

# The addition of oxygen to tetramesityldigermene

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Received 15 March 2001; accepted 30 April 2001

Dedicated to Professor O. Nefedov on the occasion of his 70th birthday

## Abstract

The addition of atmospheric oxygen to tetramesityldigermene under a variety of conditions was studied. The addition of oxygen to the digermene, prepared by the photolysis of hexamesitylcyclotrigermane in THF, cleanly afforded 3,3,4,4-tetramesityl-3,4-digermadioxetane (**7**). The photolysis of hexamesitylcyclotrigermane in toluene in the presence of triethylsilane under the ambient atmosphere gave a very complex product mixture, from which 2,2,4,4-tetramesityl-2,4-digermadioxetane (**9**), tetramesityldigermoxirane (**10**) and 2,2,4,4,5,5-hexamesityl-2,4,5-trigermadioxolane (**11**) were isolated and identified. The structures of compounds **9** and **11** were determined by X-ray crystallography. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Germanium; Digermene; Dioxygen reactions; Digermadioxetane

## 1. Introduction

Although oxygenation is, perhaps, the most ubiquitous reaction of digermenes [1], there are only two reports concerning this important and fundamental reaction. Masamune and co-workers have investigated the oxygenation reactions of tetrakis(2,6-diethylphenyl)digermene (**1a**) and tetrakis(2,6-diisopropylphenyl)digermene (**1b**) [2] and, Weidenbruch and co-workers have investigated the addition of oxygen to a (*Z*)-diaminodisilyldigermene (**5**) [3].

Triplet oxygen adds to the tetraaryldigermenes, **1**, to provide the corresponding 1,2-digermadioxetanes (**2**) that undergo photochemical rearrangement (254 nm) to the 1,3-digermadioxetanes (**3**). The 1,2-digermadioxetanes undergo thermal isomerisation to give 1-oxa-2-germacyclopent-3-enes (**4**) (Scheme 1).

In contrast, the addition of oxygen to the (*Z*)-diaminodisilyldigermene **5** furnished the 1,3-digermadioxetane **6**, stereospecifically. No evidence for the intermediate formation of a 1,2-digermadioxetane was reported (Scheme 2).

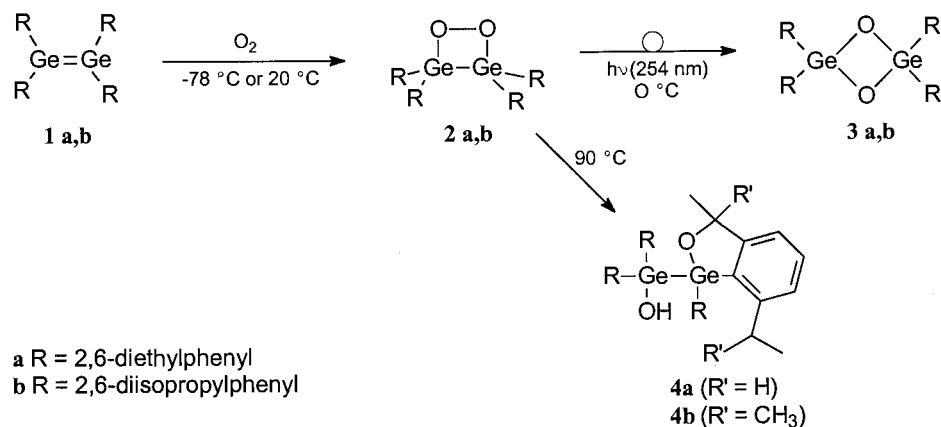
Tetramesityldigermene is a well-known, readily synthesised digermene derivative [4,5]. However, despite the extensive investigations of the reactivity of this digermene [6], the reaction of tetramesityldigermene with atmospheric oxygen has not been investigated. We report herein the oxidation of tetramesityldigermene under a variety of conditions.

## 2. Results and discussion

Photolysis of hexamesitylcyclotrigermane in toluene at  $-70\text{ }^{\circ}\text{C}$  in the presence of triethylsilane followed by bubbling compressed air into the solution yielded a 1:1 mixture of the 1,2-digermadioxetane **7** and the silylgermane **8** [6f], as determined by  $^1\text{H-NMR}$  spectroscopy. Removal of the solvent in vacuo and addition of benzene to the crude product mixture caused precipitation of **7**. Compound **7** was identified by NMR spectroscopy and mass spectrometry.

The  $^1\text{H-}$  and  $^{13}\text{C-NMR}$  spectra both showed the presence of only one type of mesityl group. The mass spectrum indicated the presence of a cluster of peaks centred at 654 amu, corresponding to the molecular ion. The precise mass of this ion was determined to be 654.179 amu, in good agreement with the calculated

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Scheme 1.

mass of 654.177. Although the spectral data are also consistent with 2,2,4,4-tetramesityl-2,4-digermadioxetane, the data do not match that of the 1,3-digermadioxetane, which has been unambiguously identified (*vide infra*) (Scheme 3).

The addition of compressed air to a solution of tetramesityldigermene (produced by the photolysis of hexamesitylcyclotrigermene and triethylsilane) at  $-70\text{ }^\circ\text{C}$  in THF yielded *only* the 1,2-digermadioxetane, **7**. No evidence for the formation of the silylgermane **8** was found. Addition of benzene to the THF solution caused **7** to precipitate from the solution as a fine white solid.

The absence of  $\text{Et}_3\text{SiGe}(\text{H})\text{Mes}_2$  (**8**) or any products derived from the germylene,  $\text{Mes}_2\text{Ge}:$ , was surprising. THF is expected to form a donor complex with  $\text{Mes}_2\text{Ge}:$  [7]. THF donor adducts of dimethylsilylene have been shown to decrease the rate of addition of the silylene to various reagents [8]. Thus, it appears that the THF-complexed germylene reacts with  $\text{Et}_3\text{SiH}$  at an appreciably slower rate. However, dimerisation of the germylene to the digermene must still occur at a reasonable rate. This is further corroborated by the isolated yield of the 1,2-digermadioxetane **7**. If the yield of **7** is calculated based on the assumption that one equivalent of cyclotrigermene produces one equivalent of digermene, one obtains a yield of greater than 100%. However, a reasonable yield of 89% is obtained if the cyclotrigermene is assumed to produce 1.5 equivalents of the digermene.

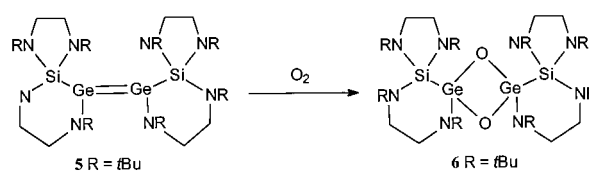
Photolysis of hexamesitylcyclotrigermene in toluene in the presence of triethylsilane at  $-70\text{ }^\circ\text{C}$  under the ambient atmosphere, yielded a complex mixture of products including **8–11**, and a small amount of **7** (Scheme 4).

The products were separated by preparative thin layer chromatography. There were two or three other products present in the crude product mixture that could not be isolated or identified. Although the  $^1\text{H}$ -

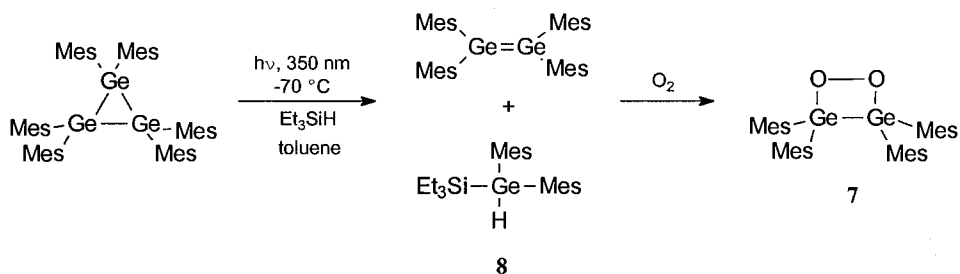
NMR ( $\text{CDCl}_3$ ) and mass spectral data of **9** are in complete accord with published data for this known compound [9], the  $^1\text{H}$ -NMR chemical shifts in  $\text{C}_6\text{D}_6$  were not consistent with the known values [10]. However, **9** was unequivocally identified by a single-crystal X-ray structure determination. The molecular structure of the molecule is presented in Fig. 1.

The molecular structure of **9** possesses two crystallographic twofold axes which bisect an almost square and perfectly planar cyclodigermozane ring. The mesityl groups are attached to the cyclodigermozane ring in a roughly helical fashion. The Ge–O bond distances are all equal at  $1.812(1)\text{ \AA}$ , the Ge–Ar bond distances are all equal at  $1.949(2)\text{ \AA}$  and the Ge–Ge distance is  $2.6073(6)\text{ \AA}$ . The Ge–O–GeA and O(1)–Ge–O(1A) bond angles are  $92.03(9)$  and  $87.97(10)^\circ$ , respectively. These values agree well with the published structure of the tetraaryl-substituted 1,3-digermadioxetane (**1a**) prepared by Masamune and co-workers [2].

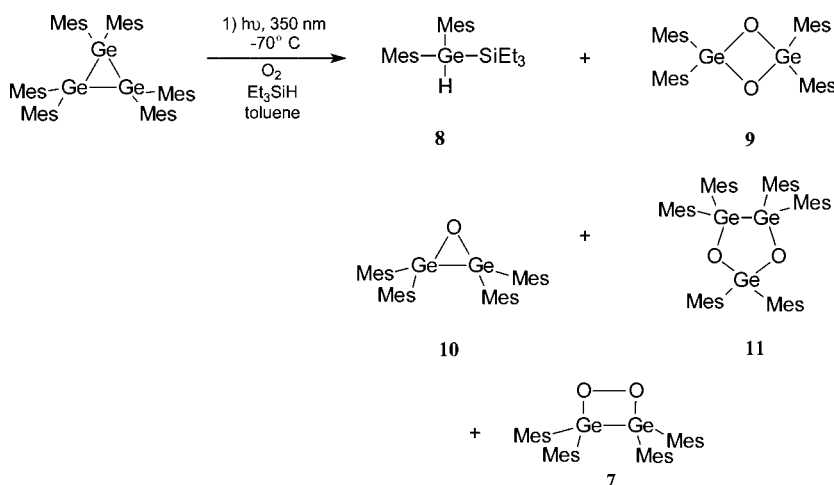
Since **9** was only obtained from the cophotolysis reactions of the cyclotrigermene with oxygen, compound **9** is believed to arise from the photochemical rearrangement of the 1,2-digermadioxetane **7** which is formed from the initial addition of oxygen to tetramesityldigermene. At this time it is not known whether this rearrangement is also thermal. The 1,2-digermadioxetane **7** was found to rearrange in solution and as a solid to the 1,3-digermadioxetane at room temperature; however, no measures were taken to exclude light.



Scheme 2.



Scheme 3.



Scheme 4.

Compound **10** was identified from  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy and mass spectrometry. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra both showed the presence of only one type of mesityl group. The mass spectrum indicated the presence of a cluster of peaks centred at 638 amu, corresponding to the molecular ion with a precise mass of 638.1827, which is in good agreement with the calculated mass of 638.1825. This compound appears to be relatively stable, as it was stored as a solid for several months under the ambient atmosphere without any signs of further oxidation to the 1,3-digermadioxetane. We were unable to obtain a crystal of **10** suitable for a single-crystal X-ray structure determination. West et al. successfully prepared the disilaoxirane of  $\text{R}_2\text{Si}=\text{SiR}_2$  ( $\text{R} = 2,4,6$ -triisopropylphenyl) by reaction with an equimolar amount of *m*-chloroperbenzoic acid [11]. An attempt was made to synthesise **10** by addition of *m*-chloroperbenzoic acid to a solution of tetramesityldigermene and  $\text{Et}_3\text{SiGe}(\text{H})\text{Mes}_2$  in toluene. However, analysis of the product mixture by  $^1\text{H}$ -NMR spectroscopy showed it to be a mixture of **9** and **11**, a compound which has been tentatively assigned as (triethylsiloxy)-dimesitylgermanol (**12**), and only a small amount of **10**.

Compound **11** was unequivocally identified by a single-crystal X-ray structure determination. The molecular structure of the molecule is presented in Fig. 2. The five-membered ring in **11** is almost planar. The mesityl groups are attached to the trigermadioxolane ring in a roughly helical fashion. The Ge–O bond distances in the trigermadioxolane are 1.777(1), 1.785(1), 1.804(1) and 1.808(1) Å and the Ge–Ar bond distances range from 1.968(2) to 1.988(2) Å. The Ge–O–Ge and O–Ge–Ge bond angles are 124.22(7), 124.11(7)° and 94.57(4), 94.29(4)°, respectively, and the O–Ge–O bond angle is 102.79(6)°. These values agree well with the only other published structure of a 2,4,5-trigermadioxolane, 2,2-di-*tert*-butyl-4,4,5,5-tetraphenyl-2,4,5-trigermadioxolane, prepared by Puff and co-workers [12] who reported values of 1.783(1)–1.800(1) Å for the Ge–O bond lengths and values of 1.93(2)–1.97(2) Å for the Ge–Ar bond lengths. They also observed bond angles of 120.7(6), 120.0(5)° and 95.7(3), 97.1(3)° for the Ge–O–Ge and O–Ge–Ge bond angles, respectively. The O–Ge–Ge angle was found to be 105.1(5)°.

The  $^1\text{H}$ -NMR spectrum of **11** in  $\text{C}_6\text{D}_6$  was very misleading as it did not show the presence of two different mesityl groups. A  $^1\text{H}$ – $^{13}\text{C}$  HMBC spectrum showed that the signals assigned to both *p*-methyl

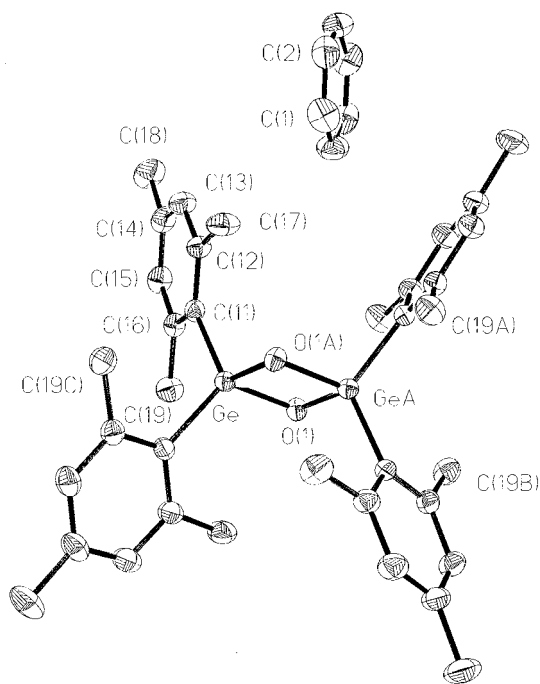


Fig. 1. Molecular structure of **9**. Important bond lengths (Å) and bond angles (°): Ge–O(1) = 1.8119(15), Ge–C(11) = 1.949(2), Ge–GeA = 2.6073(6); O(1A)–Ge–O(1) = 87.97(10), Ge–O(1)–GeA = 92.03(9), O(1A)–Ge–C(11) = 114.61(6), O(1)–Ge–C(11) = 107.74(6), C(11)–Ge–C(11A) = 119.85(12), O(1A)–Ge–GeA = 43.99(5), C(11)–Ge–GeA = 120.08(6), C(16)–C(11)–C(12) = 119.4(19), C(16)–C(11)–Ge = 116.63(15), C(12)–C(11)–Ge = 123.63(15).

groups in the  $^1\text{H}$  dimension were accidentally coincident at 2.06 ppm and the signals assigned to the

aromatic hydrogens of the mesityl groups in the  $^1\text{H}$  dimension were also accidentally coincident at 6.63 ppm. The observed precise mass of 965.267 is in good agreement with the calculated mass of 965.263 for the molecular ion.

The formation of compound **11** can be explained easily by insertion of  $\text{Mes}_2\text{Ge}$ : into the oxygen–oxygen bond of the 1,2-digermadioxetane, **7**. To provide evidence for this hypothesis, a solution of equimolar amounts of hexamesitylcyclotrigermane and **7** was photolysed in toluene at  $-70^\circ\text{C}$ . The reaction was quenched by the addition of methanol. Analysis of the product mixture by  $^1\text{H}$ -NMR spectroscopy revealed a 1:2:4 mixture of **9**, **11** and **13**. The results provide support for the suggestion that  $\text{Mes}_2\text{Ge}$ , formed during the photolysis of hexamesitylcyclotrigermane, may indeed insert into the oxygen–oxygen bond of **7** to produce **11**. Furthermore, since the reaction was performed in the absence of air, **11** cannot be a direct oxidation product of the cyclotrigermane. Compound **9** is believed to be formed from the competitive photochemical rearrangement of **7**. Tetramesityldigermene is stable under the reaction conditions and, upon addition of methanol, the methanol adduct **13** [13] of the digermene is obtained (Scheme 5).

Cophotolysis of a solution of hexamesitylcyclotrigermane,  $\text{Et}_3\text{SiH}$ , and air in THF, rather than toluene, produced a product mixture similar in its complexity. The notable difference between the two reactions is that in THF, compound **8**, derived from addition of  $\text{Et}_3\text{SiH}$  to  $\text{Mes}_2\text{Ge}$ :, is present in only small amounts, consistent

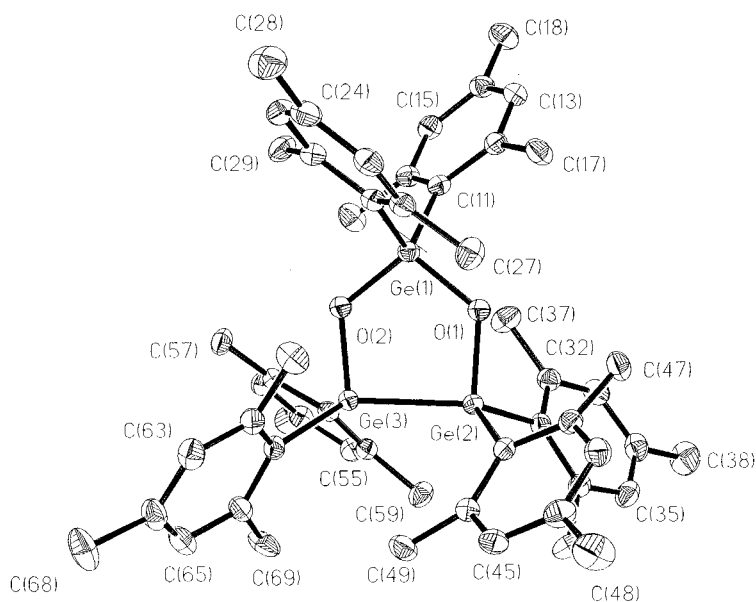
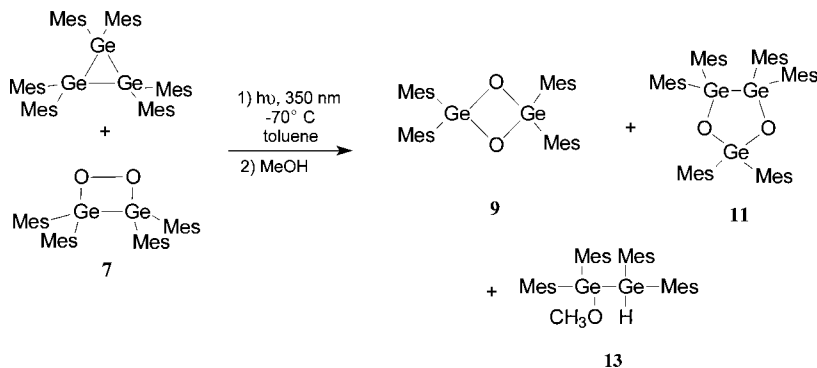


Fig. 2. Molecular structure of **11**. Important bond lengths (Å) and bond angles (°): Ge(1)–O(1) = 1.777(1), Ge(1)–O(2) = 1.785(1), Ge(1)–C(21) = 1.968(2), Ge(1)–C(11) = 1.970(2), Ge(2)–O(1) = 1.804(1), Ge(2)–C(31) = 1.985(2), Ge(2)–C(41) = 1.988(2), Ge(2)–Ge(3) = 2.504(3), Ge(3)–O(2) = 1.808(1), Ge(3)–C(51) = 1.978(2), Ge(3)–C(61) = 1.982(2); O(1)–Ge(1)–O(2) = 102.79(6), O(1)–Ge(2)–Ge(3) = 94.57(4), O(2)–Ge(3)–Ge(2) = 94.29(4), Ge(1)–O(1)–Ge(2) = 124.22(7), Ge(1)–O(2)–Ge(3) = 124.11(7).



Scheme 5.

with the previous conclusion that the rate of reaction of the THF-complexed germylene with triethylsilane is appreciably slower.

In summary, the oxidation of tetramesityldigermene closely parallels the oxidation of tetraaryldigermenes **1a** and **1b**. The direct addition of oxygen to digermenes yield a 1,2-digermadioxetane which can photochemically (and, possibly, thermally) rearrange to the 1,3-isomer. The cophotolysis of the cyclotrigermane and oxygen produced a complex mixture of products, as a consequence of the method used to generate the digermene and competing photochemical processes. Interestingly, the use of THF as a solvent reduced the complexity of these reactions presumably because of the reduced reactivity of the THF donor adduct of dimesitylgermylene.

It is interesting to compare the oxygenation of digermenes with their silicon analogues. There have been several publications which describe the usual course of the oxidation [14]. Typically, oxygenation of disilenes in solution gives the 1,2-disiladioxetane as the major product accompanied by a smaller quantity of the disilaoxirane. The 1,2-dioxetanes undergo thermal rearrangement to give the corresponding 1,3-disiladioxetanes. Direct formation of the 1,3-disiladioxetanes is also observed.

Dimetallenes with sterically demanding ligands, such as the disilene,  $\text{Tip}_2\text{Si}=\text{SiTip}_2$  (Tip = 2,4,6-triisopropylphenyl) and the digermene,  $\text{Dep}_2\text{Ge}=\text{GeDep}_2$  (Dep = 2,6-diethylphenyl) undergo the thermal rearrangement of their 1,2-dimetalladioxetanes to compounds with the 1-oxa-2-metallacyclo-pent-3-ene structure. This type of rearrangement has not been observed for less bulky dimetallenes such as the mesityl-substituted dimetallenes.

### 3. Experimental

#### 3.1. General

All experiments were carried out in flame-dried glassware under an inert atmosphere of Ar, unless otherwise

stated. Tetrahydrofuran was distilled freshly from sodium/benzophenone ketyl prior to use. Toluene and  $\text{Et}_3\text{SiH}$  were distilled from  $\text{LiAlH}_4$  prior to use. *m*-Chloroperbenzoic acid was obtained from the Aldrich Chemical Co. Hexamesitylcyclotrigermane was prepared following the published procedure [15]. Chromatography was carried out on silica gel preparative plates obtained from BDH Co.

Photolyses were carried out at 350 nm 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 ( $-70^\circ\text{C}$ ) MeOH through a vacuum jacketed Pyrex immersion well. Melting points (m.p.) were measured using a Gallencamp metal block apparatus and are uncorrected. NMR spectra were recorded on a Varian Gemini 200 (200.1 MHz for  $^1\text{H}$ , 50.3 MHz for  $^{13}\text{C}$ ), a Varian XL or a Gemini 300 (299.9 MHz for  $^1\text{H}$ , 75.4 MHz for  $^{13}\text{C}$ ), or a Varian Inova 400 (399.8 MHz for  $^1\text{H}$ , 100.5 MHz for  $^{13}\text{C}$ ) using benzene- $d_6$  as a solvent, unless otherwise noted. The standards were as follows: residual  $\text{C}_6\text{D}_5\text{H}$  7.15 ppm for  $^1\text{H}$  spectra;  $\text{C}_6\text{D}_6$  central transition 128.00 ppm for  $^{13}\text{C}$ -NMR spectra. Literature  $^1\text{H}$ -NMR chemical shifts were comparable to  $\pm 0.01$  ppm. IR spectra were recorded ( $\text{cm}^{-1}$ ) as thin films on a Perkin-Elmer System 2000 FTIR spectrometer. A Finnigan MAT model 8200 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 and a Finnigan 4615B GC/MS quadrupole mass spectrometer (San Jose, CA) was used to obtain potassium ( $\text{K}^+$ ) ionisation of desorbed species ( $\text{K}^+\text{IDS}$ ) spectra. The detailed experimental procedure to perform  $\text{K}^+\text{IDS}$  has been described elsewhere [16].

#### 3.2. Addition of air to tetramesityldigermene in toluene

$\text{Ge}_3\text{Mes}_6$  (50 mg, 0.054 mmol) and  $\text{Et}_3\text{SiH}$  (0.1 ml, excess) were dissolved in toluene (4 ml) and photolysed

(350 nm) at  $-70\text{ }^{\circ}\text{C}$  for 16 h. After irradiation, the reaction mixture was clear and bright yellow in colour. Air was bubbled through the solution until the colour completely faded ( $\sim 30$  s). The solvent was removed to yield an oily white residue. The residue was analysed by  $^1\text{H-NMR}$  spectroscopy and it was found to be an approximately 1:1 mixture of **7** and **8** [6f].

### 3.2.1. 3,3,4,4-Tetramesityl-3,4-digermadioxetane (**7**)

M.p.:  $142\text{--}143\text{ }^{\circ}\text{C}$ ;  $^1\text{H-NMR}$ :  $\delta$  6.62 (s, 8H, Mes CH), 2.64 (s, 24H, Mes  $o\text{CH}_3$ ), 2.01 (s, 12H, Mes  $p\text{CH}_3$ );  $^{13}\text{C-NMR}$ :  $\delta$  142.92, 139.82, 135.67 (Mes C), 129.25 (Mes CH), 22.64 (Mes  $o\text{CH}_3$ ), 21.09 (Mes  $p\text{CH}_3$ ); MS;  $m/z$ : 654 [ $\text{M}^+$ , 2], 632 [ $\text{M}^+ - \text{O}$ , 1], 533 [ $\text{M}^+ - \text{Mes}$ , 4], 516(4), 429 [ $\text{GeMes}_3$ , 6], 415 [ $\text{M}^+ - \text{Mes}_2$ , 5], 311 [ $\text{Mes}_2\text{Ge}$ , 12], 192 [ $\text{MesGe}$ , 20], 119 [ $\text{Mes}$ , 12], 84 (100); HRMS: Found, 654.179. Calc. for  $\text{C}_{36}\text{H}_{44}\text{ }^{72}\text{Ge}^{74}\text{GeO}_2$ : 654.177.

### 3.3. Addition of air to tetramesityldigermene in THF

$\text{Ge}_3\text{Mes}_6$  (63 mg, 0.068 mmol) and  $\text{Et}_3\text{SiH}$  (0.1 ml, excess) were dissolved in THF (4 ml) and photolysed (350 nm) at  $-70\text{ }^{\circ}\text{C}$  for 16 h. After irradiation, the reaction mixture was clear and bright yellow in colour. Air was bubbled through the solution until the colour completely faded ( $\sim 30$  s). The solvent removed in vacuo to yield **7** (59.6 mg, 89%) as an off-white crystalline solid.

### 3.4. Photolysis of hexamesitylcyclotrigermene in toluene under the ambient atmosphere

$\text{Ge}_3\text{Mes}_6$  (50 mg, 0.054 mmol) and  $\text{Et}_3\text{SiH}$  (0.1 ml, excess) were dissolved in toluene (4 ml) and photolysed (350 nm) at  $-70\text{ }^{\circ}\text{C}$  for 16 h under the ambient atmosphere. After irradiation, the reaction mixture was clear and colourless. The solvent was removed under vacuum from the reaction mixture. The  $^1\text{H-NMR}$  spectrum of the crude product showed varying amounts of **7–11** and an unidentified compound ( $^1\text{H-NMR}$ :  $\delta$  2.09, 2.37, 6.72).  $\text{C}_6\text{D}_6$  (0.5 ml) was added to the crude product. Compound **9** crystallised from the solution (5 mg, 14%) as clear, colourless crystals. The crystals were filtered from the solution and the remaining products were separated by preparative thin layer chromatography (50/50  $\text{CH}_2\text{Cl}_2$ –hexanes) to give **10** contaminated with traces of **9** and **11** (5 mg, 15%) as a waxy white solid and a mixture of **8** and **11** (14.7 mg). The solid **8** was air-oxidised to the germanol by allowing the germane to stand under the ambient atmosphere over a period of at least 3 weeks. The resulting mixture was separated by preparative thin layer chromatography (30/70  $\text{CH}_2\text{Cl}_2$ –hexanes) to give **11** (6.4 mg, 17%). The dioxolane was recrystallised from hexanes to give **11** as clear, colourless crystals.

### 3.4.1. 2,2,4,4-Tetramesityl-2,4-digermadioxetane (**9**)

M.p.:  $149\text{--}150\text{ }^{\circ}\text{C}$ ; IR (thin film,  $\text{cm}^{-1}$ ): 3364 (w), 2919 (m), 1603 (m), 1558 (s), 1449 (s), 1412 (m), 1377 (m), 846 (s), 803 (s);  $^1\text{H-NMR}$ :  $\delta$  6.63 (s, 8H, Mes CH), 2.52 (s, 24H, Mes  $o\text{CH}_3$ ), 2.06 (s, 12H, Mes  $p\text{CH}_3$ );  $^{13}\text{C-NMR}$ :  $\delta$  143.21, 139.33, 135.21 (Mes C), 129.40 (Mes CH), 23.09 (Mes  $o\text{CH}_3$ ), 21.01 (Mes  $p\text{CH}_3$ ); MS;  $m/z$ : 654 [ $\text{M}^+$ , 15], 623 [ $\text{M}^+ - \text{O}_2$ , 8], 535 [ $\text{M}^+ - \text{Mes}$ , 45], 415 [ $\text{M}^+ - \text{Mes}_2$ , 32], 327 [ $\text{Mes}_2\text{GeO}$ , 72], 311 [ $\text{Mes}_2\text{Ge}$ , 28], 235 (38), 221 [ $\text{MesGeOO}$ , 32], 119 [ $\text{Mes}$ , 100], 105 [ $\text{GeO}_2$ , 72];  $\text{K}^+$ IDS MS;  $m/z$ : 687–701 [ $\text{M}^+ + 39$  cluster].

### 3.4.2. Tetramesityldigermoxirane (**10**)

IR (thin film,  $\text{cm}^{-1}$ ): 3649 (w), 2923 (s), 2854 (s), 1718 (m), 1602 (m), 1558 (w), 1451(m), 1410 (w), 1378 (w), 1289 (m), 1031(m), 907 (w), 847 (m), 803 (w);  $^1\text{H-NMR}$ :  $\delta$  6.67 (s, 8H, Mes CH), 2.41 (s, 24H, Mes  $o\text{CH}_3$ ), 2.08 (s, 12H, Mes  $p\text{CH}_3$ );  $^{13}\text{C-NMR}$ :  $\delta$  143.56, 138.87, 138.08 (Mes C), 129.62 (Mes CH), 23.62 (Mes  $o\text{CH}_3$ ), 20.95 (Mes  $p\text{CH}_3$ ); MS;  $m/z$ : 638 [ $\text{M}^+$ , 13], 536 (9), 431 [ $\text{Mes}_3\text{Ge}$ , 23], 329 [ $\text{Mes}_2\text{GeO}$ , 100], 311 [ $\text{Mes}_2\text{Ge} - \text{H}$ , 43], 192 [ $\text{MesGe}$ , 66], 119 [ $\text{Mes}$ , 93]; HRMS: Found, 638.1827. Calc. for  $\text{C}_{36}\text{H}_{44}\text{ }^{72}\text{Ge}^{74}\text{GeO}$ : 638.1825.

### 3.4.3. 2,2,4,4,5,5-Hexamesityl-2,4,5-trigermadioxolane (**11**)

M.p.  $302\text{--}303\text{ }^{\circ}\text{C}$ ; IR (thin film,  $\text{cm}^{-1}$ ): 2920 (m), 1603 (m), 1558 (w), 1457 (m), 1409 (m), 1378 (m), 847 (m), 809 (s);  $^1\text{H-NMR}$ :  $\delta$  6.63 (s, 12H, Mes CH), 2.56 (s, 12H, Mes  $o\text{CH}_3$ ), 2.35 (s, 24H, Mes  $o\text{CH}_3$ ), 2.06 (s, 18H, Mes  $p\text{CH}_3$ );  $^{13}\text{C-NMR}$ :  $\delta$  143.27, 142.92, 141.25, 138.72, 138.50, 137.27 (Mes C), 129.27, 129.20 (Mes CH), 24.67, 22.80 (Mes  $o\text{CH}_3$ ), 21.06, 20.97 (Mes  $p\text{CH}_3$ ); MS;  $m/z$ : 966 [ $^{72}\text{Ge}^{74}\text{Ge}$ ,  $\text{M}^+ - \text{H}$ , 12], 845 (84), 724 (22), 623 [ $\text{Mes}_4\text{Ge}_2 - \text{H}$ , 46], 503 [ $\text{Mes}_2^{72}\text{Ge}^{74}\text{GeMes}$ , 31], 431 [ $\text{GeMes}_3$ , 100], 311 [ $\text{Mes}_2\text{Ge} - \text{H}$ , 91], 192 [ $\text{MesGe}$ , 21], 119 [ $\text{Mes}$ , 15]; HRMS: Found, 965.263. Calc. for  $\text{C}_{54}\text{H}_{66}\text{ }^{72}\text{Ge}^{74}\text{Ge}_2\text{O}_2 - \text{H}^+$ , 965.267.

### 3.5. Addition of *m*-chloroperbenzoic acid to tetramesityldigermene in toluene

$\text{Ge}_3\text{Mes}_6$  (50 mg, 0.054 mmol) and  $\text{Et}_3\text{SiH}$  (0.1 ml, excess) were dissolved in toluene (4 ml) and photolysed (350 nm) at  $-70\text{ }^{\circ}\text{C}$  for 18 h. After irradiation, the reaction mixture was clear and bright yellow in colour. *m*-Chloroperbenzoic acid (12.2 mg, 85% pure, 0.060 mmol) dissolved in dried, degassed toluene (3 ml) was added to the reaction mixture via cannula. Upon addition, the yellow colour of the reaction mixture faded to clear and colourless. The reaction mixture was washed with saturated  $\text{Na}_2\text{SO}_3$  (30 ml total), followed by a wash with water (30 ml total). The solvent was removed

under vacuum to yield a white residue (65 mg). The products were separated by preparative thin layer chromatography (90/10 CH<sub>2</sub>Cl<sub>2</sub>–hexanes) to give **9** (3 mg, 9%), a small amount of **10** (1.6 mg, 5%), **11** (7.8 mg, 15%), and an oily yellow product which has been tentatively assigned as **12** (9.2 mg, 37%).

### 3.5.1. (Triethylsilyloxydimesityl)germanol (**12**)

IR (thin film, cm<sup>-1</sup>): 3435 (s), 3023 (w), 2957 (m), 2921 (m), 2876 (m), 2052 (w), 1603 (m), 1653 (m), 1457 (m), 1261 (m), 1021 (m), 847 (m), 803 (m); <sup>1</sup>H-NMR: δ 6.72 (s, 4H, Mes CH), 2.49 (s, 12H, Mes oCH<sub>3</sub>), 2.10 (s, 6H, Mes pCH<sub>3</sub>), 0.89–0.98 (m, 15H, CH<sub>2</sub>CH<sub>3</sub>); MS; *m/z*: 460 [M<sup>+</sup>, 3], 445 [M<sup>+</sup> – CH<sub>3</sub>, 9], 431 [M<sup>+</sup> (<sup>72</sup>Ge) – CH<sub>2</sub>CH<sub>3</sub>, 31], 415 [M<sup>+</sup> (<sup>72</sup>Ge) – CH<sub>3</sub>, – CH<sub>2</sub>CH<sub>3</sub>, – H, 36], 401 [M<sup>+</sup> (<sup>72</sup>Ge) – (CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, – H, 24], 329 [Mes<sup>74</sup>GeOH, 51], 312 [Mes<sup>74</sup>Ge, 100], 192 [Mes<sup>74</sup>Ge – H, 94], 119 [Mes, 74].

### 3.6. Photolysis of hexamesitylcyclotrigermane in the presence of **7**

Ge<sub>3</sub>Mes<sub>6</sub> (21.4 mg, 0.023 mmol) and **7** (15 mg, 0.023 mmol) were dissolved in toluene (4 ml) and photolysed (350 nm) at –70 °C for 17 h. After irradiation, the reaction mixture was clear and bright yellow in colour. Methanol (1 ml, excess) was added to the cold reaction mixture and the yellow colour completely faded. The solvent was removed under vacuum to yield a pale yellow solid (53.3 mg). The residue was analysed by <sup>1</sup>H-NMR spectroscopy and found to be mainly a 1:2:4 mixture of **9**, **11** and **13** [13].

### 3.7. Photolysis of hexamesitylcyclotrigermane in THF under the ambient atmosphere

Ge<sub>3</sub>Mes<sub>6</sub> (50 mg, 0.054 mmol) and Et<sub>3</sub>SiH (0.1 ml, excess) were dissolved in THF (4 ml) and photolysed (350 nm) at –70 °C for 16 h under the ambient atmosphere. After irradiation, the reaction mixture was clear and colourless. The solvent was removed under vacuum from the reaction mixture. The <sup>1</sup>H-NMR spectrum of the crude product showed varying amounts of **7**–**11** and two, possibly three, other compounds which could not be identified. C<sub>6</sub>D<sub>6</sub> (0.5 ml) was added to the crude product. Compound **9** crystallised from the solution (3.6 mg, 10%) as clear, colourless crystals. The crystals were filtered from the solution and the remaining products were separated by preparative thin layer chromatography (CH<sub>2</sub>Cl<sub>2</sub>) to give **10** (2 mg, 6%) and **11** (15.2 mg, 29%).

### 3.8. X-ray structure determination of **9**

Colourless plate crystals of **9** were grown from a concentrated benzene solution at room temperature.

Diffraction data using a crystal with the dimensions of 0.32 × 0.32 × 0.12 mm were collected on a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. Of a total of 21 869 reflections collected up to 2θ = 52.8° (0 ≤ *h* ≤ 15, 0 ≤ *k* ≤ 25, 0 ≤ *l* ≤ 18) in ω–2θ mode using graphite monochromated Mo–K<sub>α</sub> radiation, 1868 were independent (*R*<sub>int</sub> = 0.057). These data were corrected for absorption using the integration method. Hydrogen atoms were calculated geometrically and were either riding, or in the case of methyl groups, riding as rigid groups on their respective carbon atoms. There were four molecules in the unit cell and thus symmetry was imposed on the molecule. Only one mesitylene group needed to be refined and the germanium atom and the oxygen atom were on special positions and given a site occupancy of 1/2. Similarly for the benzene of solvation, only 1½ carbon atoms were found and the rest of the molecule was generated by symmetry. Non-hydrogen atoms were refined anisotropically based on *F*<sup>2</sup> by full-matrix least-squares method. A molecular structure drawing is shown in Fig. 1. The X-ray crystallographic and processing parameters are given in Table 1.

Table 1  
X-ray crystallographic and processing parameters for **9**·C<sub>6</sub>H<sub>6</sub> and **11**·hexane

	<b>9</b> ·C <sub>6</sub> H <sub>6</sub>	<b>11</b> ·hexane
Empirical formula	C <sub>36</sub> H <sub>44</sub> Ge <sub>2</sub> O <sub>2</sub> ·C <sub>6</sub> H <sub>6</sub>	C <sub>54</sub> H <sub>66</sub> Ge <sub>3</sub> O <sub>2</sub> ·C <sub>6</sub> H <sub>14</sub>
Colour, habit	colourless plates	colourless block
Wavelength (Å)	0.71073	0.71073
Crystal system	orthorhombic	triclinic
Space group	<i>Ccca</i>	<i>P</i> $\bar{1}$
Crystal size (mm)	0.32 × 0.32 × 0.12	0.34 × 0.27 × 0.26
Unit cell dimensions		
<i>a</i> (Å)	12.0626(4)	12.8435(2)
<i>b</i> (Å)	20.5462(5)	13.0922(2)
<i>c</i> (Å)	14.7391(4)	16.2660(3)
α (°)	90	83.2037(11)
β (°)	90	85.2049(10)
γ (°)	90	83.0911(10)
<i>Z</i>	4	2
Diffractometer	Nonius Kappa-CCD	Nonius Kappa-CCD
Method of collection	φ–ω Scans	φ–ω Scans
Reflections collected	21 869	26 281
<i>R</i> <sub>int</sub>	0.057	0.031
2θ Range for data collection (°)	6–53	3–53
Absorption coefficient (mm <sup>-1</sup> ) and type	1.68 Integration	1.706 Integration
Data/restraints/parameters	1868/0/109	10 859/0/606
final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0333, <i>wR</i> <sub>2</sub> = 0.0901	<i>R</i> <sub>1</sub> = 0.0296, <i>wR</i> <sub>2</sub> = 0.0739
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0391, <i>wR</i> <sub>2</sub> = 0.0952	<i>R</i> <sub>1</sub> = 0.0355, <i>wR</i> <sub>2</sub> = 0.0774
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Treatment of H atoms	Calc. geometrically (riding model)	Calc. geometrically (riding model)

### 3.9. X-ray structure determination of **11**

Colourless plate crystals of **11** were grown from a concentrated hexanes solution at room temperature. Diffraction data using a crystal with the dimensions of  $0.34 \times 0.27 \times 0.26$  mm were collected on a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. Of a total of 26 281 reflections collected up to  $2\theta = 52.8^\circ$  ( $0 \leq h \leq 16$ ,  $-16 \leq k \leq 16$ ,  $-20 \leq l \leq 20$ ) in  $\omega$ - $2\theta$  mode using graphite monochromated Mo-K $_{\alpha}$  radiation, 10 859 were independent ( $R_{\text{int}} = 0.031$ ). These data were corrected for absorption using the integration method. Hydrogen atoms were calculated geometrically and were either riding, or in the case of methyl groups, riding as rigid groups on their respective carbon atoms. The hexane of solvation was well behaved and refined satisfactorily. Non-hydrogen atoms were refined anisotropically based on  $F^2$  by full-matrix least-squares method. A molecular structure drawing is shown in Fig. 2. The X-ray crystallographic and processing parameters are given in Table 1.

### 4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 158909 and 158910 for compounds **11** and **9**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

### Acknowledgements

We thank the NSERC (Canada) for financial support and Dr W.J. Simonsick (Dupont Co., Philadelphia, PA) for useful discussions and the K<sup>+</sup>IDS mass spectra.

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