On the Synthesis, Structure, and Reactivity of Tetramesityldigermene

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Tetramesityldigermene (**1**) can be synthesized cleanly and quantitatively by photolysis of hexamesitylcyclotrigermane (**2**) in THF at low temperature. A solution of tetramesityldigermene (**1**) in THF is stable for several weeks at room temperature; the digermene does not dissociate or rearrange. The molecular structure of tetramesityldigermene (**1**) has been determined using X-ray crystallography. The effectiveness of the new protocol for the synthesis of tetramesityldigermene (**1**) and its derivatives has been demonstrated in the study of the addition of carboxylic acids to tetramesityldigermene (**1**).

Introduction

The synthesis of solid, stable derivatives of digermenes a quarter century ago was significant for two key reasons. The X-ray structures of the solid derivatives greatly facilitated the understanding of the bonding in these and related compounds.[1] Furthermore, digermenes, like alkenes, serve as excellent substrates for the synthesis of numerous organogermanium derivatives.[1] More recently, there has been much interest in the reactivity of dimers on germanium surfaces. It is our hypothesis that the reactivity of molecular digermenes can guide the understanding of the reactivity of the dimers, and particularly the symmetrical dimers found on the Ge(100)-p(2×1) surface.[2] For these reasons, new and/or improved syntheses of digermenes are of ongoing importance.

Our group has had a long-standing interest in the chemistry of digermenes and employs tetramesityldigermene (**1**) as a prototypical substrate.[3] The mesityl substituents are bulky enough to kinetically stabilize the digermene, but not too bulky so as to facilitate dissociation of the digermene **1** to germylenes. Digermene **1** is most easily synthesized by the photolysis[3a] of hexamesitylcyclotrigermane (**2**) in the presence of triethylsilane in toluene at low temperature, but can also be produced by thermolysis (Scheme 1).[4] The silane is necessary to react irreversibly with dimesitylgermylene (**3**) (also formed during the reaction), which drives the reaction to completion. As a consequence, chromatographic separation of dimesityl(triethylsilyl)germane (**4**) and the product(s) derived from digermene **1** is usually required.

Surprisingly, co-photolysis of **2** and triethylsilane at −70 °C *in THF* did not produce silylgermane **4** as a product; only products derived from digermene **1** were isolated.[5] If indeed tetramesityldigermene (**1**) can be produced cleanly and reliably using this protocol, several advantages may be realized. Since the photolysis of 1 equiv of **2** should result in the formation of 1.5 equiv of **1**, the reaction is more atom economical in comparison to the photolysis in toluene. Furthermore, since a co-product is not formed, chromatographic separation is likely unnecessary and, thus, may result indirectly in better yields of the derivatives of digermene **1**. Given that the development of more efficient routes for the preparation of digermenes is of continuing interest, our previous results compelled us to further examine the general usefulness of this method for the preparation of **1** and its derivatives.

Results and Discussion

To enable us to directly compare the previously established method for the synthesis of **1** (method A: photolysis of cyclotrigermane **2** at −70 °C in toluene in the presence of Et_3SiH) and the new protocol (method B: photolysis of cyclotrigermane **2** at −70 °C in THF), **1** was converted to known isolable adducts. Methanol and chloroform were selected as the test reagents because the additions of these reagents to **1** have been reported to proceed cleanly, albeit in low isolated yields.[6,7] Low yields are typical for adducts of **1** produced by method A because of the chromatographic separation required and the nonquantitative conversion of **2** to **1**. By comparing the isolated yields of the adducts, we were able to qualitatively evaluate the relative effectiveness of the two methods for the preparation of derivatives of **1**.

In a typical procedure for method B, a solution of **2** in THF was irradiated (350 nm) at −70 °C, followed by addition

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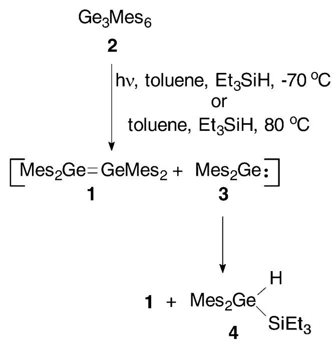
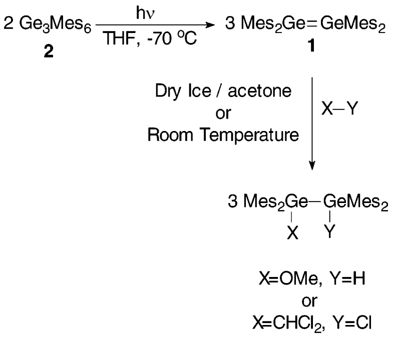
Scheme 1



Scheme 2



of the reagent to the cold solution (dry ice/acetone) of **1** (Scheme 2). If the characteristic bright yellow color of **1** did not dissipate within a few hours after addition, the solution was allowed to warm to room temperature. The results are summarized in Table 1, along with the reported isolated yields using method A. Although the crude product of each reaction was fairly clean by ^{1}H NMR spectroscopy, purification of the adducts by chromatography was still necessary to obtain acceptable purities. Nevertheless, an improvement in the isolated yields (~10%) for both products using the new protocol (method B) was consistently achieved.

The decision to add the reagent to the solution of **1** at low temperature stems from our earlier observation that **1** rearranges to the isomeric mesityl(trimesitylgermyl)germylene (**5**) under mild conditions (lower than room temperature) when Et_3SiH is present (Scheme 3).[8] However, when **2** was photolyzed at −70 °C in THF (in the absence of a germylene trap) and the solution was subsequently warmed to room temperature, the distinctive yellow color of **1** persisted, even after 6 h. When methanol was added to this solution at room temperature, the color immediately faded. Analysis of the ^{1}H NMR spectrum of the crude product revealed complete and clean conversion of **1** to 1,1,2,2-tetramesitylmethoxydigermane,[6] indicating that **1** is in fact stable at room temperature in THF in the absence of a trap. No evidence for the formation of products derived from the addition of methanol to either **3** or **5** was observed; **1** retains its structural integrity in THF at room temperature. The clean conversion of the digermene **1** to the final product at room temperature negated the need for a chromatographic separation. As a result, the isolated yield of the product improved dramatically (see Table 1, method C). Analogous results were obtained when chloroform was added to **1** under these conditions.

The irreversible conversion of **2** to **1** is likely assisted by the complexation of **3** with THF. Transient germylenes are well-known to be stabilized by Lewis bases. In fact, germylene−Lewis base complexes have been previously characterized in solution,[9,10] in matrixes,[11] and in the solid state.[3f,12] Furthermore, several intramolecularly base-stabilized germylenes have been synthesized and characterized.[13] Moreover, it has been demonstrated that the reactivity of the Lewis acid−base complex of diphenylgermylene and THF is less than the free germylene. The kinetics of the reaction of diphenylgermylene with CCl_4 was examined by laser flash photolysis. Diphenylgermylene exhibited an extended lifetime when the reaction was performed in THF compared to when it was carried out in hexanes.[9b,c] Although absolute rate constants for the reactions of germylenes in THF have not been determined, rate constants for reactions of silylenes have been reported to decrease when the reactions are performed in donating solvents, such as THF, compared to nondonating solvents, such as hydrocarbons.[14] Silylenes also show an increase in their lifetimes in solvents with which they form Lewis acid−base complexes, compared to nondonating solvents.[14]

A kinetic study of the complexation of dimesitylgermylene (**3**) with THF was recently reported.[9f] The rate constant for the complexation of **3** with THF was estimated to be 10^8−10^9 M^{-1} s^{-1} at 25 °C.[9f] The rate constant for the addition of **3** to Et_3SiH in hexanes, 1.1×10^5 M^{-1} s^{-1},[15] is much smaller than the rate constant for complexation with THF. Moreover, by variation of the concentration of THF, the equilibrium constant, K_{eq}, between free **3** and THF-complexed **3** was determined to be 1.1 ± 0.2 M^{-1}.[9f] The dimerization of **3** to produce **1** occurs quickly with a rate constant of 5×10^9 M^{-1} s^{-1} [9a,f] and was observed to afford digermene **1** in 93% yield.[9a] Significantly, an increase in the UV−vis absorption of **1** in the presence of a low concentration of THF was observed and was attributed to the influence of THF on the suppression of a decay pathway of **1**: most likely, the addition of free **3** to **1**.[9f]

Our results can be understood on the basis of the kinetic studies. The irradiation of cyclotrigermane **2** produces both **1** and **3** (eq 1, Scheme 4).[15] When **2** is photolyzed in THF, the complexation of **3** with THF appears to lower the reactivity of **3** sufficiently to effectively prevent the addition of **3** to digermene **1** (reverse reaction, eq 1, Scheme 4) or to Et_3SiH (eq 2, Scheme 4). Dimerization of **3** to **1**, on the other hand, appears to persist under the reaction conditions (eq 3, Scheme

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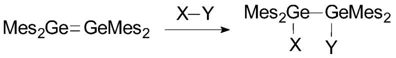
Table 1. Isolated Yields of Adducts of 1 Using Methods A, B, and C

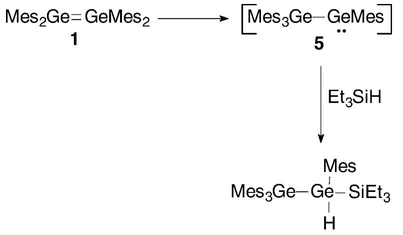


$Mes_2Ge{=}GeMes_2 \xrightarrow{X-Y} Mes_2Ge(X)-GeMes_2(Y)$

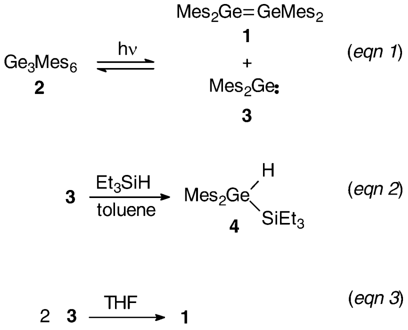
reagent X−Y	X	Y	yield method A[a]	yield method B[b]	yield method C[c]
MeOH	MeO	H	22%	30%	88%
$CHCl_3$	$CHCl_2$	Cl	25%[d]	35%	88%
t-BuCOOH	*t*-BuCOO	H		**8a**: 24%	**8a**: 53%
MesCOOH	MesCOO	H		**8b**: 42%	**8b**: 55%
$(CPhHCH_2)CHCOOH$	$(CPhHCH_2)CHCOO$	H		**8c**: 20%[e]	**8c**: 55%

[a] Method A: Photolysis (350 nm) of **2** at −70 °C in toluene in the presence of Et_3SiH, followed by the addition of the reagent to the solution of **1** cooled in a dry ice/acetone bath. [b] Method B: Photolysis (350 nm) of **2** at −70 °C in THF, followed by the addition of the reagent to the solution of **1** cooled in a dry ice/acetone bath. [c] Method C: Photolysis (350 nm) of **2** at −70 °C in THF, followed by the addition of the reagent to the solution of **1** at room temperature. [d] Reference 7. [e] The H_2O and RCOOH adducts of **1** were not separable.

Scheme 3



Scheme 4

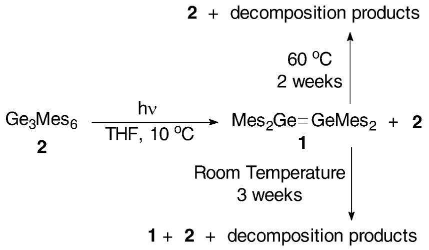


4). As such, our specific reaction conditions (irradiation of **2** in THF at −70 °C) allow for full and clean conversion of cyclotrigermane **2** to digermene **1**. Furthermore, the solution of digermene **1** can be warmed to room temperature without reversion to the cyclotrigermane **2**.

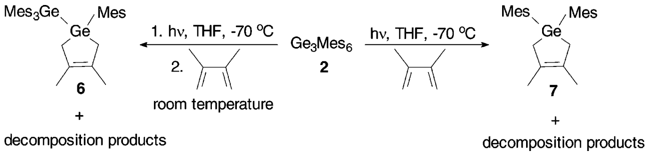
Given the stability of tetramesityldigermene (**1**) in THF at room temperature, we questioned the need for photolysis at −70 °C. Thus, we examined the photolysis of **2** in THF at 10 °C. Under these conditions, the photolysis did not go to completion; a mixture of **1** and **2** in a 1:1 ratio was observed by ^1H NMR spectroscopy. Presumably, at this elevated reaction temperature, the equilibrium constant for the formation of the THF complex of **3** decreases, producing more of free **3**. The addition of **3** to **1** must compete effectively with the dimerization of **3** at this temperature. If the mixture of **1** and **2** is allowed to stir in THF at room temperature, **1** slowly reverts to the cyclotrigermane **2** and some decomposition products. After stirring for 3 weeks, the ratio of **1** to **2** changed slightly, from 1:1 to 1:1.27. If, instead, the THF solution of **1** and **2** is heated to reflux, the loss of **1** occurs more quickly. After 2 weeks of heating, the ratio of **1**:**2** had changed significantly to 1:7.14 (Scheme 5).

To investigate the stability of digermene **1**, we examined its reactivity in the presence of a well-known germylene trap, 2,3-dimethylbutadiene.[12b,16] An excess of the diene was added to a solution of **1** in THF at room temperature. There was no noticeable color change. The solution was allowed to stir at room temperature and monitored periodically by ^1H NMR spectroscopy. Over the course of 9 days, in the presence of the diene, the formation of mesityl(trimesitylgermyl)germacyclopentene (**6**) was observed (Scheme 6). The formation of germacyclopentene **6** is best explained by a 1,2-shift of a mesityl group in **1** to give mesityl(trimesitylgermyl)germylene (**5**), followed by subsequent trapping with the diene.[16d] The rate of formation of **6** was increased by heating the reaction mixture to reflux in a sealed tube. The formation of decomposition products (presumably oligomers) was also observed; however, there was no evidence for the formation of dimesitylgermacyclopentene **7**.[16b,d] The co-photolysis of cyclotrigermane **2** and 2,3-dimethylbutadiene in THF at −70 °C was also examined. The irradiation produced germacyclopentene **7**[16b,d] and unidentified decomposition products.[17] These results demonstrate that once formed, germylene **3** can be trapped by a diene in THF. As a result, we can confidently state that there is no evidence for dissociation of **1** to germylene **3** in THF solution at temperatures less than 60 °C. In the absence of dissociation of digermene **1** to germylene **3**, the mechanism for the formation of cyclotrigermane **2** from **1** (*vide supra*) is puzzling. We postulate that, in the absence of a diene trap, **2** is formed via

Scheme 5



Scheme 6



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[17] Decomposition products (likely oligomers) were also formed in small quantities; however, they could not be separated cleanly to permit identification by spectroscopic methods. Photolysis (350 nm) of a solution of 2,3-dimethylbutadiene in THF at −70 °C in the absence of cyclotrigermane **2** also resulted in the formation of several oligomeric products.

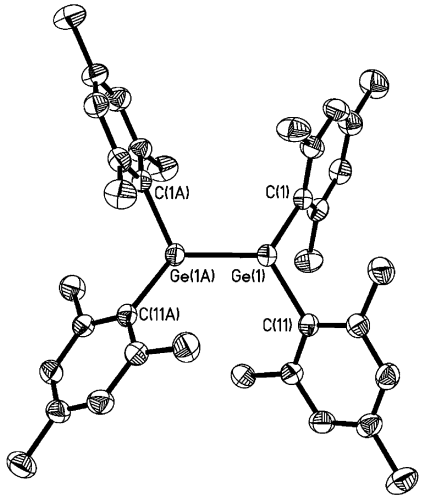


Figure 1. Structure of **1**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−Ge(1A) = 2.2856(8), Ge(1)−C(11) = 1.973(3), Ge(1)−C(1) = 1.985(3), C(11)−Ge(1)−C(1) = 113.28(15), C(11)−Ge(1)−Ge(1A) = 121.64(10), C(1)−Ge(1)−Ge(1A) = 113.22(10).

Table 2. Selected Structural Data of Representative Digermenes $R_2Ge{=}GeR_2$

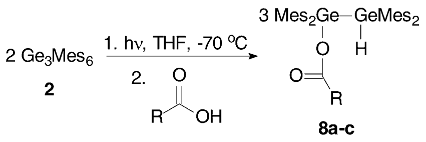
R	Ge−Ge (Å)	trans-bent angle (deg)	twist angle (deg)
Mes	2.2856(8)	33.4	2.9
2,6-diethylphenyl[a]	2.213(2)	12	10
2,4,6-triisopropylphenyl[b]	2.213(1)	12.3	13.7
(Et)(2,6-$Trip_2C_6H_3$)[c]	2.347(3)	37.9	not reported
2,3,4-Me_3-6-*t*-Bu-C_6H[d]	2.2521(8)	0	20.4

[a] Reference 19a. [b] Reference 19b. [c] Trip=2,4,6-triisopropylphenyl, ref 20. [d] Reference 21.

dimerization of the digermene with expulsion of a germylene either from the resulting cyclotetragermane or from a possible biradical intermediate. In the presence of a diene trap, however, rearrangement to the germylgermylene **5** takes place preferentially.

Crystals of digermene **1** were grown from a concentrated THF solution, and the molecular structure of tetramesityldigermene (**1**) was determined by X-ray crystallography (Figure 1). Although bond lengths and angles of **1** have been calculated,[9a] until now, there has been no experimental structural characterization of digermene **1**. The Ge−Ge double-bond length of **1** was determined to be 2.2856(8) Å, and **1** has trans-bent and twist angles of 33.4° and 2.9°, respectively. These values fall within the known range of Ge−Ge bond lengths (2.21−2.46 Å),[1g,18] trans-bent angles (0−45°),[1g,h,18] and twist angles (0−42°)[18] in digermenes. The metrics obtained are also close to the estimated values predicted by DFT calculations of **1** using uncontracted Slater-type orbitals of triple-ζ quality as the basis set with the PW91 functionals.[9a] The Ge−Ge bond length of **1** is longer than that in tetrakis(2,6-diethylphenyl)digermene and tetrakis(2,4,6-triisopropylphenyl)digermene, which both have a Ge−Ge bond length of 2.213 Å[19] despite the difference in the steric bulk of the substituents (Table 2). While the bond length of **1** is shorter than in the terphenyl-substituted digermenes,[20] it is slightly longer than the Ge−Ge bond length of the (2,3,4-Me_3-6-*t*-Bu-C_6H)-substituted digermene[21] (Table 2). Interestingly, the (2,3,4-Me_3-6-*t*-Bu-C_6H)-substituted digermene dissociates in solution at room temperature to give the corresponding germylene,[21] whereas we have shown that tetramesityldigermene (**1**) does not. As has previously been concluded, slight changes in the spatial requirements of digermene substituents produce remarkably different bond lengths and angles such that a correlation between steric bulk about a digermene and its double-bond length is not feasible.[1g,i,j] Thus, the rather long double bond in **1**, in comparison with the length of the Ge−Ge double bond in the bulkier 2,6-diethylphenyl- and 2,4,6-triisopropylphenyl-substituted derivatives, seems reasonable. With an improved method for the synthesis of tetramesityldigermene (**1**) in hand, we next wanted to demonstrate the usefulness of the procedure.

Scheme 7



a: R = *t*-Bu
b: R = Mes
c: R = *trans*-2-phenylcyclopropyl

The kinetics of the addition of carboxylic acids to transient digermenes has been examined; however, isolation of the adducts was not practical.[9a,b,d,e,10] Only one example of a carboxylic acid adduct of a digermene has been reported: the adduct between acetic acid and tetramesityldigermene (**1**).[10] The adduct, $Mes_2Ge(OAc)GeHMes_2$, was formed in good yield based on a 1:1 stoichiometry (63%); however, it was noted that the yield was lower in THF solution, although no details were given.[10] The generality of this reaction is still unknown. The addition of (deuterated) acetic acid and formic acid to the germanium dimers on the Ge(100)-2×1 surface has also been investigated.[22] The structure of the surface adduct(s) was determined using a combination of spectroscopic and computational techniques. Given the recent interest in the addition of carboxylic acids to digermenes, we selected this reaction to showcase our new protocol for the synthesis of digermene derivatives.

The addition of carboxylic acids to **1** in THF was examined at both room temperature and in the cold (dry ice/acetone bath). The formation of a digermyl ester, **8a**−**c**, was observed in all cases (Scheme 7). Despite rigorous attempts to remove all traces of water from the carboxylic acid prior to addition, the formation of the water adduct of **1** was often observed. This necessitated separation of the products by preparative thin-layer chromatography, and thus, the isolated yields were modest. All products were characterized by NMR and IR spectroscopy and mass spectrometry; the isolated yields of the products are given in Table 1.

The mass spectra of **8a**−**c** contained signals that were consistent with the formation of a 1:1 adduct between **1** and the carboxylic acid. The ^1H NMR spectra of **8a**−**c** revealed a characteristic singlet between 6.4 and 6.8 ppm, assigned to the Ge−H moiety. The IR spectra of **8a**−**c** showed absorptions between 2030 and 2092 cm^{-1}, which were assigned to the stretching vibration of the Ge−H bond.[3c,d,6,8,10,16d] The ^{13}C NMR spectra of **8a**−**c** contained signals (170−180 ppm) located in the typical chemical shift range of ester carbonyl carbons. In

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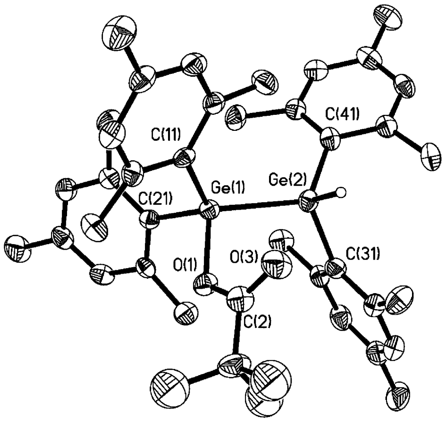

Figure 2. Structure of **8a**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms, with the exception of the Ge−H, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge(1)−Ge(2) = 2.4829(5), Ge(1)−C(11) = 1.981(4), Ge(1)−C(21) = 1.983(4), Ge(2)−C(31) = 1.968(4), Ge(2)−C(41) = 1.981(4), Ge(1)−O(1) = 1.863(3), O(1)−C(2) = 1.317(5), C(2)−O(3) = 1.210(5); C(11)−Ge(1)−C(21) = 111.67(15), C(11)−Ge(1)−Ge(2) = 116.18(11), C(31)−Ge(2)−C(41) = 107.33(15), C(41)−Ge(2)−Ge(1) = 121.15(11), C(21)−Ge(1)−Ge(2) = 120.67(10), C(31)−Ge(2)−Ge(1) = 113.39(11), O(1)−Ge(1)−C(21) = 97.05(13), O(1)−Ge(1)−Ge(2) = 103.72(8), O(3)−C(2)−O(1) = 122.6(4).

the IR spectra of **8a**−**c**, bands attributable to the stretching vibration of a carbonyl group of a germyl ester were also identified (1670−1690 cm^{-1}). None of the aforementioned ^{1}H NMR signals assigned to the Ge−H revealed a cross-peak with the ^{13}C signals assigned to the carbonyl group in the ^{1}H−^{13}C *g*HMBC spectra for adducts **8a**−**c**, and thus, the framework of **8a**−**c** was assigned as GeO(C═O)R and not Ge(C═O)OR. In addition, correlations between the signals assigned to the R groups in **8a** and **8c** in the ^{1}H dimension and their respective C═O signals in the ^{13}C dimension were observed, providing further evidence for the GeO(C═O)R arrangement. The framework of the digermyl ester **8a** was unambiguously confirmed by X-ray crystallography. Crystals of **8a** were grown by slow evaporation of C_6D_6; the molecular structure of adduct **8a** is shown in Figure 2. As expected, the Ge−Ge bond length of **8a** has increased to 2.4829(5) Å from the bond length of 2.2856(8) Å observed in digermene **1**. This is consistent with a change in bond order from two to one. The Ge−Ge bond length is slightly elongated from what is typically observed.[1d,h] The Ge−O bond length of 1.863(3) Å is representative of this type of bond.[5,23]

The structures of **8a**−**c** are consistent with those proposed to be formed on the Ge(100)-2×1 surface.[22] Bent et al. monitored the addition of acetic acid and formic acid to the Ge(100)-2×1 surface by IR spectroscopy; they recorded the IR spectra of the surface periodically during the addition of the carboxylic acid and after the reaction was complete. Absorptions corresponding to Ge−H moieties were observed, in addition to those resulting from the carbonyl and C−O functional groups.[22] Using density functional theory calculations, Bent et al. considered several possibilities for the structure of the surface adduct. The digermyl ester was found to be the most thermodynamically stable product of the addition.[22] Thus, the reactivity of the molecular digermene **1** exactly mirrors that of the Ge surface dimer. Our results are also consistent with the digermyl ester structures proposed to be formed in laser flash photolysis kinetic studies of the reaction of carboxylic acids with digermenes[9a,b,d,e,10] and are consistent with the structure of the acetic acid adduct of **1**, which was determined by NMR and IR spectroscopy and mass spectrometry.[10]

Conclusion

In summary, we have evaluated a new protocol for the synthesis of tetramesityldigermene (**1**): photolysis of cyclotrigermane **2** in THF at −70 °C. Digermene **1** was shown to be stable in THF at room temperature; no evidence for dissociation to dimesitylgermylene (**3**) or rearrangement to germylgermylene **5** was observed. Using the new protocol, we were able to characterize digermene **1** by NMR spectroscopy and mass spectrometry and determine its molecular structure by X-ray crystallography. The benefits of our new protocol were demonstrated in a study of the reaction between digermene **1** and three carboxylic acids. Moreover, it was shown that the reactivity between molecular digermenes and carboxylic acids mirrors the reactivity of the symmetric Ge dimers found on the Ge(100)-2×1 surface. It is our belief that digermenes can be used as molecular models of these surface dimers and can assist in the understanding of surface functionalization reactions.

Experimental Section

General Procedures. Unless otherwise indicated, all reactions were carried out in flame-dried glassware under an inert atmosphere of argon using a dual-manifold vacuum line or prepared under a nitrogen atmosphere using an MBraun Labmaster 130 glovebox. THF was purged with nitrogen and then passed through an alumina column (Innovative Technology Ltd.) prior to use. Toluene was purged with nitrogen and then passed through an alumina column and copper catalyst (Innovative Technology Ltd.) prior to use. Methanol was distilled from magnesium and chloroform was distilled from phosphorus pentoxide prior to use. Triethylsilane was distilled from $LiAlH_4$ prior to use. 2,3-Dimethylbutadiene was purchased from the Aldrich Chemical Co. and used without further purification. 2,4,6-Trimethylbenzoic acid and *trans*-2-phenylcyclopropane-1-carboxylic acid were purchased from the Aldrich Chemical Co.; pivalic acid was purchased from the Eastman Kodak Co. All carboxylic acids were dissolved in THF (1 mL) and allowed to sit over 4 Å molecular sieves for 24 h prior to use. Hexamesitylcyclotrigermane (**2**) was prepared according to the literature procedure.[24] If solutions of **2** were not prepared in an inert atmosphere glovebox, the solutions were degassed by successive freeze−pump−thaw cycles.

NMR spectra were recorded on Varian Mecury 400 or Inova 400 or 600 NMR spectrometers. The standards used were as follows: residual C_6D_5H (7.15 ppm) for ^{1}H NMR spectra; C_6D_6 central transition (128.00 ppm) for ^{13}C NMR spectra. *J* values are reported in hertz. EI- and GC-mass spectra were recorded on a Finnigan MAT model 8400 mass spectrometer with an ionizing voltage of 70 eV. IR spectra were recorded on a Perkin-Elmer System 2000 FT IR spectrometer. Photolyses were performed in a Rayonet photochemical reactor (Southern New England Co.) equipped with 12 bulbs. Samples were cooled by circulating methanol through a vacuum-jacketed quartz or Pyrex immersion well using an Endocal model ULT-70 low-temperature external bath circulator. Melting point data are uncorrected.

Single-crystal X-ray analyses of **1** and **8a** were performed using an Enraf-Nonius Kappa CCD X-ray diffractometer. The structures were solved and refined using SHELXTL/PC V6.14 software. A

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Table 3. Crystallographic Data for 1 and 8a

	1	8a
empirical formula	$C_{36}H_{44}Ge_2{\cdot}C_4H_8O$	$C_{41}H_{54}Ge_2O_2$
fw	694.00	724.02
temperature (K)	150(2)	150(2)
wavelength (Å)	0.71073	0.71073
cryst syst	orthorhombic	monoclinic
space group	*Pbcn*	*P*2(1)/*c*
a (Å)	11.816(2)	12.8332(4)
b (Å)	14.413(3)	14.0900(3)
c (Å)	20.729(4)	20.2794(6)
β (deg)	90	94.320(13)
volume (Å^3)	3530.4(12)	3656.50(18)
Z	4	4
calcd density (g/cm^3)	1.306	1.315
absorp coeff (mm^{-1})	1.732	1.677
F(000)	1456	1520
cryst size (mm^3)	0.15 × 0.14 × 0.05	0.47 × 0.23 × 0.08
θ range for data collection (deg)	2.04−27.48	2.04−27.48
no. of reflns collected	25 363	15 532
no. of indep reflns	4049 [$R_{int} = 0.063$]	8310 [$R_{int} = 0.076$]
completeness to $\theta = 25.03°$ (%)	99.9	99.0
absorp corr	semiempirical from equivalents	semiempirical from equivalents
max. and min. transmn	0.9184 and 0.7812	0.8845 and 0.5030
no. of data/restraints/params	4049/0/189	8310/18/414
goodness-of-fit on F^2	1.058	1.043
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0565$, $wR_2 = 0.1582$	$R_1 = 0.0522$, $wR_2 = 0.1243$
R indices (all data)	$R_1 = 0.0825$, $wR_2 = 0.1778$	$R_1 = 0.0944$, $wR_2 = 0.1414$
largest diff peak and hole (e Å^{-3})	2.309 and −0.912	0.896 and −0.920

summary of the crystal data collection and refinement for **1** and **8a** is presented in Table 3. Complete X-ray experimental details are given in the Supporting Information.

Preparation of Tetramesityldigermene (1). A clear, colorless solution of **2** (100 mg, 0.11 mmol) in THF (8 mL) was prepared in a Pyrex Schlenk tube. The solution was irradiated (350 nm) at −70 °C for 18 h, at which point the solution was bright yellow in color.[25] THF was removed *in vacuo* from **1** to yield a yellow powder. Analysis of the powder by ^{1}H NMR spectroscopy revealed that the conversion of **2** to **1** was complete. The melting point of **1** was obtained under an inert (N_2) atmosphere. **1**: Mp: 124−127 °C (dec). ^{1}H NMR (ppm): 6.72 (s, 8H, Mes C*H*), 2.39 (s, 24H, Mes *o*-CH_3), 2.06 (s, 12H, Mes *p*-CH_3). ^{13}C NMR (ppm): 143.57 (*i*-Mes*C*), 142.24 (*o*-Mes*C*), 138.21 (*p*-Mes*C*), 128.58 (Mes *C*H), 25.46 (Mes *o*-CH_3), 21.09 (Mes *p*-CH_3). High-resolution EI-MS: Exact mass calcd for $C_{36}H_{45}{}^{70}Ge_2$ ($M^+ + H$) 617.201, found 617.199.[26]

Addition of Methanol to 1. Method C. Addition of methanol (1 mL, excess) to the yellow solution of **1** (0.17 mmol) in THF (8 mL) at room temperature resulted in an instantaneous and complete loss of color. The solvent was removed by rotary evaporation to yield 1,1,2,2-tetramesitylmethoxydigermane[6] (97.7 mg, 88%).

Method A. A solution of **2** (50 mg, 0.05 mmol) and Et_3SiH (1 mL, excess) dissolved in toluene (4 mL) was prepared in a Pyrex Schlenk tube. The solution was irradiated (350 nm) at −70 °C for 16 h, at which point the solution was bright yellow in color. Methanol (1 mL, excess) was added to the cooled solution (dry ice/acetone), and the mixture was slowly warmed to room temperature, resulting in complete loss of color. The solvent was removed by rotary evaporation to yield a pale yellow oil. The product mixture was purified by preparative thin-layer chromatography (silica gel; 70/30 CH_2Cl_2/hexanes) to give (hydroxydimesitylgermyl)-dimesitylgermane,[16d] dimesityl(triethylsilyl)germane,[8] and 1,1,2,2-tetramesitylmethoxydigermane[6] (7.29 mg, 22%).

Addition of Chloroform to 1. Addition of chloroform (1 mL, excess) to the yellow solution of **1** (0.17 mmol) in THF (8 mL) at room temperature resulted in the complete loss of color within 2 min. The solvent was removed by rotary evaporation to yield 1,1,2,2-tetramesityl-1-chloro-2-(dichloromethyl)digermane[7] (111 mg, 88%).

Addition of 2,3-Dimethylbutadiene to 1. 2,3-Dimethylbutadiene (0.1 mL, excess) was added to a yellow solution of **1** (0.17 mmol) in THF (8 mL). After 9 days of stirring at room temperature, the color of the solution had faded to pale yellow. The solvent and excess 2,3-dimethylbutadiene were removed by rotary evaporation to yield a white powder identified as 1-mesityl-3,4-dimethyl-1-(trimesitylgermyl)-1-germacyclopent-3-ene[16d] (**6**) contaminated with a small amount of decomposition products[17] (96.4 mg, 85% of **6**).

Co-photolysis of 2,3-Dimethylbutadiene and 2. A solution of 2,3-dimethylbutadiene (0.1 mL, excess) and **2** (50 mg, 0.05 mmol) in THF (4 mL) was irradiated (350 nm) for 16 h. The solvent and excess 2,3-dimethylbutadiene were removed by rotary evaporation to yield 1,1-dimesityl-3,4-dimethyl-1-germacyclopent-3-ene[16b,d] (**7**) and decomposition products[17] (54.8 mg) as determined by ^{1}H NMR spectroscopy.

Addition of Pivalic Acid to 1. A solution of pivalic acid (25.3 mg, 0.25 mmol) dissolved in THF (1 mL) was added to the bright yellow solution of **1** (0.17 mmol) in THF (8 mL). After 5 min at room temperature, the color of the solution had faded to pale yellow. The solvent was removed by rotary evaporation to yield an oily, yellow residue. The product mixture was purified by preparative thin-layer chromatography (silica gel; 70/30 CH_2Cl_2/hexanes) to give excess pivalic acid, (hydroxydimesitylgermyl)-dimesitylgermane,[16d] and **8a** (65.1 mg, 53%) as colorless crystals. **8a**: Mp: 190−192 °C (dec). IR (cm^{-1}): 2964 (m), 2959 (m), 2923 (m), 2870 (m), 2085 (w), 2033 (w), 1685 (s), 1559 (s), 1458 (s), 1290 (m), 1177 (s), 1028 (m), 848 (m), 738 (m), 668 (m), 648 (m), 546 (m). ^{1}H NMR (ppm): 6.69 (s, 8H, Mes C*H*), 6.51 (s, 1H, Ge*H*), 2.39 (s, 12H Mes *o*-CH_3), 2.36 (s, 12H, Mes *o*-CH_3), 2.07 (s, 6H, Mes *p*-CH_3), 2.04 (s, 6H, Mes *p*-CH_3), 1.20 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (ppm): 179.27 (*C*=O), 143.85, 143.17 (*o*-Mes*C*), 138.91, 138.42 (*p*-Mes*C*), 138.03, 135.62 (*i*-Mes*C*), 129.76, 129.09 (Mes *C*H), 39.78 (*C*(CH$_3$)$_3$), 27.91 (C(*C*H$_3$)$_3$), 24.98, 24.41 (Mes *o*-*C*H$_3$), 20.97, 20.93 (Mes *p*-*C*H$_3$). EI-MS (*m/z*): 724 (M^+ ^{72}Ge^{74}Ge, 3), 623 ($M^+ -$ O(CO)*t*-Bu, 3), 605 ($M^+ -$ Mes, 1), 502 (Mes$_3$^{72}Ge$_2$H,

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(25) For the UV−visible spectrum of **1**, see refs 9f, 11c,e, and 15.

(26) The low-resolution mass spectrum of **1** revealed the presence of oxidation product(s) likely formed during the introduction of the sample into the mass spectrometer. EI-MS (*m/z*): 654 ($M^+ + O_2$, ^{72}Ge^{74}Ge, 34), 638 ($M^+ + O$, ^{72}Ge^{74}Ge, 17), 623 ($M^+ + H$, ^{72}Ge^{74}Ge, 23), 535 (Mes$_3$^{72}Ge^{74}GeO$_2$, 47), 517 (Mes$_3$^{72}Ge$_2$O, 47), 429 (Mes$_3$^{72}Ge, 58), 415 (Mes$_2$^{72}Ge$_2$O$_2$H, 44), 329 (Mes$_2$^{74}GeOH, 100), 311 (Mes$_2$^{72}GeH, 83), 192 (Mes^{72}GeH, 55), 119 (Mes, 87).

1), 431 ($Mes_3{}^{74}Ge$, 18), 413 ($M^+ - Mes_2{}^{72}GeH$, 100), 311 ($Mes_2{}^{72}GeH$, 28), 293 ($M^+ - Mes_3{}^{74}Ge$, 5), 192 ($Mes^{72}GeH$, 15), 119 (Mes, 8). High-resolution EI-MS: Exact mass calcd for $C_{41}H_{54}{}^{72}Ge^{74}GeO_2$ 724.256, found 724.254.

Addition of 2,4,6-Trimethylbenzoic Acid to 1. A solution of 2,4,6-trimethylbenzoic acid (41.6 mg, 0.25 mmol) dissolved in THF (1 mL) was added to the bright yellow solution of **1** (0.17 mmol) in THF (8 mL). The color of the reaction mixture faded to pale yellow within 1 min at room temperature. The solvent was removed by rotary evaporation to yield an oily, yellow residue. The product mixture was purified by preparative thin-layer chromatography (silica gel; 70/30 CH_2Cl_2/hexanes) to give excess 2,4,6-trimethylbenzoic acid, (hydroxydimesitylgermyl)dimesitylgermane,[16d] and **8b** (73.2 mg, 55%) as a white solid. **8b**: Mp: 197−198 °C (dec). IR (cm^{-1}): 3021 (m), 2964 (m), 2924 (m), 2857 (m), 2733 (m), 2092 (w), 2030 (w), 1678 (s), 1674 (s), 1668(s), 1602 (s), 1468 (s), 1462 (s), 1451 (s), 1446 (s), 1286 (s), 1173 (s), 1087 (s), 1029 (m), 848 (s), 740 (s), 668 (m), 633 (m) 546 (m). ^1H NMR (ppm): 6.78 (s, 1H, Ge*H*), 6.70 (s, 8H, Mes C*H*), 6.64 (s, 2H, acid Mes C*H*), 2.43 (s, 12H, Mes *o*-CH_3), 2.42 (s, 12H, Mes *o*-CH_3), 2.19 (s, 6H, acid Mes *o*-CH_3), 2.071, 2.067 (each s, 12H, Mes *p*-CH_3), 2.03 (s, 3H, acid Mes *p*-CH_3). ^{13}C NMR (ppm): 171.95 (*C*═O), 143.99, 143.56 (*o*-Mes*C*), 139.14, 138.47 (*p*-Mes*C*), 138.32 (*i*-Mes*C*), 138.00 (acid *p*-Mes*C*), 135.81 (acid *o*-Mes*C*), 135.69 (*i*-Mes*C*), 133.48 (acid *i*-Mes*C*), 129.79, 129.16 (Mes *C*H), 128.88 (acid Mes *C*H), 25.11, 24.86 (Mes *o*-CH_3), 20.98, 20.96 (Mes *p*-CH_3 and acid Mes *p*-CH_3), 20.41 (acid Mes *o*-CH_3). EI-MS (*m/z*): 786 (M^+ $^{72}Ge^{74}Ge$, 13), 771 ($M^+ - CH_3$, 4), 667 (M^+ − Mes, 1), 622 (M^+ − HO(CO)Mes, 3), 475 ($M^+ - Mes_2{}^{72}GeH$, 100), 431 ($Mes_3{}^{74}Ge$, 14), 356 ($M^+ - Mes_3{}^{72}GeH$, 13), 312 ($Mes_2{}^{74}Ge$, 31), 192 ($Mes^{72}GeH$, 22), 119 (Mes, 18). High-resolution EI-MS: Exact mass calcd for $C_{46}H_{56}{}^{72}Ge^{74}GeO_2$ 786.272, found 786.269.

Addition of *trans*-2-Phenylcyclopropane-1-carboxylic Acid to 1. A solution of *trans*-2-phenylcyclopropane-1-carboxylic acid (40.0 mg, 0.25 mmol) dissolved in THF (1 mL) was added to the bright yellow solution of **1** (0.17 mmol) in THF (8 mL). The solution was allowed to stir at room temperature for 5 min, after which the color of the solution had completely faded to pale yellow. The crude product mixture was purified by preparative thin-layer chromatography (silica gel; 70/30 CH_2Cl_2/hexanes) to give excess *trans*-2-phenylcyclopropane-1-carboxylic acid, (hydroxydimesitylgermyl)dimesitylgermane,[16d] and **8c** (72.8 mg, 55%) as a pale yellow oil. **8c**: IR (cm^{-1}): 2964 (m), 2960 (m), 2922 (m), 2859 (m), 2078 (w), 2033 (w), 1688 (s), 1682 (s), 1602 (s), 1462 (m), 1451 (m), 1446 (m), 1402 (m), 1196 (m), 848 (m), 698 (m), 546 (m). ^1H NMR (ppm): 7.06−6.96 (m, 3H, *m*,*p*-Ph*H*), 6.86−6.83 (m, 2H, *o*-Ph*H*), 6.71 (s, 4H, Mes C*H*), 6.69 (s, 4H, Mes C*H*), 6.38 (s, 1H, Ge*H*), 2.55 (ddd, 1H, C*H*Ph, $J = 9.1$, 6.1, 4.1 Hz), 2.42 (s, 6H, Mes *o*-CH_3), 2.40 (s, 6H Mes *o*-CH_3), 2.38 (s, 12H, Mes *o*-CH_3), 2.07 (s, 3H, Mes *p*-CH_3), 2.06 (s, 3H, Mes *p*-CH_3), 2.050, 2.046 (each s, 6H Mes *p*-CH_3), 1.97 (ddd, 1H, C*H*COOGe, $J = 8.4$, 5.2, 4.0 Hz), 1.56 (ddd, 1H, CH_2, $J = 9.2$, 5.2, 4.2 Hz), 0.98 (ddd, 1H, CH_2, $J = 8.3$, 6.3, 4.3 Hz). ^{13}C NMR (ppm): 173.66 (*C*═O), 144.03, 143.91, 143.14, 143.05 (*o*-Mes*C*), 141.11 (*i*-Ph*C*), 139.02, 139.00, 138.53 (*p*-Mes*C*), 137.62, 137.47, 135.11 (*i*-Mes*C*) 129.85, 129.83, 129.15 (Mes *C*H), 128.60 (*m*-Ph*C*), 126.45 (*o*-Ph*C*), 126.32 (*p*-Ph*C*), 26.63 (*C*HCOOGePh), 26.16 (*C*HPh), 24.84, 24.80, 24.27, 24.20 (Mes *o*-CH_3), 20.98, 20.97, 20.94 (Mes *p*-CH_3), 16.94 (CH_2). EI-MS (*m/z*): 784 (M^+ $^{72}Ge^{74}Ge$, 8), 769 ($M^+ - CH_3$, 1), 665 (M^+ − Mes, 2), 622 ($M^+ - HO(CO)CHCH_2CHPh$, 3), 549 ($M^+ - {}^{74}GeO(CO)CHCH_2CHPh$, 1), 502 ($Mes_3{}^{72}Ge_2H$, 1), 473 ($M^+ - Mes_2{}^{72}GeH$, 100), 431 ($Mes_3{}^{74}Ge$, 14), 355 ($Mes_2{}^{72}GeO(CO)H$, 56), 312 ($Mes_2{}^{74}Ge$, 58), 192 ($Mes^{72}GeH$, 79), 119 (Mes, 34). High-resolution EI-MS: Exact mass calcd for $C_{46}H_{54}{}^{72}Ge^{74}GeO_2$ 784.256, found 784.254.

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Supporting Information Available: ^1H NMR spectra of compounds **1** and **8a**−**c**. X-ray experimental details and a CIF file giving crystallographic information for **1** and **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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