.600(25)
C(2)′–C(3)′	—	1.533(19)
C(2)′–C(4)′	—	1.527(19)
C(2)′–C(5)′	—	1.527(19)
Si–Ge–C(11)	122.7(1)	123.1(2)
Si–Ge–C(21)	123.5(1)	127.6(2)
C(11)–Ge–C(21)	103.7(2)	100.7(3)
Si–Ge–C(1)	66.0(3)	64.0(6)
C(11)–Ge–C(1)	106.0(3)	118.7(6)
C(21)–Ge–C(1)	132.4(3)	120.7(6)
Ge–Si–C(31)	124.4(1)	121.8(2)
Ge–Si–C(41)	124.2(1)	123.7(2)
C(31)–Si–C(41)	103.0(2)	104.9(3)
Ge–Si–O(1)	85.6(3)	90.3(6)
C(31)–Si–O(1)	106.1(3)	105.1(6)
C(41)–Si–O(1)	109.7(3)	107.3(7)
Ge–C(1)–O(1)	95.6(5)	95.8(12)
Ge–C(1)–C(2)	114.5(7)	123.2(14)
Ge–C(1)–C(3)	120.8(8)	—
O(1)–C(1)–C(2)	104.5(9)	103.5(17)
O(1)–C(1)–C(3)	106.6(9)	—
C(1)–C(1)–C(3)	111.7(9)	—
Si–O(1)–C(1)	104.0(5)	99.1(12)
C(1)–C(2)–C(3)	—	116.0(19)
C(1)–C(2)–C(4)	—	119.5(17)
C(1)–C(2)–C(5)	—	103.4(17)
C(3)–C(2)–C(4)	—	106.9(20)
C(3)–C(2)–C(5)	—	99.1(18)
C(4)–C(2)–C(5)	—	109.8(17)
Si′–Ge′–C(1)′	62.9(5)	61.7(6)
C(31)–Ge′–C(1)′	107.1(4)	114.0(6)
C(41)–Ge′–C(1)′	132.4(5)	126.8(7)
Ge′–Si′–O(1)′	89.5(4)	88.3(6)
C(11)–Si′–O(1)′	105.9(4)	108.9(6)
C(21)–Si′–O(1)′	108.3(4)	104.4(6)
Ge′–C(1)′–O(1)′	95.8(8)	88.3(6)
Ge′–C(1)′–C(2)′	120.1(12)	126.3(15)
Ge′–C(1)′–C(3)′	111.2(11)	—
O(1)′–C(1)′–C(2)′	107.6(13)	111.2(17)
O(1)′–C(1)′–C(3)′	106.5(14)	—
C(1)′–C(1)′–C(3)′	113.3(13)	—
Si′–O(1)′–C(1)′	102.9(8)	102.5(11)
C(1)′–C(2)′–C(3)′	—	106.1(19)
C(1)′–C(2)′–C(4)′	—	111.0(19)
C(3)′–C(2)′–C(4)′	—	114.2(20)
C(1)′–C(2)′–C(5)′	—	104.1(18)
C(3)′–C(2)′–C(5)′	—	101.1(20)
C(4)′–C(2)′–C(5)′	—	119.1(22)

2.414 Å ($-x, 1-y, -z$) in **2a** and H(4B′) . . . H(33), 2.399 Å ($x-0.5, y+0.5, z$) and H(17A) . . . H(38C), 2.415 Å ($1-x, 2-y, 0.5+z$) in **2b**. (4) The thermal parameters of all the atoms are found to be normal. Furthermore, the final residual electron density is not located near the "disordered" atoms.

From the crystal structures, it is clear that the oxygen of the carbonyl group selectively adds to the silicon of the germasilene to give a 2,3-silager-

TABLE 2 Selected Bond Lengths in Model Compounds

Compound		*Bond Lengths (Å)*	*Reference*
	Si–O	1.68(1)	[2]
	Si–C	2.028(4)	
	Si–O (ring)	1.696	[9]
	Si–C (ring)	1.963	
	Si–O	1.688(4)	[31]
	Si–O	1.693(4)	[6]
	Si–C	1.886(5)	
	Ge–O	1.827(3)	[11]
	Ge–C (ring)	2.031(4)	
	Ge–O	1.83(1)	[11]
		1.82(1)	
	Ge–C (ring)	2.07(2)	
		2.04(2)	

[a] Ad = 1-adamantyl; Is = 2,4,6-triisopropylphenyl.

maoxetane, the first example of this heterocyclic system. In the addition of benzaldehyde to the germasilene, we obtain a [2 + 2] adduct regioselectively, and, by extension, we assume it is the 2,3-silagermaoxetane.

EXPERIMENTAL

All experiments were carried out in flame-dried glassware under an atmosphere of argon. Toluene and benzene were distilled from sodium/benzophenone prior to use. $SiGe_2Mes_6$ [21] was prepared according to the literature procedure. Pivalaldehyde was purified by washing 2 times with a 10% w/w solution of sodium carbonate, followed by a distilled water wash, 1 N HCl wash, and two further water washes. After drying over magnesium sulfate, the aldehyde was fractionally distilled under argon at constant temperature (79°C). Acetone was purified by fractional distillation at constant temperature (56°C), after initial drying with $MgSO_4$. Chromatography was carried out on silica gel plates using a Chromatotron (Harrison Research), on a column, or on conventional preparative plates, unless noted otherwise.

NMR spectra were recorded on a Varian Gemini 200 (200.1 MHz for ^1H), an XL-300, or a Gemini 300 (299.9 MHz for ^1H, 75.4 MHz for ^{13}C and 59.6 MHz for ^{29}Si) spectrometer using deuterated benzene as a solvent, unless otherwise noted. The standards used were as follows: residual C_6D_5H 7.15 ppm for ^1H NMR spectra; C_6D_6 central transition, 128.00 ppm for ^{13}C NMR spectra; and Me_4Si as an external standard, 0 ppm for ^{29}Si NMR spectra. The DEPT [22] pulse sequence was used to assist in the ^{13}C NMR signal assignments. IR spectra were recorded as neat films (unless otherwise noted) on a Perkin Elmer System 2000 FT IR spectrometer (recorded in cm^{-1}); a Finnegan MAT model 8230 instrument was used with an ionizing voltage of 70 eV to obtain electron impact mass spectra (reported in mass-to-charge units, *m/z*, with ion identity and intensities of peaks relative to the base peak in parentheses).

Typical Thermolysis Experiment. $SiGe_2Mes_6$ (0.10 g, 0.11 mmol), acetone (0.5 mL, excess), and toluene (2.5 mL) were placed in a 10 mm screw cap NMR tube and heated to 105°C for 8 hours. During this time, a yellow color developed which then slowly faded during the course of the reaction. Following solvent removal, the residue was separated by chromatography (Florisil) using hexane/CH_2Cl_2 as the eluent, or by fractional crystallization with hexane to give **2a** (62% yield) and **3**. A 70% yield of **2a** was achieved by photolysis of **1** in the presence of acetone.

Typical Photolysis Experiment. $SiGe_2Mes_6$ (0.11 g, 0.12 mmol), pivalaldehyde (0.5 mL, excess), and toluene (2 mL) were placed in a 10 mm screw cap NMR tube and photolyzed (8 hours, 350 nm, 15°C). Following solvent removal, the light tan residue was separated by chromatography using hexane/CH_2Cl_2 as the eluent to give **2b** (55%) and **4**.

Typical Low-Temperature Photolysis Experiment. $SiGe_2Mes_6$ (0.030 g, 0.034 mmol), triethylsilane (0.25 mL, excess), and toluene (4 mL) were placed in a Schlenk tube. The mixture was photolyzed (3.5 hours, 350 nm, −72°C), after which time acetone was added to the cold mixture, which was kept cold (−70°C) for at least 3 hours. After solvent removal, the products were characterized by ^1H NMR spectroscopy.

4,4-Dimethyl-2,2,3,3-tetramesityl-2,3-silagermaoxetane, **2a.** IR: 3015 (str), 2919 (str), 1604 (str), 1449 (str), 1166 (med), 1104 (med), 1028 (med), 944 (med), 847 (str), 765 (med). ^1H NMR: 6.69 (s, 8H, Mes-H), 2.56 (bs, 12H, *o*-CH_3), 2.31 (s, 12H, *o*-CH_3), 2.09 (s, 6H, *p*-CH_3), 2.08 (s, 6H, *p*-CH_3), 1.65 (s, 6H, $-C(CH_3)_2$). ^{13}C NMR: 142.56 (appears to be two accidentally equivalent Mes-C's), 141.87, 139.10, 137.75, 135.23 (Mes-C), 129.46, 129.03 (Mes-CH), 90.63 ($-\underline{C}(CH_3)_2$), 33.53, 25.38, 24.10, 21.00, 20.87 (CH_3). ^{29}Si NMR{^1H}: 23.82. MS (CI/Isobutane): 637 (2, M^+ + H), 578 (7, Mes_4GeSi), 517 (7, M^+-Mes), 385 (8, Mes_3Si), 311 (4, Mes_2Ge), 266 (8, Mes_2Si), 239 (7, Mes_2 + H), 161 (21), 121 (100, Mes + 2H). High-resolution MS: calcd for $C_{39}H_{50}GeSiO$ + H, 637.2921; found, 637.2966. **3**. ^1H NMR: 6.70 (s), 2.50 (s, 2H), 2.08 (s), 1.47 (s, 1H).

4-tert-Butyl-2,2,3,3-tetramesityl-2,3-silagermaoxetane, **2b.** IR: 2953 (str), 2863 (str), 1605 (str), 1449 (str), 1410 (med), 1376 (w), 1030 (med), 968 (med), 931 (w), 896 (w), 848 (s), 828 (med). ^1H NMR: 6.75 (s, 2H, Mes-CH), 6.67 (s, 4H, Mes-CH, acc. equiv.), 6.61 (s, 2H, Mes-CH), 5.25 (s, 1H, C–H), 2.81 (s, 6H, *o*-CH_3), 2.41 (s, 6H, *o*-CH_3), 2.28 (s, *o*-CH_3), 2.1–2.38 (very bs, 12H total, *o*-CH_3), 2.13, 2.12 (each s, 6H total, *p*-CH_3), 2.02 (s, 6H, *p*-CH_3, acc. equiv.), 1.14 (s, 9H, *tert*-Bu). ^1H NMR at 65°C: 6.75 (s), 6.68 (s), 6.67 (s), 6.61 (s), 5.23 (s), 2.79 (s), 2.38 (s), 2.26 (s), 2.24 (bs), 2.13 (s), 2.12 (s), 2.04 (s), 2.03 (s), 1.12 (s). ^{13}C NMR ($CDCl_3$): 144.23, 143.62, 142.59, 141.92, 141.25 (bs), 139.81, 138.90, 138.61, 137.70, 137.25, 133.55, 133.24 (Mes-C), 128.98, 128.55, 128.46, 128.32, (Mes-CH), 94.76 (C–H), 38.00 ($-\underline{C}(CH_3)_3$), 27.49 ($-C(\underline{C}H_3)_3$), 26.40, 24.14, 23.05, 20.99, 20.91 (Mes-CH_3). ^{29}Si NMR {^1H}: 21.84. MS (CI/Isobutane): 663 (1, M^+-H), 593 (14, $Mes_4GeSiCH_3$ or Mes_4GeSiO-H), 578 (64, Mes_4GeSi), 545 (8, M^+-Mes), 475 (14, Mes_3GeSiO), 385 (100, Mes_3Si), 311 (6, Mes_2Ge), 265 (8, Mes_2Si). High-resolution MS: calcd for $C_{36}H_{43}GeSiO$ (M^+-BuCH), 593.2295; found, 593.2287.

3,5-Di-tert-butyl-2,2-dimesityl-2-germa-1,4-diox-

olane, **4**. IR: 2955 (str), 2868 (str), 1603 (med), 1491 (str), 1462 (str), 1402 (str), 1361 (med), 1214 (w), 1154 (w), 1088 (str), 1054 (med), 1038 (med), 978 (str), 909 (w), 848 (med), 735 (w), 684 (w), 655 (w). ^{1}H NMR: 6.69 (s, 2H, Mes-H), 6.67 (s, 2H, Mes-H), 4.42 (s, 1H, C–H), 4.34 (s, 1H, C–H), 2.53 (bs, *o*-CH$_3$), 2.52 (s, 12H total, *o*-CH$_3$), 2.05 (s, 3H, *p*-CH$_3$), 2.01 (s, 3H, *p*-CH$_3$), 1.16 (s, 9H, CH$_3$), 1.15 (s, 9H, CH$_3$). ^{13}C NMR (CDCl$_3$): 143.27, 142.95, 139.13, 138.80, 136.37, 133.74 (Mes-C), 129.36, 128.74 (Mes-CH), 106.34, 86.19 (CH), 35.70, 35.44 ($\underline{C}$(CH$_3$)$_3$), 27.87, 25.15 (C($\underline{C}$H$_3$)$_3$), 24.44, 24.30, 21.02, 20.98 (Mes-CH$_3$). MS (CI/Isobutane): 485 (84, M$^+$ + H), 398 (100, M$^+$-BuCHO), 312 (75, Mes$_2$Ge), 279 (55, MesGe-BuCHO), 192 (17, MesGe-H), 189 (36), 121 (27), 97 (38), 87(44). High-resolution MS: calcd for C$_{28}$H$_{42}$GeO$_2$ (M$^+$ + H), 485.2475; found, 485.2467. **5**. ^{1}H NMR: 7.33 (s, 1H), 6.67 (s, 4H), 2.44 (s, 12H), 2.04 (s, 6H), 1.19 (s, 9H). IR: 2100 (GeH), 1673 (C=O) cm^{-1}. MS (EI): 413 (6, M$^+$ − 1), 313 (53, Mes$_2$GeH), 294 (62, M$^+$-MesH), 193 (52, MesGe), 119 (35, Mes), 105 (29), 1 (23), 57 (100, Bu). High-resolution MS: calcd for M$^+$ − H, 413.1536; found, 413.1486.

2,2,3,3-Tetramesityl-4-phenyl-2,3-silagermaoxetane, **2**. Yield: 65%. IR: 3022.8 (str), 2959.2 (str), 2918.7 (str), 1603.0 (str), 1551.0 (med), 1491.2 (med), 1450.7 (str), 1410.1 (med), 1028.4 (med), 953.0 (str) 848.8 (str), 756.2 (str), 804.4 (str). ^{1}H NMR: 7.25–7.22, 7.00–6.88 (m, 5H, phenyl-H); 6.75, 6.70, 6.66, 6.53 (s, 8H, Mes-H); 6.36 (s, 1H, C–H); 2.75 (s, 6H, *o*-CH$_3$); 2.47 (bs, 6H, *o*-CH$_3$), 2.40 (s, 6H, *o*-CH$_3$); 2.12, 2.11, 2.05, 1.99 (s, 12H, *p*-CH$_3$); 1.93 (s, 6H, *o*-CH$_3$). ^{13}C NMR (CDCl$_3$): 144.49, 143.71, 143.65, 143.62, 141.73, 141.15, 139.36, 139.19, 137.94, 137.86, 135.43, 133.42, 133.01 (Mes-C, Ph-C), 129.06, 128.69, 128.52, 127.98, 127.29, 126.19, 125.75 (Mes-CH, Ph-CH), 86.76 (C-H), 24.97, 23.96, 23.90, 23.20, 21.09, 21.00, 20.96, 20.85 (Mes-CH$_3$). ^{29}Si NMR (CDCl$_3$) {^{1}H}: 25.83. MS: 684 (0.4, M$^+$), 593 (20, Mes$_4$GeSiO), 577 (7, Mes$_4$GeSiH), 475 (4, Mes$_3$GeSiO), 385 (100, Mes$_3$Si), 311 (6, Mes$_2$Ge), 266 (6, Mes$_2$Si), 193 (6, MesGe), 147 (6, MesSi), 105 (2, PhCO). High-resolution MS: calcd for C$_{43}$H$_{50}$GeSiO, 684.2924; found, 684.2843.

trans-2,2-Dimesityl-4,5-diphenyl-2-germa-1,3-dioxolane, **6**. Yield: 42%, IR: 2952 (str), 2920 (str), 1600 (str), 1448 (str), 1412 (med), 1122 (med), 1047 (med), 848 (med), 824 (med). ^{1}H NMR: 7.24–7.20, 7.04–7.00 (m, 10H, Ph-H), 6.72 (s, 4H, Mes-H), 4.98 (s, 2H, C-H), 2.68 (s, 12H, *o*-CH$_3$), 2.07 (s, 6H, *p*-CH$_3$). ^{13}C NMR (CDCl$_3$): 143.09, 140.41, 132.44, 130.87 (Mes-C, Ph-C); 129.04, 127.92, 127.51, 127.26 (Mes C-H, phenyl C-H), 84.65 (O-C-H), 22.70 (*o*-CH$_3$), 21.17 (*p*-CH$_3$). MS: 524 (2.5, M$^+$), 418 (55, M$^+$-PhCHO), 312 (100, Mes$_2$Ge), 279 (37), 196 (50, Ph$_2$C$_2$H$_2$O), 193 (40, MesGe), 167 (58), 149 (65). High-resolution MS: calcd for C$_{32}$H$_{34}$GeO$_2$, 524.1696; found, 524.1771.

X-ray Structure Determinations

Colorless and transparent crystals of 4,4-dimethyl-2,2,3,3-tetramesityl-2,3-silagermaoxetane, **2a**, and 4-*tert*-butyl-2,2,3,3-tetramesityl-2,3-silagermaoxetane, **2b**, were obtained from mixtures of CH$_2$Cl$_2$/EtOH and mounted on glass fibers in air. The X-ray diffraction experiments were performed employing a similar procedure as given subsequently. All the measurements were made on an Enraf Nonius CAD4F diffractometer [23] at room temperature (296 K). The intensity data were collected using graphite monochromated Mo K_α radiation (λ = 0.71073 Å). Three standard reflections were monitored at regular intervals of time. Crystal orientation checks were done for every 250 units of data. The data were processed using NRCVAX crystal structure programs [24] running on a SUN 3/80 workstation and were corrected for absorption using an empirical method [25]. The crystal systems and the Laue symmetries were determined from inspection of Niggli matrices and symmetry equivalent reflections, respectively. The space groups were deduced from the systematic absences [26]. Fractional search procedures in the reciprocal space confirmed that the cell obtained is not part of a larger unit cell. The structures were solved by direct methods using the software SHELXS-86 [27] and subsequent difference Fourier routines, and initial full-matrix least-squares refinements on F were done using SHELX-76 [28] software. The final full-matrix least-squares refinements on F^2 were made using SHELXL-93 software [29] running on either CD4680 or SUN 3/80 Unix computers. The phenyl rings were treated as regular hexagons with C–C distances of 1.395 Å. Ge, Si, and all the methyl carbon atoms of the mesityl groups were assigned anisotropic thermal parameters and refined in the least-squares cycles.

Crystal **2a**. The cell dimensions were obtained from least-squares refinement of 21 high-angle (23.2 $\leq 2\theta \leq$ 31.3°) reflections. A total of 5413 reflections were collected in the 2θ range 0–46° ($-13 \leq h \leq 1$, $-13 \leq k \leq 13$, $-13 \leq l \leq 13$), with a scan speed from 1.37 to 4.12 deg·min^{-1}. The maximum and minimum transmission factors are 0.810 and 0.765 (μ = 8.1 cm^{-1}). The distribution of E (mean abs $E^2 - 1$, 0.976; expected for centric, 0.968, and acentric, 0.736) suggested a centrosymmetric space group. For Z = 2, the space group $P\bar{1}$ was assumed. The Ge and Si sites were found to be partially disordered as revealed by the ratio of the peak heights of the two strongest peaks in the SHELXS-86 solution, which was found to be 1.238 rather than 2.3. Furthermore, during early stages of the refinement, the isotropic thermal parameter of the Si atom refined to a negative value, indicating the presence of a greater number of electrons at that site. Thereafter, these sites were treated as Ge with

TABLE 3 Crystallographic Data

		2a	**2b**
Compound		$C_{39}H_{50}O_1Ge_1Si_1$	$C_{41}H_{51}O_1Ge_1Si_1$
Formula weight		635.52	663.57
Crystal system, space group		triclinic	monoclinic
Space group		$P\bar{1}$	Cc
Cell dimensions	a =	12.318(3)	11.306(2) Å
	b =	12.436(2)	21.292(4) Å
	c =	11.884(2)	16.524(2) Å
	α =	100.13(1)°	
	β =	103.80(2)°	106.83(1)°
	γ =	89.97(2)°	
Cell volume (Å^3), Z		1738.8(5), 2	3808(1), 4
Density, g · cm^{-3}, calcd		1.214	1.157
Radiation, wavelength (Å)		MoK_α, 0.71073	
Abs coeff (cm^{-1})		8.1	8.2
Reflections collected		5413	3004
Independent reflections		4825	2974
Data/restraints/parameters		822/6/227	2974/28/239
Goodness-of-fit on F^2		0.987	1.064
Final R indices [$I > 2\sigma(I)$]			
	R_1 =	0.0600	0.0621
	wR_2 =	0.1363	0.1681
R indices (all data)	R_1 =	0.1084	0.1081
	wR_2 =	0.1532	0.1967
Extinction coeff		0.0018(8)	
Largest difference Fourier Peak and hole, e Å^{-3}		0.598 and −0.355	0.493 and −0.329

$R_1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$.

$wR_2 = \sqrt{[\Sigma w(Fo^2 - Fc^2)^2)/(\Sigma wFo^4)]}$.

GooF = $s = \sqrt{[\Sigma w(Fo^2 - Fc^2)^2)/(n - p)]}$, where n is the number of reflections and p is the total Number of parameters refined.

a common fixed isotropic thermal parameter (U = 0.04), and the occupancy factors were refined to 0.758 and 0.625. From this, the total number of electrons in the two sites is calculated to be 44.3 electrons (expected 46 electrons), indicating that it is "Ge–Si" and not "Ge_2". In terms of Ge/Si disorder, this corresponds to 63% of Ge and 37% of Si in site 1 and vice versa in site 2. Two disorder O–C(Me_2) fragments attached to "Si–Ge" were found in the subsequent difference Fourier routines. The occupancy factors of 0.63 and 0.37 were assigned for O–Si–Ge–C(Me_2) and (Me_2)C′–Ge′–Si′–O′, respectively, based on "Si–Ge" refined occupancies. The hydrogen atoms for all the methyl groups were placed using the option HFIX 137 in SHELXL-93 software. The rest of the hydrogen atoms in the phenyl rings were placed in the calculated positions (C–H = 0.96 Å). Common isotropic thermal parameters for each type of hydrogen atom were refined in the least-squares cycles. The same positional and anisotropic displacement parameters were used for the Ge and Si atoms occupying the same sites using EXYZ and EADP options in SHELXL-93 (the least-squares refinements were unstable otherwise). Three bad reflections close to the beam stop (010, 001, and 0–11) were suppressed in final cycles. An extinction parameter was refined as suggested from the observation of the analysis of variance. In the final least-squares refinement cycles, the data converged at R_1 = 0.0600 and wR_2 = 0.1363 for 2955 ($I \geq 2\sigma(I)$) observations and 227 variables using the weighting scheme $w = q/[\sigma^2(Fo)^2 + (aP)^2 + bP + d + e \cdot \sin\theta]$, where $P = [f * \text{maximum of } (0 \text{ or } Fo^2) + (1 - f) * Fc^2]$; a = 0.0490 and b = 4.803. The residual electron density in the final difference Fourier synthesis ranges from 0.598 to −0.355 e Å^{-3}; of these, the top three peaks (with electron density greater than 0.50 e Å^{-3}) were associated with C34, C15, and C13 atoms (at distances 0.74 to 0.87 Å). The maximum shift/esd in the final cycle was −0.082 for torr H18A.

The space group $P1$ was also considered. The structure was solved readily using SHELXS-86 software. The peak heights of the top four peaks (711 and 658) in molecule 1 and (625 and 467) molecule 2 indicate that the disorder persists in this noncentrosymmetric space group also. This was confirmed by the successful location of the two disordered four-membered rings in each molecule. The refinements in this space group ($P1$) were not processed further due to severe correlations and convergence problems. The problem of twinning

TABLE 4 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\times 10^3$) for **2a**

Atom	*x*	*y*	*z*	*U(eq)*
M(1)	2444(1)	2633(1)	−969(1)	46(1)
M(2)	2514(1)	2951(1)	1027(1)	43(1)
O(1)	2893(5)	4168(5)	1015(6)	49(2)
C(1)	2430(8)	4309(9)	−221(12)	42(4)
C(2)	3305(9)	5033(9)	−475(10)	62(3)
C(3)	1339(8)	4872(9)	−249(10)	63(3)
O(1′)	2104(8)	3774(8)	−1022(9)	37(2)
C(1′)	2570(12)	4358(12)	216(19)	30(5)
C(2′)	3680(12)	4895(13)	259(15)	47(4)
C(3′)	1706(14)	5169(14)	501(17)	59(5)
C(11)	3830(3)	2468(3)	−1600(3)	49(2)
C(12)	4836(3)	2126(3)	−979(3)	52(2)
C(13)	5795(2)	2164(3)	−1400(3)	60(2)
C(14)	5748(3)	2545(4)	−2443(4)	65(2)
C(15)	4741(3)	2888(3)	−3064(3)	62(2)
C(16)	3782(3)	2849(3)	−2642(3)	51(2)
C(21)	1284(3)	1606(2)	−2186(3)	41(1)
C(22)	1482(2)	497(3)	−2275(3)	49(2)
C(23)	673(3)	−270(2)	−2984(3)	54(2)
C(24)	−335(3)	71(3)	−3604(3)	52(2)
C(25)	−533(2)	1179(3)	−3516(3)	54(2)
C(26)	276(3)	1947(2)	−2807(3)	45(1)
C(31)	1162(3)	3063(3)	1705(3)	46(2)
C(32)	134(3)	2537(3)	1122(3)	49(2)
C(33)	−778(2)	2688(3)	1628(3)	58(2)
C(34)	−660(3)	3363(4)	2718(4)	71(2)
C(35)	368(3)	3889(3)	3301(3)	67(2)
C(36)	1279(3)	3739(3)	2795(3)	55(2)
C(41)	3643(3)	2332(3)	2223(3)	47(2)
C(42)	3415(3)	1251(3)	2281(3)	49(2)
C(43)	4213(3)	682(2)	2958(4)	60(2)
C(44)	5238(3)	1194(3)	3576(3)	64(2)
C(45)	5466(3)	2275(3)	3518(3)	64(2)
C(46)	4669(3)	2844(2)	2841(4)	54(2)
C(17)	4997(6)	1663(7)	126(6)	91(3)
C(18)	6821(7)	2630(7)	−2887(8)	108(3)
C(19)	2732(6)	3243(6)	−3369(6)	70(2)
C(27)	2547(5)	51(5)	−1641(6)	62(2)
C(28)	−1234(6)	−805(6)	−4350(6)	69(2)
C(29)	−17(6)	3124(5)	−2794(6)	74(2)
C(37)	−88(5)	1766(6)	−39(6)	81(2)
C(38)	−1663(7)	3518(7)	3297(9)	120(4)
C(39)	2341(6)	4374(6)	3479(6)	73(2)
C(47)	2326(5)	626(5)	1655(6)	61(2)
C(48)	6142(7)	528(7)	4259(7)	97(3)
C(49)	5009(6)	4004(6)	2824(7)	81(2)

The M(1) site is occupied by Ge:Si in the ratio 63:37, and similarly the M(2) site is occupied by Si:Ge in the ratio 63:37. The occupancies for the primed and the corresponding unprimed atoms are 37 and 63, respectively.

was considered for **2a**, where *a* and *b* axes are almost equal and γ is close to 90°. Refinement of the twinning model was performed using the software SHELXL-93 (with the option TWIN 0 1 0 1 0 0 0 0 −1 and BASF 0.5). The BASF scale factor was refined to 0.088(4), and hence the crystal twinning was not considered further. Our original disorder model and space group were therefore retained.

TABLE 5 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\times 10^3$) for ***2b***

Atom	*x*	*y*	*z*	*U(eq)*
M(1)	0	9066(1)	0	51(1)
M(2)	2119(2)	9069(1)	335(1)	57(1)
C(1)	1243(22)	9940(9)	−31(15)	67(7)
O(1)	6(15)	9761(8)	166(11)	65(5)
C(2)	1644(16)	10549(8)	472(10)	67(7)
C(3)	754(25)	11087(12)	245(25)	115(12)
C(4)	2104(21)	10523(11)	1430(11)	76(7)
C(5)	2662(20)	10804(11)	122(17)	87(8)
C(1′)	947(21)	9961(7)	217(15)	27(5)
O(1′)	2053(14)	9775(7)	91(9)	34(4)
C(2′)	484(17)	10582(10)	−247(13)	76(9)
C(3′)	410(26)	10470(14)	−1177(14)	84(9)
C(4′)	−733(23)	10787(14)	−103(21)	97(10)
C(5′)	1600(25)	11019(12)	25(21)	81(9)
C(11)	3218(5)	8971(3)	1514(4)	45(3)
C(12)	4438(6)	9156(3)	1647(4)	53(3)
C(13)	5284(5)	9091(4)	2442(5)	67(3)
C(14)	4908(7)	8840(4)	3105(4)	82(4)
C(15)	3688(7)	8655(4)	2972(4)	69(4)
C(16)	2843(5)	8721(4)	2177(4)	70(3)
C(21)	3204(6)	8671(4)	−339(4)	50(3)
C(22)	3443(8)	8034(4)	−202(6)	74(4)
C(23)	4167(9)	7721(3)	−625(7)	93(5)
C(24)	4653(8)	8047(4)	−1185(6)	89(4)
C(25)	4414(8)	8684(4)	−1322(5)	88(4)
C(26)	3689(7)	8997(3)	−900(5)	67(3)
C(31)	−1114(6)	8957(3)	−1173(4)	55(4)
C(32)	−2212(6)	9295(3)	−1428(4)	52(3)
C(33)	−2957(6)	9254(4)	−2259(5)	80(4)
C(34)	−2604(7)	8877(4)	−2835(4)	68(4)
C(35)	−1506(8)	8539(4)	−2580(5)	75(4)
C(36)	−761(6)	8580(4)	−1749(5)	68(3)
C(41)	−882(6)	8654(3)	738(5)	60(3)
C(42)	−1352(7)	8056(3)	509(5)	54(3)
C(43)	−2039(8)	7757(3)	970(6)	68(4)
C(44)	−2257(8)	8057(4)	1661(6)	88(4)
C(45)	−1788(8)	8655(4)	1890(5)	78(3)
C(46)	−1100(7)	8954(3)	1429(5)	64(3)
C(17)	4988(14)	9533(9)	1044(11)	164(9)
C(18)	5728(19)	8801(9)	4054(10)	138(8)
C(19)	1527(17)	8349(14)	1966(18)	267(16)
C(27)	3085(13)	7662(7)	401(11)	89(5)
C(28)	5364(14)	7712(7)	−1737(11)	128(7)
C(29)	3021(18)	9620(8)	−1305(12)	175(7)
C(37)	−2712(13)	9570(9)	−741(12)	129(7)
C(38)	−3553(18)	8761(12)	−3700(11)	182(12)
C(39)	361(13)	8262(11)	−1631(9)	187(11)
C(47)	−949(12)	7655(6)	−160(11)	87(6)
C(48)	−3146(22)	7748(10)	2116(19)	199(11)
C(49)	−984(24)	9679(7)	1547(14)	185(10)

The M(1) site is occupied by Ge:Si in the ratio 47:53, and similarly the M(2) site is occupied by Si:Ge in the ratio 47:53. The occupancies for the primed and the corresponding unprimed atoms are 53 and 47, respectively.

Crystal **2b.** It was thought that a bulkier substituent, such as a *tert*-butyl group, instead of methyl groups at the C_1 carbon atom might resolve this disorder problem. Hence, the X-ray analysis of 4-*tert*-butyl-2,2,3,3-tetramesityl-2,3-silagermaoxetane, **2b**, was undertaken. The cell dimensions were obtained from least-squares refinement of 21 high-angle ($24.8 \leq 2\theta \leq 29.9°$) reflections. A total of 3004 reflections were collected in the 2θ range 0–46° (h, −12 to 12; k, −23 to 1; and l, −1 to 18), with a scan speed from 1.37 to 4.12 $\text{deg} \cdot \text{min}^{-1}$. The maximum and minimum transmission factors are 0.825 and 0.764 ($\mu = 8.2\ \text{cm}^{-1}$). The systematic absences suggested that the space group could either be *Cc* or *C2/c*. The distribution of E (mean $E^2 - 1$, 0.875) did not distinguish between the centric and noncentric space groups (expected for centric, 0.968, and acentric, 0.736).

The space group *C2/c* (No. 15) was considered first. This space group with $Z = 4$ imposes a twofold symmetry in the molecule. The structure was readily solved. This imposes 50:50 disorder due to crystallographically imposed twofold symmetry in the molecule. Hydrogen atoms were included for the mesityl groups only, and a common isotropic thermal parameter was refined in the least squares. All the methyl groups and the Ge atom were assigned anisotropic thermal parameters and refined in the least-squares cycles. The model converged at $R_1 = 0.0773$, $wR_2 = 0.2034$, and GooF = s = 1.102 for 1550 ($Fo > 4\sigma(Fo)$) and 134 parameters. R_1 = 0.1290, $wR_2 = 0.2389$, and GooF = 0.984 for all 2643 data. The maximum shift/esd = −0.021 for torr H17A. The residual electron density in the final difference Fourier varies from 0.62 to −0.36 e Å^{-3}.

The space group *Cc* was considered next. The structure was solved using SHELXS-86 software. Similar to **2a**, a crystallographic twofold disorder was also found. In the least-squares cycles, the Si site was treated as Ge, a common fixed isotropic thermal parameter ($U = 0.05$) was assigned to both the disorder sites, and the occupancy factors were refined to 0.718 and 0.705. This corresponds to the total number of electrons in two sites equal to 45.5 electrons (expected 46 electrons for Ge and Si atoms). Two disordered O–CH(*tert*-Bu) fragments attached to "Si–Ge" were found. The occupancy factors of 0.53 and 0.47 were assigned for O–Si–Ge–CH(*tert*-Bu) and (*tert*-Bu)HC′–Ge′–Si′–O′, respectively. The hydrogen atoms for all the methyl groups were placed using the option HFIX 137 in SHELXL-93 software, and the rest of the hydrogen atoms in the phenyl rings were placed in the calculated positions (C–H = 0.96 Å). Riding models were used for the thermal parameters of hydrogen atoms. The same positional and anisotropic displacement parameters were used for the Ge and Si atoms occupying the same sites using the SHELXL-93 option EXYZ and EADP. In the final least-squares refinement cycles, the data converged at R_1 = 0.0621, $wR_2 = 0.1681$, and GooF = s = 1.065 for 1817 ($I \geq 2\sigma(I)$) observations and 239 variables using the weighting scheme $w = q/[\sigma^2(Fo)^2 + (aP)^2 + bP + d + e \cdot \sin\theta]$, where $P = [f * \text{maximum of } (0 \text{ or } Fo^2) + (1 - f) * Fc^2]$; $a = 0.1231$ and b = 1.4478. The residual electron density in the final difference Fourier synthesis ranges from 0.49(7) to −0.33(7) e Å^{-3}. The maximum shift/esd in the final cycle was −0.008 for x of C(3). The Flack parameter was refined to 0.182(56).

For the inverted model, the full-matrix least-squares cycles on F^2 converged at $R_1 = 0.0625$, wR_2 = 0.1691, and GooF = s = 1.056 for 1817 ($Fo > 4\sigma(Fo)$) and 239 parameters, and $R_1 = 0.1078$ and $wR_2 = 0.198$ for all 2974 data. The Flack parameter refined to 0.32(6). The maximum shift/esd = 0.055 for z of C(3). The residual electron density in the final difference Fourier varies from 0.509 to −0.339 e Å^{-3}. Between *C2/c* and *Cc*, the noncentrosymmetric space group, *Cc* was chosen since the disorder present in the molecule was not crystallographically imposed in this space group. In addition, the agreement factors and R_{int} were better for *Cc* (R_{int} = 0.0168 and 0.0245 for *Cc* and *C2/c*, respectively).

The experimental details and crystal data are given in Table 3. The positional and thermal parameters for **2a** and **2b** are shown in Tables 4 and 5, respectively [30].

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REFERENCES

[1] M. J. Fink, D. J. DeYoung, R. West, J. Michl, *J. Am. Chem. Soc., 105*, 1983, 1070.

[2] A. Schäfer, M. Weidenbruch, S. Pohl, *J. Organomet. Chem., 282*, 1985, 305.

[3] S. A. Batcheller, S. Masamune, *Tetrahedron Lett., 29*, 1988, 3383.

[4] W. Ando, T. Tsumuraya, *J. Chem. Soc., Chem. Commun.*, 1989, 770.

[5] A. D. Fanta, D. J. DeYoung, J. Belzner, R. West, *Organometallics, 10*, 1991, 3466.

[6] A. D. Fanta, J. Belzner, D. R. Powell, R. West, *Organometallics, 12*, 1993, 2177.

[7] P. Boudjouk, B.-H. Han, K. R. Anderson, *J. Am. Chem. Soc., 104*, 1982, 4992.

[8] M. Weidenbruch, A. Schäfer, K. L. Thom, *Z. Naturforsch. B, 38*, 1983, 1695.

[9] A. G. Brook, W. J. Chatterton, J. F. Sawyer, D. W. Hughes, K. Vorspohl, *Organometallics, 6*, 1987, 1246.

[10] N. Wiberg, G. Preiner, O. Scheida, *Chem. Ber.*, *114*, 1981, 3518.

[11] M. Lazraq, C. Couret, J. Escudie, J. Satgé, M. Dräger, *Organometallics*, *10*, 1991, 1771.

[12] N. Wiberg, G. Wagner, *Angew. Chem. Int. Ed. Engl.*, *22*, 1983, 1005.

[13] A. G. Brook, S. S. Hu, W. J. Chatterton, A. J. Lough, *Organometallics*, *10*, 1991, 2752.

[14] A. G. Brook, S. S. Hu, A. K. Saxena, A. J. Lough, *Organometallics*, *10*, 1991, 2758.

[15] M. Lazraq, J. Escudié, C. Couret, J. Satgé, M. Soufiaoui, *Organometallics*, *11*, 1992, 555.

[16] K. M. Baines, J. A. Cooke, *Organometallics*, *11*, 1992, 3487.

[17] K. M. Baines, J. A. Cooke, C. E. Dixon, H. W. Liu, M. R. Netherton, *Organometallics*, *13*, 1994, 631.

[18] B. Klein, W. P. Neumann, M. P. Weisbeck, S. Wienken, *J. Organomet. Chem.*, *446*, 1993, 149.

[19] W. P. Neumann, *Chem. Rev*, *91*, 1991, 311.

[20] T. Tsumuraya, S. Sato, W. Ando, *Organometallics*, *8*, 1989, 161.

[21] K. M. Baines, J. A. Cooke, *Organometallics*, *10*, 1991, 3419.

[22] D. M. Doddrell, D. T. Pegg, M. R. Bendall, *J. Magn. Reson.*, *48*, 1982, 323; D. M. Doddrell, D. T. Pegg, *J. Am. Chem. Soc.*, *102*, 1980, 6388.

[23] "CAD4 Diffractometer Manual," Enraf-Nonius, Delft, The Netherlands, 1988.

[24] E. J. Gabe, Y. LePage, J.-P. Charland, F. C. Lee, *J. Appl. Crystallogr.*, *22*, 1989, 384.

[25] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr.*, *A24*, 1968, 351.

[26] *International Tables for X-ray Crystallography*, D. Reidel Publishing Co., Boston, vol. A (1983).

[27] G. M. Sheldrick: "SHELXS-86," *Acta Crystallogr.*, *A46*, 1990, 467.

[28] G. M. Sheldrick: "SHELX-76," University of Cambridge, Cambridge, United Kingdom, 1976.

[29] G. M. Sheldrick: "SHELXL-93," *J. Appl. Crystallogr.*, 1994, in preparation.

[30] The following materials for deposition have been sent to the Crystallograhic Data Centre, Cambridge. Tables of complete bond distances and angles, anisotropic thermal parameters, calculated hydrogen atom coordinates, structure factors, and ORTEP views of ***2a*** and ***2b***.

[31] M. Driess, H. Pritzkow, *Angew. Chem., Int. Ed. Eng.*, *31*, 1992, 316.