

Direct detection of methylphenylgermylene and 1,2-dimethyl-1,2-diphenyldigermene — Kinetic studies of their reactivities in solution

William J. Leigh, Ileana G. Dumbrava, and Farahnaz Lollmahomed

Abstract: Photolysis of 1,3,4-trimethyl-1-phenylgermacyclopent-3-ene (**5**) in hydrocarbon solvents containing isoprene, methanol, or acetic acid affords 2,3-dimethyl-1,3-butadiene (DMB) and the expected trapping products of methylphenylgermylene (GeMePh) in chemical yields exceeding 90%. The germylene has been detected in hexane solution by laser flash photolysis as a short-lived species ($\tau \sim 2 \mu\text{s}$) exhibiting a UV–vis absorption spectrum centered at $\lambda_{\text{max}} = 490 \text{ nm}$. It decays with second-order kinetics and a rate constant close to the diffusion-controlled limit, with the concomitant growth of a second longer-lived transient ($\lambda_{\text{max}} = 420 \text{ nm}$) that is assigned to a mixture of (*E*)- and (*Z*)-1,2-dimethyl-1,2-diphenyldigermene (**4**). Absolute rate constants have been determined for the reactions of the germylene with primary and tertiary amines (*n*-BuNH₂ and Et₃N, respectively), acetic acid (AcOH), a terminal alkyne and alkene, isoprene, DMB, CCl₄, and the group 14 hydrides Et₃SiH and Bu₃SnH. GeMePh is slightly more reactive than GePh₂ towards all the reagents studied in this work; both are significantly less reactive than GeMe₂ toward the same substrates. Absolute rate constants for the reactions of **4** have also been measured or assigned upper limits in every case and are compared to previously reported values for tetraphenyl- and tetramethyl-digermene with the same reagents.

Key words: germylene, digermene, kinetics, laser flash photolysis, germirane, germirene, vinylgermirane, complex, UV–vis spectrum, insertion, addition.

Résumé : La photolyse du 1,3,4-triméthyl-1-phénylgermacyclopent-3-ène (**5**) dans des solvants hydrocarbonés contenant de l'isoprène, du méthanol ou de l'acide acétique conduit à la formation de 2,3-diméthylbuta-1,3-diène (DMB) et aux produits de piégeage attendus du méthylphénylgermylène (GeMePh) avec des rendements supérieurs à 90%. Faisant appel à la photolyse éclair au laser et opérant dans une solution d'hexane, on a détecté la présence du germylène sous la forme d'une espèce transitoire (τ d'environ $2\mu\text{s}$) qui présente un spectre d'absorption UV–visible centré autour d'un λ_{max} de 490 nm. Sa décroissance présente une cinétique du second ordre et une constante de vitesse qui se rapproche de la limite d'un contrôle par la diffusion et qui est accompagnée de la croissance d'une deuxième espèce transitoire ($\lambda_{\text{max}} = 420 \text{ nm}$) qui est attribuée à un mélange (*E*)- et (*Z*)-1,2-diméthyl-1,2-diphényldigermène (**4**). On a déterminé les constantes de vitesse absolues de la réaction du germylène avec des amines primaires et tertiaires (respectivement BuNH₂ et Et₃N), l'acide acétique (AcOH), un alcyne terminal, un alcène terminal, l'isoprène, le DMB, le CCl₄ et les hydrures du groupes 14, Et₃SiH et Bu₃SnH. Le GeMePh est légèrement plus réactif que le GePh₂ vis-à-vis tous les réactifs examinés dans ce travail; les deux sont toutefois beaucoup moins réactifs que le GeMe₂ par rapport aux mêmes réactifs. Dans tous les cas, on a aussi mesuré ou attribué des valeurs limites supérieures pour les constantes de vitesses absolues de la réaction avec le composé (**4**) et on les a comparées aux valeurs rapportées antérieurement pour les réactions du tétraphényl- et du tétraméthyl-digermène avec les mêmes réactifs.

Mots clés : germylène, digermène, cinétique, photolyse éclair au laser, germirane, germirène, vinylgermirane, complexe, spectre UV–visible, insertion, addition.

[Traduit par la Rédaction]

Introduction

Germylenes are important intermediates in the thermal and photochemical reactions of germanium compounds (1),

and the study of their synthesis and chemistry continues to be of considerable interest (2–6). Of particular fundamental and practical importance is the parent molecule, GeH₂, whose chemistry has been extensively studied in the gas phase by time-resolved kinetic methods.² Studies of several simple substituted derivatives by time-resolved spectroscopic methods in matrices and in solution have been reported,³ but the solution-phase studies have been characterized by a particular lack of consistency in the spectroscopic properties and reactivities of these species (5). We have speculated that the problem is due to two main factors — the characteristic weakness of the lowest energy ($S_0 \rightarrow S_1$) electronic transition in divalent group 14 compounds and the pronounced complexity of the photochemistry of the particular organo-

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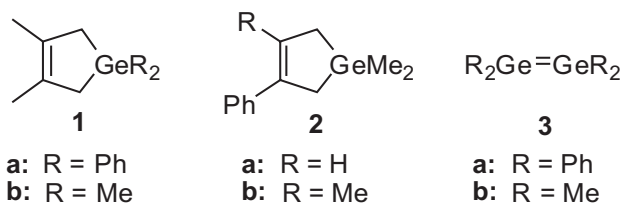
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²See refs. 5 and 6 and the refs. cited therein.

³See ref. 5 for a complete bibliography.

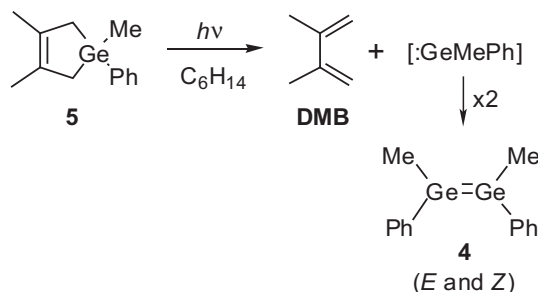
germanium compounds (typically oligogermanes and oligosilagermanes) that have been employed as germylene precursors (7). As we have recently demonstrated (8), the combination of these factors can make transient germylenes relatively difficult to detect, even when they are the major products of photolysis.

We recently reported the first comprehensive kinetic studies of the reactivities of diphenyl- and dimethyl-germylene (GePh_2 and GeMe_2 , respectively) in hydrocarbon solution, generating and monitoring them directly by laser flash photolysis of the 1,1-disubstituted germacyclopent-3-ene derivatives **1** and **2** (9–11). Trapping experiments showed that photolysis of these molecules proceeds very cleanly and with remarkably high efficiency in every case, producing the expected trapping products of the germylenes along with the corresponding conjugated dienes in chemical yields exceeding 90% and quantum yields on the order of 0.5. Absolute rate constants were reported for dimerization of the two species, which yields the transient digermene derivatives **3**, and for their reaction with a variety of representative substrates such as aliphatic amines, halocarbons (RX), aliphatic alkynes, dienes and alkenes, oxygen, acetic acid, and the group 14 hydrides R_3MH ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$; $\text{R} = \text{ethyl or } n\text{-butyl}$). Several of the reactions of these species were found to be reversible, such as the [2+1]-cycloaddition reactions with alkenes and dienes, and Lewis acid–base complexation with tertiary amines; they are nonetheless very fast, with forward rate constants on the order of $10^9\text{--}10^{10}$ ($\text{mol/L})^{-1} \text{s}^{-1}$ in hexane at room temperature. The absolute rate constants measured for the reactions of GeMe_2 with the C=C unsaturated compounds and oxygen in solution (11) were found to agree quite well with earlier data reported by Walsh and co-workers (6, 12) for reactions with the same or similar substrates in the gas phase. The solution-phase data for the two germylenes showed GeMe_2 to be significantly more reactive than its phenylated counterpart in every reaction that was studied. Rate constants were also reported for the reactions of the digermenes **3a** and **3b** in several cases, providing the first indications of the effects of methyl vs. phenyl substitution on the reactivity of digermene derivatives toward various nucleophilic and electrophilic reagents.

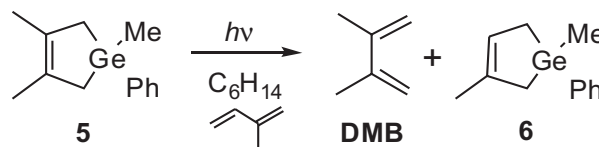


Reasonably precise determination of equilibrium constants for the (reversible) reactions with C=C bonds was possible only with GePh_2 , which has a significantly higher extinction coefficient than GeMe_2 (thus affording stronger transient absorptions) and exhibits equilibrium constants that are in an ideal range to be measured under the conditions of our experiments. Furthermore, the (transient) products of these reactions could also be detected. We were less successful in characterizing the reactions of GeMe_2 with the same substrates; there were clear indications of reversibility, but the equilibrium constants are evidently significantly higher than those for GePh_2 and close to the upper limit measurable

Scheme 1.



Scheme 2.



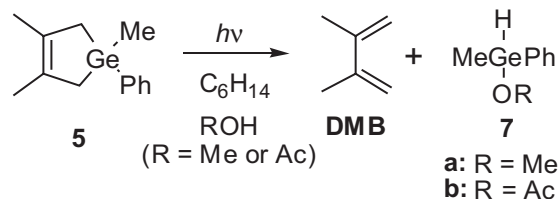
under the conditions of our experiments. While absolute rate constants for these reactions could be determined in a straightforward fashion, the weaker transient absorptions of the dialkylgermylene made it possible only to derive estimates of the equilibrium constants. The products also could not be detected, presumably because they do not absorb at sufficiently long wavelengths to enable detection with our methods.

In the present paper, we report the results of a time-resolved spectroscopic study of methylphenylgermylene (GeMePh) and (*E*)- and (*Z*)-1,2-dimethyl-1,2-diphenyldigermene (**4**, as a mixture of isomers) in hydrocarbon solution, generated by laser flash photolysis of 1,3,4-trimethyl-1-phenylgermacyclopent-3-ene (**5**, Scheme 1). This work represents the first step in a more extensive study of the effects of substituents (directly attached to germanium) on germylene and digermene reactivity, as well as an attempt to confirm and elaborate on some of the differences in the reactivity of GeMe_2 and GePh_2 towards the various substrates that have been examined so far. Our previous results for the other two germylenes lead to the expectation that the presence of a single phenyl group should provide a chromophore that would lead to stronger transient absorptions (thus enabling more precise kinetic measurements), facilitate the detection of transient products, and provide some moderation of reactivity (compared with GeMe_2) so that meaningful structure–re-activity relationships might eventually be derived.

Results

Steady state photolysis (254 nm) of a deoxygenated hexane solution of **5** (0.025 mol/L) containing isoprene (0.1 mol/L) led to the formation of 1,3-dimethyl-1-phenylgermacyclopent-3-ene (**6**) as the only detectable germanium-containing product at conversions below ca. 15% and an equal yield of 2,3-dimethyl-1,3-butadiene (DMB) (Scheme 2). The identity of **6** was established by GC coinjection of the crude photolysate with an authentic, independently synthesized sample of the compound. Similarly, photolysis of a cyclohexane-*d*₁₂ solution of **5** (0.05 mol/L) containing methanol (MeOH, 0.5 mol/L) or acetic acid (AcOH, 0.095 mol/L), with periodic monitoring of the

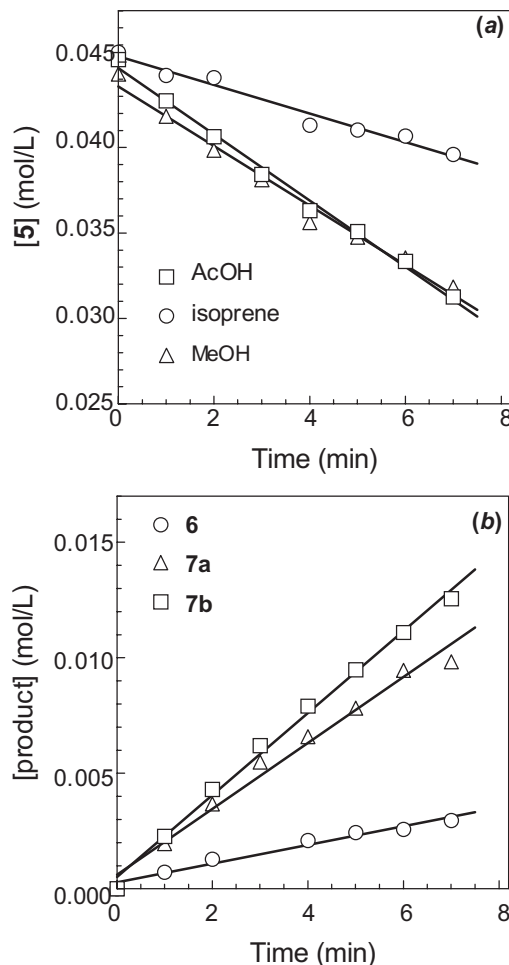
Scheme 3.



photolysates by ^1H NMR spectroscopy between 0% and ca. 25% conversion, afforded DMB and a single other product in each case. These were tentatively identified as methoxy-methylphenylgermane and acetoxymethylphenylgermane (**7a** and **7b**, respectively, Scheme 3) on the basis of their ^1H NMR spectra. The results are consistent with formal [4+1]-cycloreversion to yield GeMePh and DMB as the predominant photochemical reaction pathway of **5**. The quantum yield was not rigorously determined, but qualitative comparisons of the rate of product formation in the MeOH-trapping experiment with those for **1a** (**9**) and **2a** (**11**) under the same conditions suggest that it is similar to the value of 0.55 that had been previously reported by us (**9**, **11**) for the quantum yields for formation of GePh_2 and GeMe_2 , respectively, from these compounds. A merry-go-round experiment was carried out, in which 0.045 mol/L solutions of **5** in cyclohexane- d_{12} containing MeOH (0.25 mol/L), AcOH (0.095 mol/L), and isoprene (0.094 mol/L) were irradiated in parallel, to assess any possible differences in reaction quantum yield with trapping agent. Concentration vs. time plots, showing the consumption of **5** and the formation of the products (**6**, **7a**, and **7b**), measured by ^1H NMR spectroscopy over the 0%–20% conversion range, are shown in Fig. 1. Correction of the isoprene concentration vs. time data for primary inner filter effects (because of coabsorption of the excitation light by the substrate) leads to the conclusion that product formation using the diene as trap (at ca. 0.1 mol/L) proceeds with roughly half the efficiency as in the experiments employing MeOH or AcOH as germylene scavengers. This corresponds to a $k_Q\tau$ value of ca. 10 (mol/L) $^{-1}$ for quenching of the reactive excited state of **5** by the diene, consistent with a lifetime of 10 ns or less assuming a quenching rate constant in excess of 10^9 (mol/L) $^{-1}$ s $^{-1}$.

Laser flash photolysis of continuously flowing deoxygenated solutions of **5** (ca. 0.0015 mol/L) in anhydrous hexane with the pulses from a KrF excimer laser (248 nm, ~25 ns, ~100 mJ) led to the formation of two transient species, one that appeared to be formed within ca. 50 ns of the onset of the laser pulse ($\lambda_{\text{max}} = 490$ nm) and another ($\lambda_{\text{max}} = 415$ nm) that grew to a maximum in concentration over the first ca. 4 μs after the pulse and then decayed to baseline over the next ca. 100 μs . Figure 2 shows transient absorption spectra recorded 95–200 ns and 3.4–3.6 μs after excitation, along with typical transient decay–growth profiles recorded at 510 and 410 nm, to the red and blue, respectively, of the absorption maxima of the two species, to isolate the transient decays as completely as possible without sacrificing appreciably in signal intensity. The decay of the first-formed species fits well to second-order kinetics (eq. [1]), affording

Fig. 1. Plots of concentration vs. time showing (a) the consumption of **5** and (b) the formation of trapping products from photolysis of **5** in cyclohexane- d_{12} containing AcOH (0.095 mol/L, \square), MeOH (0.5 mol/L, Δ), and isoprene (0.094 mol/L, \circ). The data from the latter have not been corrected for inner filter effects.



a decay constant of $k\epsilon_{510} = (1.6 \pm 0.1) \times 10^7$ cm $^{-1}$. The behaviour is exactly analogous to that previously reported for **1a** and **1b** (**9**) and **2a** and **2b** (**11**) under similar conditions. We thus assign the two transients to GeMePh and its dimerization products, (*E*)- and (*Z*)-1,2-dimethyl-1,2-diphenyldigermene (**4**), respectively, (Scheme 1), which we assume are formed as a mixture of isomers.

$$[1] \quad \Delta A_t = \Delta A_0 / (1 + 2k_{\text{dim}}(\Delta A_0/\epsilon_\lambda l)t)$$

where ΔA_0 and ΔA_t are the transient absorbances at time = 0 and time = t after the laser pulse, ϵ_λ is the extinction coefficient at the monitoring wavelength, and l is the path length.

We next investigated the reactivities of the two species with various germylene scavengers (see Chart 1). Addition of AcOH, Bu_3SnH , CCl_4 , or *tert*-butylacetylene (TBE) resulted in effects consistent with irreversible⁴ scavenging of the germylene (**9**–**11**); the (germylene) absorption at 510 nm

⁴ Any reaction with a (forward) rate constant of 10^9 – 10^{10} (mol/L) $^{-1}$ s $^{-1}$ and an equilibrium constant greater than ca. 25 000 (mol/L) $^{-1}$ appears to be irreversible under the conditions of our experiments, to the extent that the reacting species decay completely to baseline with pseudo-first-order kinetics.

Fig. 2. Transient absorption spectra recorded 95–220 ns (○) and 3.4–3.6 μs (●) after the laser pulse from flash photolysis of a ca. 0.0015 mol/L solution of **5** in deoxygenated, anhydrous hexane. The inset shows representative transient decay and growth profiles recorded at 410 nm and 510 nm; the solid line in the latter is the fit of the data to second order decay kinetics

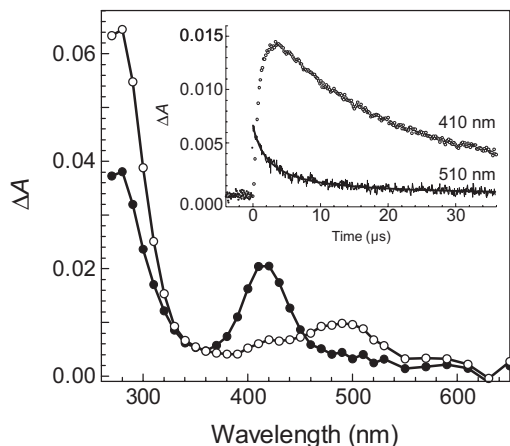
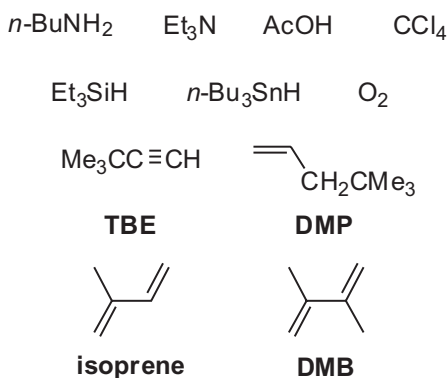


Chart 1.



decayed at increased rates, completely to baseline, with clean first-order kinetics at concentrations above those required to reduce the peak digermene signal intensities to less than ca. 50% of their values in the absence of added reagent. As well, both the peak intensities and growth time of the absorptions because of **4** (measured at 410 nm) were reduced in proportion to the concentration of added scavenger. Plots of the pseudo-first-order rate constants for gerylene decay (k_{decay}) vs. concentration were linear, consistent with the relationship of eq. [2],

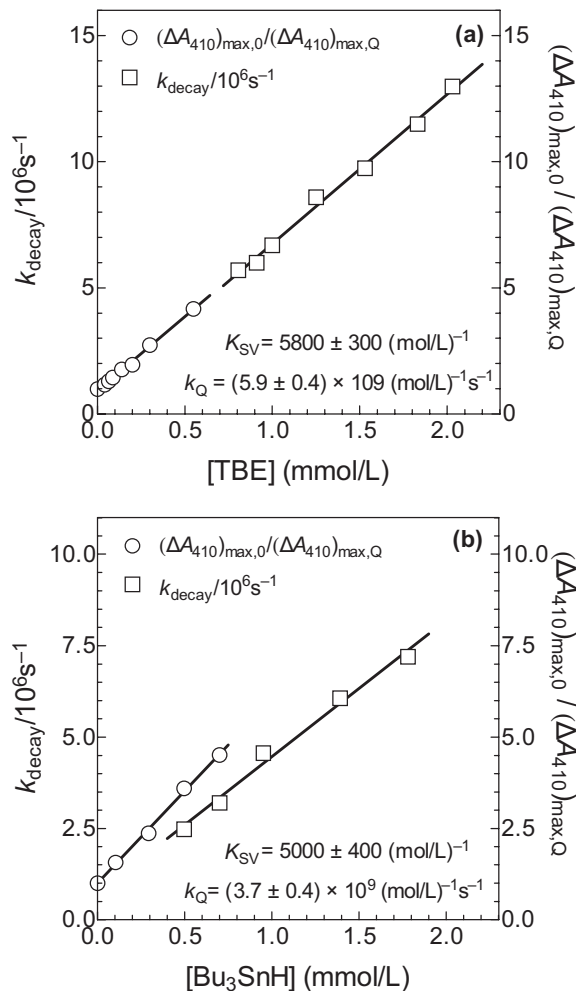
$$[2] \quad k_{\text{decay}} = k_0 + k_Q[Q]$$

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. Plots of the ratios of the peak transient absorbances due to **4**, in the absence and presence of scavenger at concentration [Q] ($\Delta A_{410,0}/\Delta A_{410,Q}$), were also linear in every case and were analyzed according to eq. [3],

$$[3] \quad (\Delta A_{410})_{\text{max},0}/(\Delta A_{410})_{\text{max},Q} = 1 + K_{\text{SV}}[Q]$$

where K_{SV} is a proportionality factor reflecting the efficiency of the gerylene scavenging reaction relative to

Fig. 3. Plots of k_{decay} (□) and $(\Delta A_{410})_{\text{max},0}/(\Delta A_{410})_{\text{max},Q}$ (○) vs. [Q] for scavenging of GeMePh by (a) 3,3-dimethyl-1-butyne (TBE) and (b) tri-*n*-butylstannane (Bu_3SnH). The solid lines are the linear least-squares fits of the data to eqs. [2] and [3], respectively. Decay and growth profiles for MePhGe and **4** were measured at 510 and 410 nm, respectively.



dimerization. Typical plots are shown in Fig. 3, from the experiments employing TBE and Bu_3SnH as scavengers. The absolute rate constants and K_{SV} values for reaction of GeMePh with the various reagents studied in this work are collected in Table 1. Also included in the table are the K_{SV}/k_Q ratios, calculated for each of the scavengers studied from the K_{SV} and k_Q values. Similar effects on the gerylene and digermene absorptions to those noted above were observed in the presence of BuNH_2 , even though its reaction with GeMePh is most likely reversible (vide infra).

In several cases, the reagent also had the effect of accelerating the decay of the digermene (**4**) signal over the concentration range where it could be detected, consistent with reaction of the scavenger with the digermene as well. The digermene decays followed reasonably good first-order kinetics in the presence of the scavenger, and plots of k_{decay} vs. [Q], according to eq. [2], were linear; the absolute rate constants obtained are also listed in Table 1. For those scavengers that did not exhibit distinctive effects on the digermene decay kinetics, upper limits of the rate constants were esti-

Table 1. Absolute rate constants (k_Q) and K_{SV} values for reactions of GeMePh and 1,2-dimethyl-1,2-diphenyl-digermene (**4**) with various substrates in dry deoxygenated hexane solution at 23 °C.

Reagent (Q)	GeMePh ^a			PhMeGe=GeMePh (4) ^b
	k_Q ($\times 10^9$ (mol/L) ⁻¹ s ⁻¹) ^c	K_{SV} (mol/L) ^{-1d}	K_{SV}/k_Q (μ s)	k_Q ($\times 10^6$ (mol/L) ⁻¹ s ⁻¹) ^b
AcOH	5.6 \pm 0.5	4 900 \pm 300	0.88	140 \pm 10
Et ₃ SiH	\leq 0.000 44	Nd ^e	—	—
Bu ₃ SnH	3.7 \pm 0.4	5 000 \pm 300	1.35	\leq 390 ^f
CCl ₄	0.017 \pm 0.002 ^g	29 \pm 2	1.72	6 \pm 1
O ₂	$<$ 0.06 ^f	50 \pm 12	$>$ 0.85	24 \pm 3
TBE	5.9 \pm 0.4	5 800 \pm 300	0.98	24 \pm 4
BuNH ₂	11.7 \pm 1.4	14 200 \pm 900	1.21	5200 \pm 600
Et ₃ N	3.9 \pm 0.4	1 120 \pm 130	0.29	—
Isoprene	8.0 \pm 0.9	3 800 \pm 100	0.48	\leq 4 ^e
DMB	4 \pm 2	175 \pm 25 ^h	0.044	\leq 12 ^e
DMP	5.1 \pm 0.7	110 \pm 100	0.21	\leq 32 ^e

^aMeasured by laser flash photolysis of deoxygenated solutions of **5** (\sim 0.0015 mol/L) in hexane. Errors are listed as $\pm 2\sigma$ from linear least-squares analyses of the data.

^bDetermined from plots of k_{decay} (for **4**, monitored at 410 nm) vs. [Q].

^cFrom plots of k_{decay} (for GeMePh, monitored at 510 nm) vs. [Q] according to eq. [2], over concentration ranges corresponding to $>$ 50% quenching of the peak ΔA_{410} value ($(\Delta A_{410})_{\text{max},0}$) because of **4**.

^dFrom plots of $[(\Delta A_{410})_{\text{max},0}/(\Delta A_{410})_{\text{max},Q}]$ vs. [Q] according to eq. [3].

^eNd (not determined).

^fCalculated from k_{decay} at the highest concentration of scavenger studied.

^gThe slope of the low concentration range of (nonlinear) plots of k_{decay} vs. [Q].

^hCorrected for primary inner filter effects.

mated from the rate constant for decay of the signal at the highest scavenger concentration investigated, obtained by fitting the transient decay profiles to single exponential decay kinetics. These data are also listed in Table 1.

Addition of Et₃N, 4,4-dimethyl-1-pentene (DMP), isoprene, and DMB resulted in behaviour consistent with reversible scavenging of GeMePh, the main indication of which is a significantly less efficient reduction in the peak intensity of digermene absorption with increasing scavenger concentration; formation of the digermene could still be readily observed even at high enough substrate concentrations to reduce the lifetime of the germylene to the point where it could no longer be detected. This effect was common to all four substrates. Other anticipated effects varied with the substrate according to the magnitudes of the forward rate constant and equilibrium constant for the particular reaction. For example, addition of Et₃N caused the germylene signals to decay with clean first-order kinetics completely to the prepulse level at all concentrations throughout the 0.3–2 mmol/L range in added substrate, similar to the behaviour observed with the irreversible substrates; this is consistent with an equilibrium constant significantly in excess of ca. 25 000 (mol/L)⁻¹ (10), the approximate upper limit of the value measurable under the conditions of our experiment given a forward rate constant in the 10⁹–10¹⁰ (mol/L)⁻¹ s⁻¹ range. On the other hand, addition of DMP and isoprene caused the germylene signal to decay with bimodal kinetics within certain concentration ranges, consisting of a fast, approximately first-order decay followed by a much longer-lived residual absorption; the decay rate of the initial component increased while the residual absorption level and its decay rate both decreased with increasing substrate concentration. To illustrate this behaviour, Fig. 4a shows a series of germylene decay traces obtained in the presence of DMP. We associate the fast initial decay with

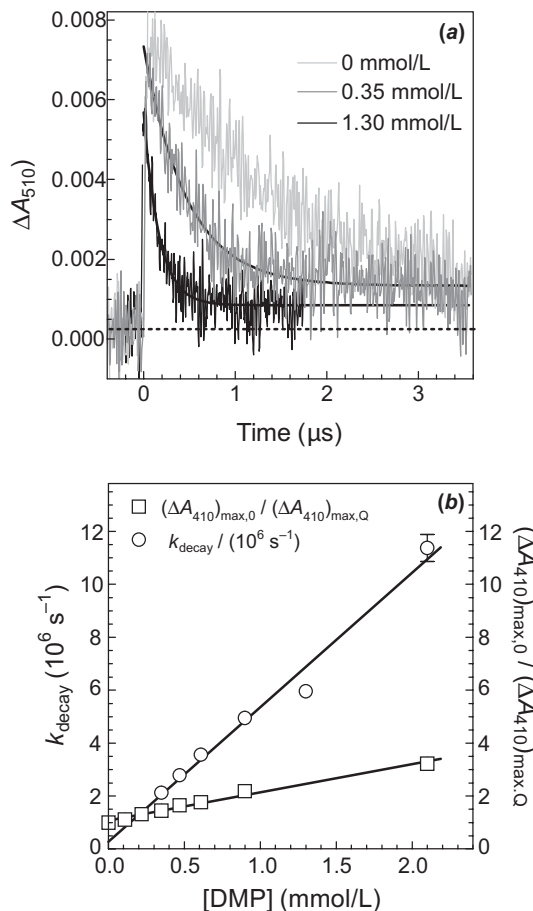
the approach to equilibrium with the scavenging product and the residual absorption as being due to residual free germylene present at equilibrium and undergoing slow dimerization. This behaviour was evident over the full concentration range in which the germylene could be detected in the case of DMP (0.35–2.1 mmol/L), but only over the 0.1–0.5 mmol/L concentration range in the case of isoprene, with the decays proceeding completely to the prepulse level (within detection limits) at higher concentrations. This is consistent with a larger equilibrium constant for reaction with isoprene compared with that for DMP.

The germylene decay profiles in the experiments with DMP and isoprene were analyzed as single exponential decays to a nonzero residual absorption, as in our earlier study (10). Plots of the decay rate constants vs. scavenger concentration exhibited excellent linearity (see Fig. 4b), and analysis of the data according to eq. [4] afforded k_Q values of $(5.1 \pm 0.7) \times 10^9$ and $(8.0 \pm 0.4) \times 10^9$ (mol/L)⁻¹ s⁻¹ for DMP and isoprene, respectively. The corresponding values of K_{SV} , obtained from analysis of the peak ΔA_{410} values due to digermene **4**, according to eq. [3], were 1060 ± 100 and 3800 ± 100 (mol/L)⁻¹. Plots of the ratios of the initial and residual germylene ΔA values, according to eq. [5], exhibited considerable scatter, mainly because of the rather low signal-to-noise that characterized the present series of experiments. It was thus not possible to determine the equilibrium constants with reasonable precision and reproducibility. Nevertheless, qualitative comparisons of the data to those previously published for GePh₂ (10) with the same substrates suggest the K_{eq} values to be in the range of 4000–8000 (mol/L)⁻¹ for DMP and 12 000–15 000 (mol/L)⁻¹ for isoprene.

$$[4] \quad k_{\text{decay}} = k_{-Q} + k_Q[Q]$$

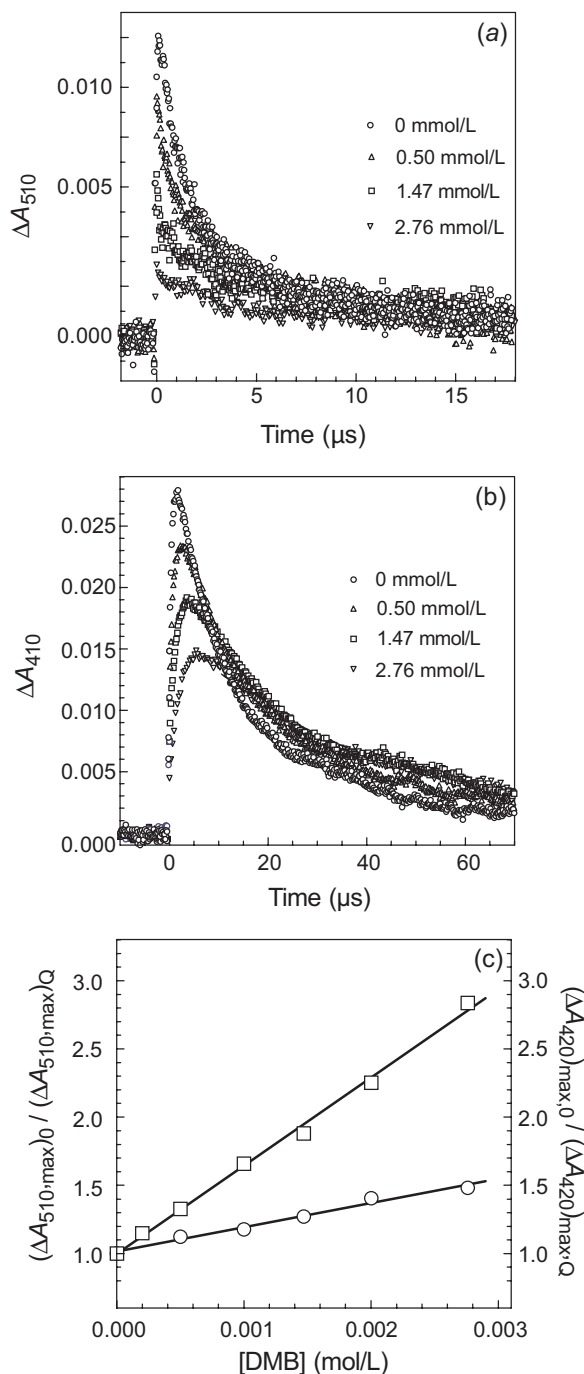
$$[5] \quad (\Delta A_{510,0}/\Delta A_{510,\text{res}})_Q = 1 + K_{\text{eq}}[Q]$$

Fig. 4. (a) Absorbance vs. time profiles for GeMePh in deoxygenated hexane containing DMP (0, 0.35, and 1.30 mmol/L), monitored at 510 nm. The solid lines are the best fits of the data to single exponential decays. (b) Plots of k_{decay} and $(\Delta A_{410})_{\text{max},0}/(\Delta A_{410})_{\text{max},Q}$ vs. [DMP], showing the fits of the data to eqs. [4] and [3], respectively.



The data obtained with DMB as scavenger were very difficult to analyze accurately. Marked reductions in the strength of the germylene signals accompanied addition of the diene over the 0.5–3 mmol/L concentration range, yet effected only minor reductions in the strength of the digermene signals and consistent lengthening of their growth times with increasing concentrations. Typical data, corrected for inner filter effects because of coabsorption of the excitation light by the diene, are shown in Fig. 5. An initial fast component to the predominantly second-order germylene decay appeared to develop over the 0–0.8 mmol/L concentration range in added diene; it became distinctive enough to allow analysis between 1.0 and 2.0 mmol/L, but was too short-lived above 2.0 mmol/L to analyze accurately, leaving behind a much weaker residual second-order decay. This behaviour is again consistent with rapid reversible reaction, but with an equilibrium constant of less than ca. $1000 \text{ (mol/L)}^{-1}$ (13). A rate constant of $k_Q = (4 \pm 2) \times 10^9 \text{ (mol/L)}^{-1} \text{ s}^{-1}$ was estimated from the decay rate constants for the fast initial component of the bimodal decay profiles from several determinations (at shorter timescales) in the presence of 1.0–2.0 mmol/L DMB, analyzed in the same way as the data obtained with DMP, while a value of $K_{\text{SV}} = 175 \pm 25 \text{ (mol/L)}^{-1}$

Fig. 5. Growth and decay profiles for the signals due to (a) GeMePh and (b) **4** in the presence of DMB (0–2.76 mmol/L), and (c) plots of the relative peak signal intensities for the germylene (\square) and digermene (\circ) absorptions vs. DMB concentration according to eq. [3].



was obtained from analysis of the digermene peak signal strengths according to eq. [3].

As is evident from the raw data shown in Figs. 4 and 5, the strength of the germylene signals decreased noticeably with addition of reactive substrate in increasing concentrations; this was generally observed with all of the substrates studied, to an extent comparable to that shown in Fig. 4 with DMP as scavenger. It may be the result of the fact that

germylene formation appears to lag slightly behind the laser pulse; this is evident from the $[\text{DMP}] = 0$ trace of Fig. 4a, which suggests that the signal grows with a rise time of ca. 50 ns, significantly longer than the ca. 25 ns width of the laser pulse. This behaviour suggests that germylene formation is not a direct excited (singlet) state process, but rather ensues from a secondary intermediate. If this is true, then a reduction in germylene signal strength with increasing scavenger concentration would be expected, as reaction of the germylene with the scavenger becomes increasingly competitive with its formation. The effect on signal strength was much more pronounced in the experiments with isoprene and DMB as scavengers, suggesting an additional mechanism for quenching of the signals beyond that exhibited by the other scavengers. Plots of the relative peak transient absorbances at 510 nm vs. concentration (cf. eq. [3]) afforded Stern–Volmer constants of $1000 \pm 150 \text{ (mol/L)}^{-1}$ and $650 \pm 40 \text{ (mol/L)}^{-1}$ for isoprene and DMB (see Fig. 5c), respectively.

On the other hand, significant increases in the strength of the transient absorptions at 260–300 nm occurred with increasing DMB concentration; these absorptions, which are centered at ca. 285 nm and are superimposed on those formed in the absence of the scavenger (vide supra), decayed over a similar timescale as the weak germylene absorption at 510 nm at low diene concentrations. Figure 6 shows a series of transient absorption spectra recorded at various time intervals after the laser pulse for the solution containing 2.76 mmol/L DMB. Higher diene concentrations could not be investigated in this case because of coabsorption at the excitation wavelength by the diene.

New long-lived transient absorptions in the 270–350 nm range were also observed in the presence of the amines and the other C–C unsaturated compounds. The absorption maximum of the species that was formed in the presence of Et_3N ($\lambda_{\text{max}} = 330 \text{ nm}$, Fig. 7a) was red-shifted sufficiently from the absorptions due to the free germylene and its oligomerization products to enable a growth in the signal to be detected at the upper end of the amine concentration range studied; the growth rate constant was found to be in reasonable agreement with that for decay of the germylene at the same amine concentration, consistent with the new species being formed by reaction of GeMePh with the amine. For example, a trace recorded at 350 nm with a solution of **5** containing 1.5 mmol/L Et_3N exhibited a growth rate constant of $(10.5 \pm 1.8) \times 10^6 \text{ s}^{-1}$, which agrees reasonably well with the decay rate constant of $k_{\text{decay}} = (6.5 \pm 0.5) \times 10^6 \text{ s}^{-1}$, measured for the germylene signal at 510 nm at the same amine concentration. We assign the species formed in the reaction to the Lewis acid–base complex **8a**. The analogous product (**8b**) is formed in the presence of BuNH_2 and exhibits $\lambda_{\text{max}} = 310 \text{ nm}$; however, the expected growth of its absorption could not be resolved because of overlap with other transient absorptions that are present in the short wavelength region at scavenger concentrations at which the germylene signal could still be detected. The same was true of the products formed in the presence of isoprene, DMP, and TBE, which absorb in the 270–285 nm range.

Transient decay profiles and spectra of the new products formed in the presence of isoprene, DMP, and TBE were re-

Fig. 6. Transient absorption spectra recorded at selected time intervals after the laser pulse for a solution of **5** (0.0015 mol/L) in deoxygenated hexane containing DMB (2.76 mmol/L). The inset shows a decay trace recorded at a monitoring wavelength of 280 nm.

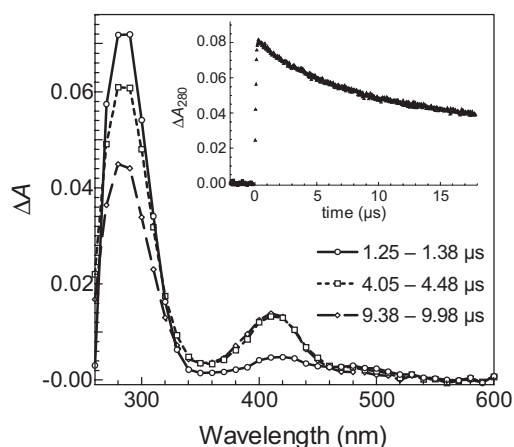
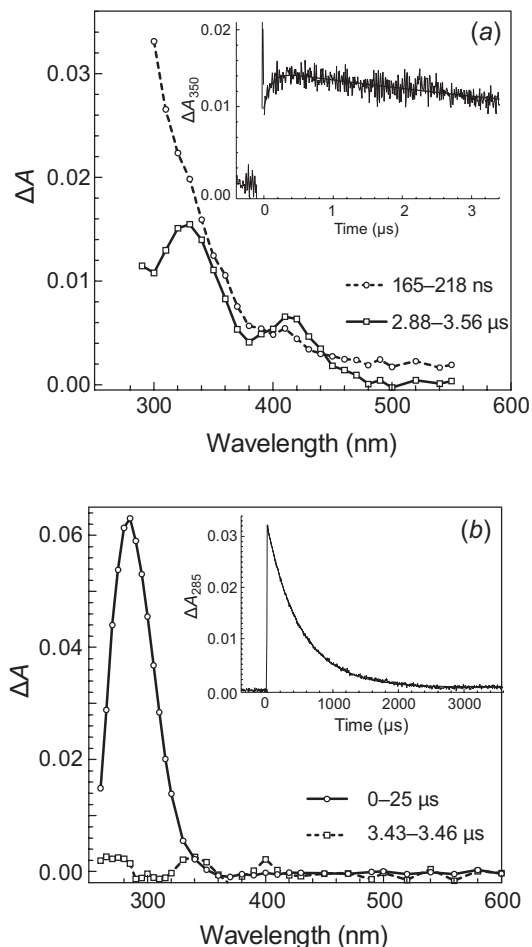
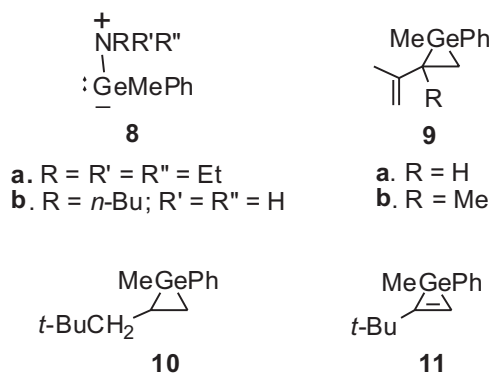


Fig. 7. Transient absorption spectra recorded by flash photolysis of a solution of **5** (ca. 0.0015 mol/L) in deoxygenated, anhydrous hexane containing (a) Et_3N (2.0 mmol/L) and (b) isoprene (20 mmol/L). The insets show growth and decay profiles recorded at 350 nm and 285 nm, respectively.



corded at relatively high (3.3–200 mmol/L) substrate concentrations to minimize contributions to the lifetimes from germylene dimerization or from overlapping transient absorptions because of GeMePh or its oligomerization products. It was possible to employ reasonably high substrate concentrations in the experiments with DMP, and the lifetime of the species formed from the alkene was found to be approximately independent of concentration over the 0.1–0.35 mol/L range. The species formed from isoprene absorbs with $\lambda_{\text{max}} = 285$ nm and decays with clean pseudo-first-order kinetics in the presence of 0.02 mmol/L diene ($\tau \sim 670$ μs). The spectra and lifetimes of these species are similar to those observed previously from GePh₂ with the same substrates (10) and we tentatively assign them to the three-membered germanocycles **9a–11**. The species absorbing with $\lambda_{\text{max}} \sim 285$ nm in the transient spectra of Fig. 6 is similarly assigned to vinylgermirane **9b**. Table 2 contains a summary of the absorption maxima and lifetimes of the primary transient products formed from reaction of GeMePh with these compounds, while Fig. 7 shows examples of the spectra and decays obtained in the presence of Et₃N and isoprene.



Saturation of a hexane solution of **5** with oxygen caused a ca. 40% drop in the peak absorbance due to digermene **4** compared with its value in deoxygenated solution, but had no discernible effect on the decay characteristics of the germylene signal. An upper limit of $k_{\text{O}_2} < 6 \times 10^7$ (mol/L)⁻¹ s⁻¹ for quenching of GeMePh was thus obtained from the pseudo-first-order rate constant for decay of the germylene in O₂-saturated hexane ($k_{\text{decay}} \sim 1 \times 10^6$ s⁻¹), using a value of 0.015 mol/L for the concentration of O₂ (14) and with the assumption that the decay of the germylene is dominated by its reaction with oxygen under these conditions. Modest reductions in the lifetime of the digermene were observed with increasing O₂ concentration, affording a value of $k_{\text{O}_2} = (2.4 \pm 0.3) \times 10^7$ (mol/L)⁻¹ s⁻¹ from analysis of the digermene decays according to eq. [2].

Discussion

As we found previously for the related compounds **1** and **2** (9), steady state photolysis of **5** in the presence of MeOH (0.5 mol/L), AcOH (0.095 mol/L), or isoprene (0.1 mol/L) affords the expected trapping products of GeMePh in high yields, along with 2,3-dimethyl-1,3-butadiene (DMB). Qualitative comparisons of the rate of product formation in the MeOH-trapping experiment to those obtained in our earlier

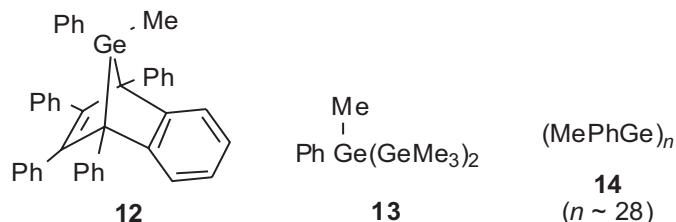
Table 2. UV absorption maxima and lifetimes of transient products from the reaction of GeMePh with amines and C—C unsaturated compounds in hexane at 23 °C.

Scavenger	Tentative assignment	λ_{max} (nm)	τ (ms) (conc. in mmol/L)
BuNH ₂	8b	310	0.015 (0.3)
Et ₃ N	8a	330	0.014 (1.5)
Isoprene	9a	285	0.670 (20)
DMB	9b	285	Nd ^a
DMP	10	275	2.6 (350)
TBE	11	270	>2000 (3.3)

^aNd (not determined).

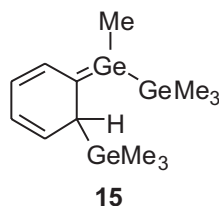
studies of **1a** and **2a**, which were carried out under the same conditions of lamp intensity and concentration, indicate similar quantum yields for germylene extrusion ($\Phi \sim 0.5$) from the three compounds.

The UV–vis spectrum of GeMePh in a 3-methylpentane (3-MP) matrix at 77 K was reported in the late 1980s by two different groups; Ando et al. (15) generated the species by photolysis of the 1,4-germanonaphthalene derivative **12** and reported a UV spectrum exhibiting $\lambda_{\text{max}} = 440$ nm, while Mochida and co-workers (16) employed the photolysis of trigermene **13** and reported $\lambda_{\text{max}} = 456$ nm in 3-MP at 77 K and $\lambda_{\text{max}} = 440$ nm in cyclohexane solution at room temperature. The latter group also reported rate constants for reaction of the species in cyclohexane solution with DMB ($k = 2.2 \times 10^6$ (mol/L)⁻¹ s⁻¹), Et₃SiH ($k = 4.1 \times 10^6$ (mol/L)⁻¹ s⁻¹), and CCl₄ ($k = 6.5 \times 10^7$ (mol/L)⁻¹ s⁻¹) (16). A transient exhibiting a similar UV absorption spectrum but much different reactivity toward DMB and CCl₄, from flash photolysis of poly(methylphenylgermylene) (**14**), was later assigned to GeMePh by the same group (17). The results reported in the present work using **5** as precursor differ significantly from those of the earlier studies, but are fully consistent with the spectroscopic and kinetic data reported by us recently for GePh₂ and GeMe₂ under similar conditions (9–11).

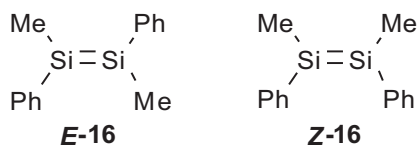


For example, the long wavelength absorption maximum of the initially formed transient from laser photolysis of **5** ($\lambda_{\text{max}} = 490$ nm) lies between those of GePh₂ ($\lambda_{\text{max}} = 500$ nm, $\epsilon_{500} = 1850$ dm³ mol⁻¹ cm⁻¹ (9)) and GeMe₂ ($\lambda_{\text{max}} = 470$ –480 nm (9, 11, 12), $\epsilon_{475} = 730$ dm³ mol⁻¹ cm⁻¹ (11)). The spectrum also shows a somewhat stronger absorption band centered at $\lambda_{\text{max}} \sim 290$ nm due to the S₀ → S₂ transition, which is shifted ca. 10 nm to the blue of the corresponding band in the spectrum of GePh₂ (9). We note that the long wavelength absorption maximum of GeMePh is the same as that reported for the silicon homologue (SiMePh) in

a hydrocarbon matrix at 77 K ($\lambda_{\max} = 490$ nm (18)). Such similarities are also evident in the UV-vis spectra of GeMe_2 and SiMe_2 ($\lambda_{\max} = 453\text{--}465$ nm (18, 19)), as well as those of GePh_2 and SiPh_2 ($\lambda_{\max} = 495$ nm (18)). It thus seems clear that the transient absorptions assigned to GeMePh in the earlier time-resolved studies in solution, using **13** and **14** as precursors, must be due to other more strongly absorbing transient products; as we have shown previously for related systems (8), the likely candidates are conjugated germene derivatives and (or) germanium-centered radicals. For example, the conjugated germene derivative (**15**) that might be anticipated from photolysis of **13** can be predicted to exhibit an absorption maximum in the 430–450 nm range and exhibit moderate reactivity toward CCl_4 and DMB, based on analogies taken from related systems (7, 8, 20).



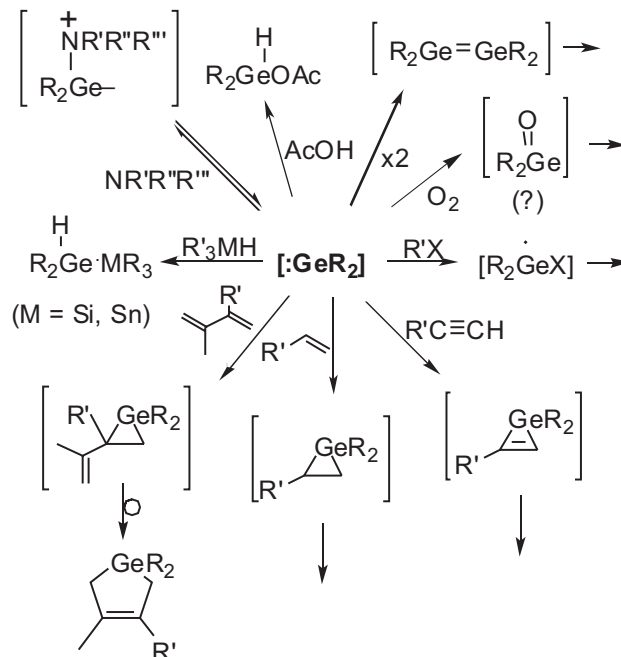
Similarly, the absorption maximum of the second-formed species ($\lambda_{\max} = 415$ nm) falls between those of Ge_2Ph_4 (**3a**, $\lambda_{\max} = 440$ nm (9)) and Ge_2Me_4 (**3b**, $\lambda_{\max} = 370$ nm (9, 11, 21, 22)) and can thus be assigned with confidence to (*E*)- and (or) (*Z*)-1,2-dimethyl-1,2-diphenyldigermene (**4**, Scheme 1), formed most likely as a mixture of isomers. The spectra of (*E*)- and (*Z*)-**4** are also quite similar to those reported by Sekiguchi et al. (23) for the silicon homologues, (*E*)- and (*Z*)-1,2-dimethyl-1,2-diphenyldisilene [(*E*)- and (*Z*)-**16**, $\lambda_{\max} = 417$ and 423 nm, respectively] in cyclohexane solution. An absorption maximum of $\lambda_{\max} = 420$ nm was reported earlier for **16** in a 3-MP glass at 77 K, formed (presumably as a mixture of isomers) by dimerization of SiMePh (18).



Absolute rate constants have been determined in this work for the reaction of GeMePh with a selection of representative germylene scavengers in hexane solution. The reactions studied include O-H insertion with AcOH, Lewis acid–base complexation with primary and tertiary amines, M-H insertions with trialkylhydrosilanes and -stannanes, reaction with terminal alkenes, alkynes, and conjugated dienes, chlorine atom abstraction from CCl_4 , reaction with oxygen, and dimerization, as summarized in Scheme 4. While product studies specific to GeMePh have not been carried out in most instances, the course of these reactions are well established for GeMe_2 and other reactive germylenes (1, 10, 11, 24, 25) and all of them have direct analogies in silylene chemistry (26).

As we found in our earlier studies of GePh_2 and GeMe_2 (10, 11), two distinct types of kinetic behaviour are observed in the signals due to GeMePh and **4**, depending on whether

Scheme 4.



scavenging of the germylene is reversible or not. A reasonably reliable indicator of reversibility in the data is the $K_{\text{SV}}/k_{\text{Q}}$ ratio, which (within certain limitations (11)) provides a normalized measure of the efficiency with which a given scavenger suppresses germylene dimerization as a result of its competing reaction with the digermene precursor (i.e., the germylene). The $K_{\text{SV}}/k_{\text{Q}}$ ratio tends toward significantly smaller values (indicating lower scavenging efficiencies) for those substrates that react with the germylene reversibly compared with those for irreversible scavengers. Because K_{SV} is measured from the relative peak intensities of the signal due to digermene **4**, its magnitude is also affected by the reactivity of the digermene with the scavenger. This leads to artificially high values of the efficiency parameter, which become particularly significant when the reactivity of the digermene toward the scavenger is within a factor of ca. 5 of that of the germylene; the smaller the differential reactivity, the greater the distortion in the magnitude of K_{SV} , and $K_{\text{SV}}/k_{\text{Q}}$, from their true values. Thus, the $K_{\text{SV}}/k_{\text{Q}}$ ratios for those reagents for which this differential reactivity is relatively small (e.g., BuNH_2 , CCl_4 , and O_2) can be expected to overestimate the efficiency (i.e., the rate relative to that of dimerization) of the scavenging reaction. For this reason, we have not attached an absolute value to the rate constant for scavenging of GeMePh by O_2 based on the K_{SV} value and report only the upper limit of the rate constant as defined by the lifetime of the germylene in O_2 -saturated solution; similarly, the value estimated previously for the reaction of GePh_2 with O_2 ($k_{\text{O}_2} \sim 3 \times 10^7$ (mol/L) $^{-1}$ s $^{-1}$) (10) should also be considered an upper limit. In any event, it is clear from the data of Table 1 that those scavengers that react at least ca. three times faster with GeMePh than with **4** fall into two groups, those with $K_{\text{SV}}/k_{\text{Q}} \geq 0.9$ (AcOH, Bu_3SnH , O_2 , CCl_4 , and TBE) and those with $K_{\text{SV}}/k_{\text{Q}} < 0.5$ (Et_3N , isoprene, DMB, and DMP). The first group is comprised of those reagents that react with GeMePh irreversibly, while the second

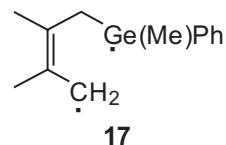
consists of the reversible scavengers. The K_{SV}/k_Q value for BuNH_2 would seem to suggest that it belongs in the group of irreversible scavengers, but as it reacts with digermene **4** only twice slower than it does with GeMePh , the K_{SV} value (and hence K_{SV}/k_Q) is likely to be significantly overestimated. This reaction is most likely reversible, like that with Et_3N (vide infra).

The absolute rate constants for the various reactions of GeMePh that have been studied in the present work are in most cases the same, within experimental error, as the corresponding values for GePh_2 (9, 10) and are consistently a factor of two to eight times smaller than those for reaction of GeMe_2 with the same substrates (11). The smallest variations throughout the series are exhibited by the rate constants for dimerization and Lewis acid–base complexation with the primary amine, which proceed within a factor of ca. 2 of the diffusional rate constant in hexane at 25 °C in all three cases (11). An estimate of $k_{\text{dim}} \sim 2 \times 10^{10} \text{ (mol/L)}^{-1} \text{ s}^{-1}$ for the rate constant for dimerization of GeMePh can be obtained from the measured second-order decay coefficient ($k/\epsilon_{510} = (1.6 \pm 0.1) \times 10^7 \text{ cm s}^{-1}$), assuming an extinction coefficient intermediate between those of GePh_2 ($\epsilon_{\text{max}} \sim 1850 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (9) and GeMe_2 ($\epsilon_{\text{max}} \sim 730 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (11). The results suggest that phenyl for methyl substitution has relatively small effects on the reactivity of simple germynes toward this diverse set of reagents, but confirm the earlier conclusion that phenyl substitution has a distinct moderating effect on gerylene reactivity (11). The present results indicate that most of the effect on the rate constant arises with substitution of the first alkyl substituent in GeMe_2 and replacing the second has much smaller consequences.

As might be expected, the equilibrium constants for the reversible reactions of GeMePh also appear to lie between those for GeMe_2 and GePh_2 , although we have not been able to measure them with reasonable precision owing to the low signal-to-noise ratios that characterize the present experiments. Nevertheless, the equilibrium constants appear to be more sensitive to gerylene substitution than the absolute rate constants for the forward component of the reaction. For example, the rate constants for reaction of the three germynes with the alkene DMP vary by less than a factor of 2, while the equilibrium constants vary between $K_{\text{eq}} \sim 2500 \text{ (mol/L)}^{-1}$ for GePh_2 (10) and $K_{\text{eq}} \sim 20\,000 \text{ (mol/L)}^{-1}$ for GeMe_2 (11); these should be compared with the qualitative estimate of 4000–8000 (mol/L)^{-1} for reaction of GeMePh with the same substrate. The estimated equilibrium constant for reaction of GeMePh with isoprene ($K_{\text{eq}} \sim 15\,000 \text{ (mol/L)}^{-1}$) also falls within the range defined by GePh_2 and GeMe_2 . The total range in K_{eq} exhibited by the reactions of DMP with the three germynes corresponds to a range of ca. 1.3 kcal/mol (1 cal = 4.184 J) in standard free energy.

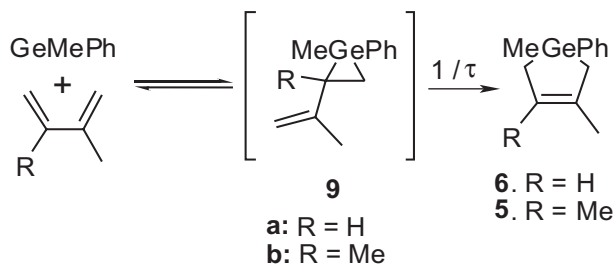
The two dienes have remarkably different effects on the gerylene and digermene growth–decay profiles, which can be attributed primarily to a substantial difference in the equilibrium constants for the reactions of these substrates coupled with similar absolute rate constants for formation of the primary products. Interestingly, they also appear to quench the formation of the free gerylene, to the extent that they cause significant reductions in the initial (peak) signal

strengths of the GeMePh absorptions in laser flash photolysis experiments with these substrates. Apparent Stern–Volmer constants on the order of 1000 (mol/L)^{-1} have been determined from analysis of the peak gerylene absorbances as a function of diene concentration over the 0–3 mmol/L concentration range, which is consistent with diffusion-controlled quenching ($k \sim 2 \times 10^{10} \text{ (mol/L)}^{-1} \text{ s}^{-1}$) of an intermediate possessing a lifetime of $\tau \sim 50 \text{ ns}$. However, product studies indicate that product formation remains efficient in the presence of isoprene in concentrations as high as ca. 0.1 mol/L; compound **6**, the expected product of trapping of GeMePh by the diene, is formed in only modestly (ca. 2 \times) lower quantum yield than the corresponding products of trapping of the gerylene by MeOH or AcOH . This indicates that whatever phenomenon is primarily responsible for the loss in signal strength in the flash photolysis experiments, it does not lead to a reduction in the yield of gerylene-derived products; this effectively rules out energy-transfer quenching of an excited state of **5** as the process responsible for the effect. In this regard, it is noteworthy that in the absence of added scavengers the gerylene signals appear to be characterized by a ca. 50 ns growth, which is discrete from the temporal characteristics of the laser pulse. This could be indicative of the involvement of an additional intermediate such as 1,5-biradical **17**, formed via Ge–C bond cleavage in the reactive excited state of **5**, which undergoes further fragmentation to yield GeMePh and DMB. Such a species would also be expected to undergo ring closure to yield **5** and **9b** competitively with fragmentation. The same temporal feature was also evident in our earlier studies of GePh_2 (generated from **1b**) (9) and GeMe_2 (generated from **2a**) (11), although the effects of added diene on the signal strengths were much less pronounced than in the present case. It is reasonable to expect that such a species might be reactive toward dienes, though again, the product studies demand that it must do so reversibly. Neumann and co-workers (27, 28) isolated products corresponding to the addition of two molecules of diene to GeMe_2 in their early studies of the reactions of GeMe_2 with aliphatic dienes; we have found no evidence for the formation of such products in the present instance, although the highest diene concentration we have employed in product studies is only 0.1 mol/L. Further work will be required to address the possible involvement of such intermediates in the photochemistry of 1-germacyclopent-3-ene derivatives and the reaction of the corresponding germynes with dienes in a more conclusive way.



Addition of the dienes leads to the formation of new strongly absorbing transients exhibiting $\lambda_{\text{max}} = 285 \text{ nm}$ in both cases, which are assigned to the corresponding vinylgermirane derivatives **9a** and **9b**. The absorption spectrum and lifetime of the species formed from reaction of GeMePh with isoprene (**9a**, $\tau \sim 670 \mu\text{s}$, Fig. 7b) are quite close to those of the analogous product from reaction of

Scheme 5.



GePh₂ with the same diene ($\lambda_{\text{max}} = 285 \text{ nm}$, $\tau \sim 500 \mu\text{s}$) (10). It should be noted that the lifetime of the isoprene-derived product has been determined in the presence of sufficiently high diene concentrations to suppress digermene formation more or less completely, and where the decay of the species follows clean first-order kinetics. We thus tentatively associate the decay rate constant with that for further (unimolecular) rearrangement to yield the stable final product of the reaction (1, 27, 29), the corresponding germacyclopent-3-ene derivative **6** (Scheme 5). Unfortunately, the greater absorptivity of DMB at the laser excitation wavelength precluded experiments at sufficiently high diene concentrations to determine a lifetime for **9b** under comparable conditions. It is interesting to note that the relative equilibrium constants for formation of **9a** and **9b** from GeMePh indicate that **9b** is ca. 1.5 kcal/mol less thermodynamically stable than **9a**, with respect to cycloreversion back to the free germylene and the diene.

The intermediates formed in the reactions of GeMePh with the alkene (DMP) and alkyne (TBE) are also relatively long-lived and have been detected as discrete species with absorption maxima in the 270–285 nm range and lifetimes of ca. 2.6 ms or greater (see Table 2). The corresponding intermediates formed in the reactions of these substrates with GePh₂ exhibit similar absorption maxima ($\lambda_{\text{max}} = 275 \text{ nm}$ in both cases), but somewhat shorter lifetimes ($\tau \sim 1.2$ and 600 ms, respectively) (10); the analogous products could not be detected from GeMe₂ under similar conditions, presumably because they absorb too far to the blue to be detectable under the conditions of our experiments (11). We similarly assign these products to the three-membered germanocycles **10** and **11**.

The significantly longer lifetimes of **9a–11** compared to those of the corresponding adducts from GePh₂ indicate that the greater degree of stabilization of the GeMePh adducts (as measured by the equilibrium constants for their formation) is also reflected in the rate constants for their further reaction. The processes responsible for the decay of the germirane (**10**) and germirene (**11**) at high substrate concentrations are unfortunately not clear; our earlier study of the reaction of DMP with GePh₂ indicated that it led to the formation of germanium-containing polymers, while the reaction with TBE produced a primary product that underwent further thermal or photochemical reaction under the conditions employed for its generation (10). Indeed, very few stable examples of such compounds are known (30–36), unlike the situation with the corresponding silicon analogues, which enjoy much greater thermodynamic stability (36–38). As mentioned previously, the reactions of GeMe₂ with alkenes, dienes, and alkynes are known to yield five-

membered ring compounds derived from reaction of the germylene with two molecules of substrate, most likely via the intermediacy of the corresponding three-membered germanocycle (1, 27). We thus suspect that the relatively slow decay of these species is due to these secondary reactions, perhaps involving biradical intermediates formed by (single) Ge—C bond cleavage processes. In the case of **10** this process occurs with a rate constant of $k \sim 500 \text{ s}^{-1}$ in the presence of 0.1–0.35 mol/L alkene, roughly half that observed for the analogous species formed from reaction of GePh₂ with DMP under similar conditions (11). The process occurs roughly 10³ times more slowly than cycloreversion to regenerate GeMePh and the alkene, based on an estimate derived from the estimated K_{eq} value and measured rate constant for the (forward) reaction of GeMePh with the alkene. The somewhat shorter lifetime observed for vinylgermirane **9a** is consistent with an additional contribution to its decay due to unimolecular isomerization, yielding **6**.

The reactions of GeMePh with BuNH₂ and Et₃N also result in the formation of detectable transient products, which can be identified as the Lewis acid–base complexes **8a** and **8b**, respectively. The equilibrium constants for formation of these complexes are in considerable excess of ca. 25 000 (mol/L)⁻¹, the approximate upper limit of K_{eq} for which residual germylene absorptions can be detected under the present experimental conditions. This was also found for the corresponding amine complexes with GePh₂ and GeMe₂ (10, 11), so it is not possible to comment on the relative stabilities of the amine complexes of this series of germylenes. Again, however, the rate constants for their formation are very similar. The only hint of a difference between the three germylenes in their reaction with amines is in the absorption spectra of the complexes, which are in both cases shifted significantly to the blue of those formed from GePh₂ (10), and significantly red-shifted compared with the complexes from GeMe₂ (11). Ando et al. (15) suggested that the positions of the absorption maxima of the complexes of amines, sulfides, phosphines, and ethers with a given germylene reflects their relative stabilities, in that they correlate broadly with Lewis base strength, shifting to the blue as the strength of the complex increases. This suggests that with a given amine, GeMePh forms the somewhat stronger Lewis acid–base complex and hence possesses somewhat higher Lewis acid strength than GePh₂. The opposite is true in regards to GeMe₂. For a given amine, the absorption maxima of the three germylene complexes vary to a much greater extent than those of the free germylenes. It is interesting to note that since the complex with BuNH₂ can be detected as a discrete, relatively long-lived intermediate, the formal H-migration process required to convert it to the putative N-H insertion product must be relatively slow. We previously reported that the reaction of GePh₂ with primary and secondary amines affords mainly polymeric material, and the germylamines derived from formal N-H insertion are formed in very low yields (10).

The effects of methyl vs. phenyl substitution on the reactivity of digermenes **3a**, **3b**, and **4** are somewhat greater and more varied than is the case with the corresponding germylenes. We have been successful in determining absolute rate constants for the reactions of **4** with four of the substrates studied (BuNH₂, AcOH, CCl₄, and O₂) and have determined

upper limits for the rate constants in the other cases. As mentioned earlier, we make the assumption that dimerization of GeMePh proceeds nonstereospecifically to yield a mixture of the (*E*)- and (*Z*)-isomers of the digermene, which seems reasonable enough considering that the reaction is fully diffusion-controlled. In most cases, the rate constants again fall between those of Ge₂Me₄ (**3b**) and Ge₂Ph₄ (**3a**), and since the mechanistic implications of these results have been discussed in some detail (11), they will not be elaborated on further here. The exception is the value for reaction with BuNH₂, which indicates somewhat greater reactivity for **4** compared with the tetraphenyl derivative. This is perhaps suggestive of a small steric effect on the rate of nucleophilic attack at the Ge=Ge bond in Ge₂Ph₄ (**3a**), which is thought to be the rate-determining step of the reaction (11).⁵ It is also interesting to note that the rate constant for reaction with O₂ is ca. 30× lower than that reported (39) for the homologous disilenes, (*E*)- and (*Z*)-**16**, providing the first quantitative indication of the differences in reactivity of digermenes and disilenes of otherwise identical substitution. The reaction of disilenes and digermenes with oxygen has been reasonably well-studied and is known to yield the corresponding 1,2-dimetallaioxetane in both cases (40–42), presumably via the intermediacy of a triplet 1,4-(metalla-oxa)-biradical intermediate (43). Comparison of the rate constants for reaction of oxygen with the series of digermenes Ge₂Me₄ (**3b**, $k_{O_2} = 5.0 \times 10^7 \text{ (mol/L)}^{-1} \text{ s}^{-1}$) (11), Ge₂Me₂Ph₂ (**4**, $k_{O_2} = 2.4 \times 10^7 \text{ (mol/L)}^{-1} \text{ s}^{-1}$), and Ge₂Ph₄ (**3a**, $k_{O_2} = 4.8 \times 10^6 \text{ (mol/L)}^{-1} \text{ s}^{-1}$) (10) indicates that phenyl for methyl substitution results in a consistent decrease in reactivity, spanning a factor of about 10 throughout the series. To our knowledge, there is little information available on the sensitivity of the rate constant to substituent for the reaction of O₂ with disilenes.

Similar trends in reactivity are evident in the rate constants for the reactions of **3a**, **4**, and **3b** with CCl₄ and AcOH (10, 11); the former is thought to proceed via initial chlorine atom abstraction to yield a (singlet) radical pair (44–46), while the latter most likely proceeds via 1,2-addition (of H-OAc) across the Ge=Ge bond, as is known for the reaction of alcohols with digermenes (9, 21) and disilenes (39, 47, 48). Interestingly, the opposite trend in reactivity is observed with the strong nucleophile, BuNH₂, for which the rate constants for the reactions with both **4** and Ge₂Ph₄ (**3a**) are ca. two orders of magnitude greater than that reported for Ge₂Me₄ (**3b**) (11). The difference in the reactivities of **3a** and **3b** toward this substrate is consistent with frontier molecular orbital control of the reaction, as the rate constants correlate with the relative LUMO energies of the two compounds (11).

Summary and conclusions

The direct detection and characterization of the reactivities of methylphenylgermylene (GeMePh) and (*E*)- and (*Z*)-1,2-dimethyl-1,2-diphenyldigermene (**4**), formed as a mixture by dimerization of the germylene, have been accomplished for the first time. The two species have been

produced by photoextrusion of GeMePh from germacyclopent-3-ene derivative **5**, which affords GeMePh in >90% chemical yield and high quantum efficiency, based on the results of steady-state trapping experiments with methanol, acetic acid, and isoprene. The germylene is detectable as a weakly absorbing transient species with $\lambda_{\text{max}} = 490 \text{ nm}$ by laser flash photolysis of **5** in hexane solution, where it decays by diffusion-controlled dimerization to yield **4** ($\lambda_{\text{max}} = 415 \text{ nm}$). The trends in the experimental UV–vis absorption spectra of GeMe₂, GeMePh, and GePh₂ mirror those in the spectra of the corresponding silylenes and similar correlations are found in the spectra of the corresponding digermenes and disilenes.

Absolute rate constants for reaction of GeMePh with several representative germylene scavengers have been measured, including primary and tertiary amines, acetic acid, triethylsilane, tri-*n*-butylstannane, O₂, CCl₄, two aliphatic dienes, and a terminal alkene and alkyne. With every reagent studied, GeMePh reacts with a similar absolute rate constant to that previously reported for GePh₂ under similar conditions and both germylenes are significantly less reactive than GeMe₂ toward the same substrates. Equilibrium constants falling between those determined earlier for GeMe₂ and GePh₂ have been estimated for the reversible reactions of GeMePh with amines, the alkene, and the dienes; the primary products of these reactions have also been detected as long-lived transient intermediates exhibiting similar UV–vis absorption spectra to the analogous products from GePh₂.

More detailed mechanistic studies of the photochemistry of arylgermacyclopent-3-ene derivatives and the reactions of transient germylenes and digermenes, including those with oxygenated substrates, are currently in progress in our laboratory.

Experimental

¹H and ¹³C NMR spectra were recorded on Bruker AV 200 or AV 600 spectrometers in deuteriochloroform or cyclohexane-*d*₁₂ solution and were referenced to the residual solvent proton and ¹³C signals, respectively. Gas chromatographic analyses were carried out using a Hewlett-Packard 5890 gas chromatograph equipped with a conventional heated injector, a flame ionization detector, a Hewlett-Packard 3396A integrator, and a SPB-5 capillary column (25 m, 0.25 μm, Supelco, Inc.). Gas chromatographic – mass spectrometric (GC–MS) separations employed a Hewlett-Packard 5890 Series II gas chromatograph equipped with a HP-5971A mass selective detector and a SPB-5 capillary column (25 m, 0.25 μm, Supelco, Inc.). High-resolution electron impact mass spectra and exact masses were determined on a Micromass TofSpec 2E mass spectrometer. Exact masses were determined for the molecular ion (M⁺), employing a mass of 12.000 000 for carbon-12. Column chromatography employed a 30 mm × 800 mm column using silica gel (120 g, acid-washed, 230–400 mesh ASTM, particle size 0.040–0.063 mm, Silicycle) and pentane as the eluant. Steady state photolyses employed a Rayonet[®] photochemical reactor (Southern New England Ultraviolet Co.,

⁵W.J. Leigh and L.A. Huck. To be published.

Branford, Connecticut) equipped with a merry-go-round apparatus and six RPR-2537 lamps (254 nm).

2,3-Dimethyl-1,3-butadiene, isoprene, phenylmagnesium bromide (3.0 mol/L solution in diethyl ether), methylmagnesium bromide (3.0 mol/L solution in diethyl ether), and magnesium were used as received from Sigma-Aldrich. Hexanes (Caledon Reagent) was dried by refluxing for several days under nitrogen with sodium-potassium amalgam followed by distillation, or by passage through activated alumina under nitrogen using a Solv-Tek solvent purification system (Solv-Tek, Inc., Berryville, Virginia). Diethyl ether (Caledon Reagent) and tetrahydrofuran (Caledon Reagent) were dried by the latter method. Each of the scavengers investigated in this work were obtained from commercial sources in the highest purity available. The amines were refluxed over solid KOH for 12 h and distilled, while triethylsilane (Et_3SiH) and tri-*n*-butylstannane (Bu_3SnH) were stirred at room temperature for 18 h over lithium aluminum hydride and distilled at atmospheric pressure (Et_3SiH) or under mild vacuum (Bu_3SnH). CCl_4 was refluxed over phosphorus pentoxide and distilled. 4,4-Dimethyl-1-pentene (DMP) was dried by passage through a silica gel column, while isoprene, DMB, and 3,3-dimethyl-1-butyne (TBE) were distilled at atmospheric pressure. 1,1-Dichloro-3,4-dimethylgermacyclopent-3-ene and 1,1-dichloro-3-methylgermacyclopent-3-ene were prepared as previously described (9, 49, 50). Deuterated solvents were used as received from Cambridge Isotopes Laboratories.

1,3,4-Trimethyl-1-phenyl-1-germacyclopent-3-ene (**5**) was synthesized by a procedure similar to that of Mazerolles and Manuel (51). In a flame-dried apparatus consisting of a 250 mL two-necked round-bottomed flask, reflux condenser, nitrogen inlet, addition funnel, and magnetic stirrer was prepared a solution of 1,1-dichloro-3,4-dimethyl-1-germacyclopent-3-ene (3.7 g, 0.016 mol) in anhydrous diethyl ether (80 mL) under nitrogen. The solution was cooled to 0 °C using an ice bath, and then a stirred solution of phenylmagnesium bromide (5.7 mL of a 3.0 mol/L solution in diethyl ether, 0.0171 mol) in dry diethyl ether (20 mL) was added dropwise over 1 h. The cooling bath was removed after 2 h and the white suspension was allowed to stir at room temperature for another 20 h. A solution of methylmagnesium bromide (6.3 mL of a 3.0 mol/L solution in diethyl ether, 0.019 mol) in anhydrous diethyl ether (20 mL) was then added dropwise over 1 h, and the reaction mixture was then stirred under reflux for a further 3 h. After cooling, the resulting yellow suspension was hydrolyzed with saturated aqueous ammonium chloride (40 mL) over 20 min, transferred to a separatory funnel, and the aqueous and organic fractions were separated. The aqueous fraction was extracted with diethyl ether (3 × 60 mL), and then the combined ether fractions were washed with distilled water (2 × 30 mL), 5% aqueous sodium bicarbonate (2 × 30 mL), dried with anhydrous magnesium sulfate (30 min), and filtered. The solvent was removed on a rotary evaporator to yield a yellow-green liquid (4.4 g). Distillation under vacuum (bp = 103–105 °C at 0.3 mm Hg, 1 mm Hg = 133.322 Pa) afforded **5** (3.78 g, 0.015 mol, 86%) as a colorless liquid. Further purification by column chromatography, using pentane as eluant, was performed until the purity of

the compound was at least 99% according to GC analysis. The compound exhibited the following spectroscopic data: ^1H NMR (CDCl_3 , 200 MHz) (δ): 0.56 (s, 3H), 1.74 (m, 10 H), 7.31–7.51 (m, 5H). ^{13}C NMR (CDCl_3) (δ): -4.5, 19.4, 26.4, 128.0, 128.5, 130.9, 133.3, 143.9. MS m/z : 248 (65), 246 (45), 244 (35), 233 (38), 231 (28), 229 (20), 166 (70), 164 (43), 151 (100), 149 (85), 147 (80). Exact mass calcd. for $\text{C}_{13}\text{H}_{18}^{74}\text{Ge}$: 248.0620; found: 248.0617.

1,3-Dimethyl-1-phenyl-1-germacyclopent-3-ene (**6**) was prepared in similar fashion. A solution of 1,1-dichloro-3-methyl-1-germacyclopent-3-ene (2.0 g, 0.009 mol) in anhydrous diethyl ether (40 mL) was introduced into a flame-dried apparatus consisting of a two-necked round-bottomed flask (100 mL), reflux condenser, nitrogen inlet, addition funnel, and magnetic stirrer. After cooling to 0 °C, a solution of phenylmagnesium bromide (3.3 mL of a 3.0 mol/L solution in diethyl ether, 0.010 mol) in dry diethyl ether (20 mL) was added dropwise over 1.5 h with stirring. The cooling bath was removed after 2 h and the suspension was stirred at room temperature for another 15 h. A solution of methylmagnesium bromide (4.1 mL of a 3.0 mol/L solution in diethyl ether, 0.012 mol) in anhydrous diethyl ether (20 mL) was then added dropwise over 1.5 h, and the resulting mixture was stirred under reflux for a further 4 h. After cooling, the resulting yellow suspension was hydrolyzed with saturated aqueous ammonium chloride (40 mL) over 20 min and transferred to a separatory funnel, where the aqueous and organic fractions were separated. The aqueous fraction was extracted with diethyl ether (3 × 60 mL) and then the combined ether fractions were washed with distilled water (2 × 30 mL), 5% aqueous sodium bicarbonate (2 × 30 mL), dried with anhydrous magnesium sulfate (30 min), and filtered. The solvent was removed on a rotary evaporator to yield a yellow oil (2.3 g), which was purified by silica gel column chromatography with pentane as the eluting solvent. This afforded a colorless oil (1.9 g, 0.008 mol, 89%) in >99% purity, according to GC analysis, which was identified as **6** on the basis of the following spectroscopic data. ^1H NMR (CDCl_3 , 200 MHz) (δ): 0.58 (s, 3H), 1.23–1.80 (m, 7 H), 5.64 (s, 1H), 7.24–7.50 (m, 5H). ^{13}C NMR (CDCl_3) (δ): -4.2, 14.2, 22.7, 31.7, 125.4, 128.1, 128.6, 130.9, 133.2, 140.3. MS m/z : 234 (35), 232 (25), 230 (18), 220 (67), 219 (36), 217 (15), 214 (10), 166 (40), 151 (100), 149 (85), 147 (50), 122 (20). Exact mass calcd. for $\text{C}_{12}\text{H}_{16}^{74}\text{Ge}$: 234.0464; found: 234.0446.

Steady state photochemical trapping experiments were carried out in quartz NMR tubes using 0.045 mol/L solutions of **5** in cyclohexane- d_{12} containing methanol (0.5 mol/L), acetic acid (0.095 mol/L), or isoprene (0.094 mol/L), monitoring the course of the reactions over the 0%–40% conversion range by ^1H NMR spectroscopy. The tubes were sealed with rubber septa and deoxygenated with a stream of dry argon for ca. 20 min prior to photolysis. The photolyses afforded equal yields of 2,3-dimethyl-1,3-butadiene (DMB; δ : 1.96, 4.88, 4.97) and a single additional major (>90%) product in each case. The identity of the isoprene adduct (**6**) was established by ^1H NMR spectroscopy, GC-MS, and GC coinjection of the crude photolysate with the authentic sample described above. The MeOH and AcOH adducts **7a** and **7b**, respectively, were identified on

the basis of comparisons of their ^1H NMR spectra to those of closely related compounds (9, 11, 53). Neither compound survived attempted GC separation without significant decomposition. Methoxymethylphenylgermane (**7a**): ^1H NMR (C_6D_{12} , 600 MHz) δ : 0.59 (d, 3H, $J = 2.3$ Hz), 3.45 (s, 3H), 5.68 (q, 1H, $J = 2.3$ Hz), 7.28 (m, 3H), 7.48 (m, 2H). Acetoxymethylphenylgermane (**7b**): ^1H NMR (C_6D_{12} , 600 MHz) δ : 0.79 (d, 3H, $J = 2.3$ Hz), 1.88 (s, 3H), 6.01 (q, 1H, $J = 2.3$ Hz), 7.28 (m, 3H), 7.58 (d, 2H).

Laser flash photolysis experiments employed the pulses from a Lambda Physik Compex 120 excimer laser, filled with $\text{F}_2\text{-Kr-Ne}$ (248 nm, ~ 25 ns, 100 ± 5 mJ) mixtures and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously (9). 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 thermostatted 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 throughout the duration of each experiment. The glassware, sample cells, and transfer lines used for these experiments were stored in a 85°C vacuum oven when not in use, and the oven was vented with dry nitrogen just prior to assembling the 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., San Diego, California) 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 (five to seven 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.

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