Time-Resolved Spectroscopic Studies of the Reactivities of Dimethylgermylene and Tetramethyldigermene in Solution

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Dimethylgermylene (GeMe$_2$) has been generated and studied by laser flash photolysis of 1,1-dimethyl- and 1,1,4-trimethyl-3-phenylgermacyclopent-3-ene (**3a** and **3b**, respectively) in hexane solution, where it exhibits $\lambda_{max} = 470$ nm and decays on the microsecond time scale with second-order kinetics. In the absence of scavengers the decay of GeMe$_2$ is accompanied by the growth of absorptions due to tetramethyldigermene (Ge$_2$Me$_4$; $\lambda_{max} = 370$ nm), which decays over the next ca. 100 μs. Absolute rate constants for reaction of GeMe$_2$ with several reagents have been determined, including acetic acid, CCl$_4$, oxygen, *n*-butyl- and triethylamine, a terminal alkene and alkyne, two dienes, and the group 14 trialkylmetallyl hydrides R$_3$MH (M = Si, Ge, Sn; R = Et or n-Bu). The rate constants agree closely with gas-phase values for the same or similar substrates. The data are compared to those for reaction of GePh$_2$ with the same set of reagents, showing GeMe$_2$ to be significantly more reactive than its phenylated analogue in every case. Evidence of reversibility is obtained for the reactions with the alkene and dienes, which are thought to yield the corresponding three-membered germanocycles as primary products; the equilibrium constants for these reactions are also considerably higher than those for reaction of GePh$_2$. Comparisons are also made with published data for SiMe$_2$ in solution. Absolute rate constants for reaction of Ge$_2$Me$_4$ have also been measured or assigned upper limits and are compared to those for the tetraphenyl analogue (Ge$_2$Ph$_4$), providing the first quantitative assessment of the effects of substituents on the reactivity of the Ge=Ge bond.

Introduction

The chemistry of germylenes, the germanium analogues of carbenes, has been of considerable interest over the past thirty years, and a great deal is known of the synthetic and preparative aspects of their chemistry.[1−4] On the other hand, relatively few mechanistic studies based on kinetics have been reported, although the parent molecule (GeH$_2$) has been extensively studied in the gas phase by direct kinetic methods,[5−16] as has the dimethyl analogue (GeMe$_2$), but in less detail.[16,17] Several time-resolved spectroscopic studies of GeMe$_2$ in solution have also been reported,[18−23] but they afford no consensus on the spectroscopic properties and kinetic behavior of the species and are in poor agreement with gas-phase data.[5,24] The problem is very likely due to the complexity of the photochemistry of many of the precursors (typically oligogermanes or oligosilagermanes[19,20,22,23]) that have been employed in these studies, coupled with the fact that the lowest energy electronic transition in simple germylene derivatives is characteristically weak,[25−27] making them difficult to detect reliably in the presence of other, more strongly absorbing transient products.[26,28]

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(1) Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311.

(2) Barrau, J.; Rima, G. *Coord. Chem. Rev.* **1998**, *180*, 593.

(3) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, *1999*, 373.

(4) Tokitoh, N.; Okazaki, R. *Coord. Chem. Rev.* **2000**, *210*, 251.

(5) Boganov, S. E.; Egorov, M. P.; Faustov, V. I.; Krylova, I. V.; Nefedov, O. M.; Becerra, R.; Walsh, R. *Russ. Chem. Bull. Int. Ed.* **2005**, *54*, 483.

(6) Becerra, R.; Boganov, S. E.; Egorov, M. P.; Nefedov, O. M.; Walsh, R. *Chem. Phys. Lett.* **1996**, *260*, 433.

(7) Becerra, R.; Boganov, S. E.; Egorov, M. P.; Faustov, V. I.; Nefedov, O. M.; Walsh, R. *J. Am. Chem. Soc.* **1998**, *120*, 12657.

(8) Becerra, R.; Walsh, R. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5301.

(9) Alexander, U. N.; Trout, N. A.; King, K. D.; Lawrance, W. D. *Chem. Phys. Lett.* **1999**, *299*, 291.

(10) Alexander, U. N.; King, K. D.; Lawrance, W. D. *Chem. Phys. Lett.* **2000**, *319*, 529.

(11) Becerra, R.; Boganov, S. E.; Egorov, M. P.; Faustov, V. I.; Nefedov, O. M.; Walsh, R. *Can. J. Chem.* **2000**, *78*, 1428.

(12) Becerra, R.; Boganov, S. E.; Egorov, M. P.; Faustov, V. I.; Nefedov, O. M.; Walsh, R. *Phys. Chem. Chem. Phys.* **2001**, *3*, 184.

(13) Becerra, R.; Walsh, R. *J. Organomet. Chem.* **2001**, *636*, 49.

(14) Becerra, R.; Boganov, S. E.; Egorov, M. P.; Faustov, V. I.; Promyslov, V. M.; Nefedov, O. M.; Walsh, R. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5079.

(15) Alexander, U. N.; King, K. D.; Lawrance, W. D. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1557.

(16) Becerra, R.; Egorov, M. P.; Krylova, I. V.; Nefedov, O. M.; Walsh, R. *Chem. Phys. Lett.* **2002**, *351*, 47.

(17) Becerra, R.; Boganov, S. E.; Egorov, M. P.; Lee, V. Ya.; Nefedov, O. M.; Walsh, R. *Chem. Phys. Lett.* **1996**, *250*, 111.

(18) Tomoda, S.; Shimoda, M.; Takeuchi, Y.; Kajii, Y.; Obi, K.; Tanaka, I.; Honda, K. *J. Chem. Soc., Chem. Commun.* **1988**, 910.

(19) Wakasa, M.; Yoneda, I.; Mochida, K. *J. Organomet. Chem.* **1989**, *366*, C1.

(20) Bobbitt, K. L.; Maloney, V. M.; Gaspar, P. P. *Organometallics* **1991**, *10*, 2772.

(21) Mochida, K.; Yoneda, I.; Wakasa, M. *J. Organomet. Chem.* **1990**, *399*, 53.

(22) Mochida, K.; Kanno, N.; Kato, R.; Kotani, M.; Yamauchi, S.; Wakasa, M.; Hayashi, H. *J. Organomet. Chem.* **1991**, *415*, 191.

(23) Mochida, K.; Tokura, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1642.

(24) Boganov, S. E.; Egorov, M. P.; Faustov, V. I.; Nefedov, O. M. In *The Chemistry of Organic Germanium, Tin and Lead Compounds, Vol. 2*; Rappoport, Z., Ed.; John Wiley and Sons: New York, 2002; pp 749−839.

(25) Kishikawa, K.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **1998**, *1998*, 239.

(26) Leigh, W. J.; Toltl, N. P.; Apodeca, P.; Castruita, M.; Pannell, K. H. *Organometallics* **2000**, *19*, 3232.

(27) Leigh, W. J.; Harrington, C. R.; Vargas-Baca, I. *J. Am. Chem. Soc.* **2004**, *126*, 16105. *Errata: ibid.* **2006**, *128*, 1394.

Recently, we reported the results of a study of the photochemistry of the 1,1-disubstituted 3,4-dimethylgermacyclopent-3-ene derivatives (**1a**−**c**) in hexane solution by steady state and laser flash photolysis methods (eq 1).[27] Photolysis of these molecules proceeds very cleanly and with remarkably high efficiency, producing 2,3-dimethyl-1,3-butadiene (DMB) and the expected trapping products of the corresponding germylene as the only detectable photolysis products. The germylenes and their corresponding Ge=Ge doubly bonded dimers, the digermenes **2a**−**c**, proved to be readily detectable in laser flash photolysis experiments with these compounds in hexane solution. Diphenylgermylene (GePh$_2$), for example, was found to exhibit λ_{max} = 500 nm and dimerize at close to the diffusion-controlled rate to yield tetraphenyldigermene (Ge$_2$Ph$_4$, **2a**; λ_{max} = 440 nm), which then decays over a much longer time scale with mixed order kinetics, presumably mainly via oligomerization. In a subsequent paper, we reported a kinetic study of the reactions of GePh$_2$ and Ge$_2$Ph$_4$ with a wide variety of representative germylene scavengers, including aliphatic amines, halocarbons (RX), an aliphatic alkyne, a diene, an alkene, oxygen, acetic acid, and the group 14 hydrides R$_3$MH (M = Si, Ge, Sn; R = ethyl or *n*-butyl).[29]

(1)

1
a. R = C$_6$H$_5$
b. R = Mes (2,4,6-Me$_3$C$_6$H$_2$)
c. R = Me

2 (Ge$_2$R$_4$)
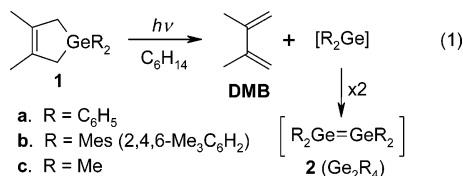
The reported spectrum of GeMe$_2$, generated by 193 nm laser flash photolysis of **1c** in hexane, agrees well with the gas-phase spectrum published by Walsh and co-workers,[17] and with the spectrum predicted by time-dependent DFT calculations.[27] Unfortunately, the need for short-wavelength laser light for excitation of this precursor severely limited our ability to study the bimolecular reactivities of GeMe$_2$ and its dimer (Ge$_2$Me$_4$; **2c**) in a meaningful way, because most reagents that are of practical interest themselves absorb appreciably at 193 nm. Thus, further study of the bimolecular reactivities of these species requires a precursor that absorbs at longer wavelengths.

We decided to investigate whether the desired characteristics might be simply achieved by affixing a phenyl substituent to the C=C bond of the germacyclopent-3-ene ring. Jiang and Gaspar showed that photolysis of a 1,1-bis(trialkylsilyl)-3-phenylsilacyclopent-3-ene derivative affords trapping products consistent with the formation of the corresponding bis(trialkylsilyl)silylene in reasonable yields,[30] so it seemed likely that the photochemistry would be productive. The main uncertainty was whether the presence of the styrenoid chromophore in such a molecule would complicate transient spectroscopic studies owing to fluorescence or competing triplet state formation.[31,32] These fears proved to be unfounded.

Accordingly, in this paper we report the results of our studies of the photochemistry of the 3-phenylgermacyclopent-3-ene derivatives **3a,b** by steady state and (248 nm) laser flash photolysis methods. To our delight, 248 nm laser excitation of these compounds affords transients with absorption character-

Scheme 1
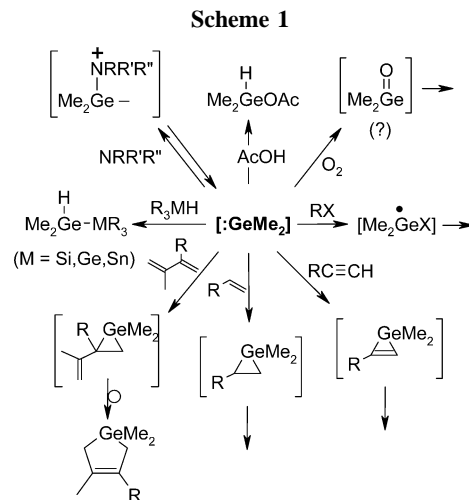
istics similar to those obtained from 193 nm laser photolysis of **1c**[27] and which are similarly assigned to GeMe$_2$ and Ge$_2$Me$_4$ (**2c**). The extinction coefficient of GeMe$_2$ at its absorption maximum has been determined, as have absolute rate constants for its dimerization and reaction with the same selection of reagents that was employed previously in our studies of GePh$_2$ in solution,[29] to allow quantitative comparisons to be made. The specific reactions of GeMe$_2$ that have been studied in the present work are shown in Scheme 1.[1] We also report absolute rate constants for reaction of Ge$_2$Me$_4$ with *n*-butylamine, acetic acid, CCl$_4$, O$_2$, triethylgermane, and tri-*n*-butylstannane and compare the results to those obtained earlier for reaction of the same reagents with Ge$_2$Ph$_4$.

3
a. R = H
b. R = Me
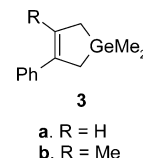
Results

1,1-Dimethyl-3-phenylgermacyclopent-3-ene[33] (**3a**) was synthesized by addition of GeCl$_2$−dioxane to 2-phenyl-1,3-butadiene (**4a**) followed by methylation of the resulting cycloadduct.[34] An analogous procedure starting from 2-methyl-3-phenyl-1,3-butadiene (**4b**) was employed for the synthesis of **3b**.

Steady state photolysis of 0.03−0.05 M solutions of **3a** in hexane or cyclohexane-*d*$_{12}$ containing DMB (0.05 M), acetic acid (AcOH; 0.25 M), or methanol (MeOH 0.24 M) was carried out using low-pressure mercury lamps (254 nm), with periodic monitoring of the photolyzates by GC or ^{1}H NMR spectroscopy. In all cases, diene **4a** and a single germanium-containing compound (**1c**, **5a**, and **5b**, respectively; eq 2) were the only products that could be detected in yields greater than 3−5%, at conversions up to 60−80%. The three products are those expected from trapping of GeMe$_2$ by the three scavenging agents. The quantum yield for formation of GeMe$_2$ from **3a** was determined to be Φ_{GeMe_2} = 0.55 ± 0.09 by 1,1-diphenylsilacyclobutane actinometry,[35] using the yield of **5b** from

(28) Harrington, C. R.; Leigh, W. J.; Chan, B. K.; Gaspar, P. P.; Zhou, D. *Can. J. Chem.* **2005**, *83*, 1324.

(29) Leigh, W. J.; Harrington, C. R. *J. Am. Chem. Soc.* **2005**, *127*, 5084.

(30) Jiang, P.; Gaspar, P. P. *J. Am. Chem. Soc.* **2001**, *123*, 8622.

(31) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 3718.

(32) Bonneau, R. *J. Am. Chem. Soc.* **1982**, *104*, 2921.

(33) Neumann, W. P.; Michels, E.; Kocher, J. *Tetrahedron Lett.* **1987**, *28*, 3783.

(34) Manuel, G.; Mazerolles, P.; Lesbre, M.; Pradel, J.-P. *J. Organomet. Chem.* **1973**, *61*, 147.

(35) Toltl, N. P.; Stradiotto, M. J.; Morkin, T. L.; Leigh, W. J. *Organometallics* **1999**, *18*, 5643.
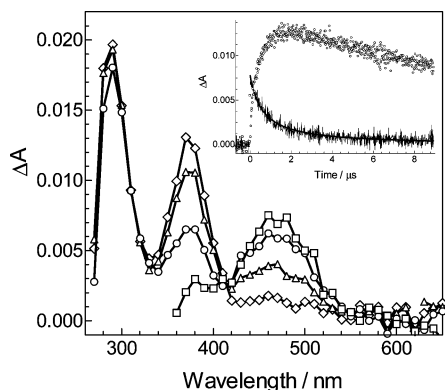
Figure 1. Transient absorption spectra from laser flash photolysis of **3a** in deoxygenated hexane solution at 25 °C, recorded 16−48 ns (□), 160−190 ns (○), 640−670 ns (△), and 2.24−2.27 μs (◇) after the laser pulse. The 16−48 ns spectrum is obscured below 360 nm due to strong emission from the sample. The inset shows typical transient growth/decay profiles, recorded at 470 nm (—) and 370 nm (○). The solid curve drawn through the 470 nm decay is the best fit of the data to eq 4.

photolysis of the compound in cyclohexane-d_{12} containing MeOH (0.24 M) as the measure of the yield of $GeMe_2$.
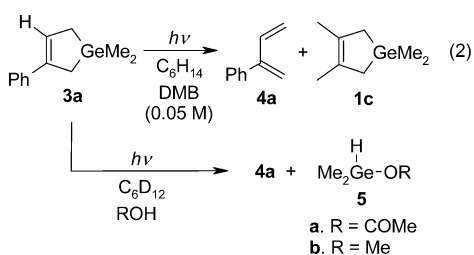
Similarly, photolysis of a 0.05 M solution of **3b** in cyclohexane-d_{12} containing AcOH (0.26 M) afforded **5a** and diene **4b** as the major (>95%) products (eq 3). The rate of product formation in the latter experiment was roughly half that observed in the photolysis of **3a** under identical conditions, suggesting a significantly lower quantum yield for germylene extrusion from **3b** compared to that from **3a**.
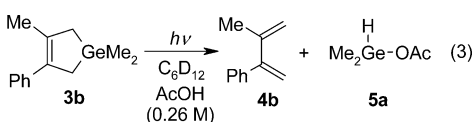
Laser flash photolysis (248 nm, ca. 25 ns, ca. 100 mJ) of continuously flowing, deoxygenated solutions of **3a** (ca. 7 × 10^{-5} M) in anhydrous hexane afforded transient absorptions that were significantly stronger than those obtained previously with **1c**,[27] but which exhibited similar spectral characteristics. Thus, a single short-lived transient species was formed with the laser pulse, exhibiting $\lambda_{max} = 470$ nm and decaying with second-order kinetics, with the concomitant growth of a second species ($\lambda_{max} = 370$ nm) that decayed with mixed order kinetics over ca. 100 μs. A third transient absorption with apparent $\lambda_{max} \approx$ 290 nm and $\tau \approx 600$ μs was also detected and appeared to be formed with the laser pulse. Time-resolved spectra and typical transient growth/decay profiles from flash photolysis of **3a** are shown in Figure 1. Similar results were obtained in experiments using **3b** as precursor (see Supporting Information), although the signals were typically somewhat weaker than those obtained from **3a**. In both cases, strong emission from the sample that

peaked at ca. 300 nm obscured transient absorptions below ca. 350 nm during the first ca. 100 ns after excitation.

The short-lived transients observed in these experiments are assigned to $GeMe_2$ ($\lambda_{max} = 470$ nm) and Ge_2Me_4 ($\lambda_{max} = 370$ nm) on the basis of the strong similarities between their spectra and kinetic behavior and those reported previously for these two species in the gas phase[17] and in solution[23,27,36] and their patterns of reactivity with various germylene and digermene scavengers (vide infra). The germylene decays fit acceptably to second-order kinetics (eq 4), affording an average value of $k_{dim}/\epsilon = (5 \pm 1) \times 10^7$ cm s^{-1} from the two precursors. This agrees quite well with the value ($k_{dim}/\epsilon_{480} = (7.5 \pm 1.7) \times 10^7$ cm s^{-1}) obtained from a second-order fit of the previously published data for $GeMe_2$, for which **1c** was employed as the precursor to $GeMe_2$.[27] The extinction coefficient for $GeMe_2$ at its absorption maximum was determined to be $\epsilon_{470} = 730 \pm 300$ dm^3 mol^{-1} cm^{-1} by benzophenone actinometry,[37] using **3a** as precursor and the quantum yield for $GeMe_2$ formation determined above.[38] This affords an absolute rate constant of $k_{dim} = (3.6 \pm 1.8) \times 10^{10}$ M^{-1} s^{-1}, in acceptable agreement with the diffusional rate constant in hexane at 25 °C ($k_{diff} = 2.1 \times 10^{10}$ M^{-1} s^{-1}) calculated from the standard Debye equation ($k_{diff} = 8RT/3000\eta$). We are unable to assign the long-lived transient absorbing below 310 nm.

$$\Delta A_{GeMe2,t} = \Delta A_{GeMe2,0}/[1 + (2k_{dim}\Delta A_{GeMe2,0}/l\epsilon)t] \quad (4)$$

Addition of *n*-butyl- ($BuNH_2$) or triethylamine (Et_3N), AcOH, triethylsilane (Et_3SiH), triethylgermane (Et_3GeH), tri-*n*-butylstannane (Bu_3SnH), carbon tetrachloride (CCl_4), oxygen (O_2), isoprene, DMB, 4,4-dimethyl-1-pentene (DMP), or *tert*-butylacetylene (TBE) led to a shortening of the lifetime of $GeMe_2$ and reductions in the intensities of the signals due to Ge_2Me_4, in proportion with the concentration of added reagent. In every case, the signal due to $GeMe_2$ decayed with good first-order kinetics in the presence of reagent concentrations sufficient to reduce the "yield" of the digermene, as defined by the peak absorbance at 370 nm ($[\Delta A_{370,max}]_Q$), to ca. 50% or less of its value in the absence of the scavenger ($[\Delta A_{370,max}]_0$). Plots of the pseudo-first-order rate constants for decay of the germylene (k_{decay}) versus scavenger concentration were linear, consistent with the relationship of eq 5, where k_Q is the second-order rate constant for reaction of the species with the added reagent (Q) and k_0 is the (hypothetical) pseudo-first-order rate constant for decay in the absence of Q. The rate constant for reaction with O_2 was estimated from the difference between the pseudo-first-order decay rate constants of $GeMe_2$ in O_2- and air-saturated solution, using a value of 0.015 M for the concentration of O_2 in O_2-saturated hexane.[39]

$$k_{decay} = k_0 + k_Q[Q] \quad (5)$$

The effects of added scavenger on the digermene peak signal intensities ($[\Delta A_{370,max}]$) provide a qualitative indication of the efficiency of germylene scavenging relative to dimerization.[29] Plots of the $[\Delta A_{370,max}]_0/[\Delta A_{370,max}]_Q$ ratios as a function of scavenger concentration [Q] according to eq 6, where K_{SV} is a

(36) Mochida, K.; Kayamori, T.; Wakasa, M.; Hayashi, H.; Egorov, M. P. *Organometallics* **2000**, *19*, 3379.

(37) Carmichael, I.; Hug, G. L. In *CRC Handbook of Organic Photochemistry, Vol. I*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, 1989; pp 369−404.

(38) Wintgens, V.; Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 5117.

(39) Battino, R.; Rettich, T. R.; Tominaga, T. *J. Phys. Chem. Ref. Data* **1983**, *12*, 163.

Table 1. Absolute Rate Constants (k_Q) and K_{SV} Values for Reactions of GeMe$_2$ and Ge$_2$Me$_4$ (2c) with Various Reagents in Dry, Deoxygenated Hexane Solution at 25 °C

	GeMe$_2$[a]			Ge$_2$Me$_4$ (2c)[d]
reagent (Q)	$k_Q/10^9$ M^{-1} s^{-1} [b]	K_{SV}/M^{-1} [c]	$(K_{SV}/k_Q)/\mu$s	$k_Q/10^6$ M$^{-1}\cdot$s^{-1} [d]
BuNH$_2$	12 ± 3	3610 ± 110	0.30	46 ± 18
Et$_3$N	8.7 ± 0.7	2030 ± 200	0.23	
AcOH	7.5 ± 0.4 (11.3 ± 2.4)	7600 ± 1300 (8300 ± 950)	1.01 (0.73)	280 ± 120
Et$_3$SiH	0.00055 ± 0.00015	1.4 ± 0.2	2.55	≤0.1
Et$_3$GeH	0.045 ± 0.015	30.9 ± 1.3	0.69	5.5 ± 0.8
Bu$_3$SnH	13.8 ± 1.8	9600 ± 1400	0.70	300 ± 40
CCl$_4$	0.08 ± 0.02	130 ± 20	1.63	22.6 ± 1.5
O$_2$[e]	0.090 ± 0.012	150 ± 80	1.67	50 ± 10
isoprene	10.8 ± 2.8	2500 ± 800	0.23	≤80
DMB	12.5 ± 5.8 (8.1 ± 0.2)	2800 ± 340 (5100 ± 1400)	0.22 (0.63)	≤40
DMP	9.6 ± 1.2	1700 ± 250	0.18	≤40
TBE	13 ± 3 (9.2 ± 1.9)	5300 ± 600 (5000 ± 600)	0.41 (0.54)	≤90

[a] Measured by laser flash photolysis of deoxygenated ∼7 × 10^{-5} M solutions of **3a** in anhydrous hexane at 25 °C; values determined using **3b** as precursor are in parentheses. [b] From plots of k_{decay} (for GeMe$_2$, monitored at 480 nm) vs [Q] according to eq 5, over concentration ranges corresponding to >50% quenching of the peak ΔA_{370} value due to Ge$_2$Me$_4$ in the absence of the scavenger (($\Delta A_{370})_{max,0}$). Errors are listed as ±2σ from the least squares analyses of the data. [c] From plots of $[(\Delta A_{370})_{max,0}/(\Delta A_{370})_{max,Q}]$ vs [Q] according to eq 6. [d] Determined from plots of k_{decay} vs [Q]; upper limits were calculated from the pseudo-first-order decay constant at the highest scavenger concentration employed. [e] Rate constant was estimated from the pseudo-first-order decay rate constants in air- and O$_2$-saturated solutions ([O$_2$] ≈ 0.003 and 0.015 M, respectively[39]).
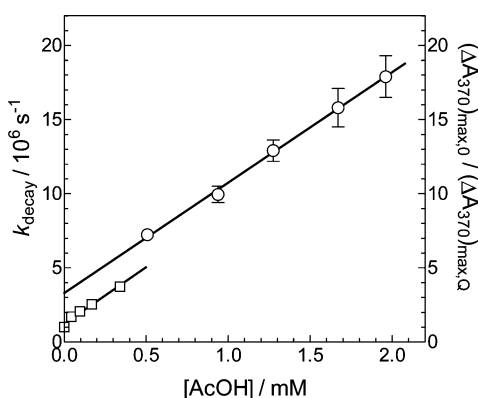

Figure 2. Effects of added AcOH on the pseudo-first-order decay rate constant of GeMe$_2$ (k_{decay}), monitored at 480 nm (○; eq 5), and the peak transient absorbance due to Ge$_2$Me$_4$, monitored at 370 nm (□; eq 6), from laser flash photolysis of **3a** in hexane solution at 25 °C.

proportionality factor reflecting the scavenging efficiency, were also linear in every case. For example, Figure 2 shows plots of k_{decay} and $[\Delta A_{370,max}]_0/[\Delta A_{370,max}]_Q$ versus [Q] for AcOH scavenging, the slopes of which are the absolute rate constant and K_{SV} value, respectively, for reaction of GeMe$_2$ with the reagent. Representative transient absorption profiles at 370 and 480 nm as a function of scavenger concentration are included in the Supporting Information for two of the substrates studied. In all cases, the K_{SV} values were determined from digermene growth/decay profiles recorded at relatively low scavenger concentrations, where the signal due to Ge$_2$Me$_4$ could still be detected, while absolute rate constants were determined from germylene decay profiles recorded at higher concentrations, where formation of the digermene is largely suppressed and the germylene decays with reasonably clean pseudo-first-order kinetics due to its preferential reaction with the scavenger. Several quenching experiments were also carried out using **3b** as precursor and afforded rate constants that were in good agreement with those determined in experiments with **3a**.

$$([\Delta A_{370,max}]_0/[\Delta A_{370,max}]_Q) = 1 + K_{SV}[Q] \qquad (6)$$

The absolute rate constants and K_{SV} values for reaction of GeMe$_2$ with the various scavengers studied in this work are summarized in Table 1. Also included in the table are the ratios

K_{SV}/k_Q (in units of μs), which provide a measure of scavenging efficiency that is independent of the actual rate constant. The K_{SV} and K_{SV}/k_Q values reported in the table warrant additional comment, as they contain a certain amount of scatter that is due to factors other than scavenging efficiency. One of these relates to the fact that K_{SV} depends on both k_Q and the *second-order* lifetime of the germylene in the absence of scavenger, where germylene decay is dominated by dimerization. Because the lifetime is governed by a second-order process and hence depends on the initial GeMe$_2$ concentration, K_{SV} varies (inversely) with the laser intensity and precursor concentration. These were kept roughly constant throughout this work with two exceptions (AcOH and TBE), for which the initial transient concentrations were ca. 20% higher than in the other experiments; thus, the K_{SV} values obtained for these two scavengers should be considered to be artificially low in comparison to the others. A similar phenomenon is responsible for the somewhat higher K_{SV} values that were obtained with **3b** as the precursor, which afforded initial germylene concentrations that were typically about 25% lower than those obtained from **3a**. Artificially high values of K_{SV} can also be obtained in cases where the scavenger is reactive toward the digermene as well as the germylene. In practice however, this leads to significant distortion of the K_{SV} value only when the rate constant for reaction of the digermene with the scavenger approaches that for reaction of the germylene, which is the case only for O$_2$ (and, to a lesser extent, CCl$_4$). With these factors in mind, it is clear from the trends in K_{SV}/k_Q values that five of the scavengers react with GeMe$_2$ considerably less efficiently than the others: the two amines, the two dienes, and the alkene. This and other aspects of the behavior observed in the presence of these scavengers are indicative of *reversible* reaction with the germylene.

In contrast to the behavior observed with the other scavengers, addition of the amines led to a lengthening of the digermene growth times with increasing concentration, which is a second indicator of reversible germylene scavenging.[29] However, in neither case could longer-lived residual absorptions be discerned in the germylene signals at 470−480 nm, indicating that the amount of germylene remaining behind after the scavenging reaction comes to equilibrium is too low to be detected. This allows the conclusion that the equilibrium constants (K_{eq}) for reaction of GeMe$_2$ with these reagents are in excess of ca. 25 000 M^{-1}; this is the approximate upper limit for K_{eq} that is

measurable under the typical conditions of our experiments. No distinct new transient absorptions were observed in the presence of either amine at concentrations up to ca. 2 mM other than the relatively strong absorptions due to competing amine photolysis, which are centered below 290 nm and decay with a lifetime $\tau \approx 2 \mu s$.[29]

Long-lived residual absorptions *were* observed in the germylene decays in the presence of DMP, isoprene, and DMB as scavengers, though only at the low end (0.1−0.5 mM) of the concentration ranges that were studied; in the case of DMB, its addition also caused the growth time of the digermene signals to lengthen as the maximum yield was reduced. As expected for reversible scavenging, the residual germylene absorptions decreased in intensity relative to the initial ΔA values with increasing scavenger concentration over this range, and could not be detected reproducibly at concentrations in excess of ca. 0.5 mM. This behavior is consistent with equilibrium constants on the order of $K_{eq} \approx 20\,000$ M^{-1}. Unfortunately, plots of the ratios of the initial and residual absorbance values according to eq 7 (where $\Delta A_{GeMe_2,0}$ and $\Delta A_{GeMe_2,res}$ are the initial and residual transient absorbances due to the germylene) from data obtained over the 0.1−0.5 mM concentration range generally exhibited considerable scatter and poor reproducibility, most likely because of the weakness of the signals that were typically obtained; these problems were compounded by a slight decrease in overall signal intensity with increasing scavenger concentration in these cases. As a result, accurate determination of K_{eq} for these reactions was not possible.

$$\Delta A_{GeMe2,0}/\Delta A_{GeMe2,res} = 1 + K_{eq}[Q] \qquad (7)$$

In our earlier study of GePh$_2$,[29] scavenging by isoprene, DMP, and TBE was accompanied by the formation of new, long-lived transient products absorbing in the 275−285 nm spectral range, which were tentatively assigned to the presumed primary products of these reactions, the corresponding three-membered germanocycles **6a**−**8a**. In the present case, addition of 10 mM isoprene to a solution of **3a** led to the complete disappearance of the signals due to GeMe$_2$ and Ge$_2$Me$_4$, but had no effect on the long-lived ($\tau \approx 600 \mu s$) transient absorption below 310 nm other than a slight reduction in maximum intensity that could be accounted for by screening of the excitation light by the diene. A similar result was obtained in the presence of 1.5 mM TBE. We thus conclude that the primary products of reaction of GeMe$_2$ with these reagents possess absorption maxima below the lower limit of ca. 270 nm that can be probed in the present experiments.

a. R = Ph
b. R = Me
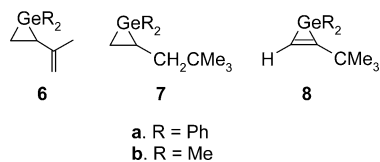
Finally, addition of six of the scavengers in the series (BuNH$_2$, AcOH, Et$_3$GeH, Bu$_3$SnH, CCl$_4$, and O$_2$) also caused discrete reductions in the decay times of the signals due to Ge$_2$Me$_4$ over the concentration ranges where the signal could be detected and pseudo-first-order decay rate constants determined. The decay constants obtained varied over a relatively small range in most cases, but they nevertheless varied linearly with scavenger concentration according to eq 5, thus allowing absolute rate constants for reaction of the scavenger with the digermene to be estimated. These are listed along with the data for GeMe$_2$ in Table 1. Those reagents that are relatively unreactive toward

Ge$_2$Me$_4$ had the effect of lengthening the decay time of the signal at 370 nm with increasing concentration, because of the accompanying decrease in digermene concentration due to scavenging of GeMe$_2$, its immediate precursor, and the fact that the digermene decays with predominant second-order kinetics in the absence of significant competitive scavenging. Only upper limits for the rate constants could be obtained in these cases, by fitting the decays at the highest scavenger concentration employed to first-order kinetics and calculating the value from the first-order decay constant (as $k_Q \leq k_{decay}/[Q]$).

Discussion

The product studies reported above verify that photolysis of **3a,b** affords the corresponding diene (**4a** or **4b**, respectively) and the trapping products of GeMe$_2$ in chemical yields of 90−95%, as was found to be the case as well with **1c** and the diarylgermylene precursors **1a,b**.[27] The formation of GeMe$_2$ from **3a** proceeds with a quantum yield ($\Phi_{GeMe_2} = 0.55 \pm 0.09$) similar to that found earlier for formation of GePh$_2$ from **1a**,[27] indicating that germylene formation proceeds with the high efficiency and absence of side-products that is necessary for the successful detection of these species in solution by time-resolved UV/vis spectroscopy. Indeed, the absorption spectra measured for GeMe$_2$ in the present work are very similar to those reported previously in the gas phase (from three different precursors)[17] and in hexane solution using **1c** as the precursor.[27] Similarly good agreement exists between the spectrum of the transient assigned to Ge$_2$Me$_4$ (**2c**) and those reported previously from other precursors.[27,36,40] There is thus little doubt that we are observing GeMe$_2$ and its dimerization product, tetramethyldigermene, in our laser flash photolysis experiments with all three of the germacyclopentene derivatives, **3a**, **3b**, and **1c**. The signals obtained for GeMe$_2$ in the present work are roughly twice as strong as those reported previously from 193 nm laser flash photolysis of **1c**,[27] but since the typical laser intensities achieved in 248 nm laser flash photolysis experiments in our laboratory are roughly twice those obtained with 193 nm excitation, we can conclude that germylene formation proceeds with similar quantum yields from **3a** and **1c**.

The good agreement between the absorption spectrum observed for GeMe$_2$ in the present work and those reported previously in the gas phase[17] and from **1c** in hexane solution[27] suggests that the germylene exists as the free species in all cases and does not form association complexes with any of the three germacyclopentene precursors (**1c**, **3a**, and **3b**) over the ca. 10 μs time window in which the germylene can be detected in the absence of added scavengers. Furthermore, the observation that the germylene decays with clean second-order kinetics indicates that it is does not react detectably with the C=C bonds in the precursors at the typical concentrations employed in our experiments (ca. 0.1 mM). The molar extinction coefficient of $\epsilon_{470} = 730 \pm 300$ dm^3 mol^{-1} cm^{-1} is roughly half that of GePh$_2$ at its absorption maximum ($\epsilon_{500} = 1850 \pm 400$ dm^3 mol^{-1} cm^{-1}),[27] in good agreement with the relative calculated oscillator strengths of the lowest energy (n,p) transitions in the two species from time-dependent DFT calculations.[27]

Table 2 provides a comparison of the absolute rate constants determined in the present work for GeMe$_2$ in hexane solution

(40) Taraban, M. B.; Volkova, O. S.; Plyusnin, V. F.; Ivanov, Y. V.; Leshina, T. V.; Egorov, M. P.; Nefedov, O. M.; Kayamori, T.; Mochida, K. *J. Organomet. Chem.* **2000**, *601*, 324.

Table 2. Comparison of the Absolute Rate Constants for Reaction of Various Substrates with GeMe$_2$ in Hexane Solution and the Gas Phase, and with GePh$_2$ and SiMe$_2$ in Hydrocarbon Solution at Ambient Temperatures

	$k_Q/10^9$ M^{-1} s^{-1} (25 °C)			
quencher	GeMe$_2$(soln)[a]	GeMe$_2$(gas)[b]	GePh$_2$(soln)[c]	SiMe$_2$(soln)[d]
BuNH$_2$	13.4 ($K_{eq} > 25\,000$ M^{-1})		10.1 ($K_{eq} > 25\,000$ M^{-1})	
Et$_3$N	8.7 ($K_{eq} > 25\,000$ M^{-1})		2.9 ($K_{eq} > 25\,000$ M^{-1})	
AcOH	7.5		3.9	
Et$_3$SiH	0.00055	<0.0036 (Me$_3$SiH)	0.00056	2.9 (3.6[42])
Et$_3$GeH	0.05	<0.24 (Me$_3$GeH)	0.028	
Bu$_3$SnH	13.8		3.49	10.1
CCl$_4$	0.08		0.011	
O$_2$	0.090	0.027	0.027	2.5
isoprene	10.9 ($K_{eq} \approx 20\,000$ M^{-1})	6.6 (1,3-butadiene)	5.5 ($K_{eq} \approx 6000$ M^{-1})	9.4 (Me$_2$C=CHCH=CMe$_2$)
DMP	8.9 ($K_{eq} \approx 20\,000$ M^{-1})	7.8 (Me$_3$CCH=CH$_2$)	4.2 ($K_{eq} \approx 2500$ M^{-1})	7.3 (1-hexene)
TBE	10.8	7.8 (C$_2$H$_2$)	5.2	8.0 (Me$_3$SiC≡CH)

[a] Hexane, 25 °C; this work. [b] Refs 5 and 17. [c] Hexane, 25 °C; ref 27,29. [d] Cyclohexane, 22 °C; ref 41.

with previously reported data for reaction of the same or similar substrates with GeMe$_2$ in the gas phase,[5,17] GePh$_2$ in hexane,[29] and SiMe$_2$ in cyclohexane.[41] The agreement between the solution-phase rate constants for reaction of GeMe$_2$ with O$_2$, isoprene, 4,4-dimethyl-1-pentene (DMP), and *tert*-butylacetylene (TBE) and the corresponding high-pressure limiting rate constants reported by Becerra et al. for reaction of the species with the same or related molecules in the gas phase[17] is excellent. Similarly, the rate constants for insertion of GeMe$_2$ into the M−H bonds of Et$_3$SiH and Et$_3$GeH in hexane are consistent with the upper limits that have been estimated for reaction of GeMe$_2$ with the trimethyl analogues of these compounds in the gas phase.[17] The present study provides absolute values of the rate constants for these reactions for the first time, which indicate that GeMe$_2$ is roughly 100 times more reactive toward Ge−H insertions than Si−H insertions. The same trend has been reported for GeH$_2$ in the gas phase,[8] although the difference in the rate constants is smaller ($k_{Et_3GeH}/k_{Me_3SiH} \approx 3.3$)[43] owing to the much higher intrinsic reactivity of the parent germylene compared to GeMe$_2$.[5,16] The present data establish a reactivity order of $k_{Sn-H} \approx 100 k_{Ge-H} \approx 25\,000 k_{Si-H}$ for insertion of GeMe$_2$ into the M−H bonds of group 14 trialkylmetallyl hydrides. This is similar to that established by us earlier for reaction of GePh$_2$ with the same substrates,[29] indicating that the two germylenes exhibit similar selectivities in their reactions with group 14 M−H bonds.

On the other hand, there is very poor agreement between the results reported here and those of earlier time-resolved studies of GeMe$_2$ in solution, where the reported absorption maximum in hydrocarbon solvents at room temperature ranges from 420 to 490 nm.[20−23] Relatively few rate constants were reported in these earlier papers, but those that were differ from the present ones by as much as 3 orders of magnitude; for example, the previously reported rate constants for reaction of GeMe$_2$ with DMB in cyclohexane at room temperature vary between 1.7×10^7 and 1.5×10^9 M^{-1} s^{-1},[20−22] which should be compared to the values of $(1.3 \pm 0.6) \times 10^{10}$ and $(1.1 \pm 0.3) \times 10^{10}$ M^{-1} s^{-1} reported here for DMB and isoprene, respectively. It is relevant to note that the precursors employed in these previous studies were all reported to afford products consistent with the formation of other transient photoproducts in addition to GeMe$_2$, unlike **3a,b**, which afford GeMe$_2$ exclusively and with quantum yields on the order of 50%. It is very likely that these other products contributed significantly to the transient absorptions that were observed, given the low extinction coefficient of the lowest energy absorption band of the germylene.

Comparison of the solution-phase kinetic data for GeMe$_2$ and GePh$_2$ reveals that GeMe$_2$ is significantly more reactive than its phenylated counterpart in almost all cases, but as might be expected, the reactivities of the two germylenes parallel each other quite closely. The rate constants for reaction of GeMe$_2$ are between ca. 1.3 and 7 times higher than those for the corresponding reactions of GePh$_2$, but the differences do not vary systematically with overall reactivity over a factor of ca. 10^4 in rate constant. The increased reactivity of GeMe$_2$ relative to GePh$_2$ is reflected as well in the absolute rate constants for dimerization, which appears to be fully diffusion-controlled in the case of GeMe$_2$ ($k_{dim} = (3.6 \pm 1.8) \times 10^{10}$ M^{-1} s^{-1}) in contrast to the value of $k_{dim} = (1.2 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1} reported for GePh$_2$ under the same conditions.[27]

The higher reactivity of GeMe$_2$ is further reflected in the equilibrium constants for reaction with isoprene and DMP; the values of $K_{eq} \approx 20\,000$ M^{-1} estimated for the two reactions with GeMe$_2$ in the present work are to be compared with the values of 6000 and 2500 M^{-1} reported previously for the reactions of GePh$_2$ with isoprene and DMP, respectively.[29] The kinetic evidence that GeMe$_2$ reacts reversibly with the dienes and alkene is somewhat more subtle than was the case with GePh$_2$, where addition of isoprene and DMP caused the germylene decay profiles to take on a distinct bimodal form over the 0.2−3.0 mM concentration range in added substrate.[29] With GeMe$_2$, analogous behavior is detectable only at concentrations less than ca. 0.5 mM, so it is clear that the K_{eq} values for reaction of these reagents with GeMe$_2$ are significantly larger than those for the phenylated derivative and close to the upper limit of ca. 25 000 M^{-1} for which such behavior can be observed under the conditions of our experiments. Unfortunately, the much weaker signals that are obtained in our experiments with GeMe$_2$ make it difficult to determine the equilibrium constants accurately. Additional verification that these reactions proceed reversibly is provided by the K_{SV}/k_Q ratios, which provide a qualitative measure of the efficiency of the scavenging reaction relative to dimerization (vide supra). Like those observed for the amines, the values of K_{SV}/k_Q obtained for the alkene and dienes fall in a narrow range centered at ca. 0.2 μs, significantly lower than the values typically exhibited by the other (irreversible) scavengers examined. The ultimate experimental manifestation of reversible scavenging is that formation of the dimerization product, Ge$_2$Me$_4$, remains readily detectable even

(41) Levin, G.; Das, P. K.; Bilgrien, C.; Lee, C. L. *Organometallics* **1989**, *8*, 1206.

(42) Shizuka, H.; Tanaka, H.; Tonokura, K.; Murata, K.; Hiratsuka, H.; Ohshita, J.; Ishikawa, M. *Chem. Phys. Lett.* **1988**, *143*, 225.

(43) Becerra, R.; Boganov, S. E.; Egorov, M. P.; Nefedov, O. M.; Walsh, R. *Mendeleev Commun.* **1997**, *7*, 87.

Scheme 2
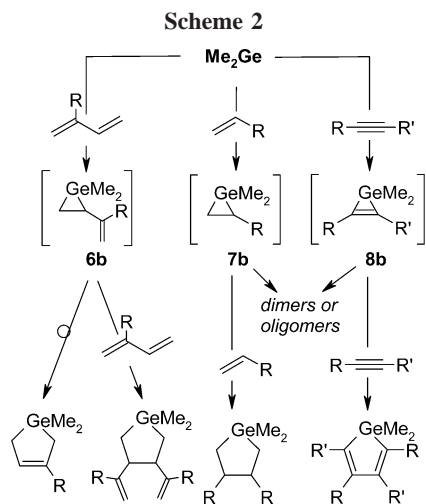
at relatively high scavenger concentrations, where GeMe$_2$ can no longer be detected.

It can thus be concluded that the ca. 2-fold increase in the forward reaction rate constants for the reactions of GeMe$_2$ with isoprene and DMP compared to those of the phenylated derivative is accompanied by a somewhat greater decrease in the rate constants for reversion of the primary reaction products to free GeMe$_2$ and substrate, consistent with a significantly higher thermodynamic stability in the primary products compared to those from the corresponding reactions of GePh$_2$. The same trend is observed in the (calculated) relative stabilities of the dimers (Ge$_2$Me$_4$ and Ge$_2$Ph$_4$, respectively) with respect to dissociation to the free germylenes.[44] Thus, all aspects of the relative reactivities of GeMe$_2$ and GePh$_2$ in solution can be understood simply in terms of a substituent effect on the relative thermodynamic stabilities of the two species.

The reactions of GeMe$_2$ with alkenes, alkynes, and dienes have been studied in detail by Neumann and co-workers, who provided compelling evidence that the primary products of these reactions are the three-membered germanocycles **6b**−**8b**; these compounds are themselves reactive toward further cycloaddition of substrate, a process that competes with thermal [1,3]-sigmatropic rearrangement in the case of vinylgermiranes (see Scheme 2).[1,33,45,46] Similar chemistry is well-known for reactive silylenes.[47,48] Our study of GePh$_2$ in solution provided spectroscopic evidence for the formation of short-lived transient products in the reaction of this germylene with isoprene, DMP, and TBE, which were assigned to the corresponding three-membered-ring compounds (**6a**−**8a**) on the basis of their UV spectra ($\lambda_{max} = 275-285$ nm) and lifetimes.[29] Unfortunately, we have been unsuccessful in detecting the analogous products in the reactions of GeMe$_2$ with these substrates, presumably because their absorption maxima lie too far to the blue for them to be detectable under the conditions of our experiments.

The rate constants for reaction of GeMe$_2$ with the two amines (Et$_3$N in particular) and AcOH are also significantly greater than those for GePh$_2$, in all cases being within a factor of 3 of the diffusion-controlled limit. In contrast to our previous study of GePh$_2$, we have been unable to obtain discrete spectroscopic evidence for formation of the corresponding amine-germylene complexes that are known to be the primary products of these reactions,[49−52] again most likely because their absorption maxima fall below the lower limit of ca. 300 nm that we are able to monitor in our experiments. GeMe$_2$ and other transient germylenes are known to form relatively stable complexes with Et$_3$N.[51] The reaction with amines is particularly difficult for us to study in detail under our conditions; this is because they absorb relatively strongly at 248 nm, the wavelength we employ in our flash photolysis experiments to generate the germylene from its precursor. The similar trend in the reactivities of GeMe$_2$ and GePh$_2$ toward AcOH and the amines suggests that reaction with the carboxylic acid proceeds via rate-determining complexation with the carbonyl oxygen, followed by rapid proton transfer to yield the overall O−H insertion product (eq 8).
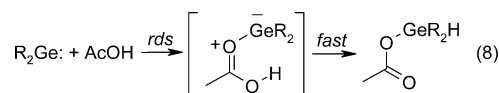
The reactions of GeMe$_2$ with halocarbons have also been extensively studied.[53−57] With CCl$_4$, for example, the major products are Me$_2$GeCl$_2$ and hexachloroethane, which have been shown to be formed by halogen atom abstraction and coupling reactions of the primary reaction products, the Me$_2$GeCl and CCl$_3$ free radicals, after their escape from an initially formed singlet radical pair (see eq 9).[54,57] Egorov and co-workers have suggested that radical pair formation is the result of chloride ion transfer within a singlet radical *ion* pair, formed by electron transfer from GeMe$_2$ to the halocarbon.[58] We have noted that the rate constants for reaction of GePh$_2$ with a series of halocarbons in hexane solution do not correlate with either the calculated C−X bond dissociation energies or the one-electron reduction potentials of the compounds.[29] The series of halocarbons studied in our earlier work included CCl$_4$, and as with GeMe$_2$ it affords the corresponding dichlorogermane, Ph$_2$GeCl$_2$, as the major germanium-containing product. The results of the present study show that GeMe$_2$ is roughly an order of magnitude more reactive than GePh$_2$ toward CCl$_4$, which is again difficult to rationalize exclusively in terms of oxidation potentials; the gas-phase ionization potential of GePh$_2$ has been estimated to be 0−0.2 eV *lower* than that of GeMe$_2$.[59] We believe that electron- or charge-transfer very likely plays a crucial role in the reactions of germylenes with halocarbons, but it is clear that the reaction kinetics in solution are affected by other factors in addition to the redox potentials of the reaction partners. One

(44) Becerra, R.; Harrington, C. R.; Gaspar, P. P.; Leigh, W. J.; Vargas-Baca, I.; Walsh, R.; Zhou, D. *J. Am. Chem. Soc.* **2005**, *127*, 17469.

(45) Schriewer, M.; Neumann, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 897.

(46) Neumann, W. P.; Weisbeck, M. P.; Wienken, S. *Main Group Met. Chem.* **1994**, *17*, 151.

(47) Bobbitt, K. L.; Gaspar, P. P. *J. Organomet. Chem.* **1995**, *499*, 17.

(48) Gaspar, P. P.; West, R. In *The Chemistry of Organic Silicon Compounds, Vol. 2*; Rappoport, Z., Apeloig, Y., Eds.; John Wiley and Sons: New York, 1998; pp 2463−2568.

(49) Barrau, J.; Bouchaut, M.; Lavayssiere, H.; Dousse, G.; Satge, J. *J. Organomet. Chem.* **1983**, *243*, 281.

(50) Riviere, P.; Castel, A.; Satge, J. *J. Organomet. Chem.* **1982**, *232*, 123.

(51) Riviere, P.; Satge, J.; Castel, A. *C. R. Acad. Sci. Paris* **1975**, *281*, 835.

(52) Zemlyansky, N. N.; Borisova, I. V.; Kuznetsova, M. G.; Khrustalev, V. N.; Ustynyuk, Y. A.; Nechaev, M. S.; Lunin, V. V.; Barrau, J.; Rima, G. *Organometallics* **2003**, *22*, 1675.

(53) Kocher, J.; Lehnig, M. *Organometallics* **1984**, *3*, 937.

(54) Kocher, J.; Lehnig, M.; Neumann, W. P. *Organometallics* **1988**, *7*, 1201.

(55) Billeb, G.; Brauer, H.; Maslov, S.; Neumann, W. P. *J. Organomet. Chem.* **1989**, *373*, 11.

(56) Kolesnikov, S. P.; Egorov, M. P.; Galminas, A. M.; Ezhova, M. B.; Nefedov, O. M.; Leshina, T. V.; Taraban, M. B.; Kruppa, A. I.; Maryasova, V. I. *J. Organomet. Chem.* **1990**, *391*, C1.

(57) Adachi, M.; Mochida, K.; Wakasa, M.; Hayashi, H. *Main Group Met. Chem.* **1999**, *22*, 227.

(58) Egorov, M. P.; Gal'minas, A. M.; Basova, A. A.; Nefedov, O. M. *Dokl. Akad. Nauk. SSSR (Engl. transl.)* **1993**, *329*, 102.

(59) Lemierre, V.; Chrostowska, A.; Dargelos, A.; Baylere, P.; Leigh, W. J.; Harrington, C. R. *Appl. Organomet. Chem.* **2004**, *18*, 676.

possibility is that the net halogen abstraction shown as the first step in eq 9 proceeds via a two-step process involving initial (reversible) formation of a Lewis acid−base complex between the germylene and the halocarbon. This would have the effect of enhancing the reactivity of GeMe$_2$ relative to GePh$_2$ because of the greater electrophilicity that is associated with the former, as evidenced by the differences in the rate constants for reaction of the two species with nucleophiles such as amines and C−C multiple bonds. Indeed, Ando and co-workers have reported spectroscopic evidence for the formation of discrete Lewis acid−base complexes between chlorocyclohexane and GeMe$_2$ and GePh$_2$ in hydrocarbon matrixes at 77 K.[60]

$$Me_2Ge: \; + \; CCl_4 \xrightarrow{e^-/\,Cl^-\; transfer} [Me_2(Cl)Ge\bullet \; \bullet CCl_3] \quad (9)$$

$$CCl_4 \downarrow \, escape$$

$$Me_2GeCl_2 + \bullet CCl_3$$

$$C_2Cl_6$$
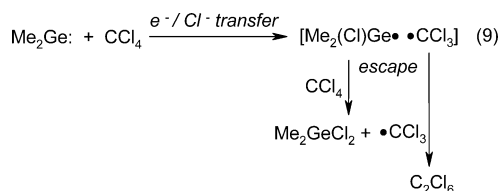
It is interesting to compare the present kinetic data for reaction of GeMe$_2$ with the group 14 hydrides and C−C unsaturated compounds to those reported previously for reaction of SiMe$_2$ with the same or similar substrates under similar conditions (see Table 2).[41,42] The largest difference in reactivity is toward insertion into the Si−H bond of Et$_3$SiH, for which the data indicate GeMe$_2$ to be ca. 5000 times less reactive than SiMe$_2$. This elaborates on the lower limit of $k_{SiMe_2}/k_{GeMe_2} > 750$ established by Walsh and co-workers for reaction of the two species with Me$_3$SiH in the gas phase at 298 K,[17,61] where only the silylene is sufficiently reactive to enable a discrete rate constant to be determined. The difference in reactivity is considerably larger than that exhibited by the parent molecules (SiH$_2$ and GeH$_2$), which are substantially more reactive than the methylated analogues and differ in rate by a factor of only ca. 3 at 298 K.[5] These reactions are thought to proceed via a two-step mechanism involving initial complexation between the vacant p-orbital on the metallylene and the silyl hydrogen (eq 10), followed by rate-controlling attack of the metallylene lone pair at silicon with concomitant cleavage of the Si−H bond.[5,62,63] As is expected for a mechanism of this type, temperature dependence studies of the reactions of SiMe$_2$[64] and the two parent metallylenes with Me$_3$SiH in the gas phase indicate that all three proceed with negative activation energies, with the barrier to the second step being largely entropic; the lower reactivity of the germylene originates in a significantly tighter transition state for the rate-determining step.[5] As might be expected, GeMe$_2$ and SiMe$_2$[41] both insert into the much weaker Sn−H bond of Bu$_3$SnH at rates that are within a factor of 2 of the diffusion limit in hydrocarbon solvents.

$$\begin{array}{c} Me_2M: \\ + \\ H\!-\!SiEt_3 \end{array} \rightleftharpoons \left[\begin{array}{c} H^{} \; \bar{}MMe_2 \\ | \\ Et_3Si \end{array} \right] \xrightarrow{rds} \begin{array}{c} H\!-\!MMe_2 \\ | \\ Et_3Si \end{array} \quad (10)$$
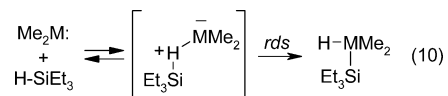
Less precise comparisons are possible between the solution-phase reactivities of SiMe$_2$ and GeMe$_2$ with C−C π-bonds because different substrates have been examined in the two

cases, but the data nevertheless suggest similar, nearly diffusion-controlled reactivities for both species, at least toward terminal alkenes and alkynes. Small differences in the rate constants appear only in the gas phase, where diffusional restrictions due to the solvent are absent, and GeMe$_2$ is known to be 3−5 times less reactive than SiMe$_2$ toward (1+2) addition to related C−C π-bonds.[5,17,63,65] Theoretical calculations for the reactions of SiH$_2$ and GeH$_2$ with ethylene indicate that both reactions proceed via the initial formation of a π-complex, which proceeds to the corresponding three-membered metallacycle essentially without enthalpic barrier.[5,14,66,67] Again, both reactions are entropically controlled, with greater entropic demands in the transition state for germylene addition. In solution, the only apparent manifestation of the smaller overall reaction exothermicities that are associated with germylene additions is the indication of reversibility in the reaction of GeMe$_2$ with the alkene and dienes. The data obtained here afford an estimate of $k \approx 5 \times 10^5$ s^{-1} for the rate constant for unimolecular dissociation of germiranes **6b** and **7b** back to GeMe$_2$ and the corresponding alkene or diene. In contrast, the thermal extrusion of dialkylsilylenes from siliranes generally occurs only at elevated temperatures, and even then proceeds several orders of magnitude more slowly.[68,69] It is interesting that despite these rather large differences in overall reaction exothermicity, the (forward) rate constants for reaction of SiMe$_2$ and GeMe$_2$ with terminal alkenes are so similar to one another. The reactivity of SiMe$_2$ toward alkenes and alkynes is known to be moderately sensitive to steric and electronic factors,[65] with the rate constants increasing with decreasing ionization potential of the C−C π-bonded compound. It will be very interesting to see in future work how the rate and equilibrium constants for reaction of the germanium analogue with substrates of this type vary with substrate structure.

Substituent Effects on Digermene Reactivity. As we found in our earlier studies of the phenylated systems,[27,29] Ge$_2$Me$_4$ is considerably less reactive than GeMe$_2$ toward most of the reagents studied, and as a result, we were able to measure absolute rate constants for its reaction with only six of them: BuNH$_2$, AcOH, Et$_3$GeH, Bu$_3$SnH, CCl$_4$, and O$_2$. Only in these cases could we discern a distinct shortening of the lifetime of the digermene within the scavenger concentration range in which it could still be detected, enabling determination of the bimolecular rate constant according to eq 5 in the usual way. In all other cases, it was possible to estimate only a crude upper limit for the rate constant. These were obtained by fitting the digermene decay at the highest scavenger concentration at which reasonable signals could still be obtained to first-order kinetics and estimating the upper limit as $k_Q < k_{decay}/[Q]$. These fits were generally quite good, but there is nevertheless no definitive proof that the decays are dominated by reaction with the scavenger; in fact, in most cases they probably are not, so the true values of the rate constants are likely to be at least a factor of 5 lower than the upper limits quoted. It is useful to note the differences between the rate constants for scavenging of Ge$_2$Me$_4$ and GeMe$_2$ for those scavengers for which both could be measured, as they provide an indication of the limits of our ability to detect slow reaction with the digermene; in general, larger differential reactivities are measurable for those scavengers that react reversibly with GeMe$_2$ than for those that react

(60) Ando, W.; Itoh, H.; Tsumuraya, T. *Organometallics* **1989**, *8*, 2759.

(61) Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. *Chem. Phys. Lett.* **1987**, *135*, 39.

(62) Su, M.-D.; Chu, S.-Y. *J. Phys. Chem. A* **1999**, *103*, 11011.

(63) Becerra, R.; Walsh, R. *Res. Chem. Kinet.* **1995**, *3*, 263.

(64) Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Walsh, R. *J. Am. Chem. Soc.* **1990**, *112*, 8337.

(65) Baggott, J. E.; Blitz, M. A.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 515.

(66) Sakai, S. *Int. J. Quantum Chem.* **1998**, *70*, 291.

(67) Su, M.-D.; Chu, S.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 11478.

(68) Driver, T. G.; Woerpel, K. A. *J. Am. Chem. Soc.* **2003**, *125*, 10659.

(69) Seyferth, D.; Annarelli, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 7162.

Table 3. Comparison of Absolute Rate Constants for Reaction of Ge$_2$Me$_4$ and Ge$_2$Ph$_4$ with Selected Substrates in Hexane Solution at 25 °C

quencher	$k_Q/10^6$ M^{-1} s^{-1} (25 °C)	
	Ge$_2$Me$_4$ (**2c**)	Ge$_2$Ph$_4$ (**2a**)[a]
BuNH$_2$	46 ± 18	3640 ± 380
AcOH	280 ± 120	≤40
CCl$_4$	23 ± 2	2.0 ± 0.2
O$_2$	50 ± 10	4.8 ± 0.8
Et$_3$GeH	5 ± 1	5.6 ± 1.6
Bu$_3$SnH	300 ± 40	410 ± 200

[a] Data from refs 27 and 29.

with the germylene irreversibly. This is illustrated by the relative rate constants for scavenging of GeMe$_2$ and Ge$_2$Me$_4$ with BuNH$_2$, a reversible germylene scavenger ($k_Q^{GeMe_2}/k_Q^{Ge_2Me_4} \approx$ 250), and AcOH, an irreversible germylene scavenger ($k_Q^{GeMe_2}/k_Q^{Ge_2Me_4} \approx 50$).

To our knowledge, only one reasonably detailed study of the chemistry of Ge$_2$Me$_4$ has been reported previously, in which the digermene was generated by photolysis of the 7,8-digermabicyclo[2.2.2]octadiene derivative **9** and trapped with dienes, MeOH, and CCl$_4$ to afford the products shown in eq 11.[36] Rate constants for dimerization ($k_{dim}/\epsilon = 6.5 \times 10^5$ cm s^{-1}) and reaction with O$_2$ ($k = 4 \times 10^8$ M^{-1} s^{-1}), DMB ($k = 5.3 \times 10^5$ M^{-1} s^{-1}), CCl$_4$ ($k = 1.2 \times 10^7$ M^{-1} s^{-1}), and ethanol ($k = 4.9 \times 10^7$ M^{-1} s^{-1}) and other alcohols in cyclohexane solution were reported, as well as upper limits of 10^4 M^{-1} s^{-1} for reaction with Et$_3$SiH and 1-hexyne, with which product studies indicated there to be no reaction at the particular substrate concentrations employed. The kinetic data are in reasonable agreement with the rate constants or upper limits determined in the present work in all cases but O$_2$, for which the reported value is ca. 30 times larger than the present one. The only product study that we are aware of for Ge$_2$Ph$_4$ (**2a**) is that of its reaction with MeOH, which affords the 1,2-addition product analogous to **10**.[27]
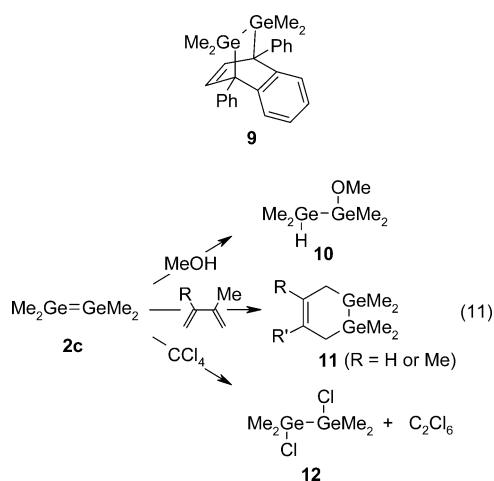

Table 3 provides a comparison of the reactivities of Ge$_2$Ph$_4$[29] and Ge$_2$Me$_4$ with those scavengers for which an absolute rate constant was measurable for at least one of the two digermenes. The two compounds exhibit distinct differences in reactivity toward BuNH$_2$, with which Ge$_2$Ph$_4$ is the more reactive of the two digermenes, and toward AcOH, CCl$_4$, and O$_2$, with which Ge$_2$Me$_4$ is the more reactive. Little or no substituent effect on the rate constants is observed for the reactions with Et$_3$GeH and Bu$_3$SnH.

The products of the reactions of Ge$_2$Me$_4$ and Ge$_2$Ph$_4$ with BuNH$_2$, AcOH, and the group 14 hydrides are unfortunately

not known and cannot be easily determined using the precursors studied here or in our earlier work because of the difficulties associated with preparative trapping experiments using precursors from which the digermene is formed as a secondary product of a primary intermediate that is itself much more reactive toward the scavenger.[28] However, on the basis of what is known from studies of other digermenes[70−72] and disilenes,[73−75] it is reasonable to assume that they react by 1,2-addition, most likely via stepwise mechanisms involving either zwitterionic or radical intermediates. Zwitterionic pathways are clearly the more likely possibilities with AcOH and BuNH$_2$, and the distinctly different responses of the rate constants to substitution in the digermenes suggest fundamentally different mechanisms, such as initial nucleophilic attack in the case of the amine and a pathway involving rate-determining protonation in the case of the carboxylic acid. In this context the results suggest that the tetramethyl derivative is more strongly nucleophilic and less electrophilic than its phenylated counterpart, which would be consistent with both the HOMO and LUMO being somewhat higher in energy in Ge$_2$Me$_4$ than in Ge$_2$Ph$_4$. DFT calculations predict the HOMO in Ge$_2$Me$_4$ to be only ca. 0.2 eV higher in energy than that in Ge$_2$Ph$_4$;[44] this and the UV/vis absorption maxima of the two compounds ($\lambda_{max} = 370$ nm for Ge$_2$Me$_4$ and 440 nm for Ge$_2$Ph$_4$) then indicate a much greater LUMO energy difference, but with the same relative ordering.

The kinetic data for reaction of the two digermenes with Et$_3$GeH and Bu$_3$SnH are consistent with a stepwise addition mechanism involving initial hydrogen abstraction, as has been proposed for the 1,2-addition of trialkyltin hydrides to tetramesityldisilene.[76] For both digermenes, the reactivities are in the order $k_{Sn−H} \gg k_{Ge−H} \gg k_{Si−H}$, following the trend in bond dissociation energies of the trialkylmetallyl hydrides.[77] The rate constants for reaction with both the germane and the stannane show little or no sensitivity to digermene structure, as would be expected on the basis of the relatively small effects of alkyl versus aryl substitution on the stabilities of germyl radicals.[77]

The product of the reaction of Ge$_2$Me$_4$ with CCl$_4$ is consistent with initial chlorine atom abstraction to yield the corresponding α-(chlorogermyl)germyl radical, which then abstracts chlorine from a second molecule of the halocarbon to yield 1,2-dichlorodigermane **12** (eq 11). The reactions of halocarbons with (stable tetrakis(trialkylsilyl)- and tetraaryl-) disilenes have been studied in some detail by Kira and co-workers[78] and are known to occur by an analogous mechanism, with coupling of the initially formed radical pair occurring competitively with cage escape and secondary disproportionation/coupling processes depending on the halocarbon. The reaction of stable digermenes with CCl$_4$ has evidently not been studied, but tetramesityldigermene (**2b**) is known to react with chloroform to yield the

(70) Baines, K. M.; Stibbs, W. G. *Adv. Organomet. Chem.* **1996**, *39*, 275.

(71) Barrau, J.; Escudie, J.; Satge, J. *Chem. Rev.* **1990**, *90*, 283.

(72) Escudie, J.; Ranaivonjatovo, H. *Adv. Organomet. Chem.* **1999**, *44*, 113.

(73) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231.

(74) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; pp 1015−1142.

(75) Sakurai, H. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley and Sons, Ltd: New York, 1998; pp 827−855.

(76) De Young, D. J.; Fink, M.; West, R. *Main Group Met. Chem.* **1987**, *10*, 19.

(77) Chatgilialoglu, C.; Newcomb, M. *Adv. Organomet. Chem.* **1999**, *44*, 67.

(78) Kira, M.; Ishima, T.; Iwamoto, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2001**, *123*, 1676.

product of addition of Cl—CHCl$_2$ across the Ge=Ge bond,[79] consistent with initial chlorine atom abstraction followed by coupling of the primary radical pair. The mechanism is further supported for both disilenes and digermenes by the recent computational studies of Su,[80] who proposed that, for reaction with a given halocarbon, the rate of the initial abstraction step is affected mainly by the magnitude of the singlet—triplet energy gap in the dimetallene; substituents that reduce ΔE_{S-T} (and with it, the M=M π-bond energy[81]) increase the rate of Cl abstraction from CCl$_4$. The explanation is equivalent to that given by Kira and co-workers, who observed that the rate constants for reaction of CCl$_4$ with bulky tetrakis(trialkylsilyl)disilenes and tetrakis-(2,4,6-triisopropylphenyl)disilene correlate inversely with the π-bond energies of the compounds.[78] We would expect Ge$_2$-Me$_4$ and Ge$_2$Ph$_4$ to have similar π-bond energies and singlet—triplet gaps; if anything, Ge$_2$Ph$_4$ is expected to have the (slightly) weaker π-bond based on the slightly (≤ 2 kcal mol^{-1}) greater stability of the triphenylgermyl radical relative to that of the trimethylgermyl radical, as measured by the Ge—H bond dissociation energies in the corresponding germyl hydrides.[82] The ca. 10-fold greater reactivity of Ge$_2$Me$_4$ relative to Ge$_2$Ph$_4$ toward chlorine atom abstraction from CCl$_4$ suggests that other factors also play a role in determining the reaction kinetics. Further mechanistic studies of the reactions of halocarbons with simple digermene derivatives are in progress in our laboratory.

Summary and Conclusions

This paper reports the first comprehensive study of the reactivities of dimethylgermylene (GeMe$_2$) and its dimer, tetramethyldigermene (Ge$_2$Me$_4$), in solution. The two species have been produced by photolysis of two closely related 3-phenylgermacyclopent-3-ene derivatives, which afford GeMe$_2$ in 90−95% chemical yield and quantum yields close to 50%. The germylene is detectable as a weakly absorbing transient species with $\lambda_{max} = 470$ nm ($\epsilon \approx 730$ dm^3 mol^{-1} cm^{-1}) in hexane solution, where it decays by diffusion-controlled dimerization to yield Ge$_2$Me$_4$. Absolute rate constants for reaction of GeMe$_2$ with several representative germylene scavengers have been measured, including primary and tertiary amines, acetic acid, group 14 trialkylmetallyl hydrides, O$_2$, CCl$_4$, two aliphatic dienes, and a terminal alkene and alkyne. In all cases for which rate constants have been measured previously in the gas phase for reaction with the same or closely related substrates, the two sets of results agree quite closely, as do the UV−vis absorption spectra. As expected, the present results for GeMe$_2$ parallel those reported earlier for diphenylgermylene under the same conditions.

With every reagent studied, GeMe$_2$ is significantly more reactive than GePh$_2$ under similar conditions. Not only are the reactions with the alkene and dienes faster than with GePh$_2$, but the products, which are thought to be the corresponding three-membered germanocycles from 1+2 cycloaddition, are significantly more stable. This conclusion is derived from comparisons of the estimated equilibrium constants for these reactions, which proceed reversibly under the conditions of our experiments, to those reported previously for reaction of GePh$_2$ with the same substrates. The reactions of GeMe$_2$ with primary and tertiary aliphatic amines have also been shown to proceed reversibly. The rate constants for M—H insertion reactions of

GeMe$_2$ with group 14 hydrides follow the order established previously for GeMe$_2$ and GeH$_2$ in the gas phase and for GePh$_2$ in solution: $k_{Si-H} \ll k_{Ge-H} \ll k_{Sn-H}$.

Absolute rate constants for reaction of Ge$_2$Me$_4$ could also be measured for six of the substrates examined, and the data have been compared to the corresponding ones for reaction of tetraphenyldigermene (Ge$_2$Ph$_4$) with the same substrates. The rate constants for reaction of the two digermenes with Et$_3$GeH and Bu$_3$SnH are very similar to one another, consistent with a mechanism involving initial H abstraction by the Ge=Ge bond, as has been proposed previously for the reaction of stable disilenes with Bu$_3$SnH. On the other hand, significant differences in reactivity are observed for reaction with BuNH$_2$, which reacts significantly faster with Ge$_2$Ph$_4$, and AcOH, O$_2$, and CCl$_4$, which react significantly faster with Ge$_2$Me$_4$. These results suggest tetramethyldigermene to be significantly less electrophilic and more nucleophilic than the tetraphenyl derivative. The greater reactivity of Ge$_2$Me$_4$ with CCl$_4$, which is thought to proceed via initial chlorine atom abstraction, does not seem to correlate with previous mechanistic proposals for the reactions of halocarbons with stable disilenes and digermenes.

1-Germacyclopent-3-enes are ideal photochemical sources for the study of reactive germylenes in solution by time-resolved spectroscopic methods. They are somewhat less well-suited as precursors of the corresponding digermenes, but are nevertheless useful for kinetic studies of the reactions of these species with a limited number of particularly reactive substrates. We are currently working to extend the methodology to the study of other reactive metallylenes and dimetallenes in solution, including representatives from silicon, germanium, and tin chemistry.

Experimental Section

The procedures employed for the synthesis of **3a,b** and semi-preparative photolysis experiments, as well as detailed spectroscopic data for the compounds reported in this work, are described in the Supporting Information.

Hexanes (EMD Omnisolv) was dried by passage through a Solv-Tek solvent purification system and contained <10 μM water as measured by Karl Fischer titration. Each of the scavengers investigated in this work were obtained from commercial sources in the highest purity available. Triethylamine and *n*-butylamine were refluxed over solid KOH for 12 h and distilled. Triethylsilane (Et$_3$-SiH), triethylgermane (Et$_3$GeH), and tri-*n*-butylstannane (Bu$_3$SnH) were stirred at room temperature for 18 h over lithium aluminum hydride and distilled at atmospheric pressure (Et$_3$SiH) or under mild vacuum (Bu$_3$SnH, Et$_3$GeH). CCl$_4$ was refluxed over phosphorus pentoxide and distilled. 4,4-Dimethyl-1-pentene (DMP), isoprene, and 2,3-dimethyl-1,3-butadiene (DMB) were purified by passage of the neat liquids through a silica gel column. 3,3-Dimethyl-1-butyne (TBE) was distilled. Glacial acetic acid was used as received from Sigma-Aldrich.

Laser flash photolysis experiments employed the pulses from a Lambda Physik Compex 120 excimer laser, filled with F$_2$/Kr/Ne (248 nm; ~25 ns; 100 $\pm$ 5 mJ) mixtures, and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously.[27] Solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was between ca. 0.7 and 0.9, and were flowed continuously through a thermo-stated 7 × 7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir, fitted with a glass frit to allow bubbling of nitrogen or argon gas through the solution for at least 30 min prior to and then throughout the duration of each experiment. The glassware, sample cells, and transfer lines used for these experiments were stored in a vacuum oven at ca. 65 °C when not in use, and the oven was vented with dry nitrogen just prior to assembling the

(79) Samuel, M. S.; Jennings, M. C.; Baines, K. M. *Organometallics* **2004**, *20*, 590.

(80) Su, M.-D. *J. Phys. Chem. A* **2004**, *108*, 823.

(81) Chen, W.-C.; Su, M.-D.; Chu, S.-Y. *Organometallics* **2001**, *20*, 564.

(82) Clark, K. B.; Griller, D. *Organometallics* **1991**, *10*, 746.

sample-handling system at the beginning of an experiment. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple inserted directly into the flow cell. Transient decay and growth rate constants were calculated by nonlinear least-squares analysis of the absorbance−time profiles using the Prism 3.0 software package (GraphPad Software, Inc.) and the appropriate user-defined fitting equations, after importing the raw data from the Luzchem mLFP software. Reagents were added directly to the reservoir by microliter syringe as aliquots of standard solutions. Rate constants were calculated by linear least-squares analysis of decay rate−concentration data (5−7 points) that spanned as large a range in transient decay rate as possible. Errors are quoted as twice the standard deviation obtained from the least-squares analyses.

The quantum yield for formation of methoxydimethylgermane (**5b**) was determined by merry-go-round photolysis of deoxygenated, optically matched solutions of **3a** (0.041 M) and 1,1-diphenylsilacyclobutane (Ph$_2$SCB; 0.037 M) in cyclohexane-d_{12} containing methanol (0.24 M) and hexamethyldisilane (0.0017 M) as internal standard, in a Rayonet photochemical reactor equipped with six RPR-2537 low-pressure Hg lamps. The course of the photolyses was monitored at time intervals between 0 and ca. 20% conversion by 600 MHz ^{1}H NMR spectroscopy. The quantum yield for the formation of **5b** from **3a** was calculated from the relative slopes of concentration versus time plots for the formation of **5b** and methoxymethyldiphenylsilane (Ph$_2$MeSiOMe; see Supporting Information) and the reported quantum yield of the latter ($\Phi =$ 0.21 $\pm$ 0.02).[35] The slopes of the plots were as follows: **3a**, −0.00145 $\pm$ 0.00019; **5b**, +0.00140 $\pm$ 0.00009; Ph$_2$SCB, −0.00067 $\pm$ 0.00002; Ph$_2$MeSiOMe, +0.00053 $\pm$ 0.00002.

Determination of the extinction coefficient for the GeMe$_2$ absorption at 470 nm was carried out by benzophenone actinometry, using the so-called intensity variation method.[37,38] The substrate and actinometer solutions were optically matched at the laser wavelength (248 nm) to ensure equal light absorption, and both were flowed through the same sample cell for sequential measurement of $\Delta A_{\lambda,0}$ values ($\lambda =$ 470 and 525 nm for GeMe$_2$ and the benzophenone triplet, respectively) as a function of laser intensity, which was controlled using neutral density filters constructed from wire screens. Both solutions were deoxygenated prior to the measurements with a stream of nitrogen and restored to their original volumes at the end of the deoxygenation procedure with fresh (deoxygenated) hexane. The resulting plots of $\Delta A_{\lambda,0}$ versus laser intensity, from whose slopes was calculated the extinction coefficient of the GeMe$_2$ absorption ($\epsilon_{470-nm} =$ 730 $\pm$ 300 M^{-1} cm^{-1}) using values of $\Phi =$ 1.0 and $\epsilon_{525-nm} =$ 6250 $\pm$ 1250 M^{-1} cm^{-1} for the benzophenone triplet[83] and the quantum yield for GeMe$_2$ formation determined above, are included in the Supporting Information.

Supporting Information Available: Details of the synthesis and characterization of compounds and photoproducts, and quantum yield, transient extinction coefficient, and kinetic data for GeMe$_2$ and Ge$_2$Me$_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0600083

(83) Carmichael, I.; Helman, W. P.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1987**, *16*, 239.